Introduction to Ground Water Geochemistry LIBRARY COPY
January 18-21, 1994 Los Alamos Inn Los Alamos, New Mexico
INSTRUCTORS: William Deutsch Patrick Longmire Richard Meyerhein
Bill Deutsch -206-343-7933 Pat Long mire-505-665-6493 Rick Meyer hein-505-841-2570

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## DO NOT MAKE CHOICES ON THIS SHEET. PLEASE MAKE ALL RESPONSES ON THE ATTACHED COMPUTER FORM.

### LANL COURSE EVALUATION FORM: Introduction to Ground Water Geochemistry

January 18-21, 1994 Los Alamos Inn Los Alamos, New Mexico

## EVALUATION KEY: A = Excellent B = Very Good C = Good D = Fair E = Poor

### Please rate the following questions using this key.

1. General rating for the short course	William J. Deutsch - Solution Chemistry		
2. Program content	11. Technical Content 12. Presentation		
3. General rating for speakers	Million I. Deutech, Chemical Equilibrium		
4. General level of speakers knowledge of topic	William J. Deutsch - Chemical Equilibrium13. Technical Content14. Presentation		
5. General quality of presentations			
6. Geographic location of the short course	Patrick Longmire - Oxidationand Reduction Reactions I		
7. Quality of facility	15. Technical Content 16. Presentation		
8. Administrative arrangements and correspondence			
SPEAKERS' EVALUATIONS:	Patrick Longmire - Oxidationand Reduction Reactions II17. Technical Content18. Presentation		
Patrick Longmire - Introduction to Hydrogeochemistry9. Technical Content10. Presentation	<b>Richard Meyerhein - Introduction to Organic Chemistry I</b> -Structure and Nomenclature 19. Technical Content 20. Presentation		

William J. Deutsch -- Carbonate System 21. Technical Content 22. Presentation

William J. Deutsch - Chemical Evolution of Ground Water 23. Technical Content 24. Presentation

Patrick Longmire - Adsorption of Solutes 25. Technical Content 26. Presentation

Richard Meyerhein - Analytical Organic Methods and Instrumentation

27. Technical Content 28. Presentation

Patrick Longmire -- Organic Geochemistry of Ground Water 29. Technical Content

30. Presentation

William J. Deutsch -- Geochemical Reaction Modeling 31. Technical Content 32. Presentation

**Richard F. Meyerhein -- Evaluation of Laboratory Analytical Data** 33. Technical Content 34. Presentation

William J. Deutsch/Patrick Longmire -- Inorganic **Problem Session** 35. Technical Content 36. Presentation

Patrick Longmire - Geochemical Processes Influencing the Fate of Organic Solutes in Ground Water 37. Technical Content 38. Presentation

**Richard F. Meyerhein -- Degradation of Organic Solutes** 39. Technical Content 40. Presentation

Patrick Longmire -- Geochemistry of Several **Contaminant Sources** 41. Technical Content 42. Presentation

All Instructors -- Organic Problem Set 43. Technical Content 44. Presentation

William J. Deutsch -- Aquifer Restoration 45. Technical Content 46. Presentation

### Additional questions

- 47. How did you hear about the short course?
  - A) Brochure B) Letter C) Magazine
  - D) Friend or associate E) Other
- 48. Which category best describes your background?
  - A) Hydrogeologist B) Engineer C) Geochemist
  - D) Hydrologist E) Regulator

Place your response to the following questions on the corresponding blanks located on the computer form.

- 49. Was any pertinent topic not covered?
- 50. Should any topic be expanded?
- 51. Should any topic be reduced/deleted?

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## COURSE SCHEDULE INTRODUCTION TO GROUND WATER GEOCHEMISTRY

January 18-21, 1994 Los Alamos Inn Los Alamos, New Mexico

### COURSE INSTRUCTORS

William J. Deutsch, Woodward Clyde Consultants, Seattle, WA

Patrick Longmire, Los Alamos National Laboratory, Los Alamos, New Mexico

Richard F. Meyerhein, New Mexico Scientific Laboratory Division, Albuquerque, New Mexico

DAY 1			
7:15 a.m.	-	8:15 a.m.	Registration
8:15 a.m.	-	9:00 a.m.	Introduction to Hydrogeochemistry Patrick Longmire
9:00 a.m.	-	9:15 a.m.	Break
9:15 a.m.	-	10:15 a.m.	Solution Chemistry William J. Deutsch
10:15 a.m.	-	10:30 a.m.	Break
10:30 a.m.	-	11:30 a.m.	Chemical Equilibrium William J. Deutsch
11:30	-	12:00 noon	Questions/Review William J. Deutsch
12:00	-	1:00 p.m.	Lunch (ON YOUR OWN)
1:00 p.m.	-	2:00 p.m.	Oxidation and Reduction Reactions-I Patrick Longmire

2:00 p.m.	-	2:15 p.m.	Break
2:15 p.m.	-	3:15 p.m.	Oxidation and Reduction Reactions-II Patrick Longmire
3:15 p.m.	-	3:30 p.m.	Break
3:30 p.m.	-	5:00 p.m.	Introduction to Organic Chemistry I - Structure and Nomenclature Richard F. Meyerhein
5:00 p.m.			Course adjourns for the day
DAY 2			
8:00 a.m.	-	9:00 a.m.	Carbonate System William J. Deutsch
9:00 a.m.	-	9:15 a.m.	Break
9:15 a.m.	-	10:45 a.m.	Adsorption of Solutes Patrick Longmire
10:45	-	11:00 a.m.	Break
11:00 a.m.	-	12:00 noon	Chemical Evolution of Ground Water William J. Deutsch
12:00 noon	-	1:00 p.m.	Lunch (ON YOUR OWN)
1:00 p.m.	-	2:00 p.m.	Introduction to Organic Chemistry-II Richard F. Meyerhein
2:00 p.m.	-	2:15 p.m.	Break
2:15 p.m.	-	3:15 p.m.	Introduction to Organic Chemistry-II Richard F. Meyerhein
3:15 p.m.	-	3:30 p.m.	Break

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3:30 p.m.	-	5:00 p.m.	Organic Geochemistry of Ground Water Patrick Longmire
5:00 p.m.			Course adjourns for the day
DAY 3			
8:00 a.m.	-	9:00 a.m.	Geochemical Reaction Modeling William J. Deutsch
9:00 a.m.	-	9:15 a.m.	Break
9:15 a.m.	-	10:15 a.m.	Evaluation of Laboratory Analytical Data Richard F. Meyerhein
10:15 a.m.	-	10:30 a.m.	Break
10:30 a.m.	-	11:30 a.m.	Evaluation of Laboratory Analytical Data Richard F. Meyerhein
11:30 a.m.	-	12:00 noon	Review/Discussion
12:00 noon	-	1:00 p.m.	Lunch (ON YOUR OWN)
1:00 p.m.	-	2:00 p.m.	Inorganic Problem Session William J. Deutsch and Patrick Longmire
2:00 p.m.	-	2:15 p.m.	Break
2:15 p.m.	-	3:15 p.m.	Discussion of Problem Session William J. Deutsch, Patrick Longmire, and Richard F. Meyerhein
3:15 p.m.	-	3:30 p.m.	Break
3:30 p.m. •	-	5:00 p.m.	Geochemical Processes Influencing the Fate of Organic Solutes in Ground Water Patrick Longmire

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5:00 p.m.			Course adjourns for the day
DAY 4			
8:00 a.m.	-	9:00 a.m.	Degradation of Organic Solutes Richard F. Meyerhein
9:00 a.m.	-	9:15 a.m.	Break
9:15 a.m.	-	10:15 a.m.	Degradation of Organic Solutes Richard F. Meyerhein
10:15 a.m.	-	10:30 a.m.	Break
10:30 a.m.	-	12:00 noon	Geochemistry of Several Contaminant Sources Patrick Longmire
12:00 noon	-	1:00 p.m.	Lunch (ON YOUR OWN)
1:00 p.m.	-	2:15 p.m.	Organic Problem Session William J. Deutsch, Patrick Longmire, and Richard F. Meyerhein
2:15 p.m	-	2:30 p.m.	Break
2:30 p.m.	-	3:30 p.m.	Aquifer Restoration William J. Deutsch
3:30 p.m.	-	4:00 p.m.	Open Discussion
4:00 p.m.			COURSE ADJOURNS

1-4

## **BIOGRAPHICAL SKETCHES**

**WILLIAM J. DEUTSCH** is a senior hydrogeochemist at Woodward-Clyde Consultants. He earned a B.S. and an M.S. degree in geological sciences at the University of Washington, Seattle. He has worked thirteen years in his technical specialty, which is low temperature aqueous geochemistry applied to water/rock interactions, ground- water contamination, and aquifer protection/restoration. He has planned, directed and participated in numerous laboratory and field hydrogeology programs dealing with site characterization, aquifer chemical simulation, geochemical modeling, and ground- water restoration. He has been involved with this course since its inception and teaches another NGWA course titled "Geochemical Modeling of Ground Water."

**DR. PATRICK LONGMIRE** is a hydrogeochemist at Los Alamos National Laboratory where he conducts applied research in the areas of geochemistry and contaminant transport. He holds a B.S., M.S., and Ph.D. in geology, with emphasis in aqueous geochemistry from the University of New Mexico. His expertise includes organic-metal interaction, geochemical equilibrium modeling and geochemical aspects of contaminant transport. Dr. Longmire is a Certified Ground Water Professional, and served on the editorial board of the Journal of *Ground Water*. Longmire has fifteen years experience dealing with geochemical aspects of ground water contamination resulting from petroleum products, uranium mill tailings, and landfills. Longmire has authored and co-authored numerous papers on ground water chemistry and given many oral presentations. He has developed and supervised laboratory and field hydrochemical programs for the University of New Mexico and Roy F. Weston, Inc. He has been involved with this course since its inception and teaches another NGWA course titled "Geochemical Modeling of Ground Water."

**RICHARD F. MEYERHEIN** has been involved in environmental chemical analyses for more than 15 years. He received his B.S. and M.S. in Chemistry from the University of New Mexico. Since 1970, he has been a supervisor in the chemistry bureau of the New Mexico Scientific Laboratory Division. Meyerhein has supervised the development of several new analytical programs for the State of New Mexico including breath and blood alcohol testing, toxicology for the state medical investigator and environmental organic chemistry. He has considerable instrumental expertise with gas and liquid chromatography and mass spectrometry. Meyerhein has instructed in numerous courses and workshops for state employees in the collection, preservation and submission of environmental samples for organic analysis, and in the interpretation of results. He has been involved with this course since its inception.

## Section 2

# Introduction to Hydrogeochemistry

Lecture by: Patrick Longmire Los Alamos National Laboratory

## SECTION CONTENTS

- Ji

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Canadian/American Conference on Hydrogeology, NWWA, June 1984, pp. 225-236
Wastewaters in the Vadose Zone of Arid Regions: Geochemical Interactions, by D.D. Runnells, <i>Ground Water</i> , November-December 1976, pp. 374-3852-19
Chemical Equilibrium and Kinetics of Geochemical Processes in Ground Water Studies, by Donald Langmuir and John Mahoney, <i>Proceedings of the First Canadian/American</i> <i>Conference on Hydrogeology</i> , NWWA, June 1984, pp. 69-952-31
Sampling and Analysis of Subsurface Water, by R.W. Hull, Y.K. Kharaka, A.S. Maest and T.L. Fries, <i>Proceedings of the</i> <i>First Canadian/American Conference on Hydrogeology</i> , June 1984, pp. 117-1262-59
Environmental Isotopies: Principles and Application in Ground Water Geochemical Studies in Alberta, Canada, by E.I. Wallick, H.R. Krouse and A. Shakur, <i>Proceedings of the</i> <i>First Canadian/American Conference on Hydrogeology,</i> June 1984, pp. 249-266
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ADDITIONAL REFERENCES:

Barcelona, M.J., 1988. Uncertainties in Ground Water Chemistry and Sampling Procedures, Chapter 24, ACS Symposium Series 416: Chemical Modeling of Aqueous Systems II, pp. 310-320.

### **OVERVIEW OF HYDROGEOCHEMISTRY**

### I. INTRODUCTION

- A. Purpose and Scope
- B. Hydrologic Cycle
- C. Hydrology
- D. Ground Water
- E. Chemical Terms in Hydrology
- F. Concept of Equilibrium -- Non-equilibrium

### II. GEOCHEMICAL PROCESSES

- A. Ion Speciation/Complexation
- B. Acid/Base and Precipitation/Dissolution Reactions
- C. Kinetics
- D. Oxidation and Reduction Reactions
- E. Adsorption Processes
  - 1. Inorganic solutes
  - 2. Organic solutes

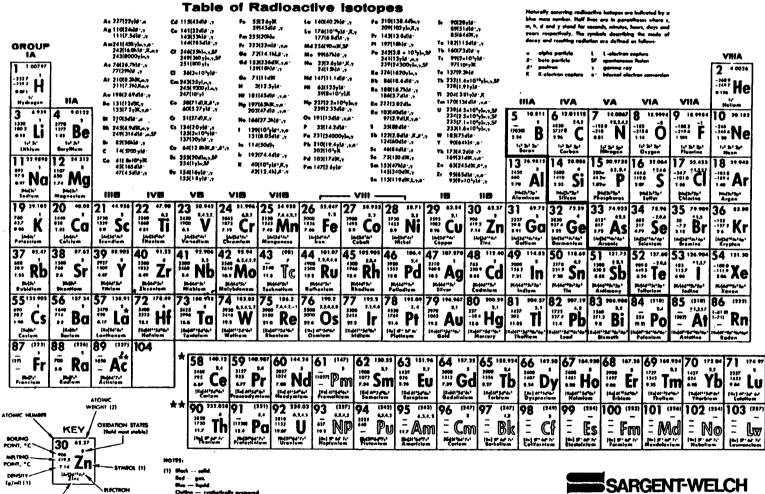
### III. GEOCHEMICAL MODELING

- A. Conceptual Model Development
- B. Types of Geochemical Models
- C. Limitations of Geochemical Models

### IV. SAMPLING AND ANALYTICAL TECHNIQUES

- A. Collecting Representative Ground Water Samples for Inorganic and Organic Analysis
- V. GEOCHEMICAL ASPECTS OF CONTAMINANT
  - A. Inorganic Solutes
  - B. Organic Solutes
- VI. GEOCHEMICAL ASPECTS OF AQUIFER RESTORATION

## PERIODIC TABLE OF THE ELEMENTS



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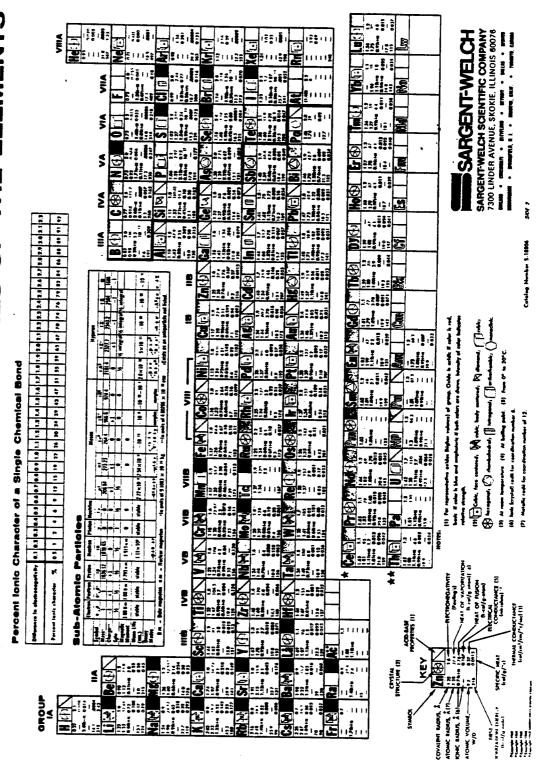
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PERIODIC PROPERTIES OF THE ELEMENTS ШО TABLE



Proceedings of First Canadian/American Conference on Hydrogeology, June 1984, p. 225-236

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## Graphical and Statistical Treatment of Standard Formation Water Analyses

### by Brian Hitchon

### Abstract

The main objective of all graphical and statistical techniques for evaluating formation water analyses is to obtain information which is not readily apparent from the analyses. The specific treatment technique depends, to a great extent, on the nature of the required information and the size of the data base. For standard formation water analyses resulting from petroleum exploration culling criteria are necessary to remove erroneous analyses, one method being the use of log-normal cumulative frequency plots of selected ions. Simple graphic procedures, of which many are available, are of limited use with large data bases or for comparing formation waters with considerable differ-ences in salinity.

Four multivariate statistical methods are applied to the same data set and comparisons made between the results obtained. Factor analysis is probably the most powerful, and intrinsically provides the most information, allowing the identification of populations by Qmode analysis and of fundamental geochemical relations by R-mode analysis. Both discriminant analysis and cluster analysis can be used to identify populations, the advantage of the former being the determination of the major discriminators in pre-selected provisional populations and of the latter the statistical selection of populations without a priori knowledge. Because many geochemical data are lognormally distributed, and extreme outliers may exert undue influence in discriminant (and especially cluster) analysis, multi-response permutation procedures (MRPP) are particularly important in confirming the efficacy of the discriminant analysis because there is no underlying distributional assumption about the data set.

Future directions in statistical applications to formation water analyses include linking multivariate statistical techniques to the results of solution-mineral relation studies, trend surface maps of a combination of statistical/solution-mineral results, and steady-state and transient models of heat-chemical-mass transport.

### Introduction

The main objective of all graphical and statistical techniques for evaluating formation water analyses is to obtain information which is not readily apparent from the analyses. The specific treatment technique depends, to a great extent, on the nature of the required information and the size of the data base. This paper is directed specifically at the evaluation of standard formation water analyses resulting from petroleum exploration. Most of the water samples were collected from drill stem tests, or surface facilities such as well heads, treaters and separators. Many of the samples do not represent true formation water but are contaminated to a greater or lesser extent. This applies particularly to drill stem test samples which may contain varying amounts of mud filtrate. In addition to these limitations, generally only the common ions, calcium, magnesium, chloride, sulfate, bicarbonate and carbonate are determined, with sodium being calculated stoichiometrically as the difference between the sum of the anions and the sum of the cations. Despite the limitations of the collection, preservation, and analysis of this standard formation water, there are a number of ways in which information from them can be applied during exploration; for example, determination of R<sub>w</sub>, the correction of hydraulic heads for variations in water density, and the identification of the specific source of the water should multiple aguifers produce into the well bore. It is clear, however, that these standard formation water analyses are of limited use in detailed studies of water-rock interaction, where precise collection and sample preservation techniques are essential.

The various graphical and statistical ways of treating standard formation water analyses are illustrated using a common data base of 78 formation waters from oil fields and gas fields of Alberta (Hitchon and Friedman 1969; Hitchon et al. 1971). These formation waters are volumetrically representative of pore water in the western Canada sedimentary basin and range in salinity from brines to fresh water. The evaluation methods are therefore of interest to those engaged in petroleum exploration, as well as ground water studies.

### **Culling Criteria**

Before any data manipulation is attempted, the initial task is to cull analyses which are not representative of the formation water in the underground environment. Samples of questionable quality include those from holding tanks or produced by bailing. As a general rule, samples recovered in the fluid column close to the tested interval are less likely to be contaminated by drilling fluid. Although poor collection procedures and inadequate sample preservation are criteria which would normally justify culling, pertinent information is commonly not available. When an equivocal analytical procedure is known this also would justify removal of the sample from the data base. Samples may also be contaminated due to water injection into the reservoir (which can be evaluated with knowledge of the reservoir history), drilling fluid, mud filtrates, acid washes, KCI muds, or washes from cement jobs. Incomplete analyses and a poor ionic balance are additional reasons for culling formation water analyses, although the latter is not a valid criterion where sodium has been determined by difference.

Once the most obviously erroneous analyses have been removed, the remaining analyses may be examined by cumulative log frequency plots, contour maps and trend surface maps. Because many geochemical data approximate a lognormal distribution, it is possible to use cumulative frequency plots of the logarithm of selected ions as a culling criterion. The most geochemically conservative ion reported in standard formation water analyses is chloride, and accordingly is the best one for constructing cumulative log frequency plots. The upper diagram in Figure 1 shows a typical plot before removal of the "tails," following examination of the individual analyses at the less than 10 percent and greater than 90 percent frequency intervals. The resulting culled plot is shown in the lower diagram in Figure 1. Several iterations may be necessary to produce a satisfactory cumulative frequency profile. Experience shows that the majority of water analyses removed by this technique were subject to either evaporation in holding tanks or contamination by drilling mud.

Contour maps of selected ions from the data base after initial culling can then be plotted to identify the remaining anomalous samples. The most useful ions at this stage are chloride and sulfate. More rigorous culling of the remaining anomalous samples can be achieved using trend surface maps. Often as little as 20 percent of the original data remain after these cull-

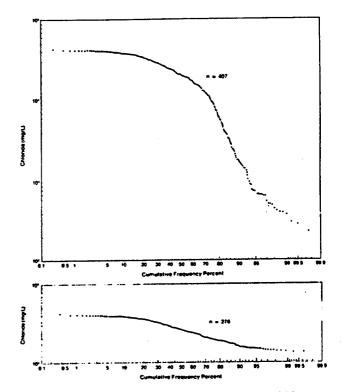


Figure 1. Cumulative frequency plots of log CI in formation water from the Lower Cretaceous Viking Formation, Cold Lake area, Alberta, Canada. Upper diagram: original data base; lower diagram: after removal of the "tails" following examination of the individual analyses.

ing procedures. Considerable confidence may be placed in regional compositional trends from the final data base, especially when regional patterns and composition gradients correspond closely with those of hydraulic-head distribution where these data have also been treated by cumulative frequency plot techniques. Figure 2 shows an example of the close correspondence of total dissolved solids (calculated, mg/L) and hydraulic-head distribution (meters) for formation water from the Wabamun-Winterburn-Grosmont Aquifer in the Peace River area, Alberta. It should be noted that this close correspondence of trends and gradients between formation water composition and hydraulichead distribution is implicit in the nature of fluid flow in sedimentary basins.

### **Simple Graphical Procedures**

Many simple graphical methods have been proposed for the classification of formation water. Most make use of only the major ions and have limited utility with large data bases. In addition to these limitations most simple graphical methods are inadequate for the representation of large concentration differences between formation waters. Although none of the proposed simple graphical methods takes account of solution-mineral reactions that control the composition of formation water, it is not difficult to visualize how such simple graphical methods could be developed.

Table 1 shows the chemical composition, stable

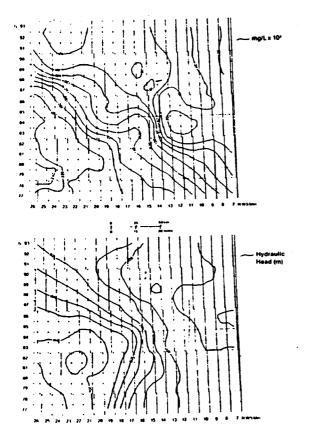


Figure 2. Comparison of regional composition trends of total dissolved solids (calculated, mg/L) (upper diagram) and hydraulic-head distribution (m) (lower diagram) for formation water from the Wabamun-Winterburn-Grosmont Aquifer, Peace River area, Alberta, Canada.

isotopes, physical properties and production data for three formation waters from the western Canada sedimentary basin (Hitchon and Friedman 1969, Table 4; Hitchon et al. 1971, Table 2). These formation waters represent compositions from fresh water to brine. They have been used in Figures 3 to 5 (fresh water to brine, respectively) to illustrate six simple graphical methods. Note that because these simple graphical methods poorly illustrate differences between formation water with large concentration differences, it was necessary to plot each analysis separately (hence the change in scales between Figures 3 and 5 for each of the graphical methods represented). Graphical comparison between formation water with large concentration differences can be achieved, however, if logarithmic (Figure 6) or frequency percent (Figure 7) scales are used. Clearly, with a little imagination, minor element, trace element, or even stable isotope and physical properties may be illustrated by simple graphical methods.

### Statistical Treatment of Large Data Bases Dummy Values and Data Transformation Techniques

With large data bases and many analytical determinations per sample, relatively complex statistical methods are required to evaluate formation water analyses. A persistent problem in statistical analysis is the lack of complete sets of variables for all samples studied. Among the reasons for incomplete sets of variables are undetermined variables in some samples and variables below detection limits. The latter reason is especially pertinent for geochemical data. To the writer's knowledge, no rigid criteria exist that can be

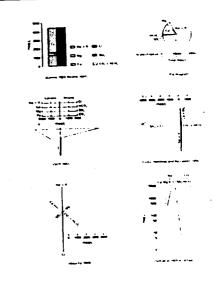
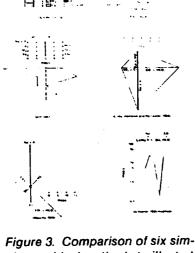


Figure 5. Comparison of six simple graphical methods to illustrate the composition of analysis W90-RCA-1165 (Table 1: total dissolved solids 256,470 mg/L). See Hem (1970) for description of construction methods for individual diagrams.



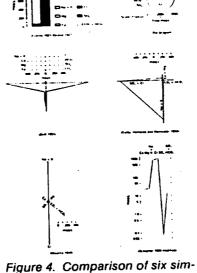


Figure 3. Comparison of six simple graphical methods to illustrate the composition of analysis W87-RCA-1065 (Table 1: total dissolved solids 2,336 mg/L). See Hem (1970) for description of construction methods for individual diagrams. Figure 4. Comparison of six simple graphical methods to illustrate the composition of analysis W29-RCA-865 (Table 1: total dissolved solids 57,080 mg/L). See Hem (1970) for description of construction methods for individual diagrams.

Analysis number	W87-RCA-1	1065	W29-RCA-	365	W90-RCA-1	165	
Stratigraphic unit	Rundle Gp.		Viking Fm.	Viking Fm.		Leduc Fm.	
Location	11-4-1-9-W4		3-33-48-21-	3-33-48-21-W4		W5	
Depth (m)	858.0-885.4		1012.9-1013.2		2047.6-2093.4		
Source	Free water knockout		Well head (	Well head (tubing)		Well head (tubing)	
Well status	Gas well		Oil well		Oil well		
Temperature (C)	34		39		68		
Pressure (MPa)	6.58		5.00		21.86		
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	
Li	0.8	0.115	3.6	0.518	40	5.764	
Na	510	22.185	21,000	913.5	65,000	2827.5	
к	70	1.789	82	2.096	2,580	65.970	
Rb	0.1	0.001	0.1	0.001	6.8	0.079	
Ca	96	4.790	469	23.403	25,200	1257.48	
Mg	58	4.771	304	25.007	3,380	278.038	
Sr	6.1	0.139	141	3.219	820	18.720	
Fe	0.57	0.020	20	0.716	0.89	0.032	
Mn	0.2	0.007	0.3	0.011	1.4	0.051	
Cu	0.09	0.003	0.12	0.004	0.5	0.001	
Zn	0.07	0.002	0.4	0.012	0.11	0.003	
в	1		_		47		
CI	320	9.027	34,300	967.603	158,000	4457.18	
Br	tr.	tr.	179	2.239	516	6.455	
I	٠		36	0.283	12	0.094	
$CO_3$	189	6.299	319	10.632	. •	-	
HCO3	1,070	17.537	176	2.884	:: 138	2.261	
SO4	9	0.187	4	0.083		10.659	
nions (anal. meq/L)	33.0		981.1		4,469.5		
Cations (anal. meq/L)	33.8		971.0		4,460.0	-	
DS (cal.)	2,336		57,080		256,470		
D (%SMOW)	- 13.2		-9.7		-5.3		
<sup>18</sup> 0 (‰SMOW)	- 15.9		-6.4		-0.3		
H (laboratory)	7.54		7.10		6.36		
Density (60 F; 15.56 C)	1.0021		1.0414		1.171	9	
Resistivity (ohm/m, 25 C)	3.62		0.139			0.0415	
Refractive index (25 C) 1.3			1.3413	1.3759			

## Table 1Chemical Composition, Stable Isotopes, Physical Properties and Production Data for FormationWater Used to Illustrate Graphical Methods of Plotting Analyses

tr. = trace; \* = below detection; - = not determined

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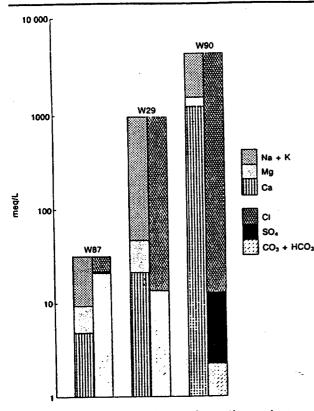


Figure 6. Comparison of three formation waters (Table 1: fresh water to brine) using log meq/L scale.

followed respecting the substitution of dummy values to fill "data holes," and much depends on the experience of the operator.

In the past, the writer has either limited statistical analysis to complete data sets where a large number of formation water samples was available (Hitchon and Horn 1974) or arbitrarily substituted a value of one-tenth the detection limit where the number of formation water samples was more limited and where less than 10 percent of the samples for any variable required the substitution of a dummy value (Hitchon et al. 1971). Another way to approach the problem of dummy values is to produce an isoconcentration map for the pertinent component and select the best value at the data hole based on concentration gradients. This technique was used by Hitchon and Filby (1984) in their study of the use of trace elements for the classification of crude oils into families. Another technique that has not been used, as far as the writer is aware, is the use of solution-mineral criteria to determine dummy values. For example, quartz is commonly at saturation in formation water. The selection of a dummy value for silica in the formation water to correspond to quartz saturation at reservoir temperature is therefore an easy matter.

A basic assumption of many multivariate statistical techniques is that the variables are normally distributed. Because many geochemical data approximate a lognormal distribution, it is important that the variables be tested for normality using both the raw data and their logarithmic transforms. Other data transforma-

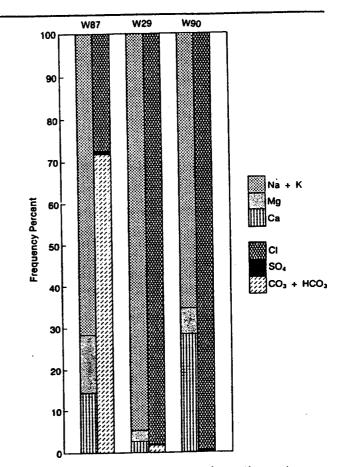


Figure 7. Comparison of three formation waters (Table 1: fresh water to brine) using frequency percent scale.

tion techniques include recalculation of the variables as a percentage of the maximum value, or as a percentage of the range. For variables of constant sum (for example, they sum 100 percent), and especially if one variable is dominant, an arc sin  $\sqrt{\text{variable transforma-}}$ tion is sometimes useful.

There are many possible interrelated physical and chemical controls that can affect the composition of formation water. This has led the writer to separate chemical, physical and isotopic data when carrying out multivariate statistical techniques.

Extreme "anomalous" values and outliers, which are common in some distributions of geochemical data, can have a profound effect on the covariant matrix commonly used as a starting point in multivariate statistics. Often the effect of these outliers is not ameliorated through the use of data transformation techniques. In this regard multi-response permutation procedures (MRPP) (to be described later in this paper) are particularly valuable because, unlike classical multivariate techniques, they do not rely on an underlying distributional assumption about the data set.

### **Factor Analysis**

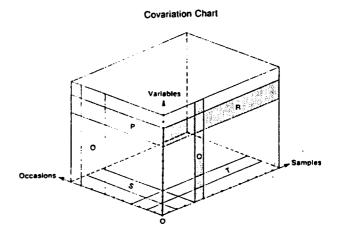
#### Theory

Of the many multivariate statistical methods that

# Table 2Summary of Predicted Group Membership for78 Formation Waters from Oil Fields and GasFields of Alberta, Canada

	• · · · · · · · · ·	Predicted group membership			
Assigned group	Number of samples	1	2	3A	3 <b>B</b>
1	12	100.0%	0.0%	0.0%	0.0%
2	12	0.0%	83.4%	8.3%	8.3%
3A	20	0.0%	5.0%	85.0%	10.0%
3B	, <b>3</b> 4	0.0%	0.0%	0.0%	100.0%

are available perhaps none is more powerful or controversial than factor analysis. Part of the mystery and controversy surrounding factor analysis techniques is the rich and intricate jargon that arose in the 1930s and 1940s through the work of experimental psychologists. These early workers divided factor analysis into several fundamental types (Figure 8) of which the most useful, for geochemical purposes, are Q-mode and R-mode methods. Q-mode factor analysis consists of a comparison of the samples in terms of the variables. This technique essentially evaluates the homogeneity of the sample or population being studied. R-mode factor analysis comprises a comparison of the relations among the variables in terms of the samples and requires a homogeneous population to be meaningful. Both start with a cross correlation matrix interrelating all the variables of the system. Mathematical manipulation (albeit a rather complex one) of the multivariate data set results in the creation of a new set of variables, which always contains more information in fewer variables than the original data set. These new variables (or factors) are derived by the extraction of the eigenvalues and eigenvectors from the correlation matrix. It is an inevitable characteristic of this procedure that at least one of these factors will be more efficient in terms of accounting for total variation than any of the original variables. It is usually observed that the first two or three factors will explain the vast majority of the variation of the data set and for this reason, factor analysis is effectively a multivariate data reduction technique. It is important to remember that factor analysis only demonstrates the relations, it does not explain them. The explanation of the factors must be in the context of known information about the variables. By the very definition of the mathematical procedure performed on the original data, it will be recalled that factors are totally independent of one another. The coefficients that the factors are given are called the factor loadings. They are the coefficients in the linear equation that the eigenvector defines and are used to compute a very important value for each sample, called the factor score. Therefore, plotting the factor scores of one factor against any other factor yields a totally uncorrelated set of data. However,



## Figure 8. Covariation chart showing fundamental types of factor analysis (Cattell 1952, Figure 14).

when a plot of this type is made it is usually found that the data have a tendency to cluster into various regions of the graph. These clusters can be rich in information and often reveal hidden subtleties.

Before considering an example of factor analysis it should be noted that three types of solution are available. The principal components solution derives orthogonal reference factor axes located in n-dimensional space such that the total amount of information, or variance, contained in the data is systematically extracted. The first factor axis explains the most variance; the second maximizes the remaining variance, and so on. In the varimax solution, orthogonal factor axes are located such that the variance of each factor is maximized. This "rotation" of orthogonal axes results in a more equitable distribution of factor loadings than that produced by the principal components method. Oblique factor solutions differ significantly from the first two methods in that the reference factor axes are not constrained to be orthogonal. A variety of analytical criteria are available to locate the exact positions of the reference axes; biguartimin, binormamin and promax are examples of these varieties. Oblique solutions are appropriate where underlying causal factors are suspected to be correlated among themselves; this is often the case in geochemical studies.

### Example

The work of Hitchon et al. (1971) will be cited as an example of the application of factor analysis to the study of formation water. These authors reported 20 major and minor chemical components for 78 formation waters from oil fields and gas fields in Alberta, Canada. They ranged in salinity from fresh water to brines, and came from stratigraphic units between the Upper Cretaceous and Middle Devonian. Initial examination indicated that all components were essentially lognormally distributed, and consequently the logarithm (base e) of the concentration of each component was used to form the correlation matrix. The first task was to determine if a very diverse data set represents a single population. Accordingly, a Q-mode factor analysis was carried out. It was found that three factors accounted for more than 98 percent of the information in the samples. When varimax factor components for these three factors were normalized and the data points plotted on a ternary diagram (Figure 9), nearly all samples fell in a narrow band along one side of the diagram, between Factor 1 and Factor 2. At first this suggested that the data set represented two populations, but when sample points on the same flow path were joined together the data set was relatively homogeneous and represented a single source (sea water) which was being subjected to two major processes. Factor 1 represented a concentration process and Factor 2, dilution by fresh water recharge. Other processes, for example that represented by Factor 3, were relatively minor. An R-mode analysis of these data was therefore justified, and in fact confirmed the single source hypothesis and identified the two major processes.

An R-mode factor analysis, using a varimax solution, was carried out on the logarithmic transforms of the same data used for the Q-mode. Tests showed that an oblique solution was justified, and when the same data were factored using the biguartimin solution the resulting factor matrix showed that much of the "noise" present in the varimax factor matrix had been removed. A matrix of correlations between the eight factors extracted indicated that they were virtually uncorrelated, with no correlation coefficient exceeding 0.25. The factors from the oblique solution may be illustrated (Figure 10) in a similar manner to that used by Spencer (1966), where rectangular boxes represent the factors and the center line of each box is a zero loading for the variable. Positive loadings occur above the center line and negative loadings below. The further a variable is from the center line the higher is its loading.

Examination of the biguartimin factor matrix indicated that many of the physical and chemical controls that are generally believed to be operative in mineralsolution reactions were not revealed by the factors extracted. This resulted from the fact that the mechanism causing concentration of the formation water was the dominant process but the increased concentration masked some of these other processes. Accordingly, an R-mode factor analysis was carried out with the salinity (total dissolved solids) partialled out by the process of running a partial correlation matrix and adjusting the analytical values accordingly. Both varimax and biguartimin factor solutions (with salinity partialled out) were carried out, but only the latter is shown here (Figure 11). The factor results showed that although some ions, such as copper and zinc, occur independently of all other components, the majority of ions exhibited direct or inverse relations, to a major or minor extent, with at least one other ion. This strong interdependence of most of the ions precluded factoring the physical properties and basic chemical data set together if the most simplistic result were desired. However, the factor scores, which represent a reduced set of new uncorrelated variables that

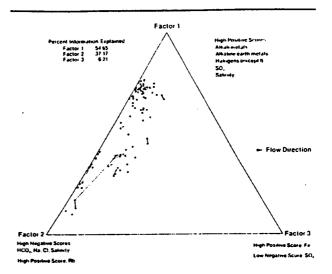


Figure 9. Ternary diagram of normalized varimax factor components for Q-mode on 78 formation waters from oil fields and gas fields of Alberta, Canada. Arrows indicate flow directions based on hydrodynamic studies (Hitchon 1969a, b).

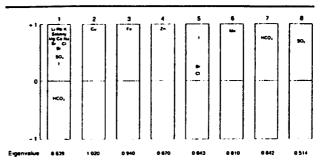


Figure 10. Diagrammatic representation of factors from R-mode biquartimin oblique solution of chemical data and salinity for 78 formation waters from oil fields and gas fields of Alberta, Canada.

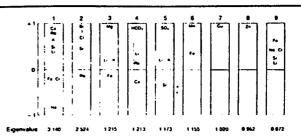


Figure 11. Diagrammatic representation of factors from R-mode biquartimin solution of chemical data, with salinity partialled out, for 78 formation waters from oil fields and gas fields of Alberta, Canada.

have essentially the same information content as the original variables can be used, together with the physical properties, in a second-order R-mode analysis.

The result of all of these factor analyses, together with information on the volume-weighted mean composition of formation water in the western Canada sedimentary basin, was the identification of the main processes controlling chemical composition of formation water in western Canada. Based on a sea water origin these included dilution by fresh water recharge, membrane filtration, solution of halite, the effects of dolomitization, bacterial reduction of sulfate, the formation of chlorite, cation exchange on clays, a contribution from organic matter, and solubility relations for carbonates and sulfates.

Because (1) factors can be considered as properties of the samples-properties which combine the complex inter-relations between the variables in the samples- and, (2) factor scores represent the "amounts" of the factors present in each sample, therefore, plotting of the factor scores in a variety of ways often yields information about the samples that would not otherwise be evident. For example, a scatter diagram illustrating the relation of formation temperature and the factor score for the cation exchange factor (Hitchon et al. 1971, Figure 5) shows increasing factor score with formation temperature; this observation is consistent with the fact that cation exchange proceeds more readily with increasing temperature. Similar conclusions could be reached by plotting maps of the factor score for the cation exchange factor by individual stratigraphic units. When variables appear with significant loadings on several factors (which indicates that their content is controlled by several processes) the relations among the variables may often be seen best by means of a three-dimensional model. This technique is illustrated in Figure 12, for the alkali and alkaline earth metals from Factors 1, 3 and 4 from the R-mode biquartimin factor solution with salinity partialled out (Figure 11). The three plots of the individual variables represent the projections of the positions of these variables onto specific twofactor planes. Each plot may be considered as a sort of two-dimensional window looking into the nine-dimensional space described by the R-mode matrix. Those variables most strongly influenced by the factors plot near the edges of the diagrams whereas those least influenced will occur toward the center. When these projections are combined into the three-dimensional model the true relations of the variables may be seen, and this is the best that can be done in our threedimensional space to illustrate the relations in the nine-dimensional space which best describes the data. Figure 12 is used for illustrative purposes and is not interpreted in this paper.

Similarly constructed diagrams can be interpreted, however; for example, Hitchon and Gawlak (1972) in their study of low molecular weight aromatic hydrocarbons in gas condensates from Alberta showed that although the relative positions of benzene, toluene, xylenes and trimethylbenzenes on one hyperplane are in the same relative proportions as their free energies of formation, they are not in thermodynamic equilibrium, and the positions could be interpreted as proportional to their solubilities.

There is no mystical power in factor analysis. It is simply a mathematical manipulation that can be performed on a set of data. Given good analytical data, and assuming the proper choice of variables, it is the writer's opinion that factor analysis is the most powerful tool for extracting the most information from a data

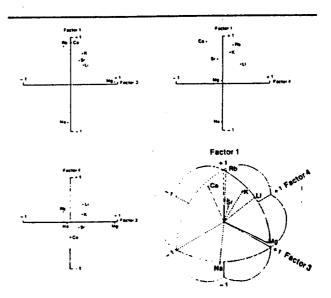


Figure 12. Plots of Factors 1, 3 and 4, used to construct a three-dimensional model showing the relations of the alkaline and alkaline earth metals in these factors.

set.

### **Cluster Analysis**

### Theory

In many geochemical studies it is desirable to group together similar samples on which many measurements have been made, and to measure the degree of similarity among the groups. Although this can be done by Q-mode factor analysis, other techniques are available. Psychologists have developed cluster analysis, which is a simple form of correlation analysis, and is a method of searching for relationships in a large symmetrical matrix. Unlike factor analysis, it does not involve reducing the information to factors, but is a straightforward, logical, pair-by-pair comparison between samples, objects or variables. The results of a cluster analysis are presented in an easily understood two-dimensional hierarchical diagram on which the "natural breaks" between groups are obvious. As with factor analysis, there is a Q-type cluster analysis in which the samples are compared, and an R-type analysis where the variables are compared. In Q-type cluster analysis the results are similar to the Q-mode factor analysis only if the variables are uncorrelated or orthogonal; the presence of several highly correlated variables can bias the results of a Q-type cluster analysis. Uncorrelated or orthogonal variables are not met very often with geochemical data and this puts some severe limitations on the value of Q-type cluster analysis. In R-type cluster analysis results are also similar to R-mode factor analysis; in cluster analysis, however, each variable as a unit is placed in a cluster, whereas in factor analysis different portions of a variable may be assigned to different factors. One feature of cluster analysis is that the raw-data matrix is normalized. column by column, in order to give equal weight to each of the variables. This results in a simple distance function which ranges from 0.0 (shortest distance equals closest similarity) to +1.0 (longest distance equals greatest dissimilarity). This function is eminently suitable for cluster analysis, but is not directly amenable to factor analysis without data transformation.

### Example

Q-type cluster analysis was carried out on the 78 samples of formation water reported by Hitchon et al. (1971); this is the same set of samples for which the factor analyses were reported previously in this paper. Four cluster groups were identified (Figure 13) of which two (3A and 3B) appear to be closely related. If the cluster group to which each sample has been assigned by the Q-type cluster analysis is indicated on the ternary diagram of normalized varimax factor components for the Q-mode factor analysis of the same data (Figure 14), some interesting similarities and differences between cluster analysis and factor analysis can be demonstrated.

Samples assigned to Cluster Group 1 are clearly associated with high components of Factor 2. All Cluster Group 2 samples have significant amounts of Factor 3, as do about one-third of the 3B samples. There appears to be considerable intermixing of samples assigned to Cluster Groups 3A and 3B in the ternary diagram. The relation between formation water composition and flow direction cannot be determined from the information in Figure 13; for example, the formation water composition changes from one cluster group to another, and back again, along the same flow path. Probably more significant, however, is the fact that the cluster dendrogram provides no information on the composition of the formation water in each cluster group, and hence without a Q-mode factor analysis, it would not have been possible to advance the hypothesis of a single sea water source.

#### **Discriminant Analysis**

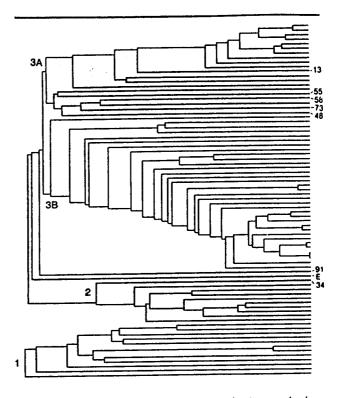
#### Theory

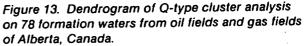
This statistical technique is designed to identify those variables which can distinguish (discriminate) a *priori* groups of samples. The value of discriminant analysis over univariate methods, such as analysis of variance, lies in its ability to treat variables which are correlated. Briefly, the technique consists of calculating equations by using various combinations of variables so that differences between the groups are maximized. In stepwise discriminant analysis the variables are entered into the equations one-by-one, until insignificant discriminating power is gained by adding another variable.

### Example

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In the case of the data from Hitchon et al. (1971) cluster analysis has already suggested that the samples may be divided into four groups. Stepwise discriminant analysis was carried out on the same data set, using logarithmic transforms of the raw data,





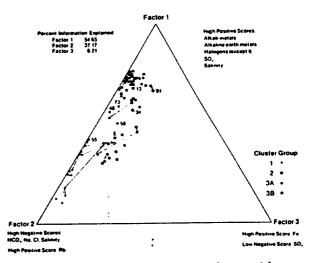


Figure 14. Plot of cluster group assignment from Q-type cluster analysis on ternary diagram of normalized varimax factor components for Q-mode on 78 formation waters from oil fields and gas fields of Alberta, Canada. Arrows indicate flow directions based on hydrodynamic studies (Hitchon 1969a, b).

because like factor analysis discriminant analysis requires that the variables in each group be normally distributed. Of the same 17 variables used in the factor and cluster analysis, it was found that only rubidium, strontium, potassium, sulfate, calcium and iodine were significant discriminators (given in order of their entry into the equations). The results are summarized in Table 2; for the 78 formation waters originally classified by groups on the basis of the cluster analysis, 93.6 percent were correctly classified on the basis of the six significant discriminators. Eigenvalue analysis of the effective dimensionality of the group centroids results in eigenvalues of 5.815, 4.635 and 0.757, with 93.2 percent of the variance associated with the first two eigenvalues and the balance with the third. This means that effectively all the total variability among the group centroids can be represented by an X-Y plot. Using calculated standardized canonical discriminant function coefficients, each group centroid and sample can be plotted (Figure 15).

Five of the samples were misclassified, and three were correctly classified but at less than 90 percent probability of belonging to the assigned group. These eight samples are indicated on Figures 13,14 and 15. There is no systematic reason for their distribution on the Q-mode ternary diagram (Figure 14), as might be expected from the nature of the mathematical manipulations used to produce that diagram. Two of the misclassified samples (91 and E) were originally assigned to Group 2 on the basis of the cluster dendrogram (Figure 13), but it is clear from the nature of that diagram that this was only for the expediency of carrying out the stepwise discriminant analysis. Sample 34 was the least related to Cluster Group 2, being assigned 85 percent probability of belonging to that group and 15 percent probability of belonging to Group 3A. This sample came from the Lower Cretaceous Mannville Group at Chauvin in east central Alberta. Although there have been no hydrodynamic studies in the Chauvin area, recent numerical modeling in the Cold Lake region, to the north, indicates that there is a small flow component upward across the Upper Devonian Ireton Formation into the Lower Mannville Group; this situation might also apply in the Chauvin area.

It is beyond the scope of this paper to supply further observations on the reason why some of the samples were misclassified or classified correctly but only at less than 90 percent probability of belonging to their assigned groups; there are clearly some problems with the Group 3A cluster because five of these samples fall within that group, three of which show mixed characteristics between Groups 3A and 3B.

### Multi-Response Permutation Procedures Theory

Multi-response permutation procedures (MRPP) are recently developed statistical techniques for the testing of a priori grouping of multidimensional data (Mielke et al. 1976). In contrast to the classical Hotelling's T<sup>2</sup> test and discriminant analysis, they are distribution-free methods, requiring no underlying assumptions of multivariate normality. The procedures are based on the Euclidean distance between objects in a multidimensional space and involve a computation of a test statistic which indicates the degree of clustering of the object in the *a priori* groups. These procedures also allow the inclusion of a residual group of objects.

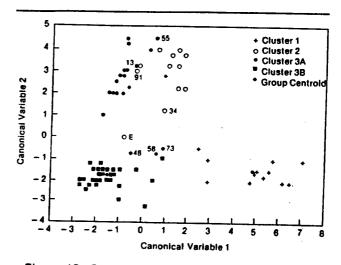


Figure 15. Canonical discrimination for 78 grouped lormation waters from oil fields and gas fields of Alberta, Canada.

The test involved is for the null hypothesis that the groupings are formed by a random allocation of objects. A low p-value (=probability of a test statistic  $\delta$  smaller than or equal to the one observed) indicates a strong tendency for within-group clustering and leads to the non-acceptance of the null hypothesis at a significance level  $\alpha$  ( $\alpha \ge$  p-value). This technique was first used with geochemical data by Hitchon and Filby (1984) to confirm the efficacy of a step-wise discriminant function analysis of trace metals in some Alberta crude oils.

### Example

Because the grouped formation waters each contain a small number of samples from which it was necessary for the discriminant analysis to derive conclusions as to their normal or lognormal distribution, it is clear that multi-response permutation procedures represent a powerful tool to test the a priori groupings used in the discriminant analysis. Using MRPP statistics, the groupings based on cluster and discriminant analysis were found to be highly significant. A separate MRPP analysis of Groups 3A and 3B indicated that these two groups are not as distinct as they might appear using cluster analysis; in fact, the significance level was only slightly better than 7 percent. Two borderline cases, Samples 91 and E, were also analyzed to determine the most suitable population to which each sample should belong. Sample 91 was found to be closest to Population 3A, and Sample E to be closest to Population 2; these observations are consistent with the results of the stepwise discriminant analysis.

### **Solution-Mineral Relations**

The 78 samples studied by means of factor, cluster, discriminant and MRPP methods represent a very diverse population, which was not collected with specific studies of solution-mineral relations in mind, inasmuch as aluminium and silica were not determined. The samples were analyzed using the computer program SOLMNEQ (Kharaka and Barnes 1973). With the exception of the two samples from the Granite Wash, all samples were saturated with respect to calcite and dolomite, and there was effectively no difference in the  $\Delta G_{diff}$  values between the cluster groups. For anhydrite and siderite, however, the range and average values of  $\Delta G_{diff}$  varied between the cluster groups (Figure 16).

Although all these formation waters show undersaturation with respect to anhydrite, there is a trend to increased undersaturation from Cluster Group 3A to Cluster Group 1. This trend is related to the fact that the formation water from Cluster Group 1 is fresh water in recharge areas, and that anhydrite is associated with some of the formation water in Cluster Groups 3A and 3B.

Most samples from Cluster Groups 1 and 2 are saturated with respect to siderite; this mineral is present as nodules in a number of the stratigraphic units from which this formation water originated. The wide range in values for siderite saturation in Cluster Groups 3A and 3B probably relates to the fact that formation water from these two groups comes from both Devonian and Cretaceous strata; formation water from Cretaceous strata is strongly represented in Cluster Groups 1 and 2.

It is beyond the scope of this paper to evaluate these relationships further, and it is sufficient to note that this information is presented as an example of one way in which information from solution-mineral relations can be linked to information from a multivariate statistical analysis of the same data.

#### **Future Directions and Conclusions**

From a discussion of simple graphical methods, this paper has progressed through four multivariate statistical techniques, to the linking of the results from these techniques with solution-mineral relations. Another approach, representing the maximum type of information generally attainable at the present, is the production of trend surface maps of a combination of statistical/solution-mineral results. Effort is being directed by several workers toward the production of heat-mass-chemical numerical models, most of which treat only steady-state conditions. Ultimately, it should prove possible to develop transient numerical models of solution-mineral reactions, that will provide the geochemist with a living picture of formation water geochemistry in the area of interest. Speculation beyond this development stage might include modeling the paleohydrodynamic and the paleohydrochemical history of a sedimentary basin, and linking this with the thermal and petroleum-generating capacity of the basin.

The essential conclusion to be drawn from this paper is that although various simple graphical and statistical techniques are available to the geochemist to assist in evaluation of formation water analyses, use of these methods does not abrogate one from the responsibility of insuring reliable sample collection,

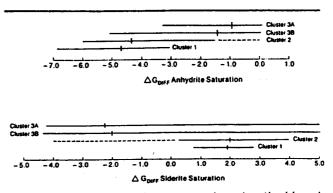


Figure 16. Range and average values (vertical bars) of  $\Delta G_{dill}$  for anhydrite and siderite saturation for each of the groups identified by cluster analysis. The dashed lines link up isolated extreme saturation points.

preservation and analytical techniques.

Ways of culling data bases of erroneous and unreliable formation water analyses have been noted, but it is the writer's experience that the resultant data bases have more generally limited utility than when formation water is collected and preserved in the field for the specific purpose of geochemical studies.

Of the four multivariate statistical techniques described in this paper, factor analysis, as a general rule, intrinsically provides the most information. Q-mode analysis allows determination of the number of populations, as well as the variables most strongly influencing those populations. R-mode analysis is a very powerful data reduction technique, and by means of threedimensional diagrams sometimes allows insight into the most fundamental properties of the data set being examined.

Once the data set has been divided into populations (based on cluster analysis, or other non-statistical criteria) discriminant analysis is the most powerful method to allow both determination of those variables which distinguish the populations and identification of misclassifield samples.

Because many geochemical data are lognormally distributed, and extreme outliers may exert undue influence in discriminant (and especially cluster) analysis, MRPP statistics are particularly important in confirming the efficacy of the discriminant analysis because there is no underlying distributional assumption about the data set.

In general, papers dealing with the statistical analysis of formation water seldom link the statistical results with solution-mineral relations of the systems under investigation. Much useful information would probably come from such linking.

Future directions in the statistical treatment of formation water analyses appear very exciting, and it is the writer's opinion that geochemists will have to broaden their perspective of geochemistry if maximum advantage is to be taken of the opportunities that will become available.

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## Wastewaters in the Vadose Zone of Arid Regions: Geochemical Interactions<sup>a</sup>

by Donald D. Runnells<sup>b</sup>

### ABSTRACT

Because of increasingly stringent laws governing discharge of fluid wastes to surface waters, the alternative of discharge to the subsurface has become attractive. The physical-chemical processes that prevail in the subsurface are not well understood, but they are clearly not identical to processes of purification in surface waters. For example, in the subsurface the process of oxidation may be of little value in significantly reducing the concentration of discharged contaminants; in contrast, oxidation plays an important role in purifying surface waters. Eleven physicalchemical processes can be identified as having potential value for purifying wastes discharged to the subsurface, as follow: dilution, buffering of pII, precipitation by reaction, hydrolysis, oxidation or reduction, filtration, volatilization, biological assimilation, radioactive decay, membrane filtration, and sorption.

Discharge to the vadose zone may be a safe means of disposal of wastes in arid regions. But it is necessary to carefully test the suitability of a particular site for a particular waste. Processes of purification in the vadose zone can be incorporated into a workable plan of discharge if adequate studies and safeguards are employed. Regulations governing subsurface discharge should take into account the physical-chemical processes that may act to purify the waste fluids. In one set of experiments, a soil from Sulfur Springs, New Mexico was capable of removing large quantities of dissolved molybdenum and copper from a synthetic mill water, and the soil was able to quantitatively retain the copper during subsequent leaching by fresh and metal-free mill waters. Such studies permit rational plans of discharge to be developed.

#### INTRODUCTION

Until fairly recent times we have generally assumed that ground water was well protected from contamination. And in many areas this seemed to

Discussion open until April 1, 1977.

be a fairly realistic view. Now, however, we know that the apparent purity of ground water was the result of our failure to look for pollution. With increasing pressures of population, and with incessant prodding from new regulations, water scientists have begun to fully recognize the widespread occurrences of contamination of ground water. Table 1 shows chemical components that have been demonstrated as being present in documented cases of contamination of ground water throughout the world (summarized from several sources, including Furiman and Barton, 1971; Scalf and others, 1973; Miller and others, 1974: Cole, 1974; van der Leeden and others, 1975). Each of these cases demonstrates that the protective capacity of subsurface materials is finite, and that this protective barrier can be overwhelmed by excessive discharge of virtually any contaminant.

The means by which contaminants may enter ground water are many and varied. Figures 1 and 2 illustrate some of the more obvious sources and pathways of contamination of ground water. The details of the hydrology of movement of

### Table 1. Chemical Components Present in Documented Cases of Contamination of Ground Water Throughout the World

chromium	cyanid <del>c</del>
cadmium	copper
zinc	sclenium
lcad	chloride (and hydrochloric acid)
fluoride	sulfate (and sulfuric acid)
iron	nitrate
barium	detergents
manganese	radium and other radioactive wastes
nickel	phenols
silver	alcohol
molybdenum	gasoline
boron	leachate from landfills
uranium	pesticides
mercury	herbicides
aluminum	solvents
lithium	

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## POSSIBLE SOURCES OF GROUNDWATER POLLUTION

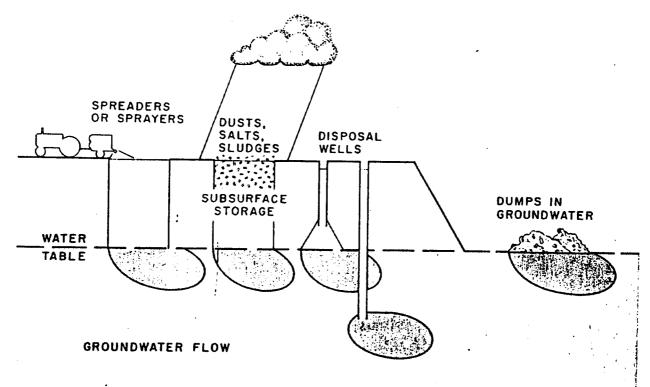
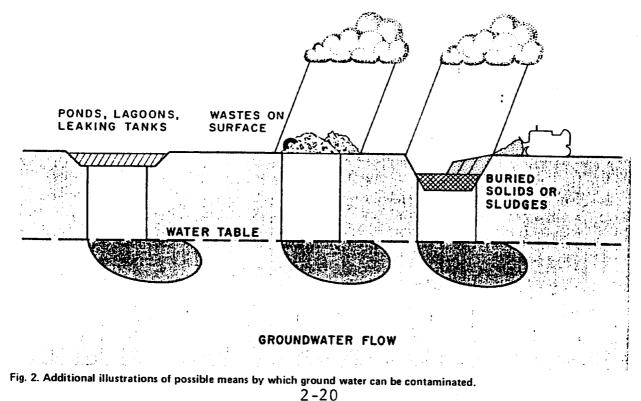


Fig. 1. Summary of some obvious pathways by which contaminants may enter ground water.

## POSSIBLE SOURCES OF GROUNDWATER POLLUTION



contaminants in the subsurface is treated in other papers in this Symposium and will not be discussed here.

Despite the fact that we are aware of hundreds of documented cases of ground-water contamination, the sobering fact is that there certainly exist thousands of similar cases of which we remain blissfully unaware. Miller and others (1974) made the important observation that most instances of ground-water contamination become known because of obvious leaks or spills at the surface, or because of complaints from subsequent users. Contamination of ground water is generally not discovered because of monitoring or routine chemical analysis. Many States in the past have not required analyses of water supplies for many toxic substances, such as barium, selenium, and silver, despite the listing of such substances in the 1962 Drinking Water Standards of the U.S. Public Health Service.

# POSSIBLE PROCESSES OF PURIFICATION Introduction

Having now emphasized the fact that ground water can surely become contaminated, let us look at some of the processes which offer protection to ground water, even in the face of significant discharges of potential contaminants to the subsurface. In Table 2 are listed eleven physicalchemical processes that may, under favorable circumstances, afford significant protection to the chemical purity of ground water. These eleven processes are listed together for the sake of completeness, but all are surely not equally effective.

The possible role and importance of each of these processes is discussed briefly in the following sections. Special emphasis is placed on their role in purifying wastes that might be discharged to the vadose zone in arid regions.

# Table 2. Eleven Physical-Chemical Processes That May Operate in the Subsurface to Purify Fluid Wastes

- 3. Precipitation by reaction of wastes with indigenous waters or solids.
- 4. Precipitation due to hydrolysis.
- 5. Removal due to oxidation or reduction.
- 6. Mechanical filtration.
- 7. Volatilization and loss as a gas.
- 8. Biological assimilation or degradation.
- 9. Radioactive decay.
- 10. Membrane filtration.
- 11. Sorption.

#### Dilution

The first process listed in Table 2, dilution, is well understood as it occurs in surface waters. However, we cannot rely on dilution to be effective over the short term in the vadose zone, especially in an arid region. And in any location, we must expect dilution of wastes *below* the water table to take place far more slowly than in surface streams. Indeed, the one outstanding characteristic of contamination of ground water is the slow rate at which it is diluted and dispersed by the natural flow system. Fryberger (1972) has presented convincing data and arguments to show how expensive and difficult it may be to reclaim a contaminated aquifer, even considering natural attenuation due to flow and dilution.

#### Buffering of pH

Natural ground waters in arid regions generally exhibit pH values between about 6 and 9. The upper limit is established in nature by the reaction between carbon dioxide gas and either limestone or caliche in the soil. The lower limit is an educated guess at the pH that might be found in shallow ground water from non-reactive rocks, such as quartz sandstone, or in ground water issuing from a mountain meadow. Trost (1974) found a range in pH from 6.0 to 9.0 in 1392 samples of ground water from southern Arizona.

The pH is a critical factor in many reactions involving contaminants, including processes that affect the stability of solid minerals and precipitates in the subsurface. If a discharged fluid has a pH outside of the range of 6 to 9, it is possible that drastic chemical reactions may occur, including the dissolution of such natural solids as calcium carbonate, iron oxyhydroxide, and manganese oxyhydroxide. Such reactions can exacerbate problems of contamination of ground water.

#### Precipitation by Reaction

This process could be quite important in purification of discharged fluids. A perusal of any handbook of chemistry will show that *in theory* it is possible to precipitate virtually any dissolved contaminant if the appropriate precipitating agent is present. In nature, however, the necessary precipitants do not commonly exist in sufficient quantities or favorable locations to cause removal of toxic substances to safe levels. For example, it is theoretically possible to reduce the concentration of dissolved sulfate in a discharge by mixing it with a natural barium-rich ground water. However, barium-rich ground waters are not common, so

<sup>1.</sup> Dilution.

<sup>2.</sup> Buffering of pH.

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this particular theoretical control will generally not operate in nature. In natural ground waters and in the enclosing solids, only certain species are normally present and available for reaction in meaningful concentrations. These species include dissolved calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, and silica. In the surrounding porous solids we find the additional abundant components of iron, aluminum, and possibly carbonate and phosphate. Dangerous or undesirable contaminants that might be reduced to safe concentrations by reaction with these species include the following: arsenic (precipitation by iron, aluminum, and calcium), barium (by sulfate and carbonate), cadmium (by sulfate and carbonate), copper (by carbonate), fluoride (by calcium and phosphate), cyanide (by many metals, including iron), iron (by silica), lead (by carbonate, sulfate, and phosphate), mercury (reduced form precipitated by carbonate and chloride), molybdenum (by iron and aluminum at proper pH), silver (by chloride), zinc (by carbonate and silica), and radium (by sulfate and carbonate). Evidence that such precipitation reactions do occur and may control concentrations in ground water has been given by many researchers. For example, Dutt and others (1968) found that the concentrations of iron and zinc in the ground waters of the Tucson Basin are apparently controlled by dissolved silica and the pH. However, despite the numerous possibilities for purification offered by precipitation reactions, a great many examples of contamination of ground water exist involving species that might be expected to precipitate; such examples demonstrate the failure of precipitation to protect ground water in many cases.

#### **Hydrolysis and Precipitation**

This type of reaction occurs when a dissolved contaminant reacts with water, with the release of either a hydrogen ion or a hydroxyl ion. The best known example involves the hydrolysis of dissolved ferric ion with precipitation of ferric hydroxide. On the acid side, molybdenum is thought to hydrolyze to bimolybdate ion and precipitate with compounds of iron and aluminum under acid conditions (LeGendre and Runnells, 1975). In an aerated environment, such as the vadose zone in an arid region, the concentration of dissolved iron can be held to very low values by hydrolysis and precipitation of ferric oxyhydroxide (Hem, 1970). However, in oxygen-deficient zones, such as commonly exist in the phreatic zone, high concentrations of iron can occur in the ferrous

(Fe<sup>2+</sup>) form. High rates of infiltration or flooding by waters into the vadose zone, such as might occur beneath a disposal lagoon, may produce anaerobic conditions and lead to solubilization of some metals.

In addition to ferric (Fe<sup>3+</sup>) iron, several other toxic metals form highly insoluble hydroxides in the range of pH of 6 to 9. These include copper (above a pH of about 6.5), chromium (the +3 form only, above a pH of about 6), nickel (above a pH of 9), and zinc (above pH 7.5). For example, Dutt and others (1968) found that the concentration of copper in ground water of the Tucson Basin seems to be controlled by either cuprous (Cu<sup>+</sup>) or cupric (Cu<sup>2+</sup>) hydroxide.

The apparent importance of hydrolysis in both the vadose and phreatic zones is the result of the simple requirement that water be present, in contrast to other precipitation reactions that demand the presence of specific precipitating agents.

#### Precipitation Due to Oxidation or Reduction

Relatively insoluble oxides of certain contaminants are known for copper, iron, manganese, mercury, and nickel. Aerobic conditions favorable for the development of these oxides will normally be found in the vadose zone and possibly in the upper parts of the phreatic zone. Deep in the phreatic zone or in swampy or flooded vadose environments, anaerobic conditions may prevail and lead to the mobilization of some species. Dutt and others (1968) in their work in the Tucson Basin found that rapid infiltration of domestic sewage caused a loss of oxidizing conditions in the vadose zone and led to increased movement of copper, zinc, manganese, nickel, and lead through the soil.

In some instances reducing conditions are most favorable for removing possible contaminants from water. One example is that of chromium, which is highly soluble and mobile in the oxidized state (+6, chromate or dichromate ion), but quite insoluble as the solid oxide or hydroxide of the reduced form (+3). Natural reducing conditions can also theoretically cause the formation of such native elements as arsenic, copper, mercury, selenium, silver, and lead, each of which is quite insoluble. We do find significant quantities of native copper, mercury, and silver in mineral deposits, and native selenium appears to be a stable phase in some soils (Goering and others, 1968). In reducing environments bacteria can convert dissolved sulfate to sulfide and dissolved nitrate to

ammonia or nitrogen gas. Reaction of the sulfide with certain metals will produce highly insoluble precipitates, such as the sulfides of arsenic, cadmium, copper, iron, lead, mercury, molybdenum, nickel, silver, and zinc.

In terms of usefulness and reliability for purification, the processes of oxidation and reduction can be of significant value if the necessary environmental conditions are maintained and managed. Considerable reliance can probably be placed on the process of oxidation for purification of wastes in the vadose zone. Processes of reduction may be more risky because some undesirable species can be mobilized, such as iron (Apgar and Langmuir, 1971) and manganese. One well-known benefit of the process of reduction is the denitrification of dissolved nitrate from sewage effluent, with significant removal of nitrogen possible under a carefully programmed mode of disposal (Bouwer, 1974).

#### **Mechanical Filtration**

The sixth process listed in Table 2, mechanical filtration, will generally be of little help in removing dissolved contaminants. Exceptions to this might occur following the formation of precipitates by means of one of the processes mentioned earlier. Such precipitates would be filtered out mechanically as the water moves through the porous medium. Iron is the species most likely to exhibit this behavior; it is well established that much of the total iron in aerated waters is present as particulate ferric hydroxide (Hem, 1970). Manganese probably behaves in a similar fashion. If these possible particulates sorb or include other dissolved species as they form, the filtration would remove these other species as well. Of course, most particulates originally present in the discharge would be filtered out quickly during downward movement through the vadose zone.

#### Volatilization and Loss as a Gas

Some inorganic species can be effectively removed from discharged waters by volatilization. Perhaps the best known example is that of the bacterial reduction of dissolved sulfate to hydrogen sulfide gas, with loss of the hydrogen sulfide to the atmosphere (Kellogg and others, 1972). Mercury in solution can also be volatilized in anaerobic environments (Lagerwerff, 1972) or by reaction with dissolved humic acids (Alberts and others, 1974). Several organic compounds of arsenic are volatile, and escape of arsenic as a gas has been demonstrated for both aerobic and anaerobic soils (Woolson and others, 1971). Based on its similarity to sulfur, we might also expect selenium to be subject to volatilization (Lakin, 1973). And of course, the microbial reduction of nitrate to ammonia and nitrogen gas is well documented (Bouwer, 1974), although the failure of this mechanism to protect ground water is demonstrated by numerous examples of pollution of ground water by nitrate (Minear and Patterson, 1973).

Volatilization as a means of purification is poorly understood, and we probably run considerable risk in relying upon it to any great extent. The exceptions to this would be the conversion of dissolved sulfate and nitrate to gases; these processes are known to be effective if managed properly.

#### **Biological Degradation**

Biological degradation or assimilation, the eighth process, is very important in removal of organic and biologic contaminants. Many organic substances would be removed or attenuated by biologic activity in the subsurface, especially in the oxidizing environment of the normal vadose zone. The biologic involvement of sulfate and nitrate have already been mentioned. In addition, arsenic, cyanide, mercury, and selenium are likely candidates for biologic fixation or volatilization. Molybdenum is strongly assimilated and concentrated by plants that are nitrogen-fixers (Johnson, 1966). And in their study in the Tucson area, Dutt and others (1968) found that grass assimilated and removed significant quantities of metals from infiltrating sewage effluent.

Biological processes could be of great value in managing discharges to the subsurface, but at present we know so little of the principles involved that each case must be studied and evaluated on its own.

#### **Radioactive Decay**

This mechanism is of value in the management of radioactive wastes by means of storage in the subsurface. Winograd (1974) has recently discussed the attractiveness of storage of high-level radioactive wastes in the vadose zone of arid environments. It seems clear that storage in this environment is possible with a high degree of safety for periods of time from thousands to hundreds of thousands of years, during which time the wastes would lose much of their activity through processes of decay. There is a substantial history of disposal of radioactive wastes to the subsurface near nuclear facilities in the United States, and in humid regions serious problems of contamination of ground water can be expected. It is the lack of recharge to move contaminants to the ground water that makes disposal to the vadose zone in arid regions so attractive.

#### Membrane Filtration

The tenth possible process of purification, membrane filtration, is a topic that is greatly in vogue at the present time in the literature of the geochemistry of subsurface waters. A summary of the phenomenon, given by Hanshaw (1972), points out that some observed data on the pressure and salinity of formational waters cannot be explained by simple gravitational flow of water or by dissolution of minerals. In such cases, the anomalous data may be related to osmotic pressures and filtration of salts across beds of shale. Pressure differentials of several hundred atmospheres can theoretically be generated across a membrane if fresh water exists on one side and a saturated brine on the other (Hanshaw, 1972).

In terms of purification of wastes in the subsurface, it is theoretically possible that a discharged wastewater could be diluted by osmotic transfer of water across a clay-rich aquitard. Conversely, one can speculate on the possibility of forcing waste fluids through a clay liner on the bottom of a disposal pond, anticipating some removal of dissolved salts and passage of a relatively more pure fluid. However, at this stage in development of the technology of disposal, careful pilot studies would be required to test the efficacy of such a scheme.

#### Sorption

Finally, and importantly, ground water may be protected by various processes of sorption. Clays, metallic oxides and hydroxides, and organic matter can all be good substrates for sorption of various dissolved species. With the exception of fractured shale or siltstone, consolidated bedrock will generally not be very effective as a sorbent. Virtually every ionic species and many non-electrolytes will be sorbed and removed to some extent as ground water moves through an aquifer; of the ions, only chloride, and to a lesser extent sulfate and nitrate, seem to pass through soils and alluvium without significant sorption.

The troubling aspect of sorption as a means of purifying waste waters in the vadose zone is that the process can be highly specific in its action, both as to the dissolved substance and the solid substrate. Molybdenum offers an interesting example. Dissolved molybdenum is sorbed strongly by most soils that exhibit an acidic reaction with water, but molybdenum will move freely through alkaline soils (Katz and Runnells, 1974). Similarly, fluoride is sorbed much more extensively by acidic soils than by alkaline soils (Bower and Thatcher, 1967). Perhaps the most revealing study of the effect of pH on sorption of ions is that by Griffin and others (1976), in which they determined the extent of removal by clay minerals of a suite of heavy metals from synthetic solutions and natural leachates from sanitary landfills. They found a very great variation in the extent of sorption, depending on the metal involved and the pH of the solution.

It is clear that the processes of sorption depend on the type of contaminant and on the physical and chemical properties of both solution and porous medium. Under favorable circumstances sorption can be wonderfully effective in purifying waters, as evidenced by the extensive use of ion-exchange media in water treatment. One should keep in mind, however, that when a contaminant ion is sorbed, some other change must also take place to compensate for loss of the charged species from solution. In ion-exchange reactions, a different ion is released by the solid to the solution. The ions released to water from a previously uncontaminated soil or alluvium will almost certainly be less harmful than most of the contaminants of concern here.

We can place considerable reliance on the processes of sorption to help us protect ground water, but each case will be different and tests must be run to assure an adequate degree of sorption and retention.

#### Summary

Eleven processes have been discussed, each of which is capable, under favorable circumstances, of contributing to the purification of liquid wastes discharged to the subsurface. However, hundreds of documented examples of ground-water contamination show that in specific instances the defensive mechanisms have been overwhelmed by discharged contaminants. It is reasonable to make an attempt to use the purifying properties of the subsurface as part of a plan of discharge, especially in the vadose zone in arid regions. However, such a plan of discharge must incorporate careful studies of the capacity and efficiency of the vadose zone for removing contaminants, and of possible later remobilization of the toxic substances.

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#### USING NATURAL PROCESSES OF PURIFICATION IN A PLAN OF DISCHARGE Introduction

Because of the potential value for purification and long-term storage of wastes in the vadose zone of arid regions, it seems reasonable to include the use of this zone in plans of discharge. In fact, Winograd (1974) presents a detailed analysis of such a plan for storage of radioactive wastes. As water scientists, we can envision similar useful applications in the discharge of other wastes. Bouwer (1974) has given an example of proper management of disposal of sewage effluent to the vadose zone in Arizona in order to maximize removal of dissolved nitrate. At the time of this writing, the New Mexico Water Quality Control Commission is considering, for possible adoption, new regulations for protection of ground water. These proposed regulations, developed chiefly by the New Mexico Environmental Improvement Agency, would permit a discharger to make use of a fraction of the purifying capacity of the vadose zone as part of his plan of discharge to the subsurface. The concept of using the vadose zone in this manner was suggested by the present writer, as a consultant to the New Mexico Environmental Improvement Agency. It is gratifying that most parties concerned, from industry on the one hand to environmental groups on the other, seem to agree that the vadose zone in arid regions can offer a safe repository for contaminants, provided that very careful study and monitoring are incorporated into the plan of discharge.

# Potential Capacity of the Vadose Zone for Purification

The capacity of the vadose zone can be large for removal and storage of contaminants. As an example of this large theoretical capacity, let us consider a hypothetical discharge of dissolved cadmium from a metal-plating plant. The assumptions involved in this example are summarized in Table 3. The concentration of 3.7 mg/l dissolved cadmium is that actually reported by Lieber and others (1964) for the well-known example of ground-water contamination on Long Island. It would be dangerous to allow a discharger to use the total capacity of the vadose zone for sorption of contaminants from his wastewater, so for purposes of this example we will assume that State regulations allow him to use 25 percent of the estimated total sorptive capacity of the unconsolidated mantle beneath his discharge pond. Based on the data listed in Table 3, the

#### Table 3. Assumptions Used in Hypothetical Example of the Capacity for Sorptive Removal of Dissolved Cadmium from Discharge to the Vadose Zone in an Arid Region

#### Assumptions:

- 1. Unconsolidated mantle with 10 weight percent clay.
- 2. Cation exchange capacity of 50 milliequivalents per 100 grams (0.22 pounds) of clay.
- 3. Density of 2 grams/cc (124.9 lbs/cubic foot).
- 4. Thickness of mantle = 100 feet (30.5 meters).
- 5. Area of disposal = 1 acre (0.405 hectare).
- 6. Efficiency of sorption is 100 percent.
- 7. Only 25 percent of the total sorptive capacity.is utilized.

discharger could store approximately 380,000 pounds (172,400 kg) of cadmium in the vadose zone. This is a *lot* of cadmium. At a concentration of 3.7 mg/l, this amount corresponds to about 38,000 acre-feet ( $4.7 \times 10^{10}$  liters) of wastewater that could be discharged from the one-acre pond.

Of course, the preceding simplistic example ignores competition or enhancement of sorption by other ions, other chemical reactions, possible channelized flow of the wastewater through the vadose zone, and a great many other complicating factors. The example does point out, however, that a significant degree of purification of wastewater and storage of dissolved contaminants is possible under the conditions that exist in an arid region.

#### Dangers and Necessity for Study

Having emphasized the great potential value of the vadose zone for discharge, we must temper our enthusiasm by recognizing that the vadose zone has a finite capacity for purification, and that there is always a danger of leakage and contamination of ground water. Referring back to Table 1, we can see that it is possible to overwhelm the protective mechanisms in the subsurface with any dissolved contaminant. This knowledge warns us of the necessity for thorough and competent studies of the hydrologic and chemical characteristics of a proposed site before discharge begins. A proposed plan of discharge must also allow for a wide margin of error in the measurements required, including such parameters as heterogeneity in the hydraulic properties of the earth materials at the site. Finally, an adequate scheme for monitoring must be included, together with contingency plans in the event that the discharged contaminants do not behave as expected.

#### **Necessary Measurements and Testing**

Our knowledge of the specific physicalchemical processes that obtain in the subsurface is primitive. We cannot predict from theory what will happen when a particular contaminant in a particular fluid matrix is discharged into a specific type of soil. We do have some general knowledge of the principles involved, as discussed in an earlier section of this paper, but we remain ignorant of many of the specifics. Now that the Safe Drinking Water Act is a reality, we can expect to see a rapid increase in research and knowledge concerning the movement of contaminants through earth materials. In fact, it would be possible to list several new publications that deal specifically with this subject. By far the most complete and satisfying such report known to this writer is that by Weir and others (1975), prepared for the Electric Power Research Institute. The purpose of the work reported by these workers was to determine if toxic ions would be leached from ash and sludge discharged into ponds by electric utilities, and to determine if such ions would move through underlying soils into ground water. Another excellent study, with greater emphasis on the hydrologic factors, is that by Papadopulos and Winograd (1974).

In order to have confidence in the probable efficacy and safety of a plan of discharge to the vadose zone, a great many factors must be considered. For example, one must have a fairly complete knowledge of the hydrogeologic conditions and homogeneity of the earth materials at the proposed site of disposal. In order to obtain such information it will certainly be necessary to conduct fairly extensive field studies, possibly including drilling, to determine the rate and paths of movement of the fluid discharge. An example of one aspect of the work that may be necessary can be found in the study of seepage of effluent from septic tanks, published by Bouma and others (1972). Hajek (1969) has given a good summary of some of the technical aspects of the tests and calculations that should be done to understand and predict the chemical interactions of wastewaters with soils. And finally, a potential discharger must look to the future, realizing that "purification" of wastewaters by the vadose zone really represents storage, either long-term or shortterm. For some chemical species, such as phosphate, zinc, and copper, the storage may be permanent because these ions can become fixed in the structure of minerals and not be available for later release by percolating solutions (Ellis and Knezek, 1972). In other cases, contaminants that have been discharged and stored in the vadose zone may be

readily available for leaching and remobilization by the next soaking rainfall, or by a subsequent change in the chemical composition of the discharged fluid. Tests must therefore be run, not only to determine the extent of removal of contaminants from the discharge, but also to determine the possibility of later remobilization and flushing to ground water. With regard to storage, Winograd (1974) has discussed the selection of a site for disposal to best avoid exhumation by the normal processes of erosion or remobilization by climatic change over periods of hundreds of thousands of years.

Discharge of any kind may pose a long-term threat to the environment, and at present, our knowledge of interactions in the vadose zone does not permit us to make unequivocal predictions from theoretical principles. Much work must be empirical, and teams of scientists and engineers must be involved in devising the plan of discharge. Perhaps most importantly, each type of discharge and potential site must be treated individually, on a case-by-case basis. No one can claim that the job of insuring non-destructive disposal of wastes to the vadose zone will be easy, but neither can they claim that the job is impossible.

#### An Example of Geochemical Testing

As part of the task of developing possible regulations to govern discharges to the subsurface in New Mexico, this writer was asked to present an example of how the geochemical portion of the testing might be conducted. The work was not intended to be complete, but was designed instead to illustrate the minimum information that would be appropriate. A very brief summary is presented here.

The soil chosen was from Sulfur Springs, New Mexico. It was dark brown in color, contained rootlets, and represented a composite of the upper six inches of the profile. A 1:2 soil:water slurry yielded a potentiometric pH of 6.4. The soil was air-dried and sieved to (-) 2 mm to remove the coarse, non-reactive fragments. A small column of soil [approximately 23.2 cc (1.42 cubic inches)] was prepared in a chromatography tube. The test solution was gravity-fed into the column at various rates, from about 0.5 to 1.6 ml/min (corresponding to a velocity of about 4 to 12 feet/day). Saturated conditions were maintained, together with a relatively high rate of flow, because of limitations of time. An actual case would require slower rates of flow and an unsaturated column. Aliquots of the effluent were 2-26

collected in volumes of about 9.5 ml (0.0025 gallons) by means of an automatic fraction collector. The porosity of the soil column was estimated in two ways: (1) addition of water to saturation and reweighing in the column and (2) measurement of volume of water withdrawn from a graduated cylinder by suction into the soil column. Density was determined by weighing and measuring the volume of soil column. The porosity was 48 ± 4 percent, and the density was  $0.88 \pm 0.03$  gm/cc (55 ± 2 lbs/cubic ft). The pore volume of the column was 11 ± 1 cubic centimeter (0.00039 cubic feet). The errors involved in this crude study are obvious, such as the disturbance and sieving of the soil, and the rough estimate of porosity and density. For an actual plan of discharge it would probably be necessary to obtain cores of the soil; ASTM methods would be used to measure the porosity and density of the core material.

The test solution was made up to simulate the aqueous discharge from a metallurgical flotation mill. The aqueous matrix was a saturated solution of gypsum, initially spiked with 1.0 ppm (mg/l) dissolved copper and 2.1 ppm (mg/l) dissolved molybdenum. The initial concentration of copper was made considerably higher than might be expected in an actual mill effluent; this was done because initial tests indicated that the soil had a large capacity for removal of copper from the test solution. The initial solution and the aliquots of effluent were analyzed for copper and molybdenum by atomic absorption and a thiocyanate colorimetric procedure, respectively. Standard additions were employed to test for sensitivity and interference in the copper analysis.

The results for molybdenum are shown in Figure 3. The results for copper are not shown because copper was generally below the limits of detection in the effluent during most phases of the study (the detection limit for dissolved copper was 0.01 parts per million).

As shown in Figure 3, an initial period of leaching by distilled water (simulated rain water) failed to release detectable amounts of molybdenum (less than 15 parts per billion dissolved). The concentration of dissolved copper was approximately 0.05 ppm in the effluent during this initial leaching, which continued for 378 ml (34 pore volumes). This initial period of leaching shows that neither the concentration of copper nor molybdenum released by heavy applications of fresh water to Sulfur Springs soil poses a threat to ground water. Next, in Figure 3, the column

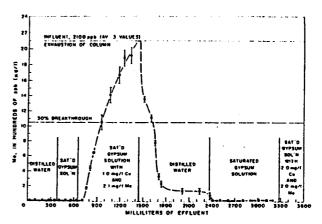


Fig. 3. Results of experimental study of leaching, removal, and remobilization of molybdenum using synthetic mill water and a New Mexico soil. Analytical error shown by vertical bars; error is approximately the diameter of the circles along the abscissa.

was leached with approximately 26 pore volumes (288 ml) of metal-free synthetic mill water. In this case, dissolved copper in the effluent averaged less than 0.01 ppm and molybdenum less than 15 ppb. Again, these results show that extensive leaching with metal-free mill water fails to leach significant quantities of either metal from the soil.

At a volume of 661 ml in Figure 3 the metal-spiked water was introduced into the column, and 72 pore volumes were passed through. No detectable copper (less than 0.01 ppm) ever appeared in the effluent. Molybdenum was first detected after 66 ml (6 pore volumes) of spiked water had flowed through the soil. Fifty percent breakthrough of molybdenum occurred after passage of 32 pore volumes. The capacity of the soil to remove molybdenum was completely exhausted after passage of 72 pore volumes of mill water (792 ml). The difference in behavior of these two metals is caused by their ionic form in solution; molybdenum occurs as an anion (MoO<sub>4</sub><sup>--</sup>), whereas copper is present as a cation (Cu<sup>++</sup>) under these conditions. This soil had a very large capacity for removal of copper.

In Figure 3, after exhaustion of the column for molybdenum, the soil was again leached with simulated rainfall and metal-free mill water to test for desorption and remobilization. Of the 792 micrograms of copper introduced, leaching by 165 pore volumes of distilled water and synthetic mill solution released only about 19 micrograms; this means that the removal of copper by this soil approaches being irreversible. The initial leaching of the soil, prior to the introduction of

the metal-rich mill water, released as much copper. In contrast, leaching of the loaded column with 83 pore volumes of distilled water remobilized nearly 60 percent of the approximately 700 micrograms of molybdenum previously added. The rate of release of molybdenum was secreasing exponentially with continued leaching by the distilled water, as shown in Figure 3. indicating that a very large volume of water would be required to remove all of the added molybdenum. Interestingly, upon initiation of leaching of the loaded soil with metal-free mill water, the concentration of molybdenum in the effluent fell to about 10 parts per billion, continuing to the end of this portion of the experiment with an additional <sup>2</sup> pore volumes (about 3280 ml on Figure 3). Calculations suggest that this decrease in desorbed molybdenum was probably due to the precipitation of solid CaMoO<sub>4</sub> in the soil due to the high concentration of dissolved calcium in the water.

Finally, in Figure 3, a new spiked mill water, containing 2 ppm copper was passed through the column in an attempt to cause breakthrough of the dissolved copper; however, breakthrough did not ccur, even after a calculated addition of 256 ppm opper to the solid phases in the soil column.

The results of this study show that the soil from Sulfur Springs, New Mexico, has an enormously high capacity to remove copper, and that the removal is essentially irreversible. A relatively high capacity for removal of molybdenum is also exhibited, with 50 percent breakthrough at 32 pore volumes of spiked mill water. This type of information would comprise an important prtion of a rational plan of discharge.

Space does not permit development here of expressions to relate the data of Figure 3 to a real situation. However, it can be shown from considerations of the distribution of the ions between the liquid and solid phases (Hajek, 1969; Tamura, 1972; Wierenga and others, 1975) that thousands of years may be required for the molybdenum in this study to reach an assumed "Iter table at a depth of 30 meters (98 feet) in the Sulfur Springs soil, depending on the rate of discharge and infiltration. Copper would require much longer to reach the ground water.

#### SUMMARY

In summary, I have tried to demonstrate that there are valid chemical and physical reasons for looking toward the subsurface, especially the vadose zone in arid regions, for disposal of some

bes of wastes. Processes that operate in this

environment can, under favorable circumstances, greatly attenuate and detoxify some wastes. On the other hand, we know of too many examples of contamination of ground water to believe that the overlying mantle of soil and sediment affords absolute protection. With these facts in mind, we must try to balance the need for protection of ground water against the economic realities of the use of water by industry, municipalities, and the general public. .

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#### ACKNOWLEDGMENTS

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#### DISCUSSION

The following questions were answered by Donald D. Runnells after delivering his talk entitled "Wastewaters in the Vadose Zone of Arid Regions: Geochemical Interactions."

**Q. by Leonard Wood.** Rain water is not distilled water. Have you used rain water in your column experiments? A. No, I have not tried to exactly duplicate the chemistry of rain water in the column studies. However, I do not believe that the observed variations in the chemistry of rain water would make a great deal of difference under most circumstances. The exception might be in regions of serious air pollution in which sulfuric acid becomes the principal control on the pH of rain water. **Q. by Mike Kaczmarek.** Would substantial increases in the Mo loading in the soil column result in comparable increases of Mo in the leachate resulting from "rain water" (distilled water)?

A. Yes, the greater the initial loading, the greater would be the slug of Mo released from a soil when remobilization due to leaching does take place.

Q. by E. E. Jones, Dale Raiston and Harry Nightingale. What percent of pore space was saturated in your experiments?

A. This particular column was filled from the bottom to drive out air, then maintained in a fully saturated condition, so the pores were nearly 100 percent filled with water. This was done because a limited amount of time was available and I had to maintain high rates of flow. A different experiment could be conducted under nonsaturated conditions, in which the rate of flow would be substantially slower.

# **Q.** by Harold Meiser. What experiments are you planning for the future?

A. We now have underway a program to test for leaching of trace elements from spent oil shale, and the reactivity of these elements with soils of the oil shale region in Colorado.

#### Q. by Neil Jaquet. How do the volumes of distilled water used in your column studies compare to rates of precipitation in the area of concern?

A. Experiments such as I described are designed to yield basic information, such as the distribution coefficient,  $K_d$ . Such information can then be used in equations involving the specific rates of precipitation and infiltration for an area. Thus, it is not necessary to model the *amount* of rainfall and infiltration, just the chemistry and rates of flow.

#### Q. by Jon O. Nowlin. Assuming contaminant "removal" bycropping, how is the crop to be disposed of?

A. The three advantages in cropping would be: (1) to convert the dissolved contaminants into solid form, or (2) to consume and transform such contaminants as nitrate, BOD, etc., or (3) to concentrate the contaminants from a large amount of fluid into a smaller volume of crop. However, in some cases, cropping would still offer no advantages because you still could not dispose of it.

# $\Omega$ . by K. E. Childs. Can these tests be used to evaluate other areas, soils, and chemicals, or are the results too qualitative for this?

A. The results are quantitatively useful for the particular parameters chosen, but new tests would have to be run for other discharges, soils, etc.

Q. by P. K. Saint: Can one quantify the sorption capacity of the soil and predict the time of passage of an ion through the vadose zone? How about desorption later on? A. Yes, the results can be used for predicting migration, and references are given in the paper to illustrate this. Figure 3 in the paper shows the results of desorption studies. **Q.** by Logan Kuiper. What barmful effects would result if the contaminants reached ground water in the case considered?

A. Molybdenum at this concentration (2.1 mg/l) could be toxic to ruminant animals, and the TDS (saturated gypsum solution) would degrade the quality of the ground water. Finally, the 1.0 mg/l copper would probably not be harmful to health, but would be undesirable because of taste.

# Q. How do different types of soils affect the leaching process?

A. The processes of removal and leaching are strongly dependent on the type of soil.

Q. by G. F. Hendricks. Any study of pick-up of copper by plants?

A. There have been several such studies by others in the past, but this was not part of our program.

Q. by Don Lundy. What mechanism retained the copper? A. I really did not get into the study of specific mechanisms. The experiments were designed only to give a general indication of capacity for removal and retention.

#### Q. by Buck Steingraber. What bappened to the sulfate in your percolating water-did it come through in the original concentration?

A. The specific conductance that was measured in the effluent suggested that the sulfate passed through the soil with little or no removal.

# $\Omega$ . What time equivalency in years of precipitation would be required to equal the amount of solution put through the soil column?

A. For a semi-arid region, with perhaps 2 centimeters of recharge per year, the total volume of solution percolating through each cubic centimeter of soil would correspond to about 10 saturated pore volumes (assuming 20% porosity) per year. In this study 1 passed about 300 pore volumes through the saturated column, corresponding to 30 years of recharge. However, the ions in the experiment were retarded by the soil and would move much more slowly than the water. Proceedings of First Canadian/American Conference on Hydrogeology, June 1984, p. 69-95

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# Chemical Equilibrium and Kinetics of Geochemical Processes in Ground Water Studies

by Donald Langmuir and John Mahoney

#### Abstract

Geochemical reactions or processes can alter the hydrologic properties of a rock. Such reactions (or the lack of them) can also render a water fit or unfit for certain uses. An understanding of equilibrium and kinetic concepts as they apply to water-rock systems can greatly improve one's ability to predict the chemical and isotopic composition of ground water, and so to better manage ground water resources. For these reasons, hydrologists need to know some ground water geochemistry. Chemical equilibrium defines the boundary conditions; i.e., what are the maximum or minimum possible concentrations of some dissolved species likely to be? Chemical kinetics defines how long it takes to reach equilibrium and by what reaction pathways it is reached. Only chemical equilibrium concepts are needed to understand ground water chemistry when the rates of reactions of interest are much faster than ground water residence times in a particular water/rock system. Thus, such concepts have been most usefully applied in deep basin artesian ground water studies. When reaction rates are comparable to or less than residence times, both kinetic and equilibrium concepts apply. This is particularly the case in shallow water table systems. Chemical equilibrium concepts, including adsorption, have successfully explained the chemical behavior of many ground water systems. In contrast, our understanding of geochemical kinetics is in relative infancy, so that only the simplest kinetic concepts have been usefully applied in ground water studies. In this paper, the principles of equilibrium (including adsorption) and of kinetics are addressed and illustrated with practical applications.

#### Introduction Purpose and Scope

Why should a hydrologist know some ground water geochemistry? First, because geochemical reactions can alter the hydrologic properties of the rock and also well performance. For example, the exchange of sodium for calcium on montmorillonite-type clays can cause swelling of formation clays. Oxidation of ground water around a pumping well can clog the aquifer and the well with precipitated ferric or manganese oxyhydroxides. The mixing of injected thermal or chemical wastes can cause encrustation and clogging of wells with such phases as silica, gypsum or calcite, or the collapse or caving of carbonate rocks.

A second reason to understand ground water geochemistry, relates to the intended use of the water. Specifically, reactions (or the lack of them) can render a water unfit (or fit) for certain uses. Thus, the adsorption or desorption of toxic, including radioactive substances can improve or aggravate ground water quality. Mining of pyrite-bearing rocks can produce acidmine water, which must be neutralized, freed of iron and manganese, and usually diluted before use. Waters associated with uraniferous rocks, mine tailings or nuclear wastes can be high in their concentrations of radioisotopes, and so unfit for drinking or industrial use. The hydrologist may develop an exact understanding of the ground water budget and safe yield of an aquifer. However, he should also understand how, where and when a ground water supply is adversely affected by its chemistry. If the causes of undesirable water quality are understood, it is sometimes possible to prevent the formation of such waters or to improve their quality using the principles of ground water geochemistry and hydrology in the siting of wells and design of well fields.

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## **Chemical Equilibrium and Chemical Kinetics**

The language of ground water geochemistry considers the reactions that occur in gas/water/rock systems, how to describe them, and how then to model and predict, and, if possible, manage them. The state of reactions can be described in terms of concepts of equilibrium or kinetics. Equilibrium models describe boundary conditions assuming attainment of equilibrium. They give no information regarding the pathways or times to reach equilibrium. Kinetic models describe the reaction pathways towards equilibrium, and the reaction position and times along those pathways. Several key questions must be answered initially in a study of reaction geochemistry. First, is the reaction sufficiently fast and reversible so that it can be regarded as chemical-equilibrium controlled, or must it be considered kinetically controlled? Second, is the reaction homogeneous (occurs within a single phase, e.g., water) or heterogeneous (occurs between two phases, e.g., water and mineral surface, or water and gas phase). Slow, irreversible, heterogeneous reactions are those most likely to require interpretation using kinetic models. Third, is there a useful volume of the water-rock system in which chemical equilibrium can be assumed? This may be called the local equilibrium assumption.

The following example should serve to illustrate some of these ideas. If we assume a simple first-order reaction (see the kinetics discussion to follow).

At equilibrium, the equilibrium constant equals

$$K_{AB} = \frac{k_{+}}{k_{-}}$$
(2)

where  $k_+$  and  $k_-$  are the rate constants for the forward (A to B) and reverse (B to A) reactions, respectively.

In an open system that is completely mixed we may write

$$T_{\rm R} = \frac{V}{g} \tag{3}$$

where  $T_{R}$  is the residence time of the water, V is the completely mixed volume, and g is the volume rate of flow. It can be shown that:

$$T_{\frac{1}{2}} = \frac{\ln 2}{k_{+}} = \frac{0.693}{k_{+}}$$
(4)

where  $T_{\frac{1}{2}}$  is the half-life of reaction (1). If the initial concentration of B is zero, one can also show:

$$\frac{C_{A}}{C_{B}} = \frac{1}{K_{AB}} + \frac{T_{1/2}}{0.693 T_{R}}$$
(5)

When  $T_R >> T_{\frac{1}{2}}$  expression (5) reduces to the equilibrium expression, and equilibrium concepts can be used (Hoffman 1981). Conversely, when  $T_R \leq T_{\frac{1}{2}}$  for a particular reaction, then kinetic concepts are necessary to explain the state of that reaction.

The composition of most deep confined ground

water and of some deeper unconfined ground water may remain constant with respect to certain dissolved species for periods of months to years. Such constancy will usually mean that reactions involving those species have come to thermodynamic equilibrium. When this is the case, the water/rock system involved can be considered a closed system in a thermodynamic sense, and equilibrium concepts can be safely applied to describe and explain the chemistry. However, in some water/rock systems, particularly shallow confined or unconfined ones, the chemistry may appear constant in time without the attainment of equilibrium. Such systems may be described as open in a thermodynamic sense, and their constancy described as reflecting steady-state conditions. Following discussion, which is based on Stumm and Morgan (1981), is intended to explain and contrast equilibrium and steady-state conditions. Figure 1 depicts schematically how such concepts apply for a reaction A = B occurring in a volume of ground water in contact with both gas and solid phases. For equilibrium concepts to apply to reaction A = B, then the total fluxes of A  $(\Sigma dn_{A})$  and of B  $(\Sigma dn_{B})$  must equal zero. The number of moles of A  $(n_A)$  and of B  $(n_B)$  must be constant, and homogeneously distributed throughout the water. The volume of water and its temperature and pressure must also be constant. If these constraints are met, then, assuming the initial concentration of B is zero, and the initial concentration of A is  $C_{A,o} = n_{A,o}/V$ , then at equilibrium  $K_{AB} = C_B / C_A$ . One can also show  $C_A =$  $C_{A,o}/(1 + K_{AB})$ , and  $C_B = C_{A,o} - C_A$ .

The mathematical description of a steady-state (also called stationary state) open system is far more complicated. For the same reaction A = B, the status of

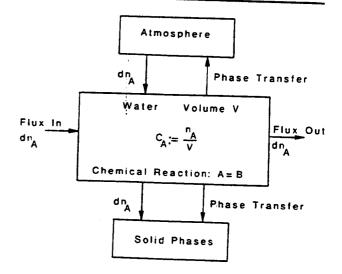


Figure 1. Schematic representation of an open ground water system and a reaction A = Boccurring in the aqueous phase, with a flux in A of  $dn_A$  taking place between the atmosphere, aqueous and solid phases.  $C_A$  is the concentration of A,  $n_A$ the number of moles of A, and V the volume of the aqueous phase.

that reaction will depend on rates of the forward reaction and reverse reaction, which in the simplest case (assuming elementary rate laws—see kinetics discussion) are described by rate constants  $k_+$  and  $k_-$  respectively, thus:

$$v_{+} = k_{+}C_{A}$$
 and  $v_{-} = k_{-}C_{B}$  (6)

where  $v_+$  and  $v_-$  are the rates of forward and reverse reactions. The rate constants themselves are functions of temperature and pressure. The time rates of change of C<sub>A</sub> and C<sub>B</sub> are:

$$dC_A/dt = -k_+C_A + k_-C_B \tag{7}$$

and

$$dC_{\rm B}/dt = +k_{\rm +}C_{\rm A} - k_{\rm -}C_{\rm B} \tag{8}$$

For the open system we must consider the material balance to the system of steady mole fluxes of A and B per unit of volume, V. These fluxes can be designated  $r\bar{C}_{A,o}$  and  $r\bar{C}_{B,o}$ , where r = Q/V, and Q is the rate of flow. In this context  $\bar{C}_{A,o}$  and  $\bar{C}_{B,o}$  are inflow concentrations. For steady-state, by definition  $dC_A/dt = dC_B/dt = O$ , and inflow and outflow rates must be equal, so that

$$dC_{A}/dt = r\bar{C}_{A,o} - k_{+}C_{A} + k_{-}C_{B} - rC_{A} = 0$$
(9)

and

$$dC_{B}/dt = r\bar{C}_{B,o} + k_{+}C_{A} - k_{-}C_{B} - rC_{B} = 0$$
(10)

Reaction stoichiometry tells us

$$C_A + C_B = \bar{C}_{A,o} + \bar{C}_{B,o} \tag{11}$$

so that for steady-state conditions

$$C_{A} = [r\bar{C}_{A,o} + k_{-} (\bar{C}_{A,o} + \bar{C}_{B,o})]/(k_{+} + k_{-} + r)$$
(12)

and

$$C_{B} = [r\bar{C}_{B,o} + k_{+} (\bar{C}_{A,o} + \bar{C}_{B,o})]/(k_{+} + k_{-} + r)$$
(13)

Obvidusly, the mathematics is considerably more cumbersome than was true of the equilibrium condition. We will say no more of steady-state conditions in this paper. Preceeding discussion is intended only to suggest that one cannot assume equilibrium exists when ground waters are of constant composition, although the assumption will usually be correct.

The essence of the equilibrium vs. kinetics discussion can be summarized as follows. When reactions are fast and reversible  $(T_R >> T_{1/2})$  equilibrium models may be used to describe the state of those reactions. On the other hand, when reactions are slow and irreversible  $(T_{1/2} \leq T_R)$  kinetic models are needed to describe the state of those reactions. We will find that in most ground water reaction half-times range from on the order of  $10^{-10}$  sec to  $10^6$  yr or longer, so that both kinetic and equilibrium models are necessary for us to understand the chemistry and isotopy of the total

water-rock system.

The relationship between residence times of different water and reaction rates of several types of reactions is depicted in Figure 2. In Table 1 are listed examples of reaction types and their approximate half times. Figure 2 shows that few reactions can be assumed at equilibrium in a raindrop, which can be considered to have constant dissolved concentrations, temperature and pressure for a few seconds or less. The most likely reactions to be at equilibrium in the raindrop will be most solute-solute or solute-water reactions. These would include most acid-base and ionization reactions (Table 1). Adsorption reactions in the raindrop may be at equilibrium when small sorbing dust particles are involved.

The dashed right arrow on the adsorption-desorption line shows rates as long as days. These longer times describe adsorption which involves diffusion into rock fragments, so that the diffusion rate controls the attainment of adsorption equilibrium. The residence times of ground water typically range from a few days in karst-type carbonate rocks and some highly permeable near-surface gravels, to millions of years in deep artesian basins. Obviously, the assumption that most chemical reactions are at equilibrium in the ground water within a deep sedimentary basin will generally be correct. Rates of radioactive decay (usually an irreversible reaction), which range from fractions of a second to billions of years, are not shown in Figure 2. Isotopic exchange rates are also widely divergent (Fritz and Fontes 1980), and so have not been plotted.

## Equilibrium Concepts

#### The Equilibrium Constant

Given the reaction: aA + bB = cC + dD, where the lower case letters denote the number of moles of their

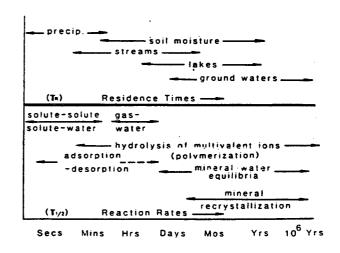


Figure 2. Schematic comparison between the halftimes of reactions  $(T_{1/2})$ , and the residence times  $(T_B)$  of some waters of the hydrosphere.

Reaction type	Approxima half time	
1. Hydration		
$H_2O + CO_2 (aq) = H_2CO_3$	~.1 s	ec
$K_{eq} = [H_2CO_3]/[CO_2]$		
2. Acid-base (also Ionization)		
$H_2CO_3 = H^+ + HCO_3^-$	~10 <sup>-6</sup> s	ec
$K_{eq} = [H^+] [HCO_3]/[H_2CO_3]$		
$HCO_{3}^{-} = H^{+} + CO_{3}^{2-}$	~10 <sup>-6</sup> s	ec
$K_{eq} = [H^+] [CO_3^{2-}]$		
3. Complexation		
$Cu^{2+} + H_2O = CuOH^+ + H^+$	~10 <sup>-10</sup> se	ec
$Fe(H_2O)_6^{2+} = Fe(H_2O)_5^{2+} + H_2O$	~10 <sup>-7</sup> se	ec
4. Polymerization and hydrolysis		
$AI(OH)_{n}^{3-n}$ + (3-n) $H_{2}O$ - $AI(OH)_{3}$ + (3-n) $H^{+}$	month	hs
5. Radioactive decay		
$^{14}C \rightarrow ^{14}N + e^{-1}$	5,570 y	rs
6. Isotopic exchange		
${}^{35}SO_4^{2-} + HS^- \rightarrow H^{35}S^- + SO_4^{2-}$	month: -vi	ns rs
7. Gas solution-exsolution		
$CO_2(g) = CO_2(aq)$	T <sub>forwar</sub>	rd
$K_{eq} = [CO_2]/P_{CO_2}$	less tha <sup>T</sup> revers (times: secs-hrs	se
8. Oxidation-reduction		
$Fe^{2+} + \frac{1}{4}O_2(g) + \frac{5}{2}H_2O = Fe(OH)_3 + 2H^+$	mins-hr	rs
$K_{eq} = [H^+]^2 / [Fe^{2+}] [P_{O_2}]^{\frac{1}{4}}$		

Table 1			
Examples of Some Reaction Types and Their Approximate Half Times			

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#### Table 1 (continued)

9. Adsorption-desorption

$$Cd^{2^{+}} + CaX = Ca^{2^{+}} + CdX$$
  
 $K_{ex} = \frac{[Ca^{2^{+}}]}{[Cd^{2^{+}}]} \cdot \frac{[CdX]}{[CaX]}$ 

#### 10. Precipitation-dissolution

$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$$
  
 $K_{eq} = [H^+] / [Ca^{2+}] [HCO_3^-]$ 

#### 11. Mineral crystallization

$$Fe(OH)_3 \cdot nH_2O(amorph) \rightarrow \alpha - FeOOH + (n+1)H_2O$$
goethite

respective reactant and product species, we can write:

Rate<sub>+</sub> =  $k_+$  [A]<sup>a</sup>[B]<sup>b</sup>, and Rate<sub>-</sub> =  $k_-$  [C]<sup>c</sup>[D]<sup>d</sup> (14)

This assumes that the forward (+) and back (-) reactions are elementary reactions (see kinetics discussion that follows). In any case, at equilibrium by definition: Rate<sub>+</sub> = Rate<sub>-</sub>. Thus:

$$\frac{k_{+}}{k_{-}} = K_{eq} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$
(15)

where the brackets denote activities (or effective concentrations) of the enclosed species.

Several conventions are adapted in the application of the law of mass action (another name for the equilibrium constant expression in Equation 15). First, for solutes (dissolved species), by definition the activity  $a_i$ of species i equals its activity coefficient  $\gamma_i$ , times its concentration  $m_i$ , or  $a_i = \gamma_i m_i$ , where the concentration is in molal units (mol/kg solution). (Molar concentrations are used by some researchers, but are not preferred because they change with temperature, whereas molal concentrations do not). When liquid water appears in a reaction, its activity is equal to the vapor pressure of water over the solution, divided by that over pure water at the same temperature and pressure. In other words:

$$[H_2O] = P_{H_2O}/P_{H_2O}^{*}$$

The activity of water in a solution is also approximately equal to its mole fraction in the solution, or  $[H_2O] = N_{H_2O}$ . For example, in sea water there are 1.14 moles of ions per kilogram, and 55.51 moles of water per kilogram, so  $[H_2O] = 55.51/(55.51 + 1.14) = 0.98$ . The approximation gives the correct answer in this case. However, in a sodium-chloride saturated brine,  $mNa^{+}$ =  $mCl^{-}$  = 6.5m at 25 C, and the correct activity of water is 0.75 based on its vapor pressure, whereas water activity computed from its mole fraction equals 0.81.

As long as pure solids and liquids (including water) are always present during a reaction, their activities are assumed equal to unity. For gases in equilibrium with the solution, gas activity may be assumed equal to gas partial pressure in bars for low total gas pressures (less than a few tens of bars). In normal dry air at sea level for example  $P_{N_2} = 0.781$  bars,  $P_{O_2} = 0.210$  bars, and  $P_{CO_2} = 0.00033$  bars. (1 bar =  $10^5$  pascals = 0.1 MPa = 0.98692 atm).

#### **Activities of Dissolved Species**

The concept of ionic strength (I) is necessary in a discussion of activities of dissolved species. By definition,  $I = \frac{1}{2} \sum m_i z_i^2$ , where z is the valence of ion i. Ionic strength is computed exactly from a total analysis of major ionic species in the water. However, when such an analysis is not available, it may be approximated closely from either the total dissolved solids (TDS) or specific conductance (SpC). The conductance approach is the more accurate of the two, in that both SpC and I are functions of total ionic content, whereas the TDS includes non-ionic species such as dissolved silica. The approximations for molal ionic strength based on TDS (ppm) are:

$I = 2 \times 10^{-5} \times TDS$	NaCI water
$I = 2.5 \times 10^{-5} \times TDS$	an 'average' water
$I = 2.8 \times 10^{-5} \times TDS$	Ca (HCO <sub>3</sub> ) <sub>2</sub> water

1 1

or in terms of specific conductance in micromhos at

esp. secs

esp > weeks

yrs

25 C: ·

I 😳 0.8 x .10 <sup>5</sup> x SpC	NaCl water
I = 1.7 x 10 <sup>-5</sup> x SpC	CaSO₄ - MgSO₄ water
I = 1.9 x 10 <sup>5</sup> x SpC	Ca (HCO <sub>3</sub> ) <sub>2</sub> water

As a first approximation, one can usually assume that activities of molecular species such as carbonic acid ( $H_2CO_3$ ) and silica ( $H_4SiO_4$ ) equal their molal concentrations, particularly in water fresher than sea water. More exactly, their activity coefficients increase with ionic strength and may be computed from the Setchenow equation, which is  $\log \gamma_i = KI$ . The constant K is called the salting-out coefficient, and in NaCl solutions equals 0.231 for  $H_2CO_3$  (Millero 1983), and 0.080 for  $H_4SiO_4$  (Marshall and Chen 1982).

For ionic strengths below about 0.1 molal (about 5000 ppm TDS), the extended Debye-Hückel equation is commonly used to compute the activity coefficients of ionic species. The equation is:

$$\log \gamma_i = (-Az_\perp^2 \sqrt{1})/(1 + Ba_i \sqrt{1})$$
(16)

A and B are functions of temperature. On a molal basis A = 0.511 and B = 0.329 at 25 C. The a, is the 'effective size' of the hydrated ion in Angstroms (Garrels and Christ 1965; Stumm and Morgan 1981). The Debye-Hückel equation is accurate for monovalent ions up to I = 0.1 m, and for divalent ions to I = 0.01 m. The equation is adequate for obtaining ion activity coefficients in fresh water (TDS  $\leq$  10,000 ppm), but not in brines (TDS > 35,000 ppm = sea water). Activity coefficients for some important ions, and ion pairs such as CaHCO<sub>3</sub><sup>+</sup> computed with the Debye-Hückel equation, are plotted in Figure 3.

The Debye-Hückel equation is based on several assumptions, which become invalid at high ionic strengths. These include that ion interactions are purely Coulombic, ion size is independent of ionic strength, and ions of the same sign do not interact. The so-called 'ion interaction' model developed by Pitzer and others (Pitzer 1979; Harvie and Weare 1981) accounts for the behavior of ions in water at high ionic strength. In highly simplistic terms, the activity coefficient of an ion based on this approach may be computed from an equation of the form

$$\ln \gamma_i = \ln \gamma_{DH} + \text{high ionic strength terms}$$
(17)

where  $\ln \gamma_{DH}$  is the Debye-Hückel contribution to the activity coefficient, and the high ionic strength terms account for two-ion (binary) and three-ion (ternary) interactions. Some of these interactions are considered 1-dependent, and some 1-independent. The ion interaction model is parameterized using a combination of theoretical and empirical information. The model has been shown to give accurate results in brines up to 20m (Harvie and Weare 1981). Model computed solubilities of gypsum, calcite and aragonite are compared to their measured solubilities in NaCl solutions in Figures 4 and 5 after Harvie (1981). The

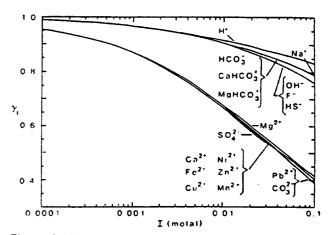


Figure 3. Activity coefficients of some ions plotted as a function of ionic strength, as computed with the Debye-Hückel equation.

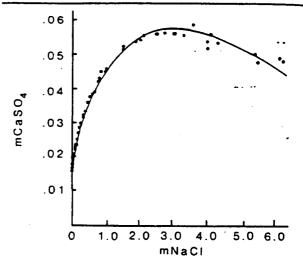


Figure 4. The molal solubility of gypsum as a function of NaCl molality. The dots are the measured solubility. The curve has been computed using Pitzer's ion interaction approach. The plot is from Harvie (1982).

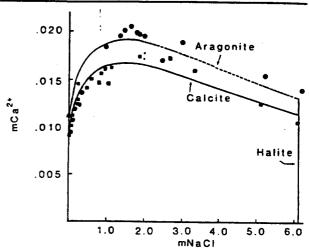


Figure 5. The molal solubilities of calcite and argonite as a function of NaCl molality  $(P_{CO_2} = 0.97 \text{ atm})$ . The points are measured. The curves have been computed using Pitzer's ion interaction approach. The plot is from Harvie (1982).

modeled and empirical results for gypsum are in excellent agreement. However, the agreement for aragonite and calcite is less perfect. This reflects the need to improve the accuracy of the high ionic strength terms involving Ca<sup>2+</sup>, Mg<sup>2+</sup> and the carbonate species in the model.

Another application of the ion interaction model is summarized in Table 2, which shows the computed saturation state of five deep brines (ionic strengths from 2.9 to 4.8m) at temperatures and pressures up to 40 C and 130 bars. The saturation state of each water with respect to individual minerals is described by its saturation index (SI) value, where SI =  $\log[M^{2^+}]$ [SO<sub>4</sub><sup>2-</sup>]/Ksp. [ $M^{2^+}$ ] [SO<sub>4</sub><sup>2-</sup>] is the product of the cation and sulfate activities in the brine, and Ksp is the theoretical solubility product of the mineral. Ion-interaction model calculations show all five brines are saturated with respect to gypsum, anhydrite and celestite, and three of the five with respect to barite. RaSO<sub>4</sub> is undersaturated in all five by from five to six orders of magnitude.

#### The Effect of Temperature and Pressure on Reactions

Most thermodynamic data for reactions is known for 25 C and 1 bar, but not for higher (or lower) temperatures and pressures. Thus, it is often necessary to correct the available data in order to apply equilibrium concepts, particularly at elevated temperatures and pressures. The following arguments are a simplified derivation of some of the expressions needed to make such corrections. The reader is referred to Garrels and Christ (1965) or Stumm and Morgan (1981) for more complete derivations and discussion.

For a reaction: aA + bB = cC + dD, we can write  $\Delta G = \Delta H - T \Delta S$ . In the latter equation,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are the Gibbs free energy, enthalpy and the entropy of the reaction, and  $\Delta G = cG_C + dG_D - bG_B$ . The free energies in this last equation are the standard state

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values for each reactant and product. Similar statements define  $\Delta H$  and  $\Delta S$  for the reaction. At equilibrium  $\Delta G = O$ , and  $\Delta H = T\Delta S$ . At 1 bar pressure  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ , and at equilibrium  $\Delta G^{\circ} = -RT1nKeq$ .

The effect of temperature on  $\Delta G$ , and thus on Keq may be predicted from

$$\frac{\partial \Delta G}{\partial T_{p}} = \Delta S, \quad \frac{\partial (\Delta G/T)}{\partial T} = -\frac{\Delta H}{T^{2}} \quad \text{or}$$

$$\frac{\partial \ln \text{Keq}}{\partial T} = \frac{\Delta H}{BT^{2}} \quad \text{(18)}$$

If  $\Delta H$  is a function of temperature, then we must know the heat capacity of the reaction, which is

$$\Delta C_{P} = \left(\frac{\partial \Delta H}{\partial T}\right)_{P}.$$

If  $\Delta H$  is constant between temperatures T<sub>1</sub> and T<sub>2</sub> (i.e., if  $\Delta C_p = 0$ ), then integration yields

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(19)

 $\Delta C_p$  is usually not zero, particularly for reactions involving ions. If  $\Delta C_p$  is constant between  $T_1$  and  $T_2$ , then integration yields

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{\Delta C_p}{R} \left(\frac{T_1}{T_2} - 1 - \ln\frac{T_1}{T_2}\right)$$
(20)

Criss and Cobble (1964) (see also Helgeson 1969) have developed a method of evaluating the average heat capacity of aqueous ionic species at elevated temperatures from the ionic entropies at 25 C. Such an approach is very useful for reactions with variable heat capacities, and can yield accurate results up to 200 C or higher in some cases. However, a more accu-

Mineral	Sawyer #1 Wolfcamp Zone 5	Sawyer #1 granite wash Zone 4	Mansfield #1 Wolfcamp Zone 1	Mansfield #1 Wolfcamp Zone 2	Zeeck #1 Wolfcamp Zone 3
Gypsum (±0.2)	+0.07	0.00	-0.08	-0.02	-0.11
Anhydrite (±0.2)	-0.12	-0.06	-0.12	-0.07	-0.20
Celestite (±0.3)	+0.05	+0.22	-0.19	-0.16	-0.09
Barite (±0.5)	-0.17	+0.34	-0.65	-0.20	-1.44
RaSO₄ (c) (±0.5)	-5.15	-6.33	-6.22	-6.16	-5.77

Table 2
 Mineral Saturation Indices for Five Palo Duro Basin (North Texas) Deep Brines

The  $\pm$  values shown in parentheses by the mineral names are the range of SI values within which a water is considered saturated with respect to that mineral. (Langmuir and Melchior 1985).

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rate approach to reactions involving ions is to write such reactions so that  $\Delta C_p$  will be practically constant, independent of temperature. This can be done by balancing the reaction with ions of the same total valence on both sides (Murray and Cobble 1980). For example,  $\Delta C_p$  must be practically constant for the reaction

$$HCO_{3}^{-} + OH^{-} = CO_{3}^{2-} + H_{2}O$$
(21)

so that with the well known data for the dissociation of water above 25 C, and a value for  $K_2$  for the reaction  $HCO_3^- = H^+ + CO_3^{2-}$  at 25 C, one can extract values for  $K_2$  above 25 C without measuring them. Another example of this approach is the reaction

$$Ca^{2+} + BaSO_4 = Ba^{2+} + CaSO_4$$
(22)

for which  $\Delta C_p = -5.1$  cal mol<sup>-1</sup>K<sup>-1</sup> at 25 C (Langmuir and Melchior 1985). Assuming a constant reaction heat capacity, with a solubility product for anhydrite (-log Ksp) of 4.64 at 56 C (our reference temperature), and the solubility product for barite from Blount (1977) we may compute  $\Delta G = 7.518$  kcal/mol and  $\Delta S = 7.95$ cal mol<sup>-1</sup>K<sup>-1</sup> for reaction (22) at 56 C. Several additional steps lead us to -log Ksp for anhydrite as a function of temperature based on the value for barite. In Figure 6 are plotted -log Ksp (anhydrite) based on this approach, and computed directly from anhydrite solubility data (Langmuir and Melchior 1985). The agreement is clearly excellent up to 100 C.

In reactions that involve gases, the effect of pressure is accounted for by writing the activity of the gas as its partial pressure (see above). The effect of pressure on reactions involving solutes, solids and liquids can usually be ignored at depths less than 300m (about 1,000 feet). Hydrostatic pressure affects reactions through the molar volume change of the reaction ( $\Delta V$ ). Higher pressure favors a lower molar volume of reactants and products. In other words, whichever of these has the lower total molar volume is favored by an increase in P. The effect of pressure on the equilibrium constant of a reaction may be computed from the expression

$$\left(\frac{\partial \ln K}{\partial P}\right)_{T} = -\frac{\Delta V}{RT}$$
(23)

(Millero 1982). The following example from Langmuir and Melchior (1985) illustrates the pressure effect. A pressure of 130 bars increases the solubility product of barite (BaSO<sub>4</sub>) at 25 C from  $-\log Ksp = 9.97$  at 1 bar to 9.87. For gypsum the effect from 1 bar to 130 bars (about 1,300m below the water table) is a change in  $-\log Ksp$  of from 5.59 to 5.52 at 25 C.

Equilibrium concepts have been used extensively to define maximum or minimum possible concentrations of dissolved species in ground water, when those concentrations are controlled by the precipitation or dissolution of minerals. The complex calculations necessary to apply such concepts, are usually carried out on a computer via computer codes such as WATEQF (Plummer et al. 1976) or PHREEQE (Park-

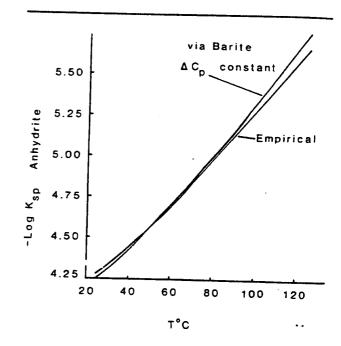


Figure 6. -Log  $K_{sp}$  for anhydrite as a function of temperature, based on empirical measurements and estimated assuming  $\Delta C_p^{\circ} = \text{constant for the}$  reaction:  $Ca^{2+} + BaSO_4 = Ba^{2+} + CaSO_4$  (Langmuir and Melchior 1985).

hurst et al. 1980). For a detailed discussion of such codes see Plummer (this volume), Nordstrom et al. (1979), or Nordstrom and Ball (1984).

### **Adsorption-Desorption Reactions**

In a water/rock or water/sediment (soil) system, dissolved substances have a tendency to partition themselves between the solution and the surfaces of mineral grains and other solids present. This partitioning is called sorption (Yariv and Cross 1979). Sorption may strictly involve a concentrating of the sorbed substance at a solid surface (adsorption), or its penetration into the interior of the solid (absorption). When adsorption involves short-range chemical bonds, it is sometimes called chemisorption. When the bonding is weaker (more physical), and reflects long-range electrostatic bonds or van der Waals bonds, it has been called physical sorption. The chemisorption process is considered limited to adsorption of up to a single surface layer, whereas physical adsorption may include the surface accumulation of multiple layers of the sorbing species (sorbate) on the solid (sorbent).

Dissolution of minerals in processes such as weathering is obviously a major source of chemical constituents in ground water. However, the opposing reaction, mineral precipitation, is much less important, in that only a few minerals are insoluble enough to reach saturation and to precipitate in any particular ground water. Stated differently, only a few dissolved species reach high enough concentrations in a given ground water to be limited or controlled by the solubility of a mineral. On the other hand, all dissolved sub-

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stances in the water/rock system are adsorbed on the surfaces of the solids present. The concentrations of these substances in the water, then, always depend upon the sorption tendencies of the solids. Mineral dissolution-precipitation controls on solute transport are only important at relatively high concentrations of the solutes when mineral saturation is approached. In contrast, adsorption controls solute transport at all concentrations below mineral saturation, and becomes most important as a process at the lowest solute concentrations. This point is perhaps best understood by looking at a plot describing the adsorption of a typical trace constituent from water onto a solid phase (Figure 7). Such a plot is often called a sorption isotherm. A tangent drawn to the empirical curve gives the ratio of the amount sorbed to its concentration in solution. At near-zero dissolved concentrations, the tangent becomes very steep. In other words, the highest proportion or percentage of a substance is sorbed at its lowest concentrations. This percentage decreases as the sorption capacity of the surface is satisfied with increasing concentrations of the sorbate. Such behavior is commonly observed for trace constituents in ground water.

Innumerable mathematical models have been developed to describe adsorption from solution. Most of the familiar ones may be classified as belonging to three types. These are the adsorption isotherm models, mass action-type models, and models that combine the first two types, with mathematics describing the detailed properties of the solution and of the socalled double-layer at the surface between the sorbent and solution. We will call the latter double-layer models in this paper. In the following discussion, we will comment on the applicability and major limitations of examples of each of these models.

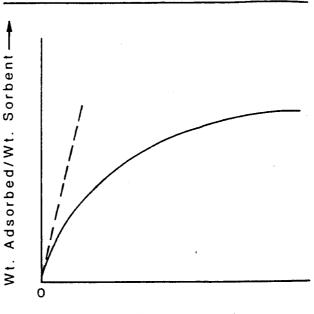
The simplest of the isotherm equations is the Freundlich equation, which may be written

$$\frac{x}{m} = KC_n$$
(24)

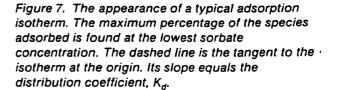
or in logarithmic terms

$$\log \frac{x}{m} = \log K + n \log C$$
 (25)

where x/m is the weight of sorbate divided by the weight of sorbent (usually  $\mu$ g/g or mg/g), K and n are constants, and C is the dissolved concentration of the sorbate. If n = 1, then K = K<sub>d</sub>. The latter is called the distribution coefficient. Because of its mathematical simplicity, K<sub>d</sub> is readily incorporated into transport equations. However, as we will see, the adsorption behavior of most substances is too complicated to be adequately modeled using a K<sub>d</sub> approach. Note that the assumption of a constant K<sub>d</sub> value is the same as assuming a linear isotherm in Figure 7, and saying that adsorption is independent of sorbate concentration and of surface coverage. Some non-ionic organics are sorbed (absorbed or partitioned) into soil organic



Sorbate Concentration ------



matter according to linear isotherm behavior (Chiou et al. 1983); however, adsorption of inorganic substances rarely obeys the  $K_d$  (linear isotherm) model.

A second familiar isotherm equation is the Langmuir isotherm, which may be written

$$\frac{x}{m} = \frac{aC}{1+bC}$$
(26)

or in a form that gives a linear plot as

$$\frac{1}{x/m} = \frac{b}{a} + \frac{1}{aC}$$
 (27)

In this case x/m and C are measured in repeated experiments, to yield the constants a and b.

In general, the isotherm equations may describe adsorption of a single species if there is no solution complexing of the sorbate species, the pH and ionic strength are constant, and there is no competitive adsorption. Perhaps the most successful applications of the isotherm equations have been to physical adsorption of trace neutral organics such as pesticides onto organic matter or soils.

A second group of adsorption models may be called mass-action type models. The models describe a process whereby one sorbate species (usually an ion) replaces a second sorbate (ionic) species on the surface of the sorbent. For a simple binary mass-action reaction (usually called an exchange reaction) we may write

$$A + BX = B - AX$$
(28)

The general equilibrium expression for the exchange reaction is

$$K_{ex} = \frac{[B]}{[A]} \left(\frac{AX}{BX}\right)^{n}$$
(29)

where the brackets enclose the activities of the aqueous ions, the parentheses the mole fractions of total surface sites occupied by each sorbate, and n is a constant.

When  $K_{ex} = n = 1$ , the adsorption-desorption reaction is said to obey Donnan exchange. If such a model fits the adsorption data, then one can assume a very simple exchange process in which the following conditions apply: (1) ion valence controls exchange, ionsize differences are unimportant; (2) the sorbent has a constant surface charge or cation exchange capacity (CEC); (3) no electronic surface effects take place; (4) sorbate ions are not complexed; (5) activity coefficients in solution and on the surface have equal ratios and are constant. Donnan exchange has been found to closely fit the adsorption behavior of major alkaline and alkaline earth ions on some clays (Langmuir 1981).

In the case that n = 1, but  $K_{ex}$  is not unity, the process may be called simple ion exchange. Corresponding conditions are: (1) ion valence and size both control exchange; (2) the surface charge is constant; (3) there are minimal electronic effects and minimal complexing of the sorbate ions; (4) activity coefficients on the surface ( $\lambda$  values) (assumed equal to unity in Donnan exchange) and for the sorbate ions in solution have constant ratios (but may not be constant themselves). Simple ion exchange accurately describes the competitive adsorption of major cations on many clays. (Major cations are those at concentrations of about 10<sup>-3</sup>m or greater).

None of the simple isotherm equations or the ion exchange equation can model completitive adsorption when the surface charge of the sorbate changes during the adsorption process, or when the sorbing ion bonds to a surface that has a net surface charge of the same sign. Such behavior is typical of trace metal adsorption onto metal oxyhydroxides as will be discussed below.

The surface charge of most solids is net positive over a range of acid pHs, and becomes net negative for a higher pH range (which may still be acid). The surface charge of most metal oxyhydroxides usually results from the adsorption of H<sup>+</sup> or OH<sup>-</sup> groups (potential determining ions. PDI's) onto surface sites which have unsatisfied bonds or broken bonds which, may be considered to expose such groups as  $-H_2O$ ,  $-HO^-$  and  $-O^{2-}$  with increasing pH. These sites may be thought of as surface acid and base sites. Thus, adsorption of H<sup>+</sup> ions onto H<sub>2</sub>O sites may result in positive H<sub>3</sub>O<sup>+</sup> sites. At some intermediate pH, the number of net positive and net negative surface sites will be equal, so that the mineral has no net surface charge. This pH is called the ZPC or zero point of

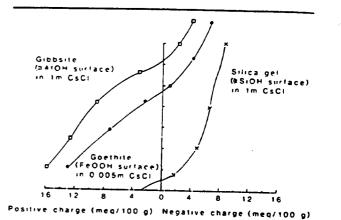


Figure 8. Curface charge of gibbsite, goethite and silica gel from pH 3 to 9. Measured charges depend on the electrolyte and concentration present during measurement (Modified after Greenland and Mott 1978).

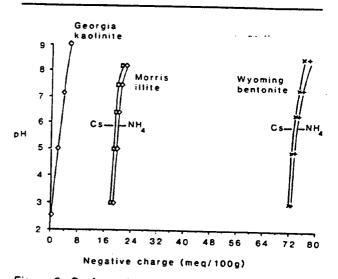


Figure 9. Surface charge of some clays in the pH range from 3 to 9, determined using 1.0M CsCl or 1.0M NH<sub>4</sub>Cl (Modified after Greenland and Mott 1978).

charge. A plot of the surface charge of silica gel, goethite and gibbsite as a function of pH is given in Figure 8, which shows that the measured ZPC's of these minerals are 2.5, 6.7 and 8.2, respectively. In other words at pH values below their ZPC's these minerals are positively charged, and can readily adsorb anions, whereas at higher pH's they become cation exchangers.

Unlike the oxides and hydroxides, the surface charge of clays (except kaolinite) chiefly results from unsatisfied negative bonds at the clay surface caused by a deficiency of cations within the clay structure. This charge deficiency may result from vacant cation sites or substitution of such ions as A1<sup>3+</sup> for Si<sup>+4</sup>, for example. To the extent that the surface charge of clays is strictly a result of structural effects, it is pHindependent. This is largely the case for smectities. The surface charge of a bentonite (a smectite) as a

function of pH is shown in Figure 9, and can be seen to

increase by less than 9 meq/100 g of clay or +10 percent between pH 3 and 9. This increase in surface charge can be ignored over a wide pH range, which is why ion exchange concepts apply rather well to the smectites. The increase is real, however, and represents a larger percentage of the net surface charge for the illite and kaolinite plotted in the same figure. It reflects the presence of broken or otherwise unsatisfied surface bonds at the corners and edges of clay particles that have acid and base properties equivalent to those exhibited by the metal oxyhydroxides. The charge characteristics of these sites then, change with pH because of the adsorption and/or desorption of the potential determining ions H<sup>+</sup> and OH<sup>-</sup>. Ignoring the effect for illite is not serious if adsorption takes place over a narrow pH range. However, in kaolinite the surface charge is almost entirely due to adsorption of H<sup>+</sup> and OH<sup>-</sup> onto an oxyhydroxide-type surface. The percentage change in the relatively small net surface charge of kaolinite with pH is obviously quite large and cannot be ignored. Ion exchange models would then be unsuitable to describe competitive cation adsorption onto kaolinite, except at a constant pH.

This same pH-dependence of kaolinite surface charge is evident from Figure 10, which shows Pb adsorption from a landfill leachate. The increase in net negative surface charge (or cation exchange capacity) with pH is manifest by the markedly greater Pb amounts that can be adsorbed at pH 6 than at pH 3. (The dashed vertical lines extending above the data points at pH 5 and 6, reflect the precipitation of lead hydroxy-carbonate at these dissolved Pb concentrations and pH's.) The plot shows that at every pH, the adsorption of lead follows a different adsorption isotherm. Clearly, the isotherm modeling approach is only qualitatively useful for such a complex problem.

In most adsorption modeling studies employing isotherm equations or ion exchange concepts, the assumption is made that the total concentration of a sorbate species is available to react with the surface of the sorbent. This assumption is roughly correct in dilute solutions in which sorbate species do not interact with other dissolved species to form complexes. Typically, neutral or negatively charged complexes are more weakly adsorbed (if adsorbed) on a net negative surface, than are cations. For example, the adsorption of Cd onto montmorillonite at different ionic strengths of NaCl solution is plotted in Figure 11 in isotherm fashion. Adsorption is seen to decrease rapidly with increasing NaCl concentrations. Cadmium is known to form strong complexes with chloride, from CdCl<sup>+</sup> to CdCl<sub>4</sub><sup>2-</sup> (Smith and Martell 1976; Long and Angino 1977). The amount of the cadmium in these complexes must increase with the chloride concentration. That adsorption decreases with chloride content indicates that the complexes are poorly adsorbed compared to Cd2+ ion.

A more general model than simple ion exchange is the power exchange function, which corresponds to Equation 29 for the competitive exchange reaction, with n typically equal to from 0.8 to 2.0 (Langmuir

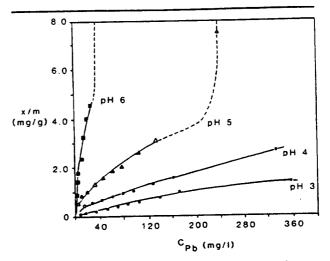
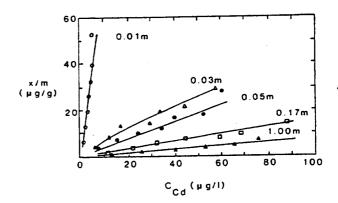
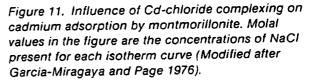


Figure 10. Adsorption of Pb from DuPage leachate by kaolinite at 25 C, as a function of pH. Dashed vertical lines show the Pb concentration at saturation with Pb hydroxy-carbonate solid (Modified after Griffin and Shimp 1976).





1981). The function is related to regular solution behavior and Freundlich isotherm behavior for certain conditions, but is otherwise strictly an empirical statement of adsorption behavior. Plotted in Figures 12 and 13 are empirical data for Cd vs. Ca adsorption onto montmorillonite using the log linearized form of the power exchange function.

$$\log \frac{[Cd^{2^+}]}{[Ca^{2^+}]} = \log K_{ex} + n \log \frac{CdX}{CaX}$$
(30)

where CdX and CaX are the mole fractions of Cd and Ca adsorbed, and the brackets enclose the activities of the ions in solution. The adsorption data is seen to closely fit three separate power exchange functions. For Cd concentrations in excess of Ca, the exchange reaction is Donnan, with  $K_{ex} = n = 1$ . However, as Cd drops below Ca in solution, a power exchange function with  $K_{ex} = 0.9$  and n = 2.00 is needed to fit the

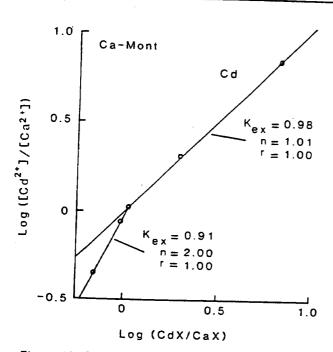


Figure 12. Power exchange function plot for Ca<sup>2+</sup> – Cd<sup>2+</sup> exchange onto Ca-montmorillonite. 'r' values are correlation coefficients (Langmuir 1981).

data. At still lower Cd concentrations (where Cd becomes a trace constituent) a third, power exchange function fits the data. It should be noted that the adsorption calculations are written in terms of the activities of free dissolved cations, corrected for ionic strength and complexing.

When the power exchange function is needed to fit the adsorption data, then some specific adsorption is taking place. In other words, there is significant adsorption of solute ions onto a surface that has the same net surface sign. This seemingly bizarre behavior is typical of trace metal adsorption. It reflects the fact that the net surface charge is just that; the sum of the surface charge due to all surface sites present, of which some will be positive and some negative, regardless of pH. Not only are such mixed charge sites always present, but the trace metal adsorption process itself produces such sites. Although the power exchange function can fit such empirical behavior, it does not explain it. The model is thus too simple to incorporate all the factors controlling adsorption we have already discussed.

Early work on trace element adsorption by metal oxyhydroxides revealed that the adsorption of trace metal cations was practically complete at pHs below the ZPC of the oxyhydroxides. In other words, specific adsorption of the metals was occurring onto surfaces having the same net surface charge as the sorbing ions. Such behavior was inconsistent with available theory. An example of such adsorption is given in Figure 14. The ZPC of the amorphous ferric oxyhydroxide is 7.9, so that virtually all the uranyl is adsorbed onto a net positive surface. The plot is called an

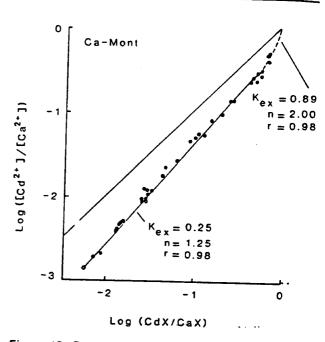


Figure 13. Power exchange function plot for Ca<sup>2+</sup> -Cd<sup>2+</sup> exchange onto Ca-montmorillonite. 'r' values are correlation coefficients (Langmuir 1981).

adsorption edge plot, and the pH of the edge (defined as the pH for 50 percent adsorbed) is near 4.

In order to explain such specific adsorption, James and Healy (1972) suggested that the adsorption free energy be written

ΔG°	= 3G°	+ 7C。	+ ∆G°
ads	coul	solv	chem
(-)	(+ or -)	(+)	(+  or  -)

where  $\Delta G_{coul}^{\circ}$  is the coluombic adsorption term. Its value is positive (inhibiting adsorption) when specific adsorption is involved.  $\Delta G_{solv}^{\circ}$  represents the energy of dehydrating the water-coordinated metal ion in order to bring it closer to the surface. This term is proportional to  $z^2$ , where z is the charge of adsorbing

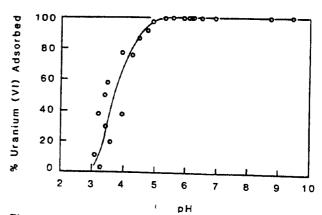


Figure 14. Adsorption of uranyl onto amorphous ferric oxyhydroxide at 25 C in CO<sub>2</sub>-free 0.1M NaNO<sub>3</sub> solutions (Hsi and Langmuir 1985).

metal ion or complex. Because  $\Delta G_{solv}^{\circ}$  is positive, it also inhibits specific adsorption. However, its z<sup>2</sup> dependence shows that  $\Delta G^{\circ}_{solv}$  becomes much less positive if a metal complex of lower valence is formed.  $\Delta G^{\circ}_{chem}$ denotes the free energy of chemical bonding, and must be negative in sign in the case of specific adsorption. That metal-hydroxy complexes are more readily adsorbed by the oxyhydroxides than are free metal ions, is clear from Figure 15. The plot shows that metals that form the strongest hydroxide complexes are adsorbed at the lowest pHs. According to Hsi (1981) (see also Hsi and Langmuir 1985) the adsorption of uranyl in Figure 14 is chiefly as the hydroxy complexes  $UO_2OH^+$  and  $(UO_2)_3(OH)_5^+$ , not free UO22+ ion. Shortcomings of the James and Healy (1972) model, are that the acid-base complex properties of the sorbate surface were not considered, and that the free energy of adsorption of all species of the same metal were considered equal.

The state-of-the-art in adsorption modeling is probably the surface-ionization and complexation-type model (Davis et al. 1978; Davis and Leckie 1979, 1980; Westall and Hohl 1980; and Hsi and Langmuir 1985). These are the first models that can deal with ion exchange and specific adsorption of anions and cations, variations in both surface charge and potential (related to pH), the effects of ionic strength, and the simultaneous adsorption behavior of several complexed and uncomplexed metal and non-metal species. The models employ a combination of mathematical functions derived from double-layer theory relating the charge, potential and capacitance in the double layer, and mass-law expressions for adsorption of species within the double layer. Rigorous application of such a model necessitates that a great many measurements be made of the solution and sorbents to adequately characterize the adsorption process. The important "fixed" basic parameters and adjustable parameters in the model are listed in Table 3.

Recent years have seen rapid development and refinement of this model approach, particularly for single sorbents and relatively simple solutions. Figures 16 and 17 show the excellent fit of model-calculated adsorption to empirical data for uranyl species adsorption involving both hydroxyl and carbonate complexing on goethite. Values are the intrinsic constants for adsorption of the aqueous species onto the corresponding surface sites indicated in the figures. Although most determinations of metal adsorption using this approach have so far dealt with pure, single minerals, the model can, in principle, also be applied to adsorption by whole rocks and soils, if the same measurements are made on these heterogeneous materials. Measurements of the co-variation in surface charge and potential on soils described by Greenland and Hayes (1978) represent a first step in the future application of these models to complex natural water-rock systems. The characterization of complex natural rock surfaces and soils in terms of the number and proportions of, for example, Si, AI and Fe(III)-type sites may allow prediction of whole rock adsorption behavior

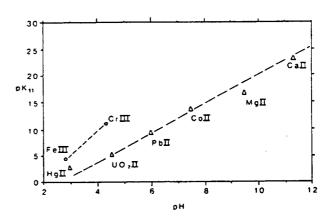


Figure 15. The pH of the 50 percent-adsorbed point taken from plots of the adsorption edge curves for the metals shown, based on published studies where the total metal concentration was about  $10^{-4}$  molal in an indifferent electrolyte. Sorbents are various oxyhydroxides. pK<sub>11</sub> is -logK<sub>11</sub> where K<sub>11</sub> is the equilibrium constant for the reaction:  $M^{n+} + H_2O = MOH^{n-1} + H^+$  (Langmuir 1983).

## Table 3 Parameters Needed in the Surface Ionization and Complexation Model

#### Fixed, experimentally determinable parameters

- 1. Surface site density, N.
- 2. Specific surface area
- 3. Intrinsic equilibrium constants for the surface reactions involving:
  - a. H<sup>+</sup> and OH<sup>-</sup>
  - b. Major cations and anions of the electrolyte
  - Other ions, including complexes of the metal of interest

#### Adjustable parameters

- 1. Inner layer capacitance, C<sub>1</sub>
- Outer layer capacitance, C<sub>2</sub> (usually assumed constant for all surfaces at 20µF/cm)

from studies of the simpler sorbent systems. This approach has been used to apply the model to the migration of metals in acid sulfate water through soils by Peterson et al. (1985) as reported in this volume.

The surface ionization and complexation adsorption model has been combined with a transport code by Jennings et al. (1982), and also by Miller (1983), and Miller and Benson (1982). The code written by

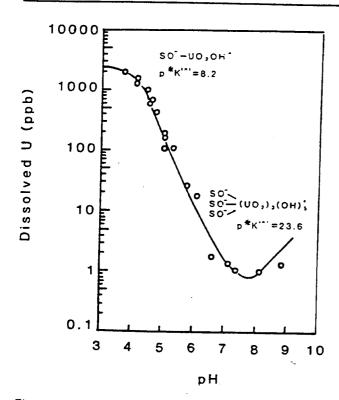


Figure 16. Adsorption of uranyl onto 1 g/L goethite in suspension in 0.1M NaNO<sub>3</sub> solutions at 25 C. Total uranium is  $10^{-5}$ M. Circles are experimental data. The solid curve is model calculated assuming the monodentate and tridentate surface complexes shown in the figure, and the presence of a dissolved  $(UO_2)_3(OH)_7$  complex, which is not adsorbed. p\*K<sup>int</sup> denotes the intrinsic stability constants of the surface complexes (Hsi and Langmuir 1985).

Miller and Benson can also compute the effect of mineral precipitation and dissolution on the transport process.

#### Summary of Adsorption/Desorption

The number of independent variables that must be quantified in order to accurately model the adsorption of most trace metals, even in a laboratory system will generally exceed ten (Table 4). These variables include properties of the solution and of the sorbent phase. In some instances many of the variables are sufficiently constant to be ignored in a particular water/rock system, and simple mathematical models such as the isotherm equations or even K<sub>d</sub> can be used to predict adsorption behavior. Before assuming their applicability, it is important to realize what simplifying assumptions are implied by each model. For example, the most accurate application of the isotherm equations is probably to non-competitive adsorption of molecular organic compounds. The simple ion-exchange model is best limited in application to competitive adsorption of major cations by smectite-group clays. Rigorous modeling of trace metal adsorption by metal oxyhydroxides or kaolinite involves specific adsorption, often

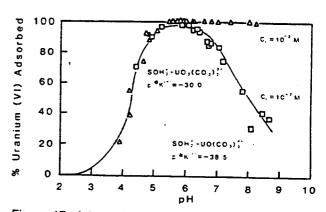


Figure 17. Adsorption of uranyl onto 1 g/L goethite in suspension in 0.1M NaNO<sub>3</sub> solutions at 25 C. Total uranium is 10<sup>-5</sup>M. C<sub>T</sub> denotes total carbonate concentrations maintained during the two sets of experiments. Symbols are experimental data. The solid curves have been model calculated considering UO<sub>2</sub>OH<sup>+</sup>,  $(UO_2)_3(OH)_5^+$ ,  $UO_2(CO_3)_2^{2-}$ , and  $UO_2(CO_3)_3^{4-}$  surface equilibria (Hsi and Langmuir 1985).

of metal-hydroxy complexes, which can be most accurately modeled using the surface-ionization and complexing model. All these adsorption models have been combined with transport codes, and successfully used to model and predict empirical field and/or laboratory data (Pearson 1984).

Because of the mathematical and conceptual simplicity of isotherm and ion exchange models, researchers often use them for adsorption modeling when it should be quite clear that the adsorption process is far too complex to make sense in terms of only two or three independent variables. Figure 18 is a plot of K<sub>d</sub> values for the sorption of neptunium(V) by 18 different minerals. Values of K<sub>d</sub> range over nearly five orders of magnitude at pH 4, and three orders of magnitude at pH 9. How can one confidently pick a single value or narrow range of values for modeling purposes? Clearly, one cannot. The adsorption data must be collected

 Table 4

 Comparison of Adsorption Models

Model	Number of independent variables
K <sub>d</sub>	1
Freundlich isotherm	2
Langmuir isotherm	3
Simple (binary) ion exchange	4
Surface-complexation + ionization model	>10

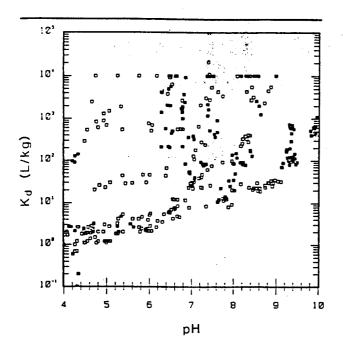


Figure 18. Sorption of trace neptunium (V) in 0.1M NaCl solutions by 18 different minerals as a function of pH, expressed in terms of  $K_d$ . Open symbols and closed symbols are oxic and anoxic waters, respectively (Myer et al. 1984).

with sufficient measurements made on both the solution and the sorbate minerals to permit parameterization of a model such as the surface ionization and complexation model, if the purpose of the work is to predict the adsorption behavior of neptunium.

#### **Kinetic Concepts**

In the introduction we discussed the general relationship between kinetic and equilibrium concepts. It was concluded that when reaction rates are comparable to or less than residence times of waters, the state of the reactions in question cannot be defined without the use of kinetic concepts. We also concluded that reactions occurring within a water (homogeneous reactions) are generally very fast, with half times of seconds or less, and so can be considered at equilibrium in most natural waters. On the other hand, reactions between the water and minerals such as precipitation/dissolution (a heterogeneous reaction) have half-times usually of days to tens of years or more. Such reactions can often be considered at equilibrium in deep artesian ground water, but not in many shallow water table systems.

In this section we will discuss fundamental concepts of kinetics with examples from among reactions of geochemical interest. The reader who wishes a more in-depth treatment of geochemical kinetics than presented here, is referred to the works of Berner (1978, 1981), Hoffman (1981), Lasaga (1981), and Helgeson et al. (1984).

Unlike chemical equilibrium concepts, which have led to the quantitative understanding of ground water

chemistry in many water/rock systems, chemical kinetic concepts are not easily applied to natural systems. This is particularly true of reactions involving minerals and the ground water. The rates of such reactions are strongly dependent on the surface characteristics of mineral grains, adsorbed trace substances on mineral surfaces, and often on the activities of organisms (Berner 1978). Laboratory rates of mineral dissolution may be orders of magnitude faster than observed in nature because of enhanced reactivities of the laboratory-prepared mineral grains, and the adsorption of dissolution-inhibiting trace species such as phosphate in the natural system. Laboratory rates of Fe(II) oxidation, for example, are much slower than naturally observed oxidation rates, when the latter are catalyzed by microorganisms.

A number of researchers have attempted to apply kinetic concepts, and in particular, the kinetics of mineral/precipitation/dissolution reactions to ground water systems (cf Claassen 1981; Paces 1983). Although the results of such studies have been qualitatively reasonable, our inability to quantify such properties as the wetted surface area of reacting minerals in an aquifer will probably preclude the rigorous application of kinetic concepts to ground water studies.

In any case, it is hoped that the following discussion of kinetics will indicate some of the useful applications of such concepts, as well as their limitations in ground water geochemical work.

#### **Reaction Types**

In kinetics, a fundamental distinction is made between elementary and overall reactions. An elementary reaction is a reaction that takes place between reactants and products on a molecular level. For example,

$$H^{+} + OH^{-} = H_{2}O$$

$$CO_{2}(aq) + OH^{-} = HCO_{3}^{-}$$

$$H_{4}SiO_{4} = SiO_{2} (quartz) + 2H_{2}O$$

are elementary reactions. The reactants and products of elementary reactions may be ions, molecular species, radicals or free atoms. For example, the breakdown of ozone to oxygen  $2O_3 - 3O_2$ , probably involves the elementary reactions

$$k_{+1}$$
  
 $O_3 = O_2 + O$  and  $O + O_3 - 3O_2$   
 $k_{-1}$ 

where one of the intermediate species is a free oxygen atom (Lasaga 1981). It is often assumed that such reaction intermediates have a highly transient existence, and that their rates of formation and disappearance quickly become equal during an overall reaction. If this is correct for the ozone breakdown reaction, and  $k_{-2} \ll k_{+2}$ , then for steady-state conditions

$$\frac{d(O)}{dt} = k_{+1}(O_3) - k_{-1}(O_2)(O) - k_{+2}(O)(O_3) = O$$

The steady-state assumption allows us to solve for the concentration of atomic oxygen and so eliminate it from further consideration in rate law calculations (Lasaga 1981). A related assumption is that when equilibrium exists in an overall reaction, then the forward and reverse rates of each elementary reaction within it must be equal. This is called the principle of microscopic reversibility.

Describing an overall reaction such as

$$Fe^{2^{+}} + \frac{1}{4}O_2 + \frac{5}{2H_2O} = Fe(OH)_3 + 2H^{+}$$

in terms of its individual elementary reactions is describing its reaction mechanism. The pathway of an elementary reaction is explicitly defined by how it is written, whereas the pathway of an overall reaction is not. Rates of overall reactions are determined by the rates of elementary reactions comprising the overall reaction. As a corollary, the rate of an overall reaction can be predicted only if the rates of its component elementary reactions are known. The rates of elementary reactions are always proportional to the concentrations of individual reactants, whereas the rates of overall reactions may not be.

The speed of an overall reaction is usually governed by a rate determining step. For sequential reactions such as

$$HCO_3 + H^+ = H_2O + CO_2(aq)$$

and

$$CO_2(aq) = CO_2(g)$$

- 24 . . . . .

the first reaction is very fast, going to completion in fractions of a second, whereas the second is orders of magnitude slower, and so rate-determining. In the case of parallel reactions, the fastest reaction is rate determining. For example, the oxidation of pyrite by dissolved oxygen gas

$$FeS_2(s) + 7/2O_2(aq) + H_2O = Fe^{2+} + 2SO_2^{2-} + 2H^+$$

is relatively slow compared to its oxidation by ferric iron

Accordingly, the second reaction is rate-determining (as long as ferric iron is available). Because rates depend on concentrations, the rate-determining step may change with concentration. For example, the rate of calcite dissolution is pH-dependent in acid water, but depends on the H2CO3 concentration at higher pHs (Plummer et al. 1979).

#### **Rate Laws**

For a hypothetical elementary reaction A = B, the rate of the forward reaction A-B is given by dA/dt =  $k_+(A)$ , the rate of the reverse reaction B-A by dB/dt =  $k_{-}(B)$ , where  $k_{+}$  and  $k_{-}$  (both functions of temperature) are the rate constants for the forward and reverse  $2-46^{-1}$  reactions, and the parentheses enclose concentrations of the species A and B.

For elementary reactions in general (Gardiner 1972) one can write for the forward and reverse rates

$$R_{+} = k_{+} II (A_{i})^{-v_{i}}$$
  
reactants

and

$$R_{-} = k_{-} II (A_{i})^{v_{i}}$$
products

where the A, terms and their exponents are the products of the concentrations of reactants and products raised to the power of their stoichiometric coefficients. At chemical equilibrium  $R_+ = R_-$  and we can write

where Keg is the equilibrium constant. This expression relates the rate constants of elementary reactions to their equilibrium constants, and shows that if  $\mathsf{K}_{\mathsf{eq}}$  and a single rate constant are known, the second rate constant need not be measured. Rimstidt and Barnes (1980) used this relationship (called the principle of detailed balancing) to obtain the rate constant for

#### Table 5 Summary of Rate Laws and Their Integrated Forms for Some Simple Reaction Orders. (Gardiner 1972; Lasaga 1981)

Zeroth order

$$dA/dt = k_{-} \qquad A = A^{\circ} + k_{-}t$$
$$-dA/dt = k_{+} \qquad A = A^{\circ} - k_{+}t$$

#### **First Order**

$$dA/dt = k_{+}A \qquad \text{In } A = \text{In } A^{\circ} - k_{+}t$$
  
$$dA/dt = k_{+} (A_{s} - A) \qquad \text{In } \frac{(A_{s} - A)}{(A_{s} - A^{\circ})} = -k_{+}t$$

Second order

$$\frac{1}{v_{A}} \frac{dA}{dt} = k_{+}A^{2} \qquad 1/A = 1/A^{\circ} - v_{A}k_{+}t$$
$$\frac{dA}{dt} = k_{+}(A)(B) \qquad \text{in } \frac{(A^{\circ})(B)}{(B^{\circ})(A)} = (B^{\circ} - A^{\circ})k_{+}t$$

dissolution of the several silica polymorphs  $(k_+)$  given their empirical solubilities ( $K_{eq}$  values) and the precipitation rate constant  $(k_-)$ .

The order of an elementary reaction is defined by the number of individual atoms or molecules involved in the reaction. For example, the rate of reaction A + 2B = C can be written  $-dC/dt = k_+(A)(B)^2$ . This reaction is first order with respect to A and C, second order in B, and third order overall.

Table 5 is a summary of the differential and integrated forms of some simple rate laws. In the integrated rate expressions the zero superscript denotes the concentration of that species at t = 0. The subscript s, indicates the concentration of a species at equilibrium or saturation with respect to a solid phase. It is useful to consider the half-life or half-time of reactions, when half of a given reactant has been depleted. For a zero order reaction the half-time is given by  $t_{1/2} = 0.5 A_o/k_+$ . The half-time of a first order reaction is  $t_{1/2} = 0.693/k_+$ .

Lasaga (1981) and Gardiner (1972) discuss the rate expressions for third and higher order reactions. These topics are beyond the scope of this paper. Some

examples of empirical rate laws for a number of reactions of geochemical interest are listed in Table 6.

#### Mineral Precipitation/Dissolution Reaction Kinetics

Only rarely do we know the elementary reactions (i.e., the reaction mechanism) of overall reactions of geochemical interest. This is particularly true of heterogeneous reactions such as mineral precipitation/dissolution. This is in spite of the fact that the empirical rate laws for a number of geochemically important overall reactions have been determined in recent years (cf Table 6).

In principle, there are several different types of processes that can control the rates of mineral precipitation and dissolution. In moving ground water these include mass transport, diffusion control and surface reaction control. Berner (1978, 1980) has observed that the dissolution of silicates including quartz, amorphous silica and feldspars, calcite and apatite all dissolve according to surface reaction control. On the other hand, the rate mechanism of dissolution of more soluble minerals such as gypsum and halite is usually transport-controlled.

	Table 6	
Some Kine	tic Data of Geochemical Interest	

### A. The FeSO $_{4}^{+}$ complex

Formation of the  $FeSO_4^+$  complex may be written (Pagenkopf 1978):

$$Fe^{3+} + SO_4^{2-} \stackrel{k_+}{=} FeSO_4^+$$

$$k_-$$

for which the forward reaction (second order) rate expression is

$$R_{+} = \frac{d[Fe^{3+}]}{dt} = \frac{d[SO_{4}^{2-}]}{dt} = k_{+} [Fe^{3+}][SO_{4}^{2-}]$$

In this expression  $k_+ = 6.37 \times 10^3$  liter mol<sup>-1</sup> sec<sup>-1</sup> at 25 C. The reverse reaction rate (first order) is given by:  $R_- = k_-$  [FeSO<sup>+</sup><sub>4</sub>]. The equilibrium constant is  $K_{eq} = 205 \text{ mol}^{-1}$ , from which because  $K_{eq} = k_+/k_-$ , we compute  $k_- = 31 \text{ sec}^{-1}$ . Calculated rates and concentrations for this reaction as a function of time are given in Figures 23a and 23b.

#### B. Radioactive decay: the example of <sup>14</sup>C

Radioactive decay is a first order, usually irreversible reaction with a rate, which is given by

$$\frac{\mathrm{dn}}{\mathrm{dt}} = -k_{+}n \tag{1}$$

which upon integration yields:  $n = n_0 \exp(-k_+t)$ , where  $n_0$  and n are the total number of molecules present at t = 0 and t. The half-time for radioactive decay is:  $T_{1/2}$  =

 $0.693/k_+$ . Radiocarbon dating is based upon the reaction

$${}^{4}_{7}N + {}^{1}_{0}n - {}^{14}_{6}C + {}^{1}_{1}H$$

which introduces <sup>14</sup>C into living organisms. Upon their death, if no new <sup>14</sup>C is introduced

$${}^{14}_{6}C \stackrel{k_{+}}{-} {}^{14}_{7}N + {}^{\circ}_{-1}e$$

so that the integrated form of Equation 1 above becomes:

$${}^{14}C = ({}^{14}C_o) \exp(-k_+ t)$$

or in natural logs:  $\ln(^{14}C) = \ln(^{14}C_o) - k_+t$ .

Transposing leads to

$$t = \frac{1}{k_{+}} \ln\left(\frac{n_{o}}{n}\right) = \frac{1}{k_{+}} \ln\left(\frac{d_{o}}{d}\right)$$
(2)

where d and d<sub>o</sub> are the disintegration rates per minute per gram of carbon (dpm/g) at t and t<sub>o</sub>. Because  $T_{\frac{1}{2}} =$ 5,570 yrs, and k<sub>+</sub> = 0.693/T<sub>1/2</sub>, then k<sub>+</sub> = 1.24x 10<sup>-4</sup> yr<sup>-1</sup>. Substituting back into (Equation 2), and converting to common logs, with d<sub>o</sub> = 15.3 dpm/g, we obtain

$$t(yrs) = 18500 \log \left(\frac{15.3}{d}\right)$$

## C. Oxidation of organic matter and sulfate reduction

There are several groups of organic substances in any sediment, each group of which has its own decay rate (Westrich and Berner 1984). Decay rates, whether oxic or anoxic, obey first-order kinetics. For each group,  $G_i$ :  $dG_i/dt = -k_iG_i$ . For the total organic material present  $G_T$ 

$$dG_T/dt = \sum_{i=1}^{n} k_i G_i$$

 $(G_{\tau}$  is assumed the total decomposable organic matter). Integration of the initial rate equation gives for  $G_i$  as a function of time

$$G_i(t) = G_{oi} [exp(-k_i t)]$$

where  $G_{oi}$  is the initial amount of  $G_i$ . Experimental observation of organic in sediment decay rates leads to

$$G_{T}(t) = G_{o1} \left[ \exp(-k_{1}t) \right] + G_{o2} \left[ \exp(-k_{2}t) \right] + G_{o2}$$
 (1)

where  $G_T$  is some measure of the total organic content in the sediment such as TOC, the first term on the right is the highly reactive fraction, the second term the less reactive fraction, and  $G_{nr}$  denotes organic matter, which is non-reactive during the study.

In their study of modern marine sediments, Westrich and Berner (1984) found  $G_{o1} = 50$  percent,  $G_{o2} = 16$ percent, and  $G_{nr} = 34$  percent of TOC. For oxic decay their empirical rate constants were:  $k_1 = 18 \text{ yr}^{-1}$  (T<sub>1/2</sub> = 0.039 yr = 14 days), and  $k_2 = 2.3 \text{ yr}^{-1}$  (T<sub>1/2</sub> = 0.3 yr = 110 days). For anoxic decay of the same organic matter, which follows the same rate equations, they obtained  $k_1 = 4.4 \, yr^{-1}$  , and  $k_2 = 0.84 \, yr^{-1}$  . If similar rates apply to natural water/rock systems, which will generally have much longer residence times than considered in this study, one can expect that organic matter similar to  $G_1$ will have disappeared (T $_{\frac{1}{2}}$  = 14 days). G<sub>2</sub> kinetics will still be important. However, rates of decomposition of more recalcitrant organics (Gnr), because they include perhaps most of the toxic organics will still be important.

If sulfate reduction is organic carbon limited in the sediment described by Westrich and Berner (1984), then the same rates of organic carbon oxidation apply. For sulfate reduction, assuming that the organic carbon may be generalized as  $CH_2O$ , the reaction may be written:

 $2CH_2O + SO_4^{2-} - H_2S + 2HCO_3^{-}$ 

The rate of sulfate reduction, R(t) may be written

 $R(t) = 1/2K G_{o} [exp(-kt)]$ 

But  $R_o = 1/2KG_o$ , so that for the overall rate we find:

 $\Sigma R(t) = R_0 1 [exp(-k_1t)] + R_{02} [exp(-k_2t)]$ 

This, of course, assumes  $G_{nr}$  is inert. From their measurements, Westrich and Berner (1984) obtained  $k_1 = 7.2 \text{ yr}^{-1}$  and  $k_2 = 1.0 \text{ yr}^{-1}$ ; rate constants nearly equal to those for anoxic decay, as expected. These constants may be compared to mean values based on the work of others of  $k_1 = 8.0 \pm 1 \text{ yr}^{-1}$ , and  $k_2 = 0.94 \pm .25 \text{ yr}^{-1}$ .

#### D. Gypsum dissolution

The dissolution of gypsum follows first-order kinetics as expressed by the equation

$$\frac{dC}{dt} = k_+ A(C_s - C)$$

where A is the mineral surface area exposed to a volume of solution at time t, and  $C_s = 0.0154$  mol kg<sup>-1</sup>in pure water at 25 C (Langmuir and Melchior 1985). The approximate rate constant at 25 C and zero flow is k<sub>+</sub> = 2x10 -4cm sec<sup>-1</sup> (Estimated from James and Lupton 1978; Claassen 1981). James and Lupton's measurements at 5, 15 and 23 C lead to E<sub>a</sub> = 10.7 kcal mol<sup>-1</sup>, and a temperature dependence of the rate constant at ground water flow rates (<0.2cm sec<sup>-1</sup>) of

 $\log k_{+} = 4.14 - 2338/T$ 

where  $k_+$  is in cm sec<sup>-1</sup>. In agreement, Liu and Nancollas suggest  $E_a = 10 \pm 1.5$  kcal mol<sup>-1</sup>. Karshin and Grigoryan (1970) obtained activation energies of 7.1 and 3.7 kcal mol<sup>-1</sup> for dissolution of the {010} gypsum crystal face and faces perpendicular to {010}, respectively. Most authors consider gypsum dissolution to be chiefly diffusion-controlled. Calculated diffusion coefficients range from 4 to  $8 \times 10^{-6}$  cm<sup>2</sup> sec<sup>-1</sup> (Barton and Wilde 1971; Christoffersen and Christoffersen 1976).

James and Lupton (1978) found that gypsum solution rate increased with ionic strength. Their rate data measured at a flow velocity of 15 cm sec<sup>-1</sup> in up to 1.7m NaCl solutions fits the equation  $k'/k'_0 = 1 + 2.2 \sqrt{1}$ . The rate constant for gypsum dissolution increases with flow velocity according to

 $k_+$  (cm sec<sup>-1</sup>) = 2x10<sup>-4</sup> + 5.8x10<sup>-3</sup>v

where the velocity, v, is in cm sec<sup>-1</sup> at 25 C (James and Lupton 1978).

#### E. Oxidation of ferrous iron

There are two overall oxidation reactions for ferrous iron below pH 3.5 (Stumm and Morgan 1981; Morel 1983). Below pH 2.2:  $Fe^{2^+} + 1/4 O_2 + H^+ = Fe^{3^+} + 1/2H_2O$ 

Above pH 2.2, but below about pH 3.5:

$$Fe^{2+} + 1/4 O_2 + 1/2H_2O = FeOH^{2+}$$

The empirical rate law for  $Fe^{2+}$  oxidation under these acid conditions (Rate law #1—Figure 24)

$$\frac{d [Fe(II)]}{dt} = -k_+ [Fe(II)] P_{O_2}$$

which is seen to be second order and pH-independent. Empirically, at 20 C  $k_{+} = 10^{-3.2} \text{ day}^{-1} \text{ atm}^{-1}$ . Under atmospheric conditions, with  $P_{O_2} = 0.2$  atm (constant), the rate becomes pseudo first-order, and  $T_{\frac{1}{2}} = -\ln 2/0.2k_{+} = 5,500 \text{ days}$  (15 yrs). Studies of the same rate with bacterial mediation show it to be about  $10^6$  times faster than the inorganic rate, so that  $T_{\frac{1}{2}} \approx 8 \text{ min.}$ 

Above about pH = 4, the rate of  $Fe^{2^{4}}$  oxidation is related to the overall reaction

$$Fe^{2+} + 1/4 O_2 + 5/2H_2O - Fe(OH)_3 + 2H^4$$

The empirical rate law (Rate law #2—Figure 24) is given by:

$$\frac{d [Fe(II)]}{dt} = -k_{+} \frac{[Fe^{2+}]}{[H^{+}]^{2}} P_{O_{2}}$$

for which  $k_{+} = 1.2 \times 10^{-11} \text{ day}^{-1} \text{ mol}^2 \text{ atm}^{-1} \text{ at } 20 \text{ C}$ . If  $P_{O_2} = 0.2 \text{ atm}$ , and pH = 6, the rate law becomes pseudo first-order, with  $k'_{+} = 2.4 \text{ day}^{-1}$ . For these conditions  $T_{1/2} = 0.693/2.4 = 0.29 \text{ days} = 7 \text{ hrs}$ . At  $pH = 7 \text{ and } P_{O_2} = 0.2 \text{ atm}$ ,  $k'_{+} = 240 \text{ day}^{-1}$ , and  $T_{1/2} = 4.2 \text{ min}$ . The activation energy for the rate law above pH 4 is about 23 kcal/mol.

#### F. Pyrite and marcasite oxidation by ferric iron

Wiersma and Rimstidt (1984) measured the rate of the overall reaction

$$FeS_2 + 14Fe^{3+} + 8H_2O \xrightarrow{k_+} 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

at pH 2.0 and 25 C. The reaction is first order, and follows the rate law

$$-\frac{d(Fe^{3+})}{dt} = k_+ \frac{A}{M} (Fe^{3+})$$

where (Fe<sup>3+</sup>) is the molal concentration of free (uncomplexed) ferric iron, and A/M the surface area of reacting mineral per mass of solution.  $k_+$  values range from  $1.0 \times 10^{-4}$  to  $2.7 \times 10^{-4}$  sec<sup>-1</sup>, and are not significantly different for pyrite and marcasite. The activation energy is 22 kcal/mol, based on rate measurements between 25 and 50 C. The rate-determining step is not known (See also Wadsworth 1979).

Oxidation of sulfides and sulfur compounds by thioacteria, which are all aerobic, can greatly speed up rates of oxidation, particularly over the inorganic rates when molecular oxygen is the oxidizing agent (Kramarenko 1969).

#### G. Calcite dissolution and precipitation

According to Plummer et al. (1979) the rate of solution or precipitation of calcite is given by

$$R = k_1 [H^+] + k_2 + k_3 [H_2O] - k_4 [Ca^{2+}] [HCO_3^-]$$
(1)

where R is in mmol,  $cm^{-2} sec^{-1}$  and rate constants  $k_1$  through  $k_3$ , correspond to the reactions:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad k_1$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^{-} \qquad k_2$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3 + OH^- \qquad k_3$$

At concentrations well below saturation with calcite, the k<sub>1</sub> term dominates the rate equation up to pHs between about 4.5 and 5.5. At higher pHs when  $P_{CO_2} >$ 0.1 bar, the k<sub>2</sub> term dominates rates. At higher pHs and lower CO<sub>2</sub> pressures, the k<sub>3</sub> term dominates above pH 5.5. In fresh water [H<sub>2</sub>O] = 1, and because [H<sub>2</sub>CO<sub>3</sub>] =  $K_{CO_2} \cdot P_{CO_2}$ , the rate law may be written

$$R = k_1 [H^+] + k_2 K_{CO_2} P_{CO_2} + k_3 - k_4 [Ca^{2+}] [HCO_3^-]$$

Temperature (K) functions for the rate constants are:

C) C)

$$\log k_1 = 0.198 - 444/T$$
  

$$\log k_2 = 2.84 - 2177/T$$
  

$$\log k_3 = -5.86 - 317/T \quad (for T < 25)$$
  

$$\log k_3 = 1.10 - 1737/T \quad (for T > 25)$$

At 25 C the rate constants are:  $k_1 = 10^{-1.29}$ ;  $k_2 = 10^{-4.46}$ ;  $k_3 = 10^{-6.92}$  (<25 C); and  $k_3 = 10^{-4.73}$  (>25 C). Corresponding activation energies are:  $E_a(k_1) = 2.0$  kcal/mol;  $E_a(k_2) = 10.0$  kcal/mol;  $E_a(k_3) = 1.5$  kcal/mol (<25 C); and  $E_a(k_3) = 7.9$  kcal/mol (>25 C).

The low activation energy for  $k_1$  suggests H<sup>+</sup> diffusion control is rate limiting at low pHs. More recently Sjoberg and Rickard (1984) have suggested that for acid pHs (where  $k_1$  is dominant), the rate of calcite dissolution is given by:

$$R = k_1 [H^+]^{0.90}$$

reflecting that the rate controlling process is not only  $H^+$  diffusion to the surface, but also reaction product diffusion away from it. The rate of dissolution at higher pHs is both surface reaction and solution product

#### Table 6 (continued)

diffusion controlled (Sjoberg and Rickard 1984).

Based on the rate equations of Plummer et al. (1979), we can compute that for ground water pHs above 6 and  $P_{CO_2}$  values less than 0.1 bar at 25 C and below, the solution rate of calcite far from equilibrium reduces to  $R = k_3$ . In other words, for these conditions (which are typical of many shallow ground waters) the reaction is zero order, as long as the surface area of the calcite is constant. This assumes no catalysis or inhibition of the rate by adsorbed substances. (Sc, Cu and PO<sub>4</sub> are strong inhibitors—Sjoberg and Rickard 1984). As equilibrium is approached, the rate equation becomes

$$R = k_3 - k_4 [Ca^{2+}] [HCO_3]$$

The value of  $k_4$  is a complex function of temperature and  $P_{CO_2}$ . Based on Figure 4 in Plummer et al. (1979) one can derive the approximate function

 $\log k_4 = -7.56 + 0.016T - 0.64 \log P_{CO_2}$  (bar)

where T is in kelvins. This function permits the rough calculation of  $k_4$  values for  $P_{CO_2} < 10^{-1.5}$  bar. The reader is referred to Berner (1980) for a discussion of calcite dissolution/precipitation rate laws near saturation in the presence or absence of rate-inhibiting substances.

## H. $SiO_2$ polymorphs, dissolution and precipitation

The reaction (which is elementary) describing the dissolution and precipitation of silica polymorphs is

$$SiO_2(s) + 2H_2O \stackrel{K+}{=} H_4SiO_4$$
 (1)

The differential rate equation is

$$\frac{d[H_4SiO_4]}{dt} = \frac{A}{M} \cdot \gamma H_4SiO_4(k_+[SiO_2][H_2O]^2 - k_-[H_4SiO_4])$$

(Rimstidt and Barnes 1980), where brackets enclose activities of the species (as usual), A/M ( $m^2/kg$ ) is the relative surface area of solid exposed to solution, divided by the mass of water. The rate constant for precipitation of quartz,  $\alpha$  and  $\beta$  cristobalite, and amorphous silica is given by

$$\log k_{-} = -0.707 - 2598/T \tag{2}$$

up to about 300 C, where T is in kelvins (Figure 20).

Because the solubilities of the four polymorphs are known as a function of temperature, the forward rate constants, k<sub>+</sub>, can be computed from the relationship  $K_{eq} = k_+/k_-$  for each elementary reaction. Thus, the solubilities of quartz and amorphous silica written as in Expression 1 are: and

 $\log K_{eq} (SiO_2$ -amorph) = 0.3380 - 7.889x10<sup>-4</sup>T - 840.1/T from which we find:

and

 $\log k_{+} (SiO_2-amorph) = -0.369 - 7890 \times 10^{-4}T - 3438/T$ 

Corresponding activation energies are:  $E_a$  (quartz) = 16.1 to 18.3 kcal/mol, and  $E_a$  (SiO<sub>2</sub>-amorph) = 14.6 to 15.5 kcal/mol. Rimstidt and Barnes (1980) examine the kinetics in terms of the activated complex (SiO<sub>2</sub>·  $2H_2O$ )=

#### I. Silicates including feldspar: dissolution and precipitation kinetics

Empirical studies of silicate rock or mineral solution rates at low temperatures, under conditions where the water is far from equilibrium with the solid, obey zero-order kinetics (cf Apps 1983; Paces 1983), also called linear kinetics (White and Claassen 1979). The best example of such behavior is the dissolution and precipitation of SiO<sub>2</sub> polymorphs (Rimstidt and Barnes 1980; Section H, this table). Linear or zero-order kinetics is observed when the area of reacting mineral in a volume of solution (also called the specific wetted surface, A, in  $m^2 \cdot m^{-3}$ ) may be considered constant with time. The general form of the empirical rate law is

$$R = \frac{dC}{dt} = Ak_+$$
(1)

where C is the aqueous concentration of a chemical species such as sodium or silica in the mineral. Paces (1983) relates this rate constant to the properties of a water-bearing formation with the equation

$$k_+ = (C-Ft)/ACt$$

where  $k_+$  is in mol m<sup>-2</sup> sec<sup>-1</sup>, C = 0 at t = 0, F is the net specific input of the chemical species from the surroundings to ground water, and A is defined as above (m<sup>2</sup>·m<sup>-3</sup>). Helgeson et al. (1984) suggest  $k_+ = 3 \times 10^{-12}$ mol m<sup>-2</sup> sec<sup>-1</sup> at 25 C for K-feldspar, albite and anorthite.

Based on laboratory dissolution rate studies of fledspars, obsidian and volcanic glass, White and Classen (1979) suggest that the initial solution rate of silicates can either obey linear kinetics as in Equation 1, or parabolic kinetics where the rate is given by:

$$R = \frac{dC}{dt} = (Ak_+/2) \cdot t_{-\frac{1}{2}}$$
(2)

 $\log K_{eq} (quartz) = 1.881 - 2.028 \times 10^{-3} T - 1560/T$ 

They point out that after long times in natural water/ 2-50

Table 6 (continued)

rock systems parabolic rates tend to become linear. Helgeson et al. (1984) show that feldspar dissolution rates are linear if the feldspar is pre-treated to remove ultrafine reactive particles. It seems likely that the assumption of linear kinetics is correct for most silicates in natural water/rock systems.

Silicate mineral dissolution is usually incongruent, with precipitation of relatively amorphous metastable products which may crystallize with time to form minerals such as gibbstite, kaolinite, illite and montmorillorite (Helgeson et al. 1984). The incongruency means that net release rates of individual components from a silicate mineral into the water may not be equal (cf White and Claassen 1979; Helgeson et al. 1984).

Aagaard and Helgeson (1982) propose general rate expressions for the dissolution of silicate minerals. They suggest that the solution rate in acid water is determined by the decomposition rate of a critical activated surface complex. The rate is given by

$$R = k_{+} [H^{+}]^{n} \cdot (1 - \exp(\Delta G/\sigma RT))$$
(3)

where [H<sup>+</sup>] is the hydrogen ion activity in solution, n a constant, and  $\sigma$  the average stoichiometric number of the reaction (Helgeson et al. 1984).  $\Delta G = -RT \ln(K_{eq}/Q)$ , where  $K_{eq}$  is the equilibrium constant, and Q the corresponding activity quotient in solution. In other words, Equation 3 may be written

$$R = k_{+} [H^{+}]^{n} \cdot (1 - Q/K_{en})$$
(4)

Based on previous work, Aagaard and Helgeson (1984) propose n values of 0.7, 0.5, and 1.2, respectively, for the hydrolysis of diopside and enstatite, bronzite, and a forsteritic olivine in Equations 3 and 4.

Far from equilibrium (Q/K<sub>eq</sub>  $\leq$  0.05) Equations 3 and 4 reduce to

$$\mathbf{R} = \mathbf{k}_{+} \left[\mathbf{H}^{+}\right]^{\mathbf{n}} \tag{5}$$

which might correspond to the leaching of silicate rocks by fast-moving acid ground water. Close to equilibrium ( $Q/K_{eq} \ge 0.8$ ) Expression 4 becomes

$$\mathsf{R} = \mathsf{k}_{+} \left[\mathsf{H}^{+}\right]^{\mathsf{n}} \cdot \left(-\ln(\mathsf{Q}/\mathsf{K}_{\mathsf{eq}})\right) \tag{6}$$

The solution rate of feldspars is pH-independent between about pH 2.9 and 8 at 25 C (Helgeson et al. 1984). For these conditions the general rate equation

The mechanism of mineral dissolution/precipitation can, however, depend on the rate of ground water flow. Berner (1978) relates transport and surface reaction rates in the expression  $dC/dt = R - k_1C$ , where dC/dt is the rate of change of concentration in a fixed volume of the system at steady-state (dC/dt = O), R the rate of dissolution (assuming first-order kinetics; R =  $k_+(C_s - C)$ ), and  $k_f$  is the flushing frequency (rate of may be written

$$R = k_{+} (1 - Q/K_{eq})$$
(7)

where  $k_+$  is the pH-independent rate constant. Far from equilibrium this becomes

$$\mathsf{R} = \mathsf{k}_{+} \tag{8}$$

Near equilibrium the rate is given by

$$R = k_{+} [-\ln(Q/K_{eq})] = k_{+} [-\ln(Q/K_{eq})]$$
(9)

(At equilibrium Q = K and R = 0). Equations 8 and 9 would perhaps apply to rates of feldspar dissolution in relatively fresh, unconfined ground water, and in older confined ground water, respectively.

Wood and Walther (1983) examined the pH-independent solution and precipitation rates of numerous silicate minerals including the  $SiO_2$  polymorphs, and concluded that their zero order rate constants could all be fit with a single equation between 25 and 700 C.

$$\log k = -6.85 - 2900/T \tag{10}$$

where T is in kelvins. Here, k is in gram atoms of oxygen per cm<sup>2</sup> sec<sup>-1</sup>. (This k value is derived from molar k values by multiplying the latter by the number of oxygens per mole of mineral). This equation corresponds to an activation energy of 13.25 kcal/mol. The line of Equation 10 corrected back to molar units by Apps (1983) has been labeled "silicates" and plotted in Figure 19.

Helgeson et al. (1984) dispute Wood and Walther's results, and argue that the rate constants and activation energies of the silicates differ appreciably at both low and high temperatures. For example, based upon the temperature dependence of rate constants for the feldspars, they obtain activation enthalpies for pH-dependent dissolution of 19.0 kcal/mol for K-feldspar, and 20.6 kcal/mol for albite.  $\Delta H^{\pm}$  for the pH-independent dissolution of K-spar is 8.45 kcal/mol. These activation enthalpies are equivalent to E<sub>a</sub> values of 19.6, 21.2 and 9.04 kcal/mol (Equation 37). The magnitude of these values supports the conclusion that feldspar dissolution and precipitation is surface reaction controlled at all pHs.

flow/volume of system). For such conditions we find:  $C = k_+C_s/(k_+ + k_f)$  and  $R = k_+k_fC_s/(k_+ + k_f)$ . At high ground water flow rates  $(k_f \gg k_+)$ , these expressions reduce to  $C=C_sk_+/k_f$ , and  $R=k_+C_s$ , so that a maximum solution rate is attained, independent of flow rate. At the opposite extreme of slow ground water flow  $(k_f - O)$ ,  $C = C_s$ , and  $R = k_fC_s$ . Saturation is attained and the rate of dissolution is controlled by the ground water flow rate. In other words, at high flow the dissolution rate is surface reaction controlled, whereas at low rates it is transport controlled. The slower process is rate limiting. (Note: James and Lupton 1978, contrast the effects of flow velocity and surface reaction rates on the dissolution of gypsum and anhydrite.)

The slowest transport controlled dissolution/precipitation is that governed by aqueous diffusion. Diffusion rates can be calculated, and so we can estimate the lower limit of rates attributable to transport control. Berner (1978) suggests that the rate of diffusion controlled dissolution is given by:  $R_d = D\rho A(C_s - C)/r$ , where R is in mass/volume/time, D is the diffusion coefficient, p the porosity, A, surface area of dissolving crystals per unit volume of solution, and r the spherical radius of the dissolving crystals. It is interesting to compare the rate of dissolution that can result from diffusion to the rate from surface reaction. As a convenient example, James and Lupton (1978) report that the dissolution rate of gypsum via surface reaction is given by:  $R_{sr} = k_+A(C_s - C)$ . The ratio of the rates  $R_d/R_{sr}$  then equals  $D_p/rk_+$ . Diffusion coefficients of ions typically range from 3x10<sup>-6</sup> to 2x10<sup>-5</sup> cm<sup>2</sup> sec<sup>-1</sup> (Lerman 1979). Assuming  $D = 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ , a porosity of 0.2, crystal radius of 1 cm, and  $k_{+} = 2 \times 10^{-4}$  cm sec<sup>-1</sup> at 25 C (based on James and Lupton 1978), we find  $R_d/R_{sr} = 1/1000$ . In other words  $R_{sr} >> R_d$ , and the slower rate, diffusion, will control the dissolution rate.

#### **Temperature Dependence of Rate Constants**

Based on empirical measurements, Arrhenius proposed the expression

$$k = A \exp(-E_a/RT)$$
(32)

to describe the dependence of the rate constant on temperature (Gardiner 1972). In this expression A is called the 'A factor,' and  $E_a$  the activation energy. The A factor usually has a slight temperature dependence that can be ignored.  $E_a$  is always positive, and shows that reaction rates increase with increasing temperature. The effect of temperature on the rate constant is given by: dlogk/dt =  $E_a/2.30RT^2$ . A familiar rule of thumb is that rates about double every ten degrees near 25 C. This corresponds to an activation energy of about 12 kcal/mol at 25 C.

Taking the logarithm of expression (Equation 32) leads to:

$$\ln k = \ln A - E_a/RT$$

ог

$$\log k = \log A - E_a/2.30RT$$

The usual procedure for evaluating  $E_a$ , is to plot the log of the reaction rate vs. I/T. The slope then equals  $-E_a/2.30R$ . Such plots are given in Figures 19 and 20 for the dissolution and/or precipitation rates of a number of silicate rocks and minerals, and for the precipitation of quartz and amorphous silica.

Activation energy values provide useful insight into the nature of the reaction mechanism(s) of mineral dissolution and precipitation. Thus, aqueous diffusion

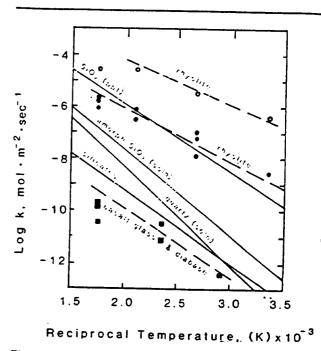


Figure 19. An Arrhenius plot of log k vs. 1/T for various silicate rocks and minerals. The data points and curves for rhyolite, basalt glass and diabase are from Apps (1983), as is the curve labeled "silicate," which Apps computed from the results of Wood and Walther (1983). Curves for the SiO<sub>2</sub> polymorphs are based on Rimstidt and Barnes (1980).

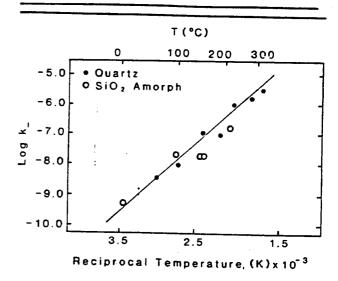


Figure 20. An Arrhenius plot of log k vs. 1/T for quartz and amorphous silica based on Rimstidt and Barnes (1980).

controlled reactions typically have activation energies of less than 5 to 6 kcal/mol (Berner 1978; Rimstidt and Barnes 1981). Minerals dissolving or precipitating via surface reaction control usually have  $E_a$  values between 10 to 20 kcal/mol (Lasaga 1981). Activation energies for solid-state diffusion in minerals at low temperatures range from about 20 to 120 kcal/mol, but are generally from 20 to 80 kcal/mol. Apps (1983) found that alteration (hydration) of obsidian and basalt glasses by diffusion had activation energies of about

22 to 23 kcal/mol. Physical adsorption has an  $E_a$  from about 2 to 6 kcal/mol, whereas activation energies for chemisorption usually exceed 20 kcal/mol. Lasaga (1981) points out that the bond-breaking and making associated with surface'reaction controlled mineral dissolution and precipitation would be expected to have activation energies similar to those of solid-state diffusion. That the former are so low may reflect that chemisorption/desorption occurs prior to mineral precipitation/dissolution. In other words the heat of chemisorption probably reduces the activation energy required for surface-controlled mineral reaction.

#### Absolute Rate (Transition State) Theory and the Activated Complex

Considerable insight into reaction mechanisms derives from the concepts of absolute rate theory. This theory is based on two assumptions: first that there is an energy maximum (barrier) between products and reactants in a reaction; and that an activated complex exists at this maximum; and second that chemical equilibrium exists among reactants, products and the activated complex. The rate determining step in a reaction corresponds to the formation and decomposition of the activated complex. Thus, for the reaction:

$$A+B \stackrel{k_+}{=} C^{\pm} = C$$

The thermodynamic equilibrium constant involving the activated complex,  $C^{\pm}$ , is (Figure 21):  $K^{\pm} = [C^{\pm}]/$ [A][B], where the brackets enclose the activities of the species. According to absolute rate theory (Wadsworth 1979), the reaction rate R is

$$R = -\frac{d(A)}{dt} = -\frac{d(B)}{dt} = \frac{k_BT}{h}C^{\pm} = \frac{k_BT}{h}K^{\pm}[A][B]$$
  
where k<sub>B</sub> and h are the Boltzmann and Planck cor

nstants ••

The constant K<sup>±</sup>, can also be written

$$\mathsf{K}^{\pm} = \frac{(\mathsf{m}\mathsf{C}^{\pm})}{(\mathsf{m}\mathsf{A})(\mathsf{m}\mathsf{B})} \cdot \frac{(\gamma^{\pm})}{(\gamma_{\mathsf{A}})(\gamma_{\mathsf{B}})}$$

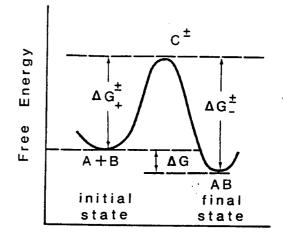
1. -

The specific rate constant at infinite dilution is equal to

$$K'_{o} = \frac{k_{B}T}{h} \cdot K^{\pm} = \frac{k_{B}T}{h} \cdot \frac{(mC^{\pm})}{(mA)(mB)} \cdot \frac{(\gamma^{\pm})}{(\gamma_{A})(\gamma_{B})}$$
(33)

If k' is the specific rate constant uncorrected for ionic strength, then

## Activated Complex Relationships (Transition State)



#### **Reaction Coordinate**

Figure 21. Free energy relationships for the activated complex  $C\pm$  in the reaction  $A + B = C \pm AB.$ 

$$k'_{o} = k' \cdot \frac{(\gamma^{\pm})}{(\gamma_{A})(\gamma_{B})}$$

and

$$\log \frac{k'}{k'_{o}} = \log \left( \frac{\gamma_{A} \gamma_{B}}{\gamma^{\pm}} \right)$$
(34)

With a model for computing the activity coefficients, we can predict the effect of ionic strength on the second order rate constant, k'. Assuming applicability of the Debye-Hückel Limiting Law (log  $\gamma_i = -Az^2\sqrt{I}$ ; see Equation 16), we can expand Equation 34 to give

$$\log\left(\frac{\mathbf{k}'}{\mathbf{k}_{o}'}\right) = -A \sqrt{1} \left[ z_{A}^{2} + z_{B}^{2} - (z_{A} + z_{B})^{2} \right]$$
(35)

which reduces to

$$\log \frac{k'}{k'_0} = 2A \sqrt{I} (z_A z_B)$$
(36)

(Lasaga 1981). Substitution shows that if A and B have the same sign, k' increases with ionic strength; if of opposite sign, k' decreases with ionic strength. Equation 36 is plotted in Figure 22, which shows for example that at  $I = 6 \times 10^{-3}$ m, the rate of a second order reaction involving divalent ions A and B is double its value in pure water.

Returning to Equation 33, we see that the specific rate constant ko is also a function of the free energy of activation ۰.

$$k_{o}^{\prime} = \frac{\kappa_{B}}{h} \exp(-\Delta G^{\pm}/RT)$$

Or replacing the free energy with the enthalpy and entropy of activation we may write

$$k_0' = \frac{k_B T}{h} \exp(-\Delta H^{\pm}/RT) \exp(\Delta S^{\pm}/R)$$

Taking the logarithm gives

$$\ln k_0' = \ln(k_B/h) + \ln T - \frac{2H^{\pm}}{RT} + \frac{2S^{\pm}}{R}$$

Assuming  $\Delta H^{\pm}$  and  $\Delta S^{\pm}$  are independent of temperature, differentiating we obtain

$$\frac{d \ln k_0'}{dT} = \frac{1}{T} + \frac{\Delta H^{\pm}}{BT^2}$$

But the Arrhenius relationship in differential form is

$$\frac{d \ln k_0'}{dT} = \frac{E_a}{RT^2}$$

so we find

$$\mathsf{E}_{\mathfrak{g}} = \mathsf{R}\mathsf{T} + \mathsf{L}\mathsf{H}^{\pm} \tag{37}$$

Because the value of RT is less than 1 kcal/mol up to about 500 K, this last expression reduces to  $E_a = \Delta H^{\pm}$ . Thus, here is a tie-in between the empirical Arrhenius equation and transition state theory, and a way that one can evaluate the enthalpy of activation of a reaction.

## Some Kinetic Data of Geochemical Interest

Given in Table 6 are some kinetic data of geochemical interest. The examples are chosen to illustrate kinetic concepts discussed in this paper, and to suggest approximately where we are in the development and application of kinetic principles to low temperature water/rock systems.

Once we have defined the detailed mechanisms of reactions such as those of mineral precipitation/dissolution, there are obviously major stumbling blocks to their application. These include: (1) the frequently observed fact that theoretical dissolution/precipitation rates can be drastically increased by catalytic processes or slowed by the surface adsorption of inhibiting substances, and (2) that the rigorous application of such concepts requires we have foreknowledge of the wetted surface area of reacting minerals in a volume of the rock. This property (related to the effective porosity) is difficult or impossible to directly quantify (cf Claassen and White 1979; Claassen 1981 and Paces 1983)

On the positive side, there is reason to believe that rate information for simple homogeneous reactions and for the least complex mineral dissolution/precipitation reactions can be more usefully applied to studies of natural systems. Such applications can now be in concert with our better developed concepts and models of chemical equilibrium as described early in this paper. When not useful for the accurate prediction of natural system reaction rates, the laboratory data, as described in Table 6, does at least provide guidelines that direct our further study and ultimate understanding of natural controls on rates.

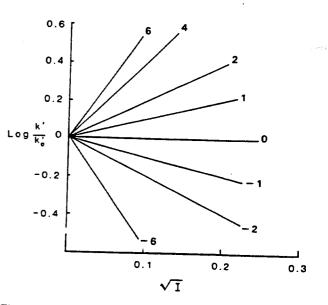


Figure 22. The predicted effect of ionic strength on the second order rate constant k prime for different values of the product of the valences of reactants A and B (i.e.,  $Z_A \times Z_B$ ). K prime = K prime<sub>o</sub> at 1 = 0.

#### Summary

Geochemical reactions or processes can alter the hydrologic properties of a rock. Such reactions (or the lack of them) can also render a water fit or unfit fc certain uses. An understanding of equilibrium and kinetic concepts as they apply to water-rock systems can greatly improve one's ability to predict the chemical and isotopic composition of ground water, and so to better manage ground water resources. For these reasons, hydrologists need to know some ground water geochemistry. Chemical equilibrium defines the boundary conditions; i.e., what are the maximum or minimum possible concentrations of some dissolved species likely to be? Chemical kinetics defines how long it takes to reach equilibrium and by what reaction pathways it is reached. Only chemical equilibrium concepts are needed to understand ground water chemistry when the rates of reactions of interest are much faster than ground water residence times in a particular water/rock system. Thus, such concepts have been most usefully applied in deep basin artesian ground water studies. When reaction rates are comparable to or less than residence times, both kinetic and equilibrium concepts apply. This is particularly the case in shallow water table systems. Chemical equilibrium concepts, including adsorption, have successfully explained the chemical behavior of many ground water systems. In contrast, our understanding of geochemical kinetics is in relative infancy, so that only the simplest kinetic concepts have been usefully applied in ground water studies. In this paper, the principles of equilibrium (including adsorption) and of kinetics were addressed and illustrated with practical applications.

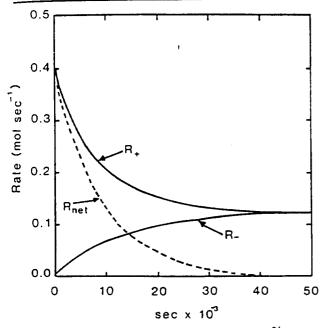


Figure 23a. Calculated concentrations of Fe<sup>3+</sup>,  $SO_4^{2-}$ , and  $FeSO_4^+$  as a function of time for the reaction  $Fe^{3+} + SO_4^{2-} = FeSO_4^+$ . Initial concentration 8.0x 10<sup>-3</sup> M (Pagenkopf 1978).

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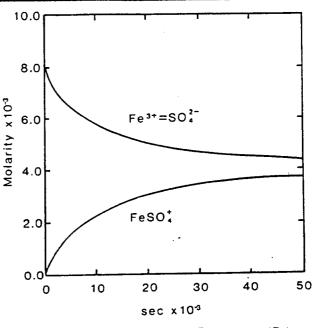


Figure 23b. Calculated forward  $(R_t)$ , reverse  $(R_r)$ , and net rates  $(R_{net})$  for the reaction  $Fe^{3+} + SO_4^{2-} = FeSO_4^+$  (Pagenkopf 1978).

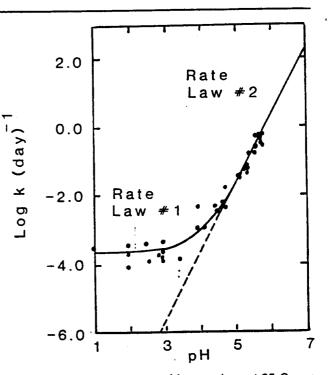


Figure 24. Oxidation rate of ferrous iron at 25 C as a function of pH. The ordinate  $k = -d \log(Fe^{2^+})/dt$ . Data points are empirical results. Rate laws #1 and #2 are described in the text (Modified after Stumm and Morgan 1981).

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# Sampling and Analysis of Subsurface Water

by Robert W. Hull, Yousif K. Kharaka, Ann S. Maest and Terry L. Fries

#### Abstract

Geochemical studies are generally more comprehensive and detailed than those required to monitor a given water supply or contamination site. These studies, which generally include the use of geochemical models, require detailed knowledge of the hydrologic and mineralogic properties of the aquifer, as well as the spatial and temporal compositions of its water and gases. This paper summarizes the methods used for the collection, preservation and chemical analysis of subsurface water.

Detailed procedures for collection include equipment and precautions necessary to ensure that the sample is "representative" of the water in a specified part of the aquifer. Field procedures for sample preservation include filtration (0.1  $\mu$ m filters for trace metals, 0.45  $\mu$ m for dissolved organics and other dissolved species), acidification, dilution for silica (in hydrothermal water), extraction of aluminum (labile, monomeric) addition of mercuric chloride or sodium azide, and potassium permanganate to preserve dissolved organics and mercury respectively, and precipitation of carbonate species for carbon isotopes and total dissolved carbonate analyses. Properties determined in the field include temperature, sulfide, pH, Eh, ammonia, alkalinity and conductivity.

Analysis of cations are performed by atomic absorption and flame emission spectrophotometry. Graphite-furnace AA with Zeeman-background correction is used for the determination of most metals. However, inductively coupled plasma atomic emission spectrometry (ICP-AES) is becoming the selected method for the determination of many cations and metals. An increasing number of anionic species, including sulfate, bromide and iodide are being determined by ion chromatographic techniques. Dissolved organics are determined by gas chromatography and other instrumentation, such as mass spectrometry.

#### Introduction

As geochemists involved in the sampling and anal-

ysis of ground water, part of our laboratory is the complex and heterogeneous geologic environment. Many of the commonly used methods of study are as yet imprecise and somewhat primitive relative to our scientific needs. In laboratory experiments one may control the temperature, pressure, pH and the concentration of some solutes. Only certain changes in this system can be allowed to occur and are then carefully measured. Since the system was created by design, the composition and the conditions of the environment can be known with precision. In the field situation, the physical and chemical environment of a water parcel are known with substantially less precision. In fact, because the hydrologic and mineralogic environment around a well or group of wells is, to a degree, heterogeneous and non-isotropic, the measured conditions are an averaged or homogenized value. In many cases the mineralogic environment must be assumed or generalized, and the hydrologic characteristics must be inferred from various tests using indirect methods. A well drilled into this environment is an intrusion with which the subsurface must try to come into equilibrium. In a sense, our attempts at studying the environment actually change it. It is our responsibility as scientists to address how this intrusion affects the results of the study and determine how effectively samples can be collected that are representative of the subsurface environment.

#### **Objectives of Ground Water Studies**

The procedures for ground water sampling and chemical analysis can vary widely in complexity depending on the objectives for collecting water samples for chemical analysis. In perhaps the simplest case a sample is collected from an existing well and is analyzed for the presence or absence of a particular chemical element or specie to meet drinking water standards. In the complex case the interactions of a suite of aqueous species and minerals must be determined within a specific geologic horizon under reducing chemical conditions. Sampling for geochemical studies may necessitate a complicated sample collection effort during the drilling of a well or under some other less than optimum conditions. For scientific investigations it is crucial to know the in situ geochemical conditions.

Chemical analyses required for these two cases will be substantially different. To determine conformance with drinking water standards it may only be necessary to use analytical methods sufficient to show that concentration levels are below the standards. The detection limits of these methods may be on the order of a few milligrams per liter (mg/L). In geochemical studies a limit of detection to within a few micrograms per liter ( $\mu$ g/L) may be required for a number of chemical constituents in a complex sample matrix.

#### Origin and Chemical Composition of Ground Water

Often the objective of geochemical studies is to establish the origin of subsurface water. Frequently this is done with the use of hydrogen and oxygen isotopes ( $\delta D$  and  $\delta^{18}$ 0), as well as the chemical composition (Fritz and Fontes 1980; Kharaka and Carothers 1985). Most natural water is meteoric (originally in contact with the atmosphere) or connate (trapped with sediments at the time of deposition). Diagenetic water that was released from solid phases, and water that was involved in metamorphism are only of local significance. Juvenile or primary water from igneous sources is not volumetrically important to most studies.

Physical, chemical and biological processes act on this water to chemically alter their composition. Physical processes can generate hydraulic pressure gradients that result in the circulation of subsurface water, often causing the mixing of chemically different water, filtration by clay membranes and contact with various geologic environments. Chemical interaction of water, solutes, solids, gases and other fluids (e.g., oil) produces water of widely varying composition. Aqueous concentrations may be affected by dissolution-precipitation, sorption, ion exchange and oxidation-reduction reactions and the formation of colloids (Garrels and Christ 1965; Hem 1970; Drever 1982). The chemistry of natural water from a few selected geologic environments is shown in Table 1 (White, Hem and Waring 1963). All of this water is meteroric, and its chemical composition is largely related to the mineralogic composition of the rock type (e.g., limestone shows high calcium and bicarbonate).

Ground water at depths of less than a few hundreds of feet is commonly referred to as shallow. Much of the water is currently or recently (geologically) recharged by meteoric sources carrying with it traces of its contact with the earth's atmosphere. The isotopic composition of this water and the chemical and isotopic composition of the gases and dissolved species indicate if a water is meteroic and how recently it has been recharged. Meteoric water recharged during the 1950s

Table 1
Chemical Composition of Subsurface Water from Several Geologic Environments
(White et al. 1963)

Dissolved concentration (mg/L)	Catahoula Sandstone, Collins, MS	Edwards Limestone, Uvalde, TX	Peebles Dolomite Bainbridge, OH	Granite, West Warwick, RL	Olivine Basalt tuff-beccia, Buell Park, AZ
SC*	38	570	663	76	458
pH**	6.2	7.0	7.6	7.6	8.2
Na	2.6	24	3.5	5.9	19***
к	2.0	7.0	1.7	.8	
Mg	.5	9.5	72	: 2.6	42
Ca	2.4	74	28	6.5	20
Sr	_	_		<u> </u>	-
Fe	.41	.08	.48	.19	· <u> </u>
CI	2.5	24	5.0	5.0	7
Br		_	-		—
SO₄	1.4	19	28	.9	22
NO <sub>3</sub>	.0	4.1	31	1.5	2.5
HCO <sub>3</sub>	18	277	398	38	279
SiO <sub>2</sub>	25	11	11	20	31

\*Specific conductance in micromhos per centimeter at 25 C

\*\*In pH units

\*\*\*Analysis includes K

and 1960s may contain measurable quantities of tritium, carbon-14. cesium-137, strontium-90 and other isotopes related to the atmospheric testing of nµclear weapons. Shallow ground water is also affected by contamination from landfills, septic tanks, liquid waste storage and disposal sites, mine excavations and operations, irrigation and other agricultural practices, and domestic and industrial activities (Todd and McNulty 1976).

Water within deeper strata may be connate or meteroic with some mixing with diagenetic water. This water tends to have greater than 10,000 mg/L dissolved solids and tends to be Na-Cl or Na-Ca-Cl- $SO_4$  type water. This high salinity water results mainly from the increased dissolution of many minerals (including evaporites) and the increased membrane efficiency of shales in these higher temperature and pressure environments. Higher salinity is also caused by contamination from waste injection, sea water encroachment and interflow between zones in abandoned wells and oil test holes.

#### Ground Water Sampling

Geochemical studies require data that are representative of water in the subsurface environment. Geology, hydrology, well construction, sampling and analysis must each be examined for their influence on collecting a typical sample. Certain questions should be asked:

• What spatial distribution of water samples is needed?

• In what hydrostratigraphic zone(s) will samples be collected?

Are there existing wells at these locations?

• Is the well construction appropriate for the zone(s) of interest?

• Do new wells or test holes need to be constructed?

• Can water samples be collected in a manner consistent with the objectives, and will they be representative of the zone(s) of interest?

• Are chemical analyses available so that you know what to expect from sampling?

Aquisition of all available geologic and hydrologic information from the literature and other sources should provide answers to some of these questions. A knowledge of the ground water flow path, the geologic section, and the hydraulic characteristics of the aquifer units should be obtained. If much of the information is not available, it may be necessary to drill one or more exploratory wells or test holes. These can provide cores or cuttings of rock material at intervals frequent enough to discern the vertical variability in mineralogic composition. Testing of the hydraulic characteristics of different zones may be needed to determine interborehole flow during the construction or after a well is completed. Geophysical logging and discrete interval sampling may help in deciding well completion and subsequent sampling procedures. Multicompletion wells and wells that allow interborehole flow (Figure 1) are to be used with caution as the collection of representative samples from these wells is difficult. Water analyses from these wells are most often not indicative of a particular hydrostratigraphic zone. A good reference concerning the entire aspect of collecting representative samples is Claassen (1982). It should be noted that although it may be commonly accepted that deeper ground water migrates slowly, there may be reason to sample with frequency. If other wells, especially high capacity production wells are nearby or if sources of high pressure such as a reservoir or holding pond are close and are hydraulically connected to the zone of interest, then the frequency of sampling should be examined carefully (Schmidt 1977). If changes in water chemistry are expected for any reason, then the best plan is to choose a short time interval for sampling. The sampling interval should be increased or decreased as examination of the data reveal a suitable periodicity to observe changes.

#### Wells, Well Construction and Testing

Drilling fluids are probably the major sources of contamination of ground water obtained from recently drilled wells (Claassen 1982). Wells can be drilled with gas, water or oil, in combination with foams, emulsions and muds. Additives are introduced to change the physical or chemical character of the drilling fluids so as to engineer the well to specifications (Gray and Darley 1980). It is virtually impossible to remove all the materials introduced during the construction of a well by the time it is completed. Subsequent well develop-

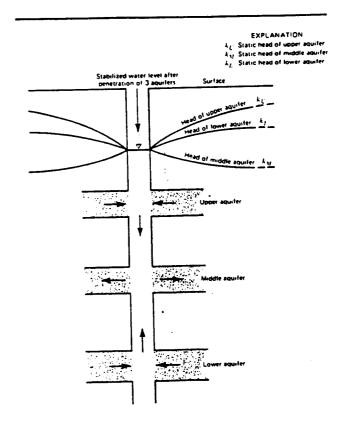


Figure 1. Head distribution in a multiple completion zone well showing inter-borehole flow (modified from Bennett and Patten 1962)

ment (pumpage to increase capacity) will, however, generally remove most of the residual materials. It is important to be convinced that drilling fluids have been removed from the well prior to sampling.

Construction materials for the well may also be a source of contamination. Metal casings will, of course, corrode and may thereby introduce metals to the water altering its true chemistry. Depending upon the hydrogeologic environment of the well, materials may be used after setting the casing to prevent interconnection of water-producing zones. These materials range from various cements and clays to broken pecan shells.

The use of drilling fluids should be minimized especially when penetrating the zone(s) of interest. If at all possible, drilling with rotary air or nitrogen or by cable tool can help reduce possible effects. Additives to fluids should be severely limited and used only when absolutely necessary. Some of these additives contain materials such as starches, which are biodegradable and form a substrate for microbial growth, which can produce gas and other dissolved species that change the inorganic and organic composition of the ground water.

#### Sampling Devices and Representative Samples

There are numerous good references on sampling techniques (Rainwater and Thatcher 1960; Ball et al. 1976; Wood 1976; Gibb et al. 1981; Scalf et al. 1981; Claassen 1982; Lico et al. 1982). No one technique is appropriate for all of the possible sampling conditions and environments. Wells that are deep or highly saline, or that produce hot water, gases or oil exhibit particular problems. In most instances, when sampling these types of wells the methods of sampling will be dictated by the "plumbing" at the well head, especially if it belongs to a commercial operation.

Ground water sampling is carried out in one of two places: downhole or at the surface. Surface sampling is the most common, because it requires less in the way of equipment and time, and it is often the only way a sample may be collected. For the sampling of shallow wells where the water is for all intents and purposes in chemical and physical equilibrium with the atmosphere, most commonly used sampling methods will be adequate. The exception would be when collecting trace inorganics or organic substances. Attention here must be paid to the composition of collection bottles and equipment coming into contact with the sampled water. Contamination by the collection materials or sorption onto or off of them may be an important factor (Gibb and Barcelona 1984).

Surface sampling of all wells that are not equilibrated with the atmosphere or are under high in situ pressure or temperature is significantly more difficult. As these samples travel up the casing (by artesian pressure, pump or gas lift) they move into a lower pressure-temperature environment that may cause the precipitation of minerals from solution or induce some colloid formation. If high concentrations of dissolved gas exist in situ, then outgassing would be expected

as the water rises to the surface. It is not uncommon to observe the encrustation of pipes by salt or carbonate minerals as a result of these conditions. An additional problem is created by contact with the atmosphere if the subsurface water is reducing. If there is an influx of oxygen to samples that contain oxidizable aqueous species (e.g., Fe<sup>++</sup>), then redox reactions will proceed until the oxygen is used or the reduced species have all been oxidized. If this process results in the precipitation of some minerals (e.g., iron oxyhydroxides), then co-precipitation and scavenging of charged metal complexes may also occur. This process may lead to pH changes and numerous other shifts in the chemistry of the sample. Apparatuses for collecting gases and precipitating carbonate from a well head without contact with the environment are shown in Pearson et al. (1978) and Lico et al. (1982).

For wells that do not have sufficient pressure to produce water at the well head, there are many mechanisms for bringing it to the surface. These consist of air-lifting or jetting, swabbing the casing with a suction swab, and the use of various pumps. Surface pumps include centrifugal, pitcher and peristaltic varieties. Subsurface pumps such as the electric submersible, gas or fluid bladder, and syringe should be considered over the surface types with the exception of the peristaltic for actual sample collection. See Claassen (1982) for a discussion of the pros and cons of these devices.

Because of the need in geochemical studies to collect representative samples, the use of downhole samplers is increasing. These samples may be collected where water enters the well screen or openhole zone or at some other point prior to arrival at th surface. It is generally assumed that this type of sampling is preferred over surface sampling, but it may also not be optimal. For example, some wells have water levels that are too far beneath the well head for centrifugal, pitcher, or peristaltic pumps. They may also have too small an internal diameter to allow submersible pumps. Sample collection from these wells is with a bailing device or swab (Claassen 1982). The problem is that water standing in the well casing must be removed before a sample should be collected. The rule of thumb is that a well standing dormant for some time should be flushed five times before sampling to ensure a fresh sample. Even a well that is frequently used should be allowed to discharge the equivalent of two casing volumes before a sample is collected. Therefore, although bailing will allow in situ collection, it may not give samples of the quality needed, because of the time needed to flush the well.

A recent paper by Barcelona et al. (1984) discusses several commercially available sampling mechanisms. They found that the positive displacement bladder sampler had the best overall results for collecting various organics, gases, common ions and metals. In the deeper ground water environments, mechanisms have been designed that allow for water sampling at high temperature (Fournier and Morgenstern 1971) and high pressure (Hull and Stevens, unpublished, Figu 2) environments. The Hull and Stevens sampler allow. for samples to be collected at temperatures and pressures up to about 150 C and 700 megapascals (MPa). This sampler was also designed to sample environments with high dissolved gas concentrations, but can easily be modified to sample trace volatile organics. It performs under positive gas/water displacement with minimal pressure drop across the sampling orifice because of the slow movement of the syringe-type piston.

The chemistry of samples collected at a well head may vary with time or discharge rate (Hull and Martin 1980) as a result of hydraulic properties of the water producing zone(s) and their water chemistry. Commonly an aquifer or water-producing zone will show variable permeability and minerology with depth. The combination of these circumstances will produce mixing of water within the borehole during discharge at the well head. The most common way to decide if a sample is suitable for collection is to monitor a few field measurements with time and discharge.

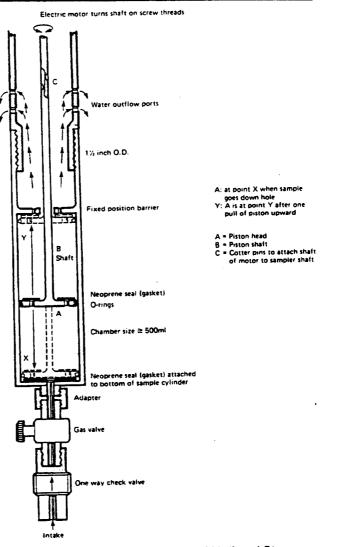
At some time before sampling at the well head, a monitoring log of pH, specific conductance, and temperature with time and flow rate should be started. For 'a new well the values measured should plot asymptotic to the steady-state value when plotted with time and should not vary with flow rate. If the values do not achieve steady-state, then in situ sampling should be considered.

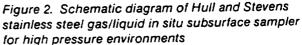
#### Field Tests and the Preservation of Samples

The instability of some chemical constituents makes it necessary to perform certain chemical analyses or chemical stabilization in the field. Alkalinity, pH,  $H_2S$ , ammonia and conductivity can be measured in the field on unfiltered samples. Samples for the determination of labile aluminum, carbon isotopes, total carbonate and silica (from hydrothermal water) require field extraction, precipitation and dilution, respectively, for later laboratory analysis (Presser and Barnes 1974; Lico et al. 1982).

Filtration of most dissolved constituents requires a 0.45  $\mu$ m pore size. However, since inorganic and organic colloids and some clay particles can pass through this size filter, it is recommended that 0.1  $\mu$ m filter paper be used for the collection of samples for trace element analysis (Kennedy et al. 1974).

Measurement of field pH and alkalinity should be performed as quickly after collection as possible and as near to the in situ conditions as practical. For samples from reducing environments, it is necessary to prevent oxidation by the atmosphere. Maest (unpublished) has designed a device that allows the filtration and filling of sample containers under a nitrogen atmosphere (Figure 3). The measurement of pH is done using a flow-through cell and a water bath (Wood 1976). Buffers to be used in determining pH are kept in the water bath at the temperature of the samples at the well head. Actual measurement of pH and alkalinity should be made by such methods as these described by Barnes (1964). If the presence of organic acid anions are expected then the titration of alkalinity





should proceed down to a pH of 2.5 (Carothers and Kharaka 1978), since the inflection point will be closer to 3.5 than to 4.5.

If radiochemical constituents are to be analyzed the procedures are those generally recommended for the particular environment (Ball et al. 1976; Wood 1976; Thatcher et al. 1977; Lico et al. 1982). However, some of the radiochemical elements exhibit less stability at the low pH recommended for sample preservation (Thatcher et al. 1977). Where problems are to be expected, it would be wise to consult the literature relative to the particular element in question.

Sampling and preservation of organic materials poses some special problems and requires special treatment. Contamination, adsorption and degradation are the most common problems (Gibb and Barcelona 1984). They may be largely avoided if the sample is only allowed to contact non-carbonaceous materials, filtered through silver filter paper (0.45  $\mu$ m) and

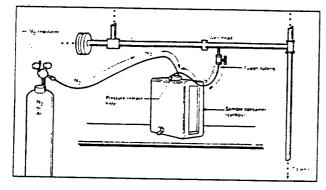


Figure 3a. Well head sampling apparatus for collection of subsurface water under reducing conditions

stored at or near freezing. Some recommend that solutions of  $HgCl_2$  (40 mg Hg/L) or NaN<sub>3</sub> (1,000 mg/L) be used as bactericides. Methods for the preservation of organics are described in Goerlitz and Brown (1972). Wershaw et al. (1983), and in Minear and Keith (1984).

Perhaps the most misunderstood field test is Eh, the measurement of the oxidation-reduction potential of a water. Problems with its measurement by the standard potentiometric method (Wood 1976) are several. First, some of the redox species found in natural water are not electroactive at the interface of the platinum electrode used in the measurement. Carbon is a good example. Secondly, most redox species in natural environments are in sufficiently low concentrations that exchange currents are too low to allow for the measurement of a Nernstian Eh (Whitfield 1974; Lindberg and Runnels 1984). Lastly, direct measurements of individual redox couples in many environments suggest that these redox couples are not in equilibrium with each other, and therefore Eh measurements would detect mixed potentials that cannot be interpreted (Lindberg and Runnells 1984). Oxidation-reduction states of natural water have been studied using several chemical couples (Nordstom et al. 1978; Cherry et al. 1979; Kharaka et al. 1980).

#### Laboratory Analysis of Water Inorganic Constituents

The literature is replete with methods for the chemical analysis of water as described in recent reviews (Fist.man et al. 1983; Polcyn 1984). Recent literature has compared the state-of-the-art techniques for lowered detection limit capabilities for individual elements (Eaton et al. 1982; Nadkarni et al. 1982; Parsons et al. 1983). Today it is possible to measure many elements at the nanogram level (Parsons et al. 1983). For the analysis of much of the natural and polluted water, this is far below the theoretical detection limit because of interferences and matrix effects. Methodologies have been developed by researchers for the analysis of certain types of geothermal (Presser and Barnes 1974; Watson 1978) and oil field water (Lico et al. 1982).

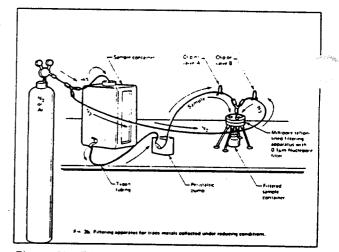


Figure 3b. Filtering apparatus for trace metals collected under reducing conditions

The authors have found that the following methods have been suitable for analyzing water with a salinity that ranges from fresh ground water (0 to 1,000 mg/L total dissolved solids (TDS)) to brines (greater than 100,000 mg/L TDS).

Major cations are measured by atomic absorption spectroscopy as described in Lico et al. (1982). Major anions are done by various methods (Lico et al. 1982). Ion chromatographic techniques, however, are now used for iodide (Elsheimer and Law, written communication 1985), sulfate and bromide (Johnson and Haak 1983). Metals are now generally measured by graphit furnace AA with Zeeman-background correction. ICP-AES has also been applied to the analysis of cations and metals (Garbarino and Taylor 1979; Thompson and Walsh 1983).

Parsons et al. (1983) have summarized the advantages and disadvantages of the atomic spectroscopy instrumentation (Table 2). In general, we have used the graphite-furnace AA (GFAA) when the detection limit required was below that for the flame AA (FAA) and the ICP or when a complicated matrix necessitated dilution below the detection limit for FAA or ICP. For samples with background interferences, the GFAA requires that sample volumes be reduced, internal gas rate be increased and background correctors be used (Beaty 1978). For samples with chemical interferences, one may use standard additions, matrix matching, or the use of peak area instead of peak height for the GFAA. The Zeeman GFAA is the best technique for trace metals analysis when the detection limit is below the ICP and the ionic strength is much greater than 0.5 molar (Slavin et al. 1983; Mulford 1966). Matrix modifiers will control chemical and background interferences in water at least up to 0.5 molar. Standard additions may be used with samples of low metal concentrations in high ionic strength matrices.

In general, ICP-AES is comparable to FAA in terms of detection limits and precision. However, ICP-AE offers several advantages: 1) it is relatively tree from chemical interferences due to the high temperature of the plasma; 2) it has multielement capability, and 3) it has a wide dynamic range covering five or more orders of concentration magnitude. Although sample dilution and/or matrix matching of samples and standards is required for high ionic strength, corrections must be made for background and spectral interferences in ICP-AES, the reduced sample handling time and highsample throughput make this technique a valuable alternative to FAA.

#### **Organic Constituents**

Less than 10 percent of the dissolved organic constituents in natural water has been identified (Leenheer 1984). While waste water may contain up to several thousand mg/L of total organic carbon, shallow ground water generally have less than 10 mg/L (Leenheer 1984). In shallow ground water, up to 90 percent of the total organic carbon may consist of high molecular weight fulvic and humic acids (Thurman 1984). Oil field water generally has much higher concentrations of TOC (up to 2,000 mg/L). Short-chain aliphatic acid anions (mainly acetate and propionate) were identified (Willey et al. 1975; Carothers and Kharaka 1978). Because of the latest techniques for concentration, partitioning and isolation, and improved analytical instrumentation, a greater percentage of these compounds are now being identified (Leenheer 1984).

Analytical techniques using gas chromatography (GC) (Schwarzenbach et al. 1984), mass spectrometry (MS) (Hass and Norwood 1984), high performance liquid chromatography (HPLC) (Bombough 1984), and infrared spectrometry (IR) (Kawahara 1984) are now used for analysis of waste and natural water. These instruments may be used separately or in sequence (i.e., GC-MS) to acquire the necessary detection level. In addition to techniques for specie identification there are methods to separate organic materials by their chemical characteristics. One procedure identifies acid, base and neutral hydrophobic and hydrophilic solute fractions, which can be useful in the study of organic transformations and sorption processes (Leenheer and Huffman 1979).

#### **Quality Control**

Quality control of samples is an essential part of any well-posed scientific study. Interlaboratory comparisons have shown that even for commonly analyzed species such as sulfate (Ellis 1976), the range in reported values may be considerable. The use of blanks, artificial samples, diluted and spiked samples provide a means of determining the accuracy of chemical analyses from a given laboratory. It is recommended that the preceding procedures be followed if the analyses are performed by an outside laboratory. Publications by Wilson (1952), the American Chemical Society (1980), and Friedman and Erdmann (1982) provide some guidance for setting up a quality assurance program.

## Extrapolation of the Chemical Data To Subsurface Conditions

Geochemical studies often require the use of com-

#### Table 2 Comparison of Four Spectrometric Methods: (FAES)<sup>1</sup>, (FAAS)<sup>2</sup>, (GFAA)<sup>3</sup> and (ICPS)<sup>4</sup>

	Method			
Comparison	FAES	FAAS	GFAA	ICPS
Advantages				
Inexpensive instrument	х	х	Χ.	
Inexpensive maintenance	х	х	х	
Wide dynamic range	x			х
Low matrix interferences				х
Low spectral interferences	х	X	х	
Multi-element				х
Small sample capacity			x	
Disadvantages				
Expensive instrument				х
Expensive maintenance				x
Limited dynamic range		х	х	
High matrix interferences	х	х	х	
High spectral interferences				х.
Single element	x	. <b>X</b>	х	
Poor precision			x	

' Flame atomic emission

<sup>2</sup> Flame atomic absorption

<sup>3</sup> Graphite-furnace atomic absorption

Inductive coupled plasma (modified from Parsons et al. 1983)

puter models to interpret chemical processes in subsurface water. In our studies, we use SOLMNEQ II (Kharaka et al. 1985) to calculate the distribution and activities of aqueous species on the assumption of thermodynamic equilibrium in the aqueous phase. The thermodynamic data base for this model includes inorganic and organic aqueous species (250), and minerals (300) over the temperature range from 0 to 350 C, and pressures from 0.1 to 100 MPa.

The reason for using this model in the analysis of subsurface water is that it allows the calculation of pH at in situ temperature and pressure conditions. Higher hydrostatic pressure almost always increases the solubility of minerals and becomes significant in sedimentary basins, especially in geopressured zones and at temperatures greater than about 100 C. During the collection of subsurface samples, the pH can change from the loss of volatile gases such as  $CO_2$  and  $H_2S$ , but changes in temperature and pressure alone will result in pH changes due to variations in the stabilities of hydrogen-bearing aqueous species (Kharaka et al. 1980). SOLMNEQ II will compute the subsurface pH where known quantities of  $CO_2$  and  $H_2S$  were lost prior to the surface measurement of pH.

Geochemical models and their application to subsurface water are covered in Jenne (1979) and in Plummer (this volume).

#### Summary

Geochemical studies of subsurface water require detailed information about the hydrologic and geologic environment such as ground water flow path, hydraulic characteristics of the aquifer, the geologic section and the mineralogy of the zone of interest. Wells where interborehole flow may occur should be used with caution. The entire history of a new well should be documented along with construction materials and fluids used (types and volumes) downhole.

Ground water sampling should proceed when it has been determined that a representative sample may be collected at the well head or in situ. The in situ sample is generally preferred because it is more likely to be representative. Samples should be collected at the well head when pH, alkalinity, temperature and conductivity achieve steady-state measurements. Samples should be collected, filtered and preserved in the field as appropriate as soon after collection as possible. Care should be taken to minimize air contact with the samples, especially if in situ reducing conditions are expected.

Analysis of subsurface water should be in accordance with the study objectives and the required level of detection. Methods for the analysis of certain types of water have been published and should be consulted because of the many difficulties of analyzing brines and geothermal water. Quality control of chemical analyses should be documented by the use of blanks, dilutions, spiked samples and standard reference samples. If the pH of the sample varies substantially after collection, it may be necessary to calculate the subsurface pH by using a computer model such as SOLMNEQ II if the volumes of volatile gases lost prior to the surface pH measurement are known.

#### Disclaimer

Use of trade names (i.e., Zeeman) in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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# Environmental Isotopes: Principles and Applications in Ground Water Geochemical Studies in Alberta, Canada

by Edward I. Wallick, H. Roy Krouse and Asif Shakur

#### Abstract

Isotopic ratio determinations of hydrogen, oxygen, carbon and sulfur are among the most useful of parameters in the study of ground water geochemical systems. Hydrogen has two stable isotopes, protium and deuterium, having masses one and two, and atomic abundances of 99.985 and .015 percent, respectively. The main mass-dependent processes by which hydrogen isotope abundances are altered are evaporation and condensation of water in the hydrological cycle of the earth. Tritium (mass three, half life 12.3 years) is produced by cosmic rays in the upper atmosphere and in thermonuclear bomb explosions. Tritium levels are affected mainly by losses due to radioactive decay, through exchange with atmospheric water vapor, and through dilution in the oceans. Oxygen has three stable isotopes having masses 16 (most abundant), 17 (.01 percent), and 18 (.08 percent). The main mass-dependent processes that affect the abundance of oxygen isotopes are evaporation, condensation and exchange reactions. Carbon has three isotopes of environmental importance having masses 12, 13 and 14. The average abundances for the two stable nuclides are 98.9 and 1.1 percent, respectively, while carbon-14 is radioactive and has a half-life of 5,730 years. Inasmuch as carbon is the building block of life, biological processes play the dominant role in the fractionation of carbon isotopes. Sulfur consists of four stable isotopes having masses 32 (95.01 percent), 33 (0.75 percent), 34 (4.21 percent) and 36 (.02 percent). Sulfur is also important in the biological cycle and the wide range in valence states, (-2 to +6), and the fact that sulfur compounds occur in all three phases and in organic, as well as inorganic compounds, make it especially prone to isotopic fractionation.

Alberta has long been a successful proving ground for environmental isotope applications because of the extremely varied topography and climate, giving rise to large variations in the stable isotope composition of precipitation. In addition, the unconsolidated Cretaceous deposits are rich in organic matter containing sulfur, and isotopes of carbon and sulfur have proven useful in studying the processes that occur during formation and mining of oil sands, coal and sour gas deposits. A number of interesting examples of environmental isotope applications studies in Alberta are presented. One study involved the determination of potential for impacts of sour gas processing plant operation on soil and water chemical quality. Another entailed the environmental asessment of the Alsands Oil Sands open pit mining operation in the Athabasca Oil Sands of northern Alberta. A method for determining the hydraulic character of prairie potholes is discussed. Studies of the processes governing carbon dioxide production in mine spoil and determination of the source of sulfate in ground water are also presented.

#### Overview

This paper consists of two parts: Part I deals with principles of isotope research including basic definitions and factors affecting isotope abundance variations in nature. Part II cites examples of the use of environmental isotopes in a variety of hydrogeochemical investigations in Alberta during the past decade. These include assessment of ground water-surface water communication; identifying sources of pollutants and tracing their fates in subsurface environments; evaluating the influence of bacterial activity on ground water composition; and assessment of dissolution, transport and precipitation of minerals.

Specific problems for study included determination of the source of anomalously high  $CO_2$  partial pressures in reclaimed mine spoils; delineating natural

and anthropogenic soluble S-compounds in surface and ground water near sour gas processing plants; upward migration of deep saline formation water to a shallow aquifer as a consequence of open pit mining; and origin of a sodium-sulfate/carbonate ground water evaporite deposit.

#### Part I: Principles of Isotope Research

lsotopes of an element differ in their masses because of different numbers of neutrons in their nuclei. Isotopes are usually designated by superscripts to the left of the symbol for the element. Therefore, <sup>34</sup>S designates the 16 protons common to all sulfur nuclei and the particular isotope with 18 neutrons giving a total nucleon number of 34.

By convention, the isotopic composition of an element is measured and reported using the "del" notation. Absolute abundances of isotopes are not usually measured. Rather the relative difference in the abundance ratio of the heavy isotope to the light isotope of the sample with respect to a reference is determined. The fractional difference "d" is given by:

$$d = \frac{R_{sample} - R_{reference}}{R_{reference}}$$

where the R's are, for water, the <sup>18</sup>O/<sup>16</sup>O or the D/H isotope concentration ratios. Positive "d" values show the samples to be enriched in the heavy isotope species with respect to the reference (in this case SMOW, acronym for Standard Mean Ocean Water). Negative "d" values correspond to samples relatively depleted in the heavy isotope species. Inasmuch as the differences between samples and reference are usually quite small, it is convenient to define a del scale in which the "d" values are multiplied by one thousand.

d(%∞) = x 1,000

High reproducibilities of del values can be obtained (0.1% of for  $^{18}\!O$  and 1% for D) whereas the errors in determining the absolute isotope composition of a sample would be typically two orders of magnitude larger. Del values are an intrinsic property of water and can be used in tracing and mixing computations in hydrology. The high precision of del determinations, coupled with the large natural variations in del values, usually means that sources of water masses and mixing phenomena can be determined more effectively with isotopic data than with chemical compositional differences.

Isotope ratio mass spectrometry, featuring the simultaneous collection of two or more ion beams corresponding to the isotopes of interest, is the most frequently used instrument for stable isotope abundance determinations, and occasionally for studies involving radionuclides. However, for measurement of the content of radioctive isotopes, beta spectroscopy using either gas proportional counters or liquid scintillation counters is preferred. The fractionation reactions that affect sulfur isotope abundances fall principally into the two categories of isotope

exchange and kinetic isotope effects. These processes occur during chemical and biochemical conversions.

A chemical exchange reaction can be represented by the equation

$$aA_1 + bB_2 - aA_2 + bB_1$$
, where

'a' and 'b' represent the number of moles of molecules 'A' and 'B' containing the element of interest. The subscripts '1' and '2' refer to lighter and heavier isotopic species respectively. The equilibrium constant K generally is not equal to 1 and has a basic temperature dependence of  $lnK = f(1/T^2)$ (Urey 1947).

When the same molecule occurs in two physical states of the same substance, e.g. liquid water and water vapor, isotope exchange can also occur. This is exemplified in the case of sulfur by the case where H<sub>2</sub>S gas is present in an aqueous system containing HS<sup>-</sup> ion.

The kinetic isotope effect is represented by the one-step competitive reactions

$$A_1 + R - P_1 + X$$
$$K_2$$
$$A_2 + R - P_2 + X$$

1

where  $A_1$  and  $A_2$  are the reactants, and  $P_1$  and  $P_2$ represent the products that contain the light and heavy isotopes respectively. R refers to other reactants and X to other products. The ratio of the isotopic rate constants  $K_1/K_2$  is generally greater than unity. This is to say that the initial product is usually depleted in the heavier isotope as compared to the reactant. Figure 1 shows that as the reaction advances, the remaining reactant becomes increasingly enriched in the heavier isotope because of the preferential conversion of the lighter isotopic species. The model of this process shown in the figure is a simplified version of the real process that has several stages where the overall isotopic behavior is a complex function of the isotopic selectivity of each step (Krouse 1983).

Because of the general nature of this presentation, it is not possible to focus upon very detailed aspects that account for the variations in isotopic abundances in nature. The approach that is used instead is to highlight the most important processes that promote isotopic fractionation. In this way the casual reader can obtain a reasonable appreciation of the potential of isotope-geochemical approaches for solving practical problems.

#### Hydrogen

Hydrogen has two stable isotopes, <sup>1</sup><sub>1</sub>H, (protium), and <sup>2</sup>H or D (deuterium), occurring with average abundances of 99.985 and .015 percent respectively. In addition, the radioactive nuclide,  ${}^{3}_{1}H$  or T (tritium), exists naturally and decays with a half-life of 12.3 years into <sup>3</sup><sub>2</sub>He.

Tritium is produced naturally in the upper atmosphere 2-7<sup>by</sup> the collision of cosmic rays (essentially very high

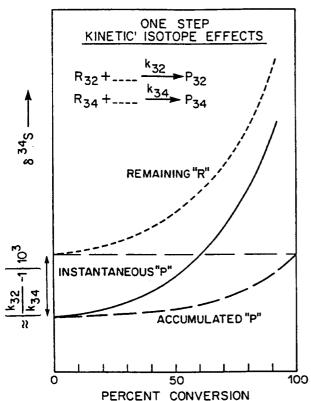


Figure 1. Kinetic isotope effect: isotopic behavior of components during a simple one-step, first-order process where the ratio of the rate constants  $k_{32}/k_{34}$  is larger than unity

energy protons) with atoms of oxygen and nitrogen to produce thermal neutrons. These neutrons, in addition to energetic protons and deuterons, collide with each other and nitrogen of the air to produce tritium. The production of cosmic ray-induced tritium is directly dependent on the neutron flux. Examples of natural tritium production are as follows:

$${}^{14}_{7}N + {}^{1}_{0}N - {}^{3}_{1}H + {}^{12}_{6}C$$
  
 ${}^{14}_{7}N + {}^{1}_{1}H - {}^{3}_{1}H + fragments$   
 ${}^{2}_{1}H + {}^{2}_{1}H - {}^{3}_{1}H + {}^{1}_{1}H$  (Evans 1966)

Tritium is also produced during thermonuclear tests and in nuclear reactors, and it is estimated that 12 times the natural inventory of tritium, about 360kg, were present in the waters of the northern hemisphere at the end of the atmospheric testing, which took place between 1958 and 1963 (Libby 1963).

The main mass-dependent processes by which hydrogen isotope abundances are altered are evaporation and condensation in the hydrological cycle of the earth. The world acts like a giant "still" for isotopic species of water with net evaporation occurring in the oceans and net precipitation occurring in continental and polar regions.

Tritium levels are affected mainly by loss due to radioactive decay, through exchange with atmospheric water vapor, and through dilution in the oceans.

#### Oxygen

There are three stable isotopes of oxygen,  ${}^{16}_{8}$ O,  ${}^{17}_{8}$ O and  ${}^{18}_{8}$ O.

The approximate abundances for <sup>18</sup>O and <sup>17</sup>O are .08 percent and .01 percent, respectively. The main mass-dependent processes that affect the abundances

SOURCE	MEAN δ <sup>34</sup> S (%)	RANGE & "S(%)
SEA WATER SO =	+ 20.3	+ 18.9 to + 20.7
MARINE EVAPORITE SULFATE MINERALS		+ 8.0 to + 32.0
PRECIPITATION SO. #	+ 6.1	· 1.5 to + 19.4
BIOGENIC H S	- 15.0	· 35.0 to + 4.0
SEDIMENTARY ROCK SULFIDE MINERALS	- 15.0	· 35.0 10 + 42.0

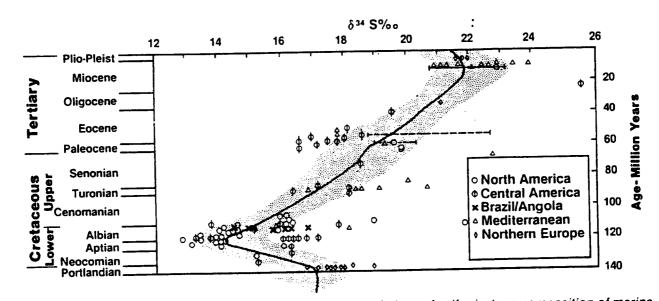


Figure 2. Range of sulfur isotope abundances in nature and variations of sulfur isotope composition of marine sulfate over geological time 2-71

SULFUR ISOTOPIC COMPOSITION OF THE PRINCIPAL SOURCES OF GROUNDWATER SULFATE

of oxygen isotopes are evaporation, condensation and exchange reactions.

## Fractionation of Hydrogen and Oxygen Isotopes in Nature

At 20 C, water vapor is lower by about 80% in del D and 10% in del <sup>18</sup>O than liquid water with which it is in isotopic equilibrium. Kinetic isotope effects during open evaporation lead to greater fractionation.

Water vapor that is evaporated from the oceans is depleted in deuterium and oxygen-18; however, it is not quite in isotopic equilibrium with the ocean. This discrepancy is due to the effects of wind, imperfect mixing and kinetic factors affecting the mass transfer between the liquid and vapor phases. The initial condensation event leads to the preferential removal of the heavier isotopes during precipitation, with the remaining vapor becoming more depleted in oxygen-18 and deuterium. Subsequent condensation is further depleted in the heavy isotopes. The major effects of this Rayleigh process (continuous removal of condensate enriched in the heavier isotopes) are:

• A gradual decrease in del <sup>18</sup>O and del D as one goes from lower to higher latitudes

• More depletion in del <sup>18</sup>O and del D in winter snow than in summer rains

• A decrease in del <sup>18</sup>O and del D in going from the coast inland on continents, and

• A decrease in del <sup>18</sup>O and del D with increasing altitude.

Figure 2 is a simple diagram that displays processes affected by the relationships between del D and <sup>18</sup>O. Water of meteoric origin (as opposed to juvenile water or water of hydration in various minerals, for example) plotted on a line with an approximate relation del D = 8 del <sup>18</sup>O + 10 (Dansgaard 1964; Craig 1966). The various processes that cause a departure from the meteoric water line are evaporation from an open water body, condensation, exchange with gases and solids, and hydration of silicate minerals.

#### Carbon

Carbon has two stable isotopes,  ${}^{12}_{6}C$ , ( ${}^{12}C$ ), and  ${}^{13}_{6}C$  or  ${}^{13}C$ , occurring with average abundances of 98.9 and 1.1 percent, respectively. In addition, the radioactive nuclide, carbon-14 (radiocarbon) exists naturally and decays with a half-life of 5,730 years into nitrogen-14.

In nature, the values of del <sup>13</sup>C (with respect to the PDB scale) range from less than -90% for some very isotopically light biogenic methanes to over +20% for a few carbonates. The biosphere and carbonates are connected to atmospheric CO<sub>2</sub> (del <sup>13</sup>C approximately -8%) and constitute the two main carbon reservoirs. As a consequence of isotopic exchange among atmospheric CO<sub>2</sub>, dissolved HCO<sub>3</sub><sup>-</sup>, and CaCO<sub>3</sub>, precipitated marine carbonates are enriched in <sup>13</sup>C, resulting in del <sup>13</sup>C values near zero per mil.

Because carbon is the building block of life, it is not surprising that biological processes play the dominant role in the fractionation of carbon isotopes. These biological processes include photosynthesis and respiration, whereby carbon is either incorporated into organic matter from free  $CO_2$  or where organic matter is oxidized.

Three photosynthetic pathways (C3, C4, and CAM) have been identified that follow the Calvin Cycle and include many trees and most cereal grains such as wheat and oats. These plants have values of del <sup>13</sup>C ranging between -30 to -22% or The C4 plants belong to the Hatch-Slack Cycle and include cane plants such as corn. They are isotopically heavier with del <sup>13</sup>C values ranging from -16 to -8% or (Hatch and Slack 1970). The CAM (crassulacean acid metabolism) plants, which include the cacti, tend to span the range of C3 and C4 plants (Troughton 1972).

Variations in the carbon isotopic composition of soil  $CO_2$  are often related to the type of plant cover because of the large amount of root respiration that contributes to the soil atmosphere. It is this  $CO_2$  that enters the ground water system and becomes part of the dissolved inorganic carbon. Carbon isotopes are therefore of great importance in understanding the chemical evolution of ground water.

Carbon-14 is produced naturally in the upper atmosphere by thermal neutron activation of nitrogen according to the reaction:

$${}^{14}_{7}N + {}^{1}_{0}n - {}^{14}_{6}C + {}^{1}_{1}p$$

The estimated production rate of  ${}^{14}C$  is about 2.2 atoms/sec/cm<sup>2</sup> of earth's surface (Lingenfelter 1963; Lal and Peters 1967).

Once formed, the radiocarbon is first oxidized to  ${}^{14}CO$  and then to  ${}^{14}CO_2$  and is subsequently dispersed throughout the atmosphere, biosphere and mixed layer of the oceans. Radiocarbon takes part in the carbon cycle of the earth to the extent of its 5,730-year half-life (8,270-year mean-life). Radiocarbon decays by the mechanism:

### ${}^{14}_{6}C - {}^{14}_{7}N + {}^{0}_{-1}\beta + \tilde{v}$

The basic chemical model for the use of natural radiocarbon in ground water age determination was developed by Munnich (1957). Munnich recognized that the principal problem in age dating was estimating the initial radiocarbon activity of recharge water inasmuch as recent shallow soil water from northwest Europe gave carbon-14 dates that were too old by as much as 2,000 years. Clearly, the recharge water contained a mixture of old and recent carbon. The recent carbon was composed of CO2 dissolved in soil water from plant root respiration and from decay of organic matter in the soil. Carbon from soil lime, containing no radiocarbon due to the great age of the parent marine limestone, was diluting the initial carbon-14 activity of the water. The dissolution of CaCO<sub>3</sub> by CO<sub>2</sub>-charged water was modeled by the reaction:  $x \cdot CaCO_3 + (x+y) \cdot CO_2 + xH_2O - 2x \cdot HCO_3^- + y \cdot CO_2$ + x • Ca\*\*, where x and y are the molar concentrations. According to the reaction, x moles per liter of recent atmospheric/biogenic CO2 dissolve the same amount

of CaCO<sub>3</sub> to produce 2x moles per liter of dissolved bicarbonate. Unreacted CO<sub>2</sub> of concentration, y, remains dissociated H<sub>2</sub>CO<sub>3</sub> and that is unable to attack further CaCO<sub>3</sub>. This CO<sub>2</sub> is referred to as "free" CO<sub>2</sub> as opposed to "fixed" CO<sub>2</sub> that is dissolved HCO<sub>3</sub><sup>-</sup> plus CO<sub>3</sub><sup>-</sup> or bound in CaCO<sub>3</sub>. Certain assumptions are inherent in the basic chemical model as follows:

• The soil biogenic and atmospheric  $CO_2$  have a radiocarbon activity of 100 percent of the modern standard.

The soil lime contains no radiocarbon.

• The dissolved carbonate in ground water originates only from dissolved CO<sub>2</sub> and carbonate minerals in the soil and unsaturated zone.

• Loss of radiocarbon is solely by radioactive decay once the water leaves the soil zone, i.e., no loss by isotopic exchange with carbonate minerals in the aquifer.

• The concentrations of carbonate species are conserved in the ground water over time. Composition of ground water remains unchanged over time, i.e., no chemical exchange.

Because the preceding assumptions rarely hold true in natural ground water systems, correction models have been developed using various chemical and isotopic equilibrium approaches in order to correct for non-ideality in the basic chemical model. These approaches have been used to correct ages deduced using the basic chemical model. These approaches have refined the estimate of the value of the initial carbon-14 content in the dissolved inorganic carbon in the recharge area (e.g. Pearson 1965; Mook 1972; Wallick 1976).

#### Sulfur

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The element sulfur consists of four stable isotopes,  $^{32}_{16}$ S,  $^{33}_{16}$ S,  $^{34}_{16}$ S and  $^{36}_{16}$ S. The approximate abundances of these isotopes are, respectively, 95.02, 0.75, 4.21 and .02 percent.

All sulfur isotope del values are reported with respect to the Cañon Diablo meteoric troilite standard. The range of sulfur isotope abundances in nature and the variations in del <sup>34</sup>S of marine sulfate over geological time are shown in Figure 3.

Sulfur, like carbon, is important in the biological cycle. The wide range in valence states, (-2 to +6), and the fact that sulfur compounds occur in all three phases and in organic, as well as inorganic forms, makes it particularly sensitive to fractionation.

The largest fractionations occur during aqueous sulfate reduction to bisulfide by bacteria such as *Desulfovibrio desulfuricans*, according to the following equation (after Berner 1972):

In the preceding equation, C represents organic carbon and  $Fe_2O_3$  represents reactive iron minerals in sediments with which water is in contact. The net effect is to convert the sulfate into an equivalent amount of alkalinity, which may precipitate as calcium or magnesium carbonate, or may build up in solution.

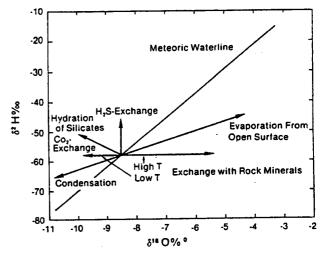


Figure 3. Meteoric water line diagram showing del D vs. del <sup>18</sup>O for generalized systems (IAEA Report No. 228, 1983)

Because there is usually incomplete conversion of sulfate to sulfide, there is isotopic fractionation, with the heavy sulfur being enriched in the aqueous sulfate. The net fractionation, del  ${}^{34}S(SO_4^{=}) - del {}^{34}S(HS^{-})$ , may exceed 70 per mil and is dependent upon many factors such as availability of nutrients and extent of conversion.

#### Part II: Isotope Applications in Alberta

Alberta has long been a successful proving ground for isotope methods in hydrology and geochemistry studies because of the supporting role they played in reconnaissance investigations. Further, almost ideal conditions exist in the province for application of the isotope tools (Hitchon and Friedman 1969; Hitchon and Krouse 1972; Hitchon, Brown and Krouse 1975). Alberta has an extremely varied topography and climate. As a result, variations of deuterium and oxygen-18 in meteroric water are very large due to major changes in altitude, latitude and temperature with respect to time and space. Furthermore, the rocks in Alberta range from Paleozoic carbonates and shales to unconsolidated Cretaceous sequences. Some are very high in organic matter (bituminous sandstones and organic-rich shales), and carbon and sulfur isotopes proved useful in elucidating major surface and subsurface processes such as formation of oil sands, coal and sour gas deposits. An additional aspect of the hydrogeological conditions in Alberta is that there are very great differences in hydraulic conductivity, which result in ground water of ages ranging from recent to many millions of years. Isotopic methods for determining the age of this ground water are needed and are in rudimentary stages of development; e.g., chlorine-36 and inert gas methods.

Unless otherwise stated, all stable isotope analyses reported in this paper were performed in the Stable Isotope Laboratory, Physics Department, The University of Calgary (H.R. Krouse, director). Tritium analyses were performed by the Radiocarbon and Tritium Laboratory, Alberta Environmental Centre, Vegreville, Alberta (L.D. Arnold, head).

#### Environmental Impact of Sour Gas Plant Operations

The oil and gas industry is a very important part of the Alberta economy. Therefore, any environmental problems that bias the public against the industry must be resolved quickly.

One study was commissioned by the Alberta Department of Environment in 1983 to assess the environmental impact of operation of gas plants near the town of Pincher Creek in southwestern Alberta (Figure 4). The work that is summarized next is taken from a component of the larger study by Wallick (1984) and was abridged in Wallick, Dabrowski and Shakur 1984).

Although the area receives an average of about 400mm/yr of precipitation, the high winds and occasional drought years make this area tenuous for agriculture. The topography is gently rolling to hummocky with numerous water-filled depressions. The upper Cretaceous sandstone and shales are covered by a thin veneer of glacial drift sediments ranging in thickness from 3 to 20m. Ground water is the only source of water for residents of the local area, and the principal aquifers consist of sands and gravels at the drift/bedrock erosional contact and fractured sandstones in the bedrock.

Two objectives of the study were (1) to determine the dimensions of the area that had been affected by the  $SO_2$  emissions and fallout of sulfur dust, and (2) to establish the degree of communication between the surface water and ground water systems. Environmental isotope methods were used along with other standard hydrogeological procedures to meet these objectives.

Sulfur isotopes had been used successfully in Alberta to differentiate between sulfur of petroliferous origin and sulfur of land plant origin by Case and Krouse (1980), Krouse and Case (1981), and Krouse, Legge and Brown (1984). The method is based upon the observation that deep sour gas occurrences have del <sup>34</sup>S values (ranging from +15 to +30 per mil) similar to associated evaporate deposits. In contrast, plant and soil sulfur in Alberta have del <sup>34</sup>S values ranging from zero down to -30 per mil (Krouse 1980).

If significant quantities of petroliferous sulfur have been added to the soil-water system, heavier values of del <sup>34</sup>S of the soil sulfur should result. Measurements of del <sup>34</sup>S of particulate sulfur and SO<sub>2</sub> extracted from the atmosphere are reported in Table 1. Note that these values are characteristic of marine sedimentary sulfate as are the del <sup>34</sup>S values obtained for the elemental sulfur and raw gas emitted from the two gas processing plants in the study area (Table 2).

The distribution of del <sup>34</sup>S in sulfur extracted from soil plugs 0 to 5cm in depth is shown in Figure 5. The area where there has been influence from the gas plant emissions is well-defined. There is a narrow corridor in which relatively positive values were obtained with respect to the soil sulfur background value represented by the point furthest west. Similar patterns emerged for samples of vegetation and lake

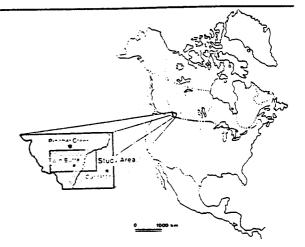


Figure 4. Location of study area for assessment of impact of gas plant operation, Twin Butte

#### Table 1 Measurements of Del <sup>34</sup>S of Particulate Sulfur and SO<sub>2</sub>Extracted from the Atmosphere, Twin Butte Area

Source of Sulfur	δ³⁴S (per mil)	
Atmosphere (~24 H Period in Oct. 1983)		
Particles captured on glass filter	+ 19.7, + 21.6, + 15.8	
- SO₂ trap #1	+ 21.3, + 16.5, + 16.4	
- SO <sub>2</sub> trap #2	+ 25.0, + 22.9, + 20.7	

Table 2Measurements of Del 34S in Elemental Sulfurand Raw Gas from Gas Plants, Twin Butte Area

Source of Sulfur		δ³⁴S (per mil)	
Elemental Sulfur			
- Shell		+ 17.0, + 17.1	
- Gulf	•	+ 18.1, + 18.2,	
		+ 18.3	
Raw Gas			
- Shell		+ 16.4	
- Gulf		+ 17.3	

sediments, i.e., a narrow east-west corridor in which the failout from the gas plant was most concentrated.

Values of del <sup>34</sup>S for aqueous sulfate indicate that sulfate anion was derived from the leaching of local soil sulfur and/or sulfide oxidation (Figure 6). Only a spring discharging approximately 0.8km downgradient from the Shell Plant had a positive value, suggesting that there is a contribution from the sulfur storage block to the shallow ground water system.

Determination of the degree of hydraulic communication between the surface water and ground water

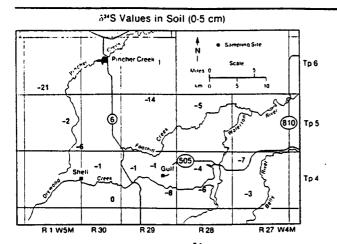


Figure 5. Distribution of del <sup>34</sup>S in sulfur from soil plugs, Twin Butte

systems was facilitated by a deuterium, oxygen-18 and environmental tritium survey. Overlap in the oxygen-18 distributions between the surface water and ground water systems (Figure 7) suggests mixing of water from the two systems occurs and that the ground water system responds readily to any surface disturbance that can change the quantity or chemical quality of recharge water.

The tritium contents of surface water in T.U. (one T.U. =  $1 \times 10^{-18}$  T/H) average approximately 50 T.U. (Figure 8). In the ground water samples, there were two groups: one group of drift wells 2.5 to 20m deep with tritium levels similar to those of surface water, and another group of bedrock wells ranging from 40 to 70m deep with tritium levels higher than recent precipitation, sometimes exceeding 100 T.U. (Figure 9).

A tentative explanation for the higher tritium levels is that about a decade is required for recharge to occur in the deeper aquifers, although rapid seasonal recharge occurs for the shallow drift units. The sulfate concentration of surface water was ambiguous as an indicator of fallout of gas plant sulfur because of the ...evaporation-concentration of salts brought about by high winds and low relative humidity. Extensive evaporation was revealed by the stable isotopes, deuterium and oxygen-18. A meteoric water line plot with both surface water and ground water data is given in Figure 10. Ground water and surface water both plot close to the meteoric water line; however, most surface water plots well below the line indicative of evaporation. Note that tritium values did not increase along the evaporation line because of the diluting effect of exchange with atmospheric moisture. These trends indicate that sulfate concentrations increased due to evaporation-concentration and not because of additional sulfur loading. In general, the conclusions reached in the Twin Butte study as a result of the application of isotope-geochemical techniques were as follows:

• The surface water system is hydraulically continuous with the shallow ground water system and recharge is rapid (on the order of several years).

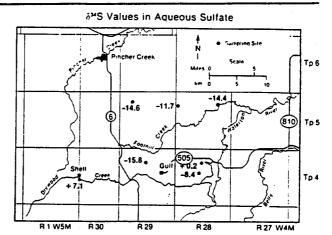


Figure 6. Distribution of del <sup>34</sup>S in aqueous sulfate, Twin Butte

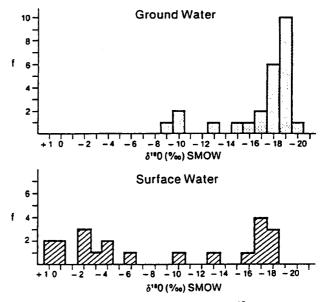


Figure 7. Frequency histogram of del <sup>18</sup>O values for surface water and ground water

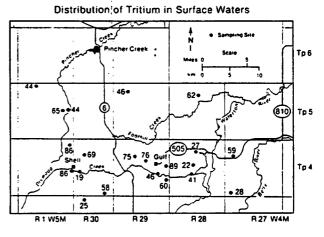
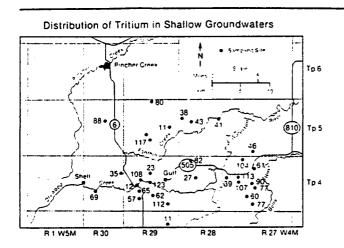
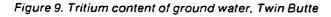


Figure 8. Tritium content of surface water, Twin Butte

 Runoff and seepage from the sulfur storage block contributes sulfate to ground water very near to the plant, and atmospheric sulfur fallout from the plant





accumulated in the soil in a corridor aligned with the direction of the prevailing westerly winds.

• Evaporation-concentration is an important geochemical process in the area and sulfate concentration levels in surface water bodies are not reliable indicators of the presence of petroliferous sulfur loading.

#### **Environmental Impact of Oil Sands Mining**

During the final stages of the work that was done to assess the environmental impact of mining of oil sands in the Alsands Project area near Fort McMurray, Alberta, (Figure 11) several fundamental questions were posed concerning the effect of open pit mining:

• Would dewatering the large open pit result in upward movement of highly saline ground water from deep aquifers?

• Is there active recharge through the oil sands in the area?

• Is the sulfate in the ground water of evaporite origin or is it derived from oxidation of reduced sulfur forms?

Figure 12 shows the stratigraphy and the distribution of aquifers and aquitards along an east-west section in the area. The Precambrian basement consists of metasediments and granites; these rocks outcrop about 70km northeast of the Alsands Project area. Overlying the Precambrian are the LaLoche and the McLean River formations, consisting respectively of clastics and evaporites. The Methy Formation is composed primarily of dolomite and ranges in thickness from 63 to 107m. Saline formation water is found in these zones. The Prairie Evaporite Formation in the study area consists of anhydrite, gypsum and silty shales, varies in thickness from 40 to 80m and constitutes a tight confining bed for the Methy Aquifer. In other locations, the Prairie Evaporite Formation can be up to 130m in thickness and acts as a low permeability membrane that separates the Middle Devonian Methy Aquifer from aquifers present in the Lower Cretaceous deposits. The Upper Devonian deposits form a base for much younger sediments of lower

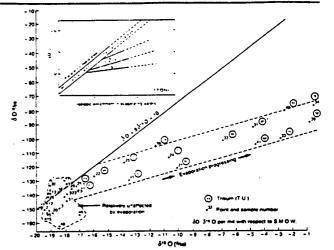


Figure 10. Meteoric water line plot of surface water and ground water from Twin Butte

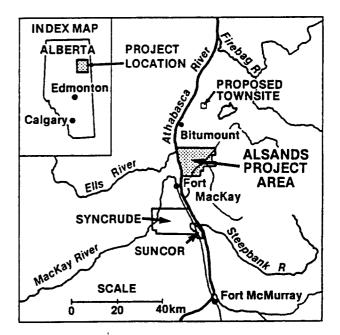


Figure 11. Location of Alsands Project Area in Athabasca oil sands, northern Alberta

Cretaceous age. Within the Alsands Project area, this consists of the McMurray Formation with the younger, locally present Clearwater Formation. In the basal part of the McMurray Formation, a residual claystone underlies massive sand deposits up to 40m thick. These sands are the Basal Aquifer and have the highest ground water yields in the project area. The Pleistocene is represented by glaciofluvial (sand and gravel) and ice contact deposits consisting of lacustrine clay and till. Recent sediments include sand, silt and clays of aeolian, fluvial and lacustrine origin. Muskeg organic deposits cover most of the project area.

The extensive ground water monitoring system in the Alsands Project area consisted of a total of 137 piezometers in the surficial aquifer, 49 piezometers in the Basal Aquifer and 7 piezometers in the Methy

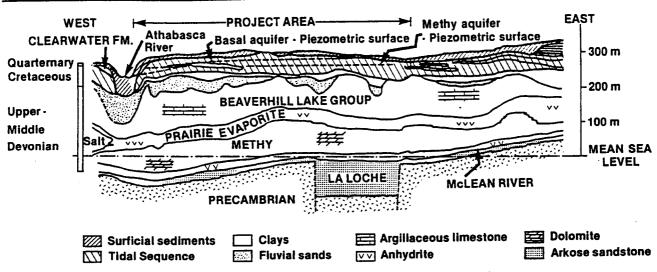


Figure 12. Stratigraphy and distribution of aquifers and aquitards, Alsands Project Area

Formation. Piezometers were of the standpipe type with a section sealed within the aquifer. The piezometers were developed with compressed air, samples were collected and static water levels were measured. Water samples and pore water (extracted from oil sands core materials by means of the toluene reflux extraction method) were analyzed for a variety of isotopic and chemical constitutents. Analyses of tritium were performed at the Centre for Applied Isotope Studies at the University of Georgia, Athens (J.E. Noakes, director).

An important objective of this study was to use the environmental isotopes to determine whether the Methy and Basal aquifers are hydraulically connected. Figure 13 is a plot of del <sup>18</sup>O vs. del D together with Craig's (1966) meteoric water line. The points representing the Methy Aquifer are the most depleted in the heavy isotopes and possess greater homogeneity than in the Basal Aquifer. One interpretation that fits the data is that ground water in the Methy is far older than ground water in the Basal Aquifer, and that the depleted isotopic composition reflects recharge during a colder climatic period. Ground water from the Basal Aquifer shows the effect of recharge and the greater scatter in the data is believed to reflect the variability in the precipitation input.

The distribution of isotopic data in Figure 13 may be compared with a plot prepared by Salati et al. (1974) for an environmental isotope study of an area in northeastern Brazil (Figure 14). Note how the older ground water in the Acu Sandstone is also lighter and isotopically more homogeneous than the ground water that occurs in a limestone aquifer or in the recharge area of the Acu Sandstone. These isotopic distributions describe ground water conditions where there is a lack of communication between two aquifers, so that so-called "fossil" ground water can be preserved. In the Alsands Project area, the Basal Aquifer does not appear to communicate hydraulically with the Methy Aquifer in a time span of less than tens of

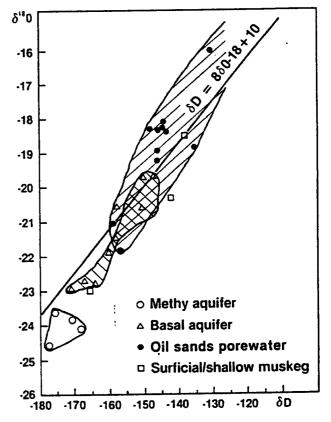


Figure 13. Meteoric water line plot of formation water from Alsands Project Area

thousands of years. It is possible that the water that is trapped in the Methy was recharged sometime during the Pleistocene or earlier epoch.

Another way of illustrating the lack of significant communication between the Basal and Methy aquifers is by means of the log (CI<sup>-</sup>) vs. del D plot in Figure 15. The Basal and Methy ground waters have neither overlap in chloride nor in del D. Because the movement of chloride is impeded the least by interaction with sediments, the deuterium is a conservative tracer

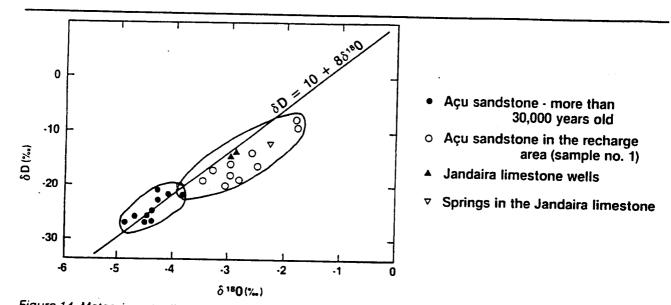


Figure 14. Meteoric water line plot of ground water from northeastern Brazil (Salati et al. 1974)

of the water molecule, any mixing between the two water masses over geological time would destroy the isotopic and geochemical zonation that exists.

Conventional hydrogeological data also confirmed that the Basal and Methy aquifers are not hydraulically connected. In the northeast part of the study area, the piezometric heads in the Basal Aquifer exceeded the Methy Aquifer by more than 10m. The reverse situation was observed in the southwest part where the piezometric head difference between the two aquifers was more than 25m. Furthermore, a 1.5 year drawdown test in the Basal Sands Aquifer, associated with the open pit mining feasibility study failed to induce any change in water level in piezometers completed in the Methy Aquifer.

The second most important objective of the study was to determine whether recharge took place through the oil sand within recent time. Oil sand deposits were believed to be impermeable based upon laboratory consolidation tests, and yet, the large volumes of water that were being pumped from the dewatering wells surrounding the pit indicated otherwise.

Analyses of del <sup>18</sup>O and del D in pore water separated from the oil sand by the toluene reflux extraction method are presented in Table 3. The mean value for del <sup>18</sup>O was -18.2 +/- 2.2 and the mean for del D was 143.7 +/- 10 per mil. Tables 4 and 5 contain the results of tritium analyses of ground water, surface water and pore water. Although no tritium was found in ground water samples collected from the Basal and Methy aquifers, the pore water contained significant levels of tritium in all except one sample (810041 EP). The two surface water samples that were analyzed had the same tritium content as the pore water.

The similarity of the stable isotopic composition of the pore water and recent surface water and the presence of significant tritium levels in the pore water suggested that recharge was taking place through the oil sand. Tritium levels were similar to those in precipi-

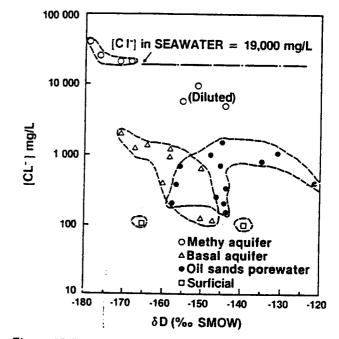


Figure 15. Log (CI<sup>-</sup>) vs. del D for formation water from Alsands Project Area

tation analyzed in Alberta over the past five or six years.

Assuming 10 percent for the effective porosity of the oil sand, using a measured hydraulic gradient of 1m per m, and a flow velocity of 75m per six years, substitution into Darcy's Law gives a hydraulic conductivity of about  $4 \times 10^{-8}$ m/sec. This value is in agreement with those obtained from pumping tests in the dewatering wells.

The third objective in which isotopic methods played an important role was in determining the source of sulfate in the ground water. Values of del <sup>34</sup>S for both Basal and Methy aquifers (Table 6) fell within the range of sea water sulfate (+18.9 to +20.7 per mil).

#### Table 3

Analyses of Del <sup>18</sup>O and Del D in Pore Water Separated from Oil Sand by Toluene Reflux Extraction, Alsands Project Area

ALSANDS #	DESCRIPTION	DEPTH (m)	δ <sup>18</sup> 0 (‱)	۵D (‱)
810004 EP	upper feed	10.2 • 20.0	.17.0	.155.5
810004 EP	lower feed A	30.0 - 54.0	-16.0	-130.6
810004 EP	lower feed B	54.0 - 75.0	-12.6	-121.2
810041 EP	upper leed	12.0 · 25.0	-21.0	-157.5
810041 EP	lawer feed	41.8 · 60.0	-18.1	-143.5
810041 EP 🕚 -	lower feed	60.5 · 75.5	-18.3	-144.5
810015 EP	lower feed	25.0 - 54.0	-21.8	-158.1
810015 EP	lower feed	54.0 - 65.0	-18.2	-143.7
810015 EP	lower feed	68.0 - 74.0	-18.9	-145.4
810043 EP	lower leed	53.0 · 65.0	-18.8	-134.7
810043 EP	upper feed	31.0 - 42.0	-18.3	-147.5
810007 EP	upper feed	52.0 - 73.0	18.2	-145.1
810007 EP	lower teed	36.9 - 52.0	-18.4	-143.0

#### $\delta^{\overline{18}}0 = -18.2 \pm 2.2\%$

ôD = 143.7 ± 10.3%.

Despite the fact that ground water from the Basal Aquifer contained much less sulfate than ground water from the Methy Formation, sulfate reduction is not the explanation for the difference. Had sulfate reduction been operative, the large negative fractionations would have severely altered the isotopic composition of the sulfate. The most likely cause is more extensive flushing by circulating ground water in the shallow Basal Aquifer than in the deeper Methy Formation to remove the residual sulfate.

## Source and Mechanism of Generation of $CO_2$ in Mine Spoil

Large-scale disturbance of the earth's surface allows oxygen to come into contact with reduced carbon, sulfur and nitrogen compounds. When oxidized, these compounds convert to CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub> gases, which hydrolyze as acids. These acids are then available to attack silicate and carbonate minerals and .. thereby contribute to the salt content of the rock.

Because of the desire to mitigate soil and water salinization during surface coal mining, there is a need to develop conceptual and mechanistic models for the formation of salts during chemical weathering in mining operations. Inasmuch as the most important drive in these weathering reactions is the carbon dioxide content, an understanding of the source and mechanism for  $CO_2$  generation is very useful in predicting which environments are particularly prone to development of high  $CO_2$  concentrations and consequently salinization problems.

Research was conducted in several phases (Wallick 1983) in the Forestburg-Halkirk area of east central Alberta (Figure 16). Dry piezometers were installed in natural undisturbed areas, in spoil piles and in reclaimed spoil. Laboratory apparatus was constructed for evacuation of gas-sampling bulbs and for gas purification. Sampling and analysis of gas were con-

#### Table 4 Tritium in Ground Water and Surface Water, Alsands Project Area

AQUIFER	WELL NUMBER	TRITIUM (pCI/L)*	TRITIUM (T.U.)**
Basal	810015 EP	<83.0	< 25.6
	810069 EP	< 83.0	< 25.6
	810051 EP	<75.8	<23.4
	\$10043 EP	< 92.8	< 28.6
	810002 EP	<79.2	<24.4
	810057 EP	<83.0	< 25.6

\*1 pCI/L = 3.7 x 10" disintegrations per second

\*\*1 T.U. = 1 x 10"" (H = 3.24 pCVL

#### Table 5 Tritium in Pore Water, Athabasca Oil Sands, Alsands Project Area

AQUIFER	WELL NUMBER	TRITIUM (pCI/L)*	TRITIUM (T.U.)**	
Methy	1481	<108.6	< 33.5	
	1717	< 67.8	< 20.9	
	1240	<88.7	<28.8	
	5039	<87.5	< 27.0	
Diluted Methy	1489	108.6 ± 24.1	32.9	
	1489	155.8 ± 24.5	48.0	
	5021	119.7 ± 22.9	36.9	
· · ·	SUI	RFACE WATER		
YPE OF SA	MPLE	TRITIUM (pCI/L)	TRITIUM (T.U	
Muskeg River		293.5 ± 21.2	90.6	
Surficial Drai	nage	250.6 ± 26.3	77.3	
Surficial Muskeg		636.3 ± 30.6	198.8	

\*1 pCl/L = 3.7 x 10<sup>11</sup> disintegrations per second

ALSANDS NO. DEPTH (M) T.U.(±) DET. LIMIT (T.U.) 610004 EP 810004 EP 30.0-54.0 54.0-75.0 98.2 (7.0) 93.8 (25.0) 25.0 18.1 93.8 (25.0) 50.0 (6.7) 23.5 (6.2) 75.3 (7.7) 64.5 (7.3) 45.0 (7.2) 73.7 (8.2) 79.4 (7.4) 72.1 (7.4) 76.5 (6.3) 115.5 (8.5) 10.2-20.0 12.0-25.0 810004 FP 25.0 810041 EP 23.0 41.8-60.0 60.5-75.5 26.0-54.0 54.0-65.0 810041 EP 29.4 27.7 27.7 810041 EP 810015 EP 810015 EP 31.4 54.0-65.0 66.0-74.0 53.0-65.0 31.0-42.0 52.0-79.0 810015 EP 27.7 810043 EP 810043 EP 22.2 115.5 (8.5) 31.4 81007 EP 81007 EP 36.9-52.0 95.1 (7.0) 29.4

ANALYSES OF TRITIUM IN PORE WATER

ducted during the fall of 1981 and during the 1982 field season. Samples were analyzed for mole percent of oxygen, nitrogen, carbon dioxide and sulfur dioxide.

Values were determined for del <sup>13</sup>C of the carbon dioxide.

#### Carbon Isotope Composition of CO<sub>2</sub>

Carbon dioxide from natural and reclaimed areas within the mine locality falls into three distinct groups on the basis of carbon isotope composition (Figure 17). The lack of overlap signifies that differentiation is possible not only between natural and undisturbed environments but also between one disturbed environment and another. Shown in the right half of Figure 17 is the range of  $CO_2$  levels found for each of the field situations: natural, undisturbed settings and the reclaimed areas (Vesta and Diplomat mines). The three

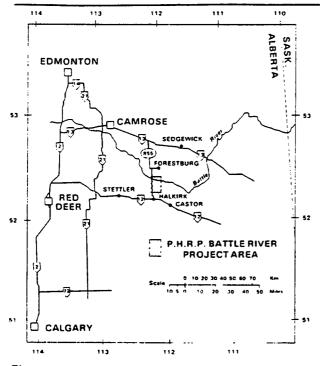


Figure 16. Location of the Forestburg/Halkirk Area. Plains Hydrology and Reclamation Project

settings have different ranges of CO<sub>2</sub> levels, with by far the highest values occurring at the Diplomat Mine.

In nature, del <sup>13</sup>C for organic carbon ranges between -21 and -27 per mil with respect to PDB, whereas marine carbonates have del <sup>13</sup>C values approximately equal to zero. The del <sup>13</sup>C values of the natural settings fall into the range of organic carbon, suggesting that oxidation of organic carbon is the likely source of the  $CO_2$ . (Any suspicion that the  $CO_2$  is derived from atmospheric contamination is ruled out because the observed del <sup>13</sup>C values were significantly lighter than the atmospheric CO<sub>2</sub> del  $^{13}$ C mean value of -7 mil PDB. In addition, the normal content of CO<sub>2</sub> in the atmosphere is 0.03 mole percent, a factor of 10 to 30 times less than the lower limits observed.) Carbon dioxide from the Diplomat Mine was most likely a mixture of oxidized organic carbon and CO<sub>2</sub> produced by reaction of sulfuric acid with marine limestone/ dolostone, which is isotopically "heavy."

#### Sources and Reaction Mechanism for CO<sub>2</sub>

The isotopic data indicate that two sources exist that yield  $CO_2$ : organic carbon and marine carbonate. The following reactions are therefore likely in the unsaturated zone.

a. 
$$C_{org} + O_2 - CO_2 t$$
  
b.  $S_{pyrite/org} + O_2 - SO_2$   
c.  $SO_2 + H_2O + 0.5 O_2 - H_2SO_4$   
d.  $H_2SO_4 + CaCO_3 - CaSO_4 + H_2O + CO_2 t$ 

If relatively equal volumes of CO<sub>2</sub> were produced by

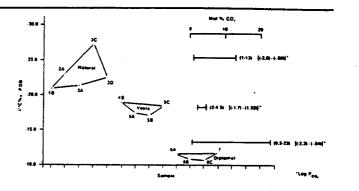


Figure 17. Carbon isotope composition of  $CO_2$  from the unsaturated zone in natural and reclaimed areas

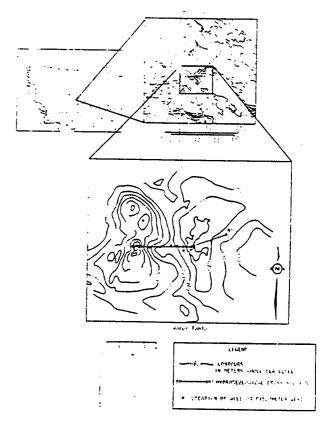


Figure 18. Horseshoe Lake area: A. location; B. regional topography; Ĉ. local water table topography (Wallick 1981)

reactions a and d above, then the isotopic composition should be about halfway between the average value for organic carbon and marine carbonate, i.e., del <sup>13</sup>C equal to approximately -12.5 per mil. This is very close to the observed value at the Diplomat Mine and consistent with CO<sub>2</sub> levels that were roughly twice those observed elsewhere. Furthermore, the overburden at the Diplomat Mine consisted mainly of till that contained a significant marine carbonate component. The fact that authigenic gypsum was detected in the till suggests that reactions of the type described previously are taking place in the spoil environment.

#### Determination of the Hydraulic Character of Prairie Potholes Using Total Dissolved Solids, Deuterium and Oxygen-18

Environmental isotopes proved useful in determining the hydraulic character of the prairie potholes in an area of east central Alberta during a study of the Horsehoe Lake sodium sulfate/carbonate deposit (Wallick 1981). Figure 18 shows the location, regional topography and local water table topography of the Horseshoe Lake area.

Prairie potholes are water-filled depressions of hummocky glacial moraine. They are important breeding grounds for water fowl and water supplies for livestock. The water is a mixture of precipitation, surface runoff and ground water seepage inflow. The ponds lose water through surface outflow, evaporation and seepage outflow to the ground water system. The ponds are quite transient in their hydrological characteristics in that the amount of seepage outflow (ground water recharge) and seepage inflow (ground water discharge) varies in time and space. Sloan (1972) studied the prairie potholes on the Coteau du Missouri in North Dakota and concluded that ground water plays a major role in the water balance of the ponds. The continuous range of ground water conditions around the potholes is shown in Figure 19,

Figure 20 shows a meteoric water line plot along with del <sup>18</sup>O and del D data for water samples collected from potholes and lakes in the Horseshoe Lake Basin. The strong effects of evaporation are evident as is the ultimate origin of much of the ponded water. If the evaporation line is extrapolated back to the meteoric water line, the intersect is very close to the snowmelt isotopic composition of the area based on a survey by Brown (1971). Plotting of del <sup>18</sup>O values vs. the TDS delineates the hydraulic character of the potholes (Figure 20). Note that two distinct situations are represented: First, there is a linear trend of the data, reasonably parallel to the calculated curves for snowmelt and ground water (Lloyd 1966). Second, there is a divergent trend, showing the insensitivity of isotopic enrichment with increasing TDS.

The first trend appears to be associated with the data for potholes that are predominantly recharge in character. In these potholes, the evaporation concentration of snowmelt is the principle mechanism for chemical evolution of the water. Hence, a linear relationship between TDS and del <sup>18</sup>O is expected and observed.

For those potholes existing in a throughflow hydraulic situation, ground water seepage inflow is offset by ground water seepage outflow. Inasmuch as the snowmelt and precipitation that is added to the pond is not as constant in character as the ground water component, the isotopic composition of the water in the pond will take on the value of evaporated ground water over time. This is observed in the plot shown in Figure 21.

The divergent trend where the del <sup>18</sup>O value of sloughs appears to level off at -8 per mil (SMOW), indicates that the simple one-step evaporation process

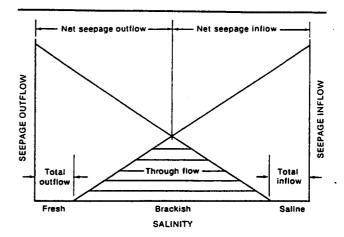


Figure 19. Continuous range of ground water conditions associated with prairie potholes (Sloan 1972)

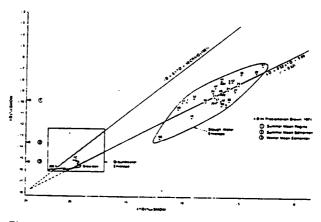


Figure 20. Meteoric water line plot of surface water from potholes and lakes from the Horseshoe Lake Basin, east central Alberta

is not applicable. In this lobe on Figure 21, the potholes and lakes have an increasing tendency to be situated in ground water discharge areas. The reason for the breakdown in the linear relation is believed to result from: (a) the holdover of water from year to year so that the initial isotopic composition and TDS are greater than that of average ground water, but more importantly, (b) repeated dilution with fresh water and evaporation of water from potholes with permanent salt crusts results in smaller oxygen-18 enrichment for a given total dissolved solids concentration.

The inset in Figure 21 illustrates how the latter mechanism (b) operates. Consider the water in the pothole to be at composition A. Evaporation results in a shift parallel to the theoretical curve to point B. At this time, an influx of water to the pothole dilutes the brine. However, because additional salts are carried into the slough by the added water and/or because some of the salt crust dissolves, the water does not move back to point A, but to point C. Repeated processes of this type may produce the observed trend toward higher TDS with less oxygen-18 enrichment.

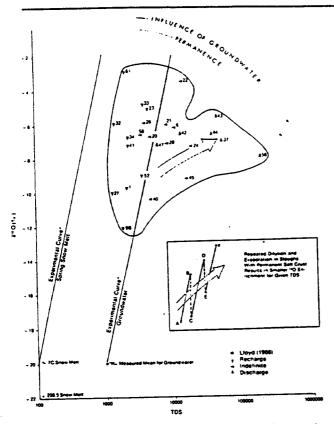


Figure 21. Enrichment of oxygen-18 with increasing total dissolved solids, surface water, ground water, snowmelt, Horseshoe Lake Basin

#### Determination of Sources of Ground Water Sulfate and Mechanism for Transport

Whereas the Horseshoe Lake sodium sulfate/carbonate deposit was shown to be derived from the evaporation concentration of ground water (Wallick 1981), any explanation of the origin of the deposit must identify the source of the sulfate ion in the ground water.

Wallick and Krouse (1977, 1980) determined the sulfur isotope composition for sedimentary sulfate, organic sulfur in coal, in addition to that of the ground water sulfate in an attempt to answer these questions. Samples of the glacial drift, bedrock and lacustrine deposits were collected by means of hollow stem auger. The samples were dried, pulverized to <0.5mm, and a saturated extract prepared for each sample according to methods given in USDA Handbook #60 (pg. 84). Sulfate was precipitated as  $BaSO_4$  and del <sup>34</sup>S values determined.

The ground water flow pattern and the sulfur isotope distribution in the form of vertical profiles of del <sup>34</sup>S and lithology are given in Figure 23, along with a summary of the mean values of del <sup>34</sup>S in sedimentary sulfate in the ground water flow region.

The data for the test hole OBS-2 represent the vertical distribution of del  $^{34}$ S in the glacial drift of the recharge area. (Values of del  $^{34}$ S ranged from -40.1 to +1.4 with a mean of -13.9 +/- 10.7 per mil.) Very negative del values were associated with zones of higher

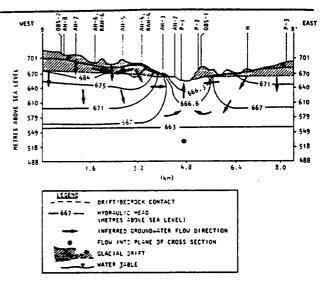


Figure 22. Ground water flow pattern, hydrogeological cross section B-B'. Horseshoe Lake Basin

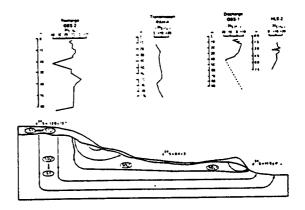


Figure 23. Summary of distribution of del <sup>34</sup>S in sedimentary sulfate from cores in the Horseshoe Lake Basin

hydraulic conductivity, e.g., the silty clay from 22.3 to 24.4m and the sandy clay at 64m, overlying a basal erosional contact.

Data for the lateral flow area (transmission zone) came from test hole RAH-4. All samples of the bedrock came from the upper Cretaceous Belly River Formation with the exception of the drift sample at 12.2m. Values of del <sup>34</sup>S ranged from +2.6 to +12.0, with a mean of +8.4 +/- 3. Little variation of the isotopic composition was observed with depth at this location.

In the discharge area, values of del <sup>34</sup>S above the basal sand and gravel deposit at 47.2m ranged from -16.9 to +6.8 with a mean of -2.7 +/- 6.4. This is significantly "heavier" isotopically than that obtained for OBS-2 in glacial drift in the recharge area. Again, however, the most negative values of del <sup>34</sup>S were closely associated with the zone of highest hydraulic conductivity between 47.2 and 56.4m. Two values of del <sup>34</sup>S for sulfate from the bedrock in OBS-1 fell within the range obtained for RAH-4 in the lateral flow region. The depth profile of del <sup>34</sup>S in the lake segments (HSL-2) shows that values averaging +15 per

# Table 6Values of Del 34S for Sulfate fromGround Water in Basal and Methy Aquifers,Alsands Project AreaSULFUR ISOTOPE RATIO IN GROUNDWATER SO4

	WELL NUMBER	534S (%o) *	(SO.=) (mg/t)
AQUIFER	1481 1717 (diluted) 1240	+ 19.6 + 19.6 + 23.2 (before installation) + 22.0 (Mar. 14	3,640.0 3,1770.0 3,734.0
	5039 1489 (diluted)	sampling) + 22.2/ + 20.3 + 23.8 (Mar. 5) + 21.0 (Mar. 15) + 19.7	4,737.0 2,726.0 1,160
	5027 (diluted) 5021	+ 13.1 + 22.0 δ = 21.3 ± 1.5%•	3,889.0

Sulfur isotope analysis are reported in standard & notation:

#### $\delta^{\omega}S = [\frac{R \text{ sample}}{R \text{ standard}} \cdot 1] \times 1,000, \text{ where } R = (\frac{\omega S}{\omega S})$

The above analyses are reported relative to the Cañon Diablo meteorite FeSstandard.

	WELL NUMBER	5×S (%+) *	$[SO_{1}^{=}](mg/l)$
AQUIFER Basel	810002 EP 810043 EP 810043 EP 810043 EP 810043 EP 810043 EP	+ 13.6 + 22.1 + 21.4, + 21.2, + 21.3 + 22.1 + 16.2, + 16.0 $\delta = 19.0 \pm 3.4\%^{\circ}$	5.0 7.0 14.0 7.0 7.0

Sulfur isotope analysis are reported in standard & notation:

 $\delta^{\mu}S = \{\frac{R \text{ sample}}{R \text{ standard}} - 1\} \times 1,000$ , where  $R = (\frac{\mu S}{33S})$ \* The above analyses are reported relative to the Califon Diablo meteorite FeS standard.

mil occur in the upper 3m of the salt deposit, decreasing to +5 per mil at 7.6m. The mean value of del  $^{34}$ S of +11.9 +/- 4 was the most positive value obtained.

Inasmuch as the Belly River Formation contained organic clay shales and coal, and the drift was estimated to be composed of as much as 85 percent reworked Belly River sandstones, siltstones and clayshales, it was important to obtain data for the distribution of del <sup>34</sup>S in organic matter. Wallick and Krouse (1980) presented data for del <sup>34</sup>S in coal samples from Alberta. These ranged from +6.3 per mil to 13.1 per mil with a mean value of +11 per mil.

Ground water samples, having an average of 213 mg/L sulfate, were collected from completed wells and piezometers in the area. Del <sup>34</sup>S values ranged from -10.2 to +9.2 per mil. Del <sup>34</sup>S values became more negative with respect to depth at a given piezometer nest.

Using the data and observations cited previously, it was possible to address the questions posed initially as to the source and mechanism for transport of sulfate in the ground water flow system.

First, it is clear that the sulfur is not of evaporite mineral origin nor is it derived from connate water (as in the Alsands study previously cited). Values of del <sup>34</sup>S were significantly lighter than the +20 per mil average for del <sup>34</sup>S of sea water sulfate. The sulfur is, more likely, derived from lighter sources such as organic sulfur and perhaps, pyrite.

With regard to the mechanism of release and transport of the sulfur, a hypothesis was advanced that

moderately positive values of del <sup>34</sup>S (+5 to +12 per mil) represent the unaltered sulfur isotope ratio of the bedrock. Glaciation, oxidation of organic sulfur and pyrite incorporated in the till, leaching and ground water flow, and bacterial sulfate reduction were responsible for the isotopically "light," highly variable del <sup>34</sup>S values in the drift profiles.

Bacterial sulfate reduction occurs under anoxic conditions when sulfate ion and a nutrient organic substrate are present. It is well-known that kinetic isotope effects during bacterial sulfate reduction concentrate "light" sulfur in the sediment as pyrite or organic sulfides, and render the remaining sulfate in solution isotopically "heavier." However, Smith and Batts (1974) pointed out that whereas the preceding applies when the rate of sulfate flow exceeds the rate of sulfate reduction, negligible isotopic fractionation occurs when the reduction rate approaches the flow rate. Ground water flow redistributed the sulfur in the basin sediments according to the existing hydraulic conductivity and flow pattern. When sulfate reduction occurred in the vicinity of a permeable zone, sulfur-34 was preferentially removed from the sediments because the rate of sulfate flow exceeded the rate of sulfate reduction. In addition, in a recharge area where the water table undergoes large vertical fluctuations, some strata will alternate between aerobic and anaerobic conditions. Conditions therefore exist whereby repeated oxidation and reduction of sulfur compounds can occur. Inasmuch as the reduced species tend to be retained in a stratum while sulfate ions are more mobile, the cumulative isotopic selectivities will produce sedimentary sulfide and sulfate that are very depleted in sulfur-34 and ground water sulfate that is enriched in sulfur-34. The redistribution of sulfur in the ground water flow system will ultimately yield a situation where sedimentary sulfur in the recharge area is isotopically lighter than the sedimentary sulfur in the discharge area. This is, in fact, the condition reflected in the generalized flow pattern and mean values of del <sup>34</sup>S shown in Figure 23. The ground water system has been operating like a huge conveyor belt: the sulfur was removed from the recharge area, and, through oxidation/reduction reactions and the kinetic isotope effect, the sulfide fraction was enriched in the light isotope of sulfur. The heavy isotope was transported downgradient and accumulated in the sodium sulfate/carbonate deposit in the discharge

area. A more recent paper on this topic reports on a study of origin of sulfate in glacial till in southern Alberta (Hendry, Cherry and Wallick 1985). Through analysis of the composition of the till and the performance of chemical weathering experiments in which fresh unoxidized till (derived 85 percent from bedrock) was exposed to air, it was found that sulfate anion was released into solution. These observations essentially confirmed that the source of the sulfate was indeed organic sulfur in the till that was derived from the bedrock sediments.

#### **Summary and Conclusions**

Isotopes of hydrogen, oxygen, carbon and sulfur are among the most useful of parameters in the study of ground water geochemical systems.

Hydrogen has two stable isotopes, protium having one proton in the nucleus, and deuterium, which has a proton and a neutron in the nucleus. The abundances of protium and deuterium are respectively 99.985 and .015 percent. Tritium is a short-lived radioisotope of hydrogen having an additional neutron in the nucleus. Tritium is a cosmic ray-induced nuclide and has a half-life of 12.3 years. Tritium is also produced in thermonuclear bomb explosions and the levels of tritium in atmospheric water vapor rose by several orders of magnitude between 1954 and 1963 when nuclear bombs were detonated in the atmosphere. The main mass-dependent processes by which hydrogen isotope abundances are altered are evaporation and condensation in the hydrological cycle of the earth. The world acts as a giant "still" for isotopic species of water with net evaporation occurring in the oceans and net precipitation occurring in continental and polar regions. Tritium is useful in determining the approximate age of ground water less than 30 years old. Tritium levels are affected mainly by loss due to radioactive decay, through exchange with atmospheric water vapor and through dilution in the oceans.

Oxygen has three stable isotopes having masses 16 (most abundant), 17 (.01 percent) and 18 (.08 percent). The main mass-dependent processes that affect the abundance of oxygen isotopes are evaporation, condensation and exchange reactions. Both hydrogen and oxygen isotopes are affected by the Rayleigh distillation process in the hydrological cycle so that the following observations result:

• Precipitation is enriched in the lighter isotopes of hydrogen and oxygen with increasing latitude.

• At a given locality, summer rains are more enriched in heavy isotopes than in winter snow.

• Travelling inland from the coast, there is a tendency for precipitation to be enriched in the lighter isotopes.

• At a given locality, increasing altitude results in water vapor that is more and more depleted in the heavy isotopes.

Carbon has three isotopes of environmental importance having mass 12, 13 and 14. The average abundances of the stable isotopes, mass 12 and 13, are 98.9 and 1.1 percent, respectively. Carbon-14 is radioactive with a half-life of 5,730 years. Because carbon is the building block of life, it is not surprising that biological processes play the dominant role in the fractionation of carbon isotopes. These biological processes include photosynthesis and respiration, whereby carbon is either incorporated into organic matter from free  $CO_2$  or where organic matter is oxidized. Carbon-14 is a cosmogenic radionuclide and is a natural tracer in the carbon cycle of the earth to the extent of its 8,270year mean-life. Carbon-14, like tritium, is useful in age determinations of ground water; however, it is subject to chemical interferences due to the fact that it is not actually part of the water molecule but is carried in the dissolved inorganic carbon.

Sulfur consists of four stable isotopes having masses 32 (95.02 percent), 33 (0.75 percent), 34 (4.21 percent) and 36 (.02 percent). Sulfur, like carbon, is important in the biological cycle. The wide range in valence states (-2 to +6), and the fact that sulfur compounds occur in all three phases and in organic, as well as inorganic forms, makes it particularly sensitive to fractionation. The largest fractionations take place during sulfate reduction to bisulfide by bacteria such as *Desulfovibrio desulfuricans*. Isotopic exchange and kinetic isotopes effects resulting from reactions involving competing rates of exchange are important mechanisms that give rise to the wide range of fractionation effects for sulfur isotopes in nature.

The western Canadian province of Alberta has long been a successful proving ground for environmental isotope applications. This is because of the extremely varied topography and climate, which give rise to large variations in the stable isotope composition of precipitation. In addition, the unconsolidated Cretaceous rocks of the province are rich in organic matter containing carbon and sulfur, and isotopes of these elements have proven valuable in studying the processes that occur during formation and mining of oil sands, coal and sour gas deposits.

A number of interesting examples of environmental isotope applications studies in Alberta over the past decade were offered to illustrate the principles discussed in the first part of the paper.

One problem that arose recently in Alberta concerned whether sour gas processing plants were affecting air, soil and water quality in an adverse way, and thereby were a hazard to the health of local residents. Application of conventional ground water geochemical and isotopic methods revealed the actual area affected by the fallout of sulfur dioxide and sulfur dust, and showed that sulfur was virtually immobile in the soil. Furthermore, the isotopic studies showed that the high concentrations of sulfate in local ponds were due to evaporation-concentration and not to large additions of sulfur from the gas plant activities. The environmental sensitivity of the area was highlighted by the presence of tritium in wells over the entire depth range sampled.

Another study was carried out during the environmental assessment of the Alsands Oil Sands open pit mining operation in the Athabasca Oil Sands of northern Alberta. Conventional hydrogeological methods and isotopic methods were used to find answers to questions regarding potential for upward movement of deep saline formation water to the surface, whether or not active recharge of ground water occurs through the bitumen-saturated oil sands deposit, and whether the sulfate in the ground water is of evaporite origin or derived from oxidation of sulfides.

An understanding of salinization processes in mine spoil was obtained by monitoring the gas composition in the unsaturated zone in natural and reclaimed sites at a plains surface coal mine. Samples were analyzed for mole percent of oxygen, nitrogen, carbon dioxide and sulfur dioxide. The carbon isotope composition of the carbon dioxide was determined. The isotopic data showed that two sources of CO2 were available. One source was from the oxidation of organic matter in shales and the coal itself, while the other source was from the oxidation of sulfide to produce sulfuric acid, which reacted with carbonates to produce CO2 in an unsaturated environment.

A method for determining the hydraulic character of surface ponds and lakes (i.e., whether the overall character of the water body is recharge, transmission, or discharge with respect to the ground water system) was devised using the relationship between the total dissolved solids and oxygen isotope composition. It was found that for recharge ponds, the water resembled evaporated snowmelt most closely. In the case of transmission ponds, the water was most like evaporated ground water. And, in the case of the discharge ponds, the oxygen isotope composition became less sensitive to increase of TDS due to evaporation because of the dissolution of permanent salt crusts.

The final example offered showed that sulfur isotopes may be used to determine the source of sulfate in ground water and that the release and redistribution of sulfur in a ground water flow system may be studied by determining the subsurface distribution of sulfur isotopes in sedimentary sulfate.

#### An Afterthought

Applications have not been restricted to the more ambitious studies described in this report. On one occasion, injection of water for secondary oil recovery was implicated as the reason for contamination of a domestic well. Since the injection water had been taken from a deep formation, its del D value was distinctly different from meteoric water at the same locality. Hence, it was relatively easy to rule out contamination from the water-injection operation. It is interesting to note that nitrate levels subsequently measured in the domestic well suggested that a feed lot operation may have been the culprit.

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## INTRODUCTION TO GROUND WATER GEOCHEMISTRY

## TOPICS

- Geochemical processes
- Organic chemistry
- Degradation of organic solutes
- Laboratory analysis and geochemical reaction modeling
- Geochemical aspects of contaminant migration
- Aquifer restoration

# TOPICS

## **GEOCHEMICAL PROCESSES**

**Solution Chemistry** 

**Chemical Equilibrium** 

**Oxidation-Reduction Reactions** 

**Carbonate System** 

**Chemical Evolution of Ground Water** 

**Adsorption of Solutes** 

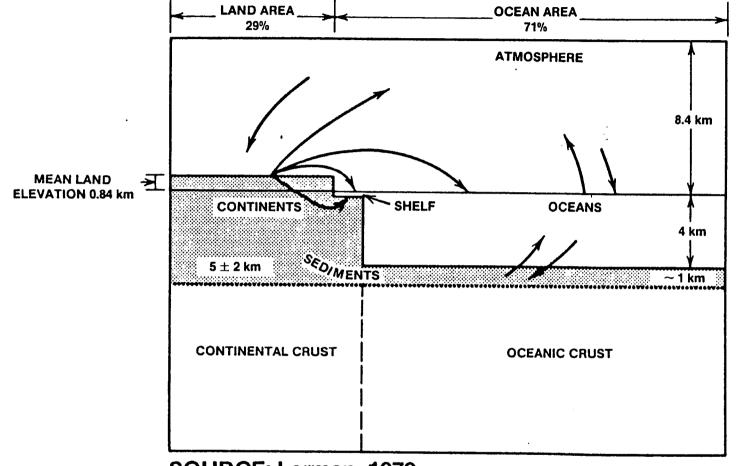
## INTRODUCTION TO GROUND WATER GEOCHEMISTRY

**OBJECTIVES** 

PROVIDE AN OVERVIEW OF GROUND WATER GEOCHEMISTRY BY CONSIDERING PRINCIPLES OF EQUILIBRIUM AND KINETICS.

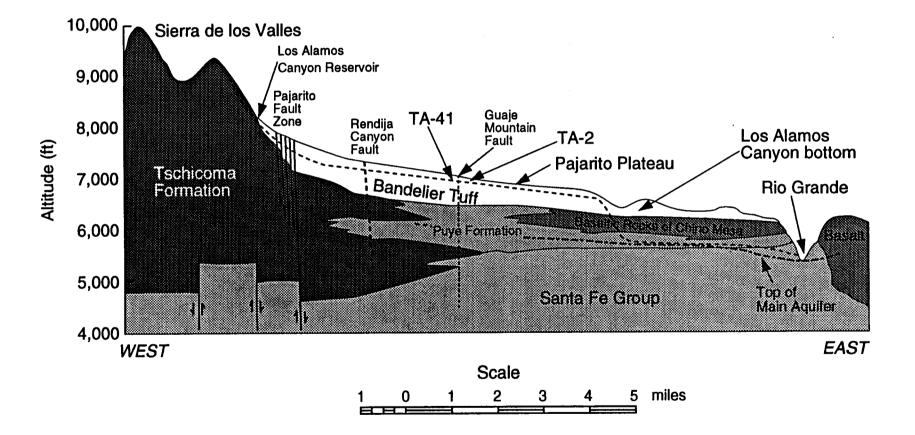
ILLUSTRATE EQUILIBRIUM CONCEPTS WITH PRACTICAL APPLICATIONS OF GEOCHEMICAL BEHAVIOR OF INORGANIC AND ORGANIC SPECIES IN WATER-ROCK SYSTEMS.

## **Geochemical Cycles**



## SOURCE: Lerman, 1979

The geochemical cycles of chemical elements or species are conceptual models of their geochemical behavior within different parts of the earth. In this short course, we are concerned with geochemical processes occurring in ground water near the earth's surface.



**Figure 4.1-1** Geologic section showing the location of TA-2 and TA-41 with respect to stratigraphy and structure from the Sierra de los Valles across the Pajarito Plateau to the Rio Grande.

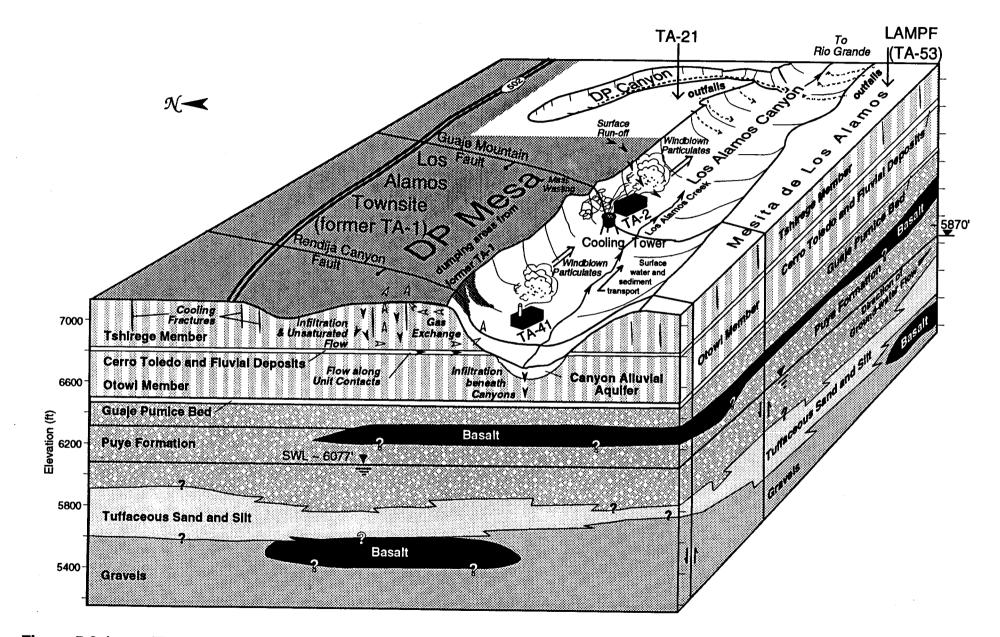
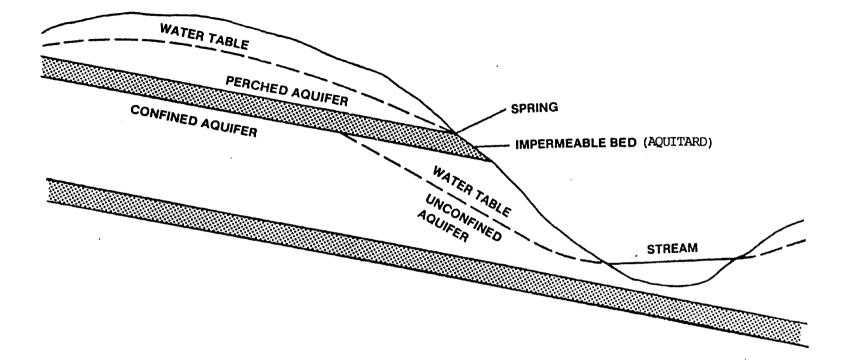


Figure 5.6-1 Three-dimensional conceptual model of TA-2 and TA-41.

2-908



## PERCHED AND CONFINED AQUIFERS

The hydrologic cycle is the endless circulation of water at or near the earth's surface. The hydrologic cycle is part of the geochemical cycle. Ground water can occur in unconfined and confined aquifers. Geochemical processes occur in both types of aquifers.

#### CLASSIFICATION OF DISSOLVED INORGANIC CONSTITUENTS IN GROUND WATER

Major constituents (greater than	5 mg/L)
Bicarbonate	Silicon
Calcium	Sodium
Chloride	Sulfate
Magnesium	Carbonic Acid
Minor constituents (0.01-10.0 m Boron Carbonate Fluoride Iron	g/L) Nitrate Potassium Strontium
Trace constituents (less than 0.1	mg/L)
Aluminum	Nickel
Arsenic	Phosphate
Barium	Platinum
Bromide	Radium
Chromium	Selenium
Copper	Thorium
Lead	Tin
Manganese	Uranium
Molybdenum	Zinc

Source: Davis and De Wiest 1966

Most dissolved solutes in ground water include calcium, magnesium, sodium, potassium, chloride, sulfate, silica, and bicarbonate  $(6.4 \le pH \le 10.3)$ . Contaminated ground waters contain other species (for example trace metals) greater than 0.1 mg/L.

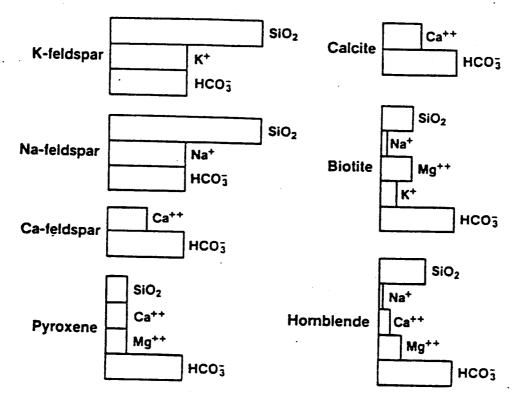
#### MEDIAN GROUND WATER ANALYTICAL DATA

pH	l = 7.3, Eh = 0.164V,	T = 12.6C, N = Log Total	715
Species	Total mg/L	Molality	Log Molality
Ca <sup>2+</sup>	48.1	-2.92	
CaSO₄°	(3.26)		-4.46
	(2.42)		-4.62
CI-	14.0	-3.40	
HCO3-	255	-2.38	
K <sup>+</sup>	2.80	-4.14	
KSO₄⁻	(0.01)		-7.03
SO42-	36.9	-3.41	
Mg <sup>2+</sup>	18.0	-3.13	
Mg HCO₃ <sup>+</sup>	(1.90)		-4.65
Mg SO₄°	(2.23)		-4.73
Na <sup>+</sup>	19.0	-3.08	
Na HCO₃°	(0.14)		-5.79
SiO <sub>2</sub> (H <sub>4</sub> SiO <sub>4</sub> )	16.0	-3.57	

SOURCE: Lindberg, 1983

Molality is defined as the amount of moles of solute/kilogram solvent. In most ground waters major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>, and Na<sup>+</sup>) occur as free or uncomplexed ions. Higher TDS waters such as seawater (TDS, 35 parts per thousand) contain complexed species in greater abundance or concentration.

### CALCULATED COMPOSITIONS OF WATERS FROM MINERAL ALTERATION



### MOLE RATIOS DISSOLVED SPECIES TO HCO<sub>3</sub> FROM GARRELS. 1967

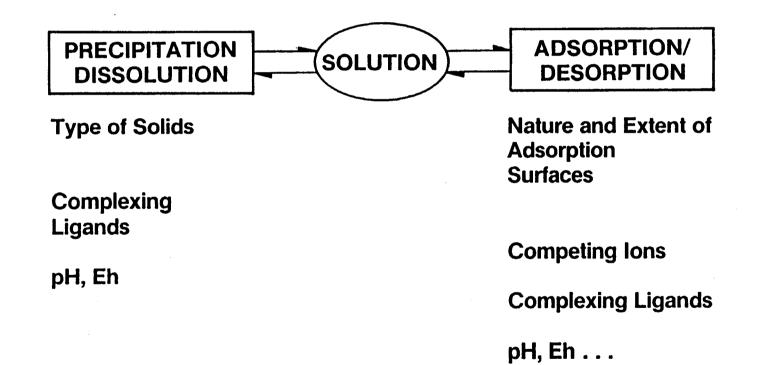
This figure shows mineral compositions and possible water compositions resulting from the alteration of silicate minerals to kaolinite  $(Al_2Si_2O_5 (OH)_4)$ .

Rocks contain different minerals that weather at different rates. For example, biotite (Mg-Fe silicate) is unstable at low temperatures and pressures and weathers at a faster rate than other minerals stable at low temperatures, such as quartz. Where does the bicarbonate come from?

Example Reaction:

2.33 NaAlSi<sub>3</sub>0<sub>8</sub> + 8.64H<sub>2</sub>0 + 2CO<sub>2</sub> (Albite) =  $^{Na}0.22^{Al}2.33^{Si}3.67^{0}10^{(OH)}2^{(OH)}2^{(Smectite)}$ + 2 Na<sup>+</sup> + 2HCO<sub>3</sub><sup>-</sup> + 3.32 H<sub>4</sub>SiO<sub>4</sub> Precipitation/dissolution and adsorption/desorption reactions control contaminant migration of inorganic and organic solutes in soil and groundwater. We will spend time describing these two important types of processes.

### **CHEMICAL ATTENUATION MECHANISMS**



#### **OVERSATURATION**

S.I. >0

#### EQUILIBRIUM

**S.I.** = 0

#### **UNDERSATURATION**

S.I. < 0

### **Saturation Index**

#### S.I. = Log<sub>10</sub> <u>ION ACTIVITY PRODUCT</u> SOLUBILITY PRODUCT

Thermodynamic stability of minerals and solid phases is estimated by the saturation index. This expression does not consider kinetics or rates of reactions.

# Table 2.7MEDIAN GROUND WATER ANALYTICAL DATA

Phase	Log IAP	Log Kt	Log IAP/Kt
Calcite	-8.67	-8.41	-0.25
Goethite	19.59	14.31	5.28
Pyrite	-169.76	-89.99	-79.77
Quartz	-3.57	-4.21	0.63
Kaolinite	13.58	6.85	6.72
Muscovite	23.48	14.88	8.60
Microcline	2.75	1.01	1.74
CO₂ (Gas)	-20.18	-18.18	-2.00

#### LOOK MIN IAP

The saturation index (SI =  $\log_{10} \frac{1AP}{K_{\pm}}$ ), is a thermodynamic expression which defines stability of a given solid phase. This table indicates that median ground water is oversaturated with repect to goethite, quartz, kaolinite, muscovite, and microcline. The solution is undersaturated with respect to calcite, pyrite, and CO<sub>2</sub> gas. The geochemical computer code, WATEQFC was used for the SI calculations.

NWWA

Primary attenuation mechanisms include precipitation reactions involving hydroxides, carbonates, and sulfides for many transition metals. Adsorption of transition metals onto these solids, including iron oxyhydroxides (goethite), is an important geochemical process.

### **PRIMARY ATTENUATION MECHANISMS**

#### **Species**

Cr(III), Fe, Al, Mn Pb, Cu, Zn, Cd, Ni

As, Cr(VI), Mo, Se

#### **Geochemical Behavior**

Precipitation (Hydroxides)

Precipitation (Hydroxides, Carbonates, Sulfides); Specific Adsorption

Precipitation (Iron?); Specific Adsorption Important factors affecting adsorption include types of adsorbents and hydrogeochemical solution properties. Iron-aluminum-manganese oxides and oxyhydroxides, clay minerals, carbonates, organic matter, and possibly amorphous aluminosilicates are the dominant adsorbents found in most soils and aquifer materials. Solution pH, Eh, competing ions, and complexing ions also influence adsorption processes.

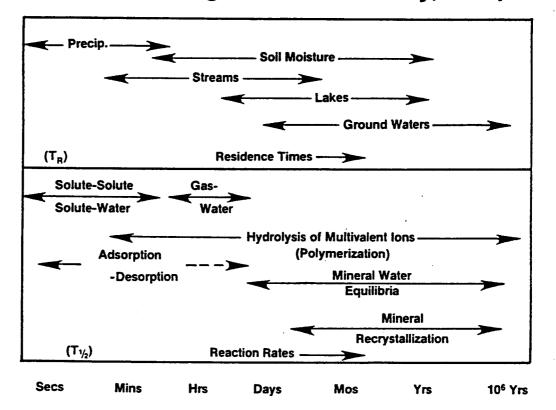
### **FACTORS AFFECTING ADSORPTION**

	Aquifer Material (Most Important Adsorbents)						nical Conditions olution Variables)		
·	Fe-Al-Mn Oxides	Clays	Amorph. Al-Silicates	Carbonates	Org C	pН	Eh	Competing Ions	Complexing lons
Oxy Anions									
(Cr, As, Se, Mo, S)	x	x	0	ο	0	x	x	0	o
Metallic Cations									
(Cd, Cu, Pb, Ni, Zn)	X	x	0	x	x	x		x	x
(Mn, Cr, V, Hg, Fe)	x	x	0	x	X	x	x	x	x
Alkali/Alkali Earth									
(Ca, Ba, Be)		x	0	x	x	x		x	x

x = Demonstrated importance

o = Anticipated importance but data absent

Schematic comparison between the halftimes of reactions ( $T_{1/2}$ ), and the residence times ( $T_R$ ) of some waters of the hydrosphere (SOURCE: Langmuir and Mahoney, 1985)



Equilibrium conditions exist when reaction rates are faster than residence times (amount of substance in reservior/flux of substance into the reservior). The residence time of water in the ocean is 3350 years (13,700 x  $10^{20}$ g/ (0.36 + 3.5) x  $10^{20}$ g/yr). Equilibrium conditions probably exist in groundwaters with long residence times ( $> 10^4$  yrs). Do equilibrium conditions exist in shallow alluvial aquifers?

# TOPICS

Organic Chemistry

- Introduction to organic chemistry
- Organic geochemistry of ground water

#### NWWA

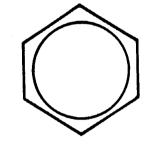
## **ORGANIC CHEMISTRY**

ORGANIC COMPOUNDS ARE CLASSIFIED ACCORDING TO THE FUNCTIONAL GROUP UNIQUE TO EACH CLASS.

THE FUNCTIONAL GROUP IS THE ATOM OR GROUP OF ATOMS THAT DEFINES THE STRUCTURE AND UNIQUE PROPERTIES OF A GIVEN CLASS OF ORGANIC COMPOUNDS.

# **EXAMPLES OF FUNCTIONAL GROUPS**

1. Aromatic Ring



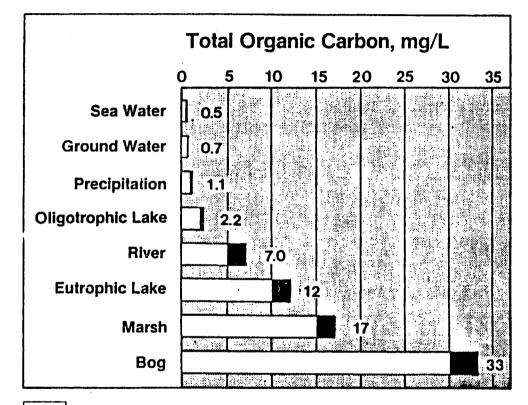
2. Alkyl Halides -F, -Cl, -Br, -I

## PHYSICAL AND CHEMICAL PROPERTIES OF ORGANIC COMPOUNDS

ORGANIC COMPOUNDS EXIST IN NATURE AS MOLECULES. BONDING IS PREDOMINANTLY COVALENT (ELECTRON SHARING).

ORGANIC COMPOUNDS ARE EITHER POLAR OR NON-POLAR. "LIKE DISSOLVES LIKE."

ORGANIC COMPOUNDS GENERALLY DO NOT DISSOCIATE TO IONS AS MANY INORGANIC COMPOUNDS DO. Humic substances are naturally occurring organic polymers found in surface and groundwater. Total organic carbon (TOC) includes dissolved organic carbon (DOC) and particulate organic carbon (POC), where DOC constitutes the majority of TOC. Solid humic substances control the fate of many anthropogenic organic contaminants.



Dissolved Organic Carbon

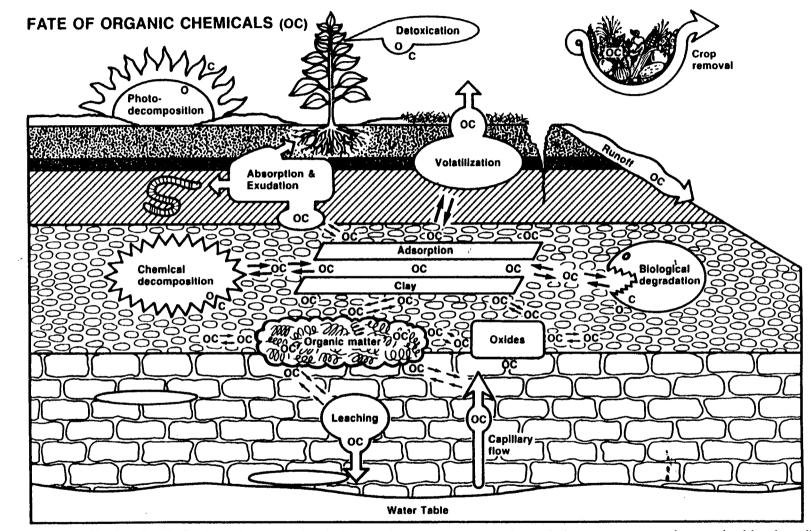
**Particulate Organic Carbon** 

SOURCE: Thurman, 1985

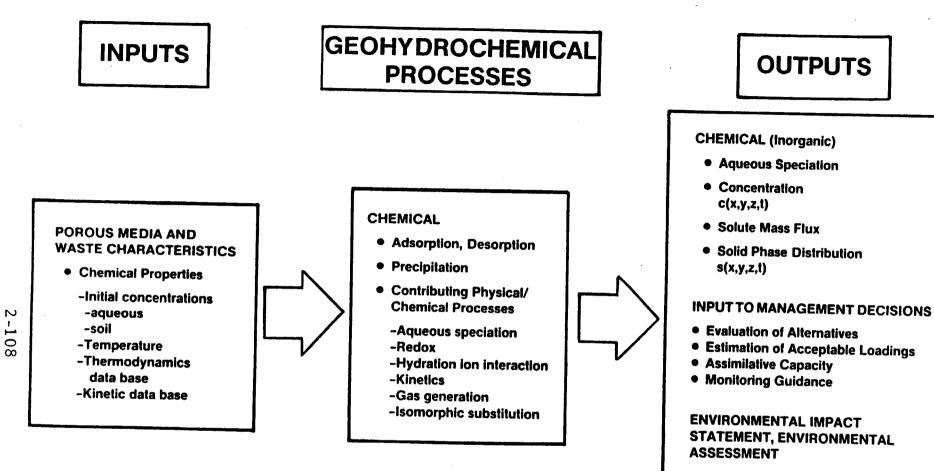
# ORGANIC SOLUTE - SOIL - WATER INTERACTIONS

THE MAJOR PROCESSES INFLUENCING THE MOBILITY OF ORGANIC COMPOUNDS IN THE SUBSURFACE INCLUDE:

- 1. SORPTION,
- 2. BIODEGRADATION, AND
- 3. CHEMICAL REACTION.

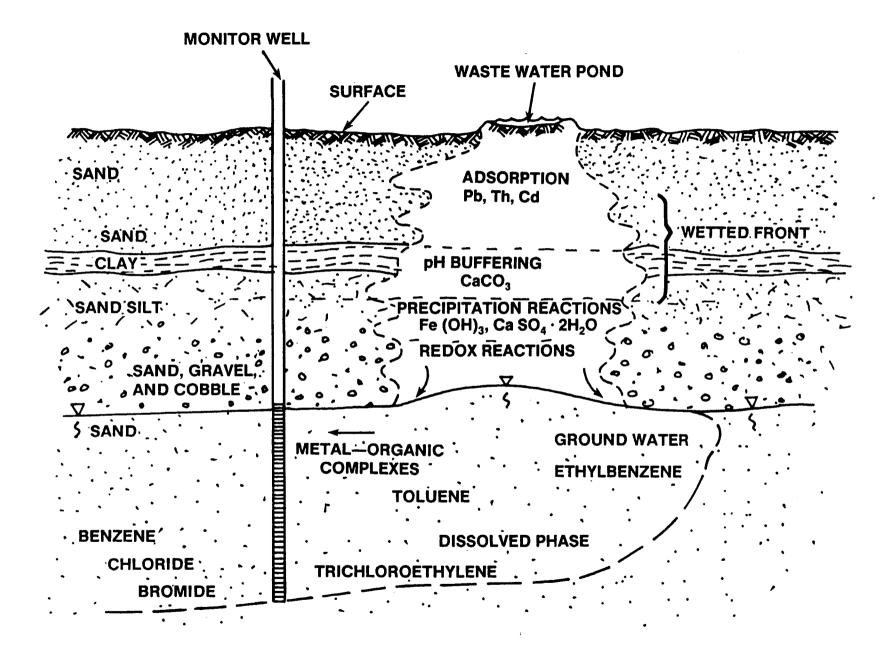


Processes affecting the dissipation of organic chemicals (OC) in the environment. Degradation processes are characterized by the splitting OC molecule. Transfer processes are characterized by the OC molecules remaining intact (Weber and Miller, 1989).



• Evaluate Potential for Ground Water Contamination

SOURCE: EPRI, 1984



2-109

REFERENCES TO INTRODUCTION TO HYDROGEOCHEMISTRY AND GROUND WATER SAMPLING

Davis, S.N. and De Wiest, R.J.M., 1966. <u>Hydrogeology</u>, Wiley, New York, 463 pages.

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Lindberg, R.D., 1983. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling, Ph.D. thesis, University of Colorado.

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#### Section 3

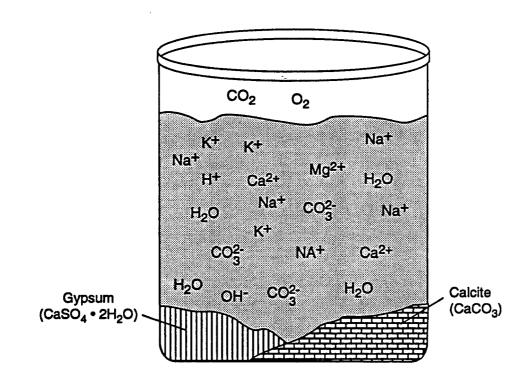
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# Solution Chemistry

Lecture by: William Deutsch Woodward-Clyde Consultants

# SECTION CONTENTS

# **Basic Geochemistry and Ion Speciation / Complexation**



### Topics

- Definitions and Units
- Chemical equilibrium
- Ion speciation / complexation

### **Definitions and Units**

Solvent: water

**Solute**: the dissolved inorganic or organic constituents

**Solution**: solvent + solutes

**Concentration Units:** 

- Mole Concept mass of Avogadro's number (6.022 x 10<sup>23</sup>) of items. A quantity of an element equal to its atomic weight contains one mole of atoms of that element
- Molarity number of moles of solute in one liter of **solution**
- Molality number of moles of solute in one kilogram of solvent

Molarity ≈ Molality for water with TDS < 10,000 mg/L and T < 100°C

### **Concentration Units**

- Milligrams per Liter (mg/l): mass of solute in milligrams dissolved in one liter of solution
   *molarity*
- Parts per Million (ppm): mass of solute in milligrams dissolved in one kilogram of solvent Molality
- Equivalents per Liter (eq/l): number of moles of solute multiplied times the valence of the solute in one liter of solution

### **Class Exercise**

1. Converting concentration units:

100 mg of  $CaCO_3$  dissolves completely in a 1 liter solution of water.

What is the molarity of  $Ca^{2+}$  and  $CO_{3}^{2-}$  in this solution?

(Molecular weight of  $CaCO_3 = 100$  g.)

2. What are the equivalents per liter of  $Ca^{2+}$  and  $CO_{3}^{2-}$  in this solution?

3. EXTRA CREDIT: How many moles of water are there in a liter of water? (molecular weight of  $H_2O = 18 g$ )  $\approx 55 \text{ proves}$ 

If a solution is 1% by weight Ca<sup>2+</sup>, how many ppm Ca<sup>2+</sup> does it contain?

Dissolved Phase only Filtered

# **Example of Calculation Procedure**

#### Conversion of Concentrations in mg/L to meq/L

Const.	Measured Conc. (mg/L)	Atomic Weight (g)	Molarity (mmol/L)	Valence	meq/L
Ca <sup>2+</sup>	92.	40.08	2.30	+2	4.60
Mg <sup>2+</sup>	34.	24.31	1.40	+2	2.80
Na⁺	8.2	23.0	0.36	+1	0.36
K⁺	1.4	39.1	0.04	+1	0.04
Fe (III)	0.09	55.8	0.002	+3	0.006
HCO <sub>3</sub>	339.	61.0	5.56	-1	5.56
SO <sub>4</sub> <sup>2-</sup>	84.	96.0	<b>0.88</b>	-2	1.7
Cl-	9.6	35.5	0.27	-1	0.27
NO3-	13.	62	0.21	-1	0.21

\* meq/L = milliequivalents/Liter

Labs have hard time getting this # correct. degassing chuses precipitateon of culcate need to analyze in field.

### **Cations/ Anion Balance Calculation**

í.

Cation / Anion Balance =	Anions - Cations Anions + Cations × 100%
Total Cations =	7.81 meq/l
Total Anions =	7.74 meq/l
Cation / Anion Balance =	$\frac{7.74 - 7.81}{7.74 + 7.81} \times 100\%$
	=-0.5% E is close enough to zero there is a good electrical balance
25,70 is	odequate balance
If the # other cation avaluate for	t is large like 20, then there are one on arions that you did Not on it. (e.g. Ammonium, aluminum magnesoum ith <sup>t</sup> , Al <sup>3+</sup> Mu <sup>44</sup> whether you Know the major catronst

### Use of Analytical Chemical Data in Geochemistry

- Accurate data can be used in equilibrium calculations to define the chemical system
- Water composition data and the equilibrium assumption can be used to predict the response of the system to environmental change.

### Chemical Equilibrium and the Equilibrium Constant

Chemical Reactions

A + B = Y + Z

The driving force of the reaction is a function of the amount of material available for interaction

Driving force of forward reaction

 $= k_1 m_A m_B$ 

where,  $k_1 = constant$ 

m<sub>A</sub> = amount of A available (molality units)

 $m_B = amount of B available$ 

### **Chemical Equilibrium and the Equilibrium Constant (continued)**

Chemical Reactions (continued)

Driving Force of Reverse Reaction

 $= k_{\gamma}m_{\gamma}m_{z}$ 

At equilibrium the amount of products being produced equals the amount of reactants produced and the driving forces are equal, therefore

 $k_1 m_A m_B = k_2 m_V m_Z$ 

Rearranging yields:

ſ

$$\lim_{\substack{p \in \mathcal{A}^{udd} \\ p = w^{2} \\ p^{2} \\ p$$

# **Equilibrium Conditions**

A + B = Y + Z

- At equilibrium the reaction continues
- Equilibrium can be approached from either direction
- The equilibrium constant applies only for the reaction as written

General equilibrium relationship:

$$aA + bB = yY + zZ$$
$$K = \frac{(Y)^{y} (Z)^{z}}{(A)^{a} (B)^{b}}$$

(lower case letters are stoichiometric coefficients)

### **Using the Equilibrium Constant**

Equilibrium constants for reactions are written in terms of activities (a), not concentrations (m)

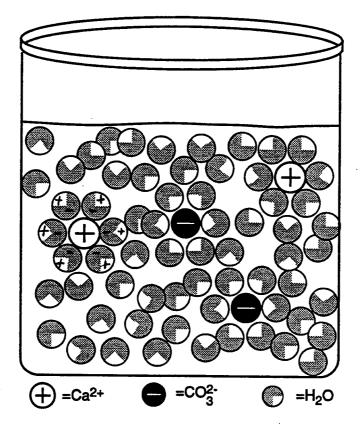
$$aA + bB = yY + zZ$$
$$K = \frac{a_Y^{y} a_Z^{z}}{a_A^{a} a_B^{b}}$$

- Concentration and activity
- Activity coefficients
- Solution ionic strength

# **Concentration and Activity**

Lab. Measured value

- Concentration is the total dissolved amount of a component in water. It is the laboratory measured value.
- Activity is the <u>effective concentration</u> of a component. It takes into account the effects of ion shielding.



# **Activity Coefficients**

$$a_x = \gamma_x m_x$$

Where,

a <sub>x</sub> =	activity of component X
$\gamma_x =$	activity coefficient of component X
m <sub>x</sub> =	concentration of component X l Lab measured value

### Solution Ionic Strength (I)

• Ionic strength is a measure of the importance of ion shielding in a solution and is used to derive activity coefficients.

 $I = 1/2 \sum_{i} (m_{i}Z_{i}^{2})$ 

 $m_i$  = concentration (molal) of species i

 $Z_i$  = valence of species i

#### **Calculating Activity Coefficients**

The charge of the ion of interest and the ionic strength of the solution are used to calculate activity coefficients.

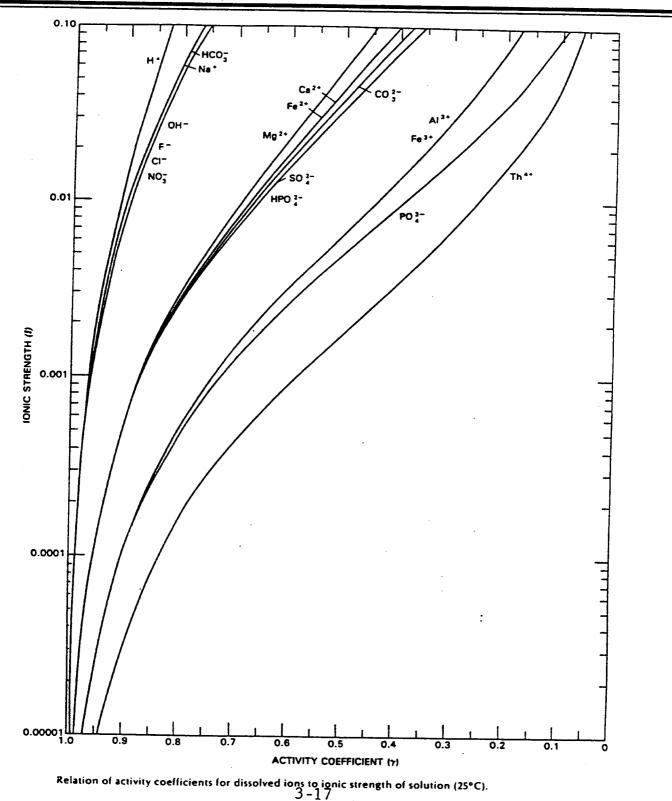
**Davies Equation** 

$$-\log \gamma = Az_{\phi}^{2} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

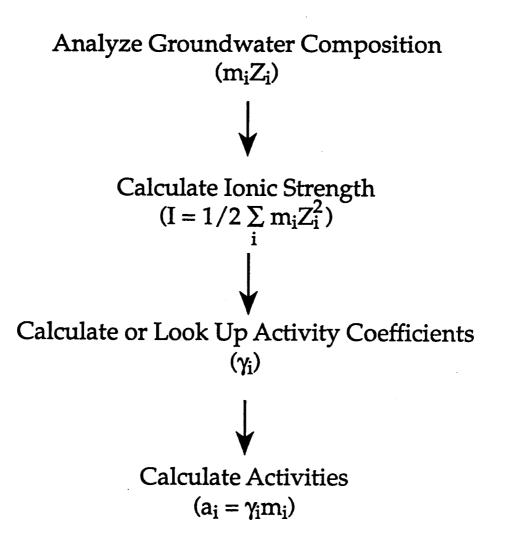
where, I = ionic strength Z = valenceA = 0.51 at 25C > Study + Interpretations of Water Quality - USGS

## Relation of Activity Coefficients for Dissolved lons to lonic Strength of Solution (25°C)

(Source: Hem. 1985, Figure 1)



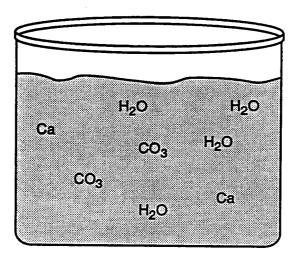
## **Determining Activities**



## Using the Equilibrium Constant

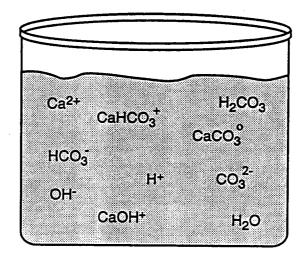
#### Ion Speciation/Complexation

Dissolve 0.001 moles of CaCO<sub>3</sub> in 1 kg of water  $= 10^{-3}$  molal CaCO<sub>3</sub> solution.



Total Ca = 
$$10^{-3}$$
 molal =  $T_{Ca}^{2+}$   
Total CO<sub>3</sub> =  $10^{-3}$  molal =  $T_{CO_3^{2-}}$   
Total H<sub>2</sub>O = 55.56 molal =  $T_{H2O}$ 

## In Speciation / Complexation



In solution, various species and complexes of calcium, carbonate and water are present.

#### Equilibrium Calculations Mass Balance

$$T_{Ca}^{2+} = m_{Ca}^{2+} + m_{CaOH}^{+} + m_{CaHCO_3}^{+} + m_{CaHCO_3}^{+} + m_{CaCO_3}^{-} = 0.001 \text{ molal}$$

$$T_{CO_3}^{2-} = m_{CaHCO_3}^{+} + m_{CaCO_3}^{0} + m_{H_2CO_3}^{+} + m_{H_2CO_3}^{0} + m_{H_2CO_3}^{$$

 $T_{H}^{+} = -m_{CaOH}^{+} + m_{CaHCO_{3}}^{+} + 2m_{H_{2}CO_{3}}^{+} + m_{HCO_{3}}^{+} + m_{H}^{+} - m_{OH}^{-} = 0.0$ 

The concentration terms appearing in these equations can be replaced with corresponding species activities using appropriate activity coefficients ( $\gamma$ ) and equilibrium constants (K)

3-21

#### Equilibrium Calculations (continued) Mass Balance

$$a_{Ca}^{2+} = (\gamma_{Ca}^{2+}) (m_{Ca}^{2+}); m_{CA}^{2+} = \frac{a_{Ca}^{2+}}{\gamma_{Ca}^{2+}}$$
  
Mass Action Equation:

Mass Action Equation:

× 7

 $Ca^{2+} + H_2O = CaOH^+ + H^+; K_{CaOH}^+ +$ 

$$\frac{(a_{CaOH}^{}+)(a_{H}^{}+)}{(a_{Ca}^{}2+)(a_{H_{2}^{}O}^{})} = K_{CaOH}^{}+$$

$$a_{CaOH}^{}+ = \frac{(K_{CaOH}^{}+)(a_{Ca}^{}2+)(a_{H2O}^{})}{a_{H}^{}+} = \gamma_{CaOH}^{}+*m_{CaOH}^{}+;$$

$$m_{CaOH}^{+} + = \frac{(K_{CaOH}^{+}) (a_{Ca}^{2}) (a_{H2O}^{-})}{(\gamma_{CaOH}^{+}) (a_{H}^{+})}$$

etc.

1

Substituting these conversions into the mass balance equation for Ca gives:

$$T_{Ca}^{2} = \frac{a_{Ca}^{2+}}{\gamma_{Ca}^{2+}} + \frac{(K_{CaOH}^{2+})(a_{Ca}^{2+})(a_{H2O})}{(\gamma_{CaOH}^{2+})(a_{H}^{++})} + \frac{(K_{CaHCO_{3}^{2+}})(a_{Ca}^{2+})(a_{H}^{2+})(a_{CO_{3}^{2-}})}{\gamma CaHCO^{+}} + \frac{(K_{CaCO_{3}^{0}})(a_{Ca}^{2+})(a_{CO_{3}^{2-}})}{\gamma_{CaCO_{3}^{0}}}$$

= 0.001 molal

(similar relationships exist for  $T_{CO_3^2}^{2-}$  and  $T_{H+}$ )

3-23

#### Calculating Concentrations of Solution Species and Complexes

•  $T_{Ca}^{2+}$ ,  $T_{CO3}^{2-}$  and  $T_{H+}$  equations are solved for

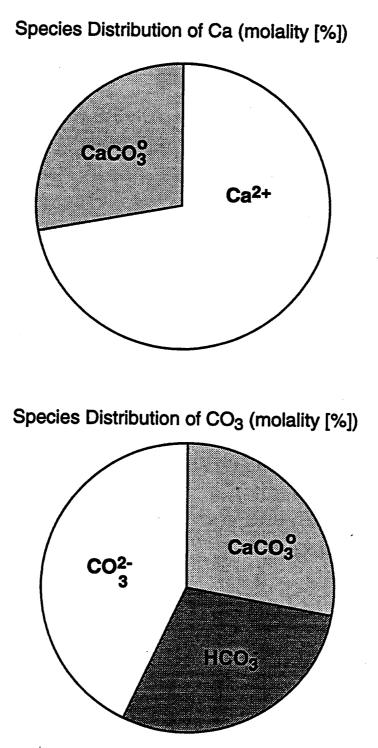
 $a_{Ca}^{2+}$ ,  $a_{CO_3}^{2-}$  and  $a_{H+}$ 

• Concentrations of species and complexes are calculated using equilibrium constants and activities of components, e.g.,

$$m_{CaOH}^{+} = \frac{(K_{CaOH}^{+}) (a_{Ca}^{2+}) (a_{H20}^{-})}{(\gamma_{CaOH}^{+}) (a_{H}^{+})}$$

# 0.001 M CaCO<sub>3</sub> Exercise Calculation Results

1



#### Summary

- In dilute solutions (TDS < 10,000 mg/L) molarity is equivalent to molality and ppm is equivalent to mg/L
- Equilibrium constants from thermodynamic data are based on the activity of the solutes not on the measured analytical concentration
- The activity of a solute may be considered its "effective concentration"
- The activity coefficient converts measured concentrations to activities
- Ion speciation and complexation are important solution processes

Section 4

C

# Chemical Equilibrium

Lecture by: William Deutsch Woodward-Clyde Consultants

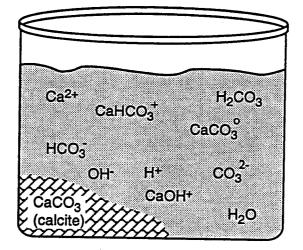
# SECTION CONTENTS

## **Topics**

- Water/solid equilibrium calculations
- Mineral solubility
- Aquifer mineral equilibria

+

# Water/Solid Equilibrium Calculations

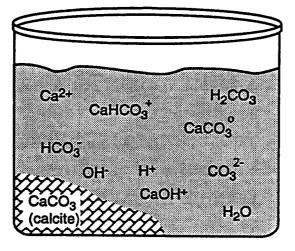


CaCO<sub>3</sub> (calcite) = Ca<sup>2+</sup> + CO<sup>2-</sup><sub>3</sub>

 $K = \underline{a_{Ca}^{2+} a_{CO_3}}_{a_{CaCO_3}} (s)$ 

 $K = a_{Ca}^{2+} a_{CO_3^{2-}}$ 

## **Calcite Equilibrium in Water**



$$CaCO_3$$
 (s) =  $Ca^{2+} + CO_3^{2-}$ ; K = 10<sup>-8.4</sup> (25° C)

At equilibrium of calcite with the solution

$$(a_{Ca}^{2+})(a_{CO_3^{2-}}) = K_{Calcite} = 10^{-8.4}$$
 (Constant

where,

 $a_{Ca}^{2+}$  = calculated activity of Ca<sup>2+</sup> in solution  $a_{CO}^{2-}_{3}$  = calculated activity of CO<sub>3</sub><sup>2-</sup> in solution

4-3

#### **Ion Activity Product**

 $a_{Ca}^{2+} a_{CO}^{2-} =$  Ion Activity Product for Calcite in the Solution

Comparing Ion Activity Product (IAP) for calcite in the solution with the equilibrium constant for calcite  $(K_{calcite})$  allows us to determine whether the solution is in equilibrium with calcite

## **Mineral Equilibrium Calculation**

If (IAP)  $_{mineral/solution} = K_{mineral}$ 

then the mineral is in equilibrium with the solution.

At equilibrium,

$$\frac{\text{(IAP)}_{\text{mineral/solution}}}{K_{\text{mineral}}} = 1$$

**Definition** 

Saturation Index (S.I.) = 
$$\log_{10} \left( \frac{IAP}{K} \right)$$

At equilibrium,

S.I. = 
$$\log_{10} 1 = 0$$

#### **Calculation Example**

Constituent	Measured/Calculated Activity
$a_{Ca}^{2+}$	10 <sup>-52</sup>
$a_{CO_{3}}^{2-}$	10 <sup>-32</sup>

Is the solution in equilibrium with calcite?

Calculate Saturation Index (SI)

 $SI = \log\left(\frac{IAP}{K}\right)$ 

To use this equation we need to know what reaction defines the equilibrium constant

$$CaCO_{3}$$
 (calcite) =  $Ca^{2+} + CO_{3}^{2-}$ ; K = 10<sup>-8.4</sup>  
K =  $a_{Ca}^{2+}$   $a_{CO_{3}}^{2-}$ , therefore  
IAP =  $a_{Ca}^{2+}$   $a_{CO_{3}}^{2-}$ 

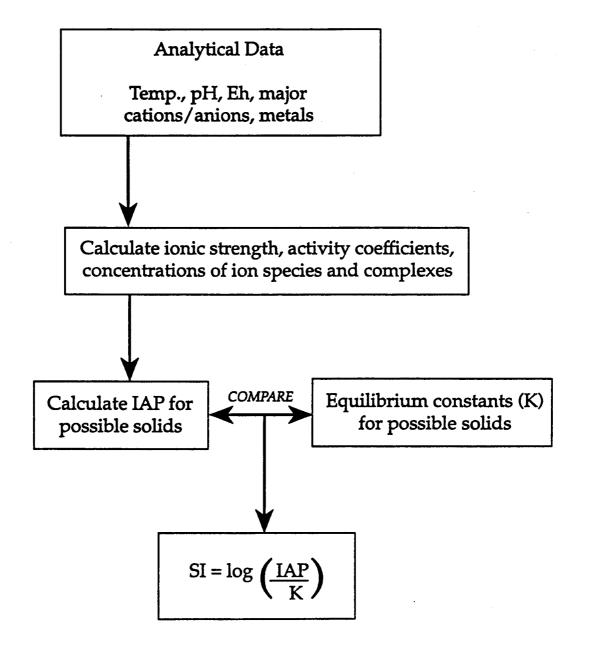
#### **Calculation Example (continued)**

S.I. = 
$$\log\left(\frac{IAP}{K}\right) = \log\left(\frac{a_{Ca}^{2+} a_{CO}^{2-}}{K_{calcite}}\right)$$
  
=  $\log\frac{(10^{-5.2})(10^{-3.2})}{10^{-8.4}} = \log\frac{10^{-8.4}}{10^{-8.4}}$   
=  $\log 1 = 0$ 

S.I. = 0; mineral is in equilibrium with solution
S.I. < 0; mineral undersaturated - mineral is not reactive</li>
S.I. > 0; mineral oversaturated - mineral is not reactive

4 - 7

## **Saturation Index Calculation Method**



#### <u>Class Exercise</u>

#### Saturation Index of Ferric Hydroxide [Fe(OH),]

affect groppobility of metals

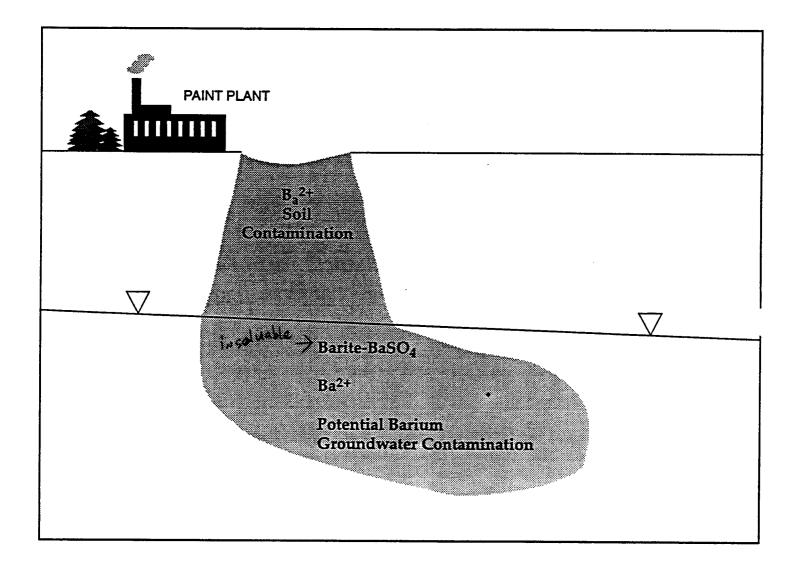
1. Consider the reation:

 $Fe(OH)_{3}(s) + 3H^{+} = Fe^{3+} + 3H_{2}O; K = 10^{6}$ 

If a solution has a pH = 8 and the activity of  $Fe^{3+} = 10^{-17}$  molal, what is the saturation index of ferric hydroxide in this solution?

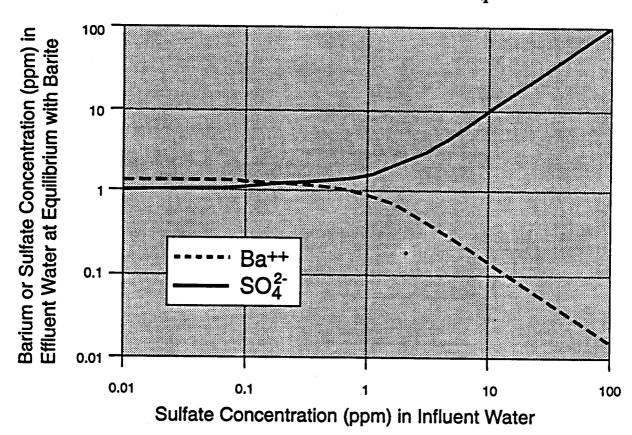
- 2. Would you expect ferric hydroxide to dissolve or precipitate from this solution in order to reach equilibrium?
- 3. EXTRA CREDIT: If the activity coefficient of  $Fe^{3+}$  in this solution is 0.5, what is the concentration in mg/L of  $Fe^{3+}$  (atomic weight of iron is 56 grams/mole)?

# Case Study: Mineral Equilibrium and Barium Mobility



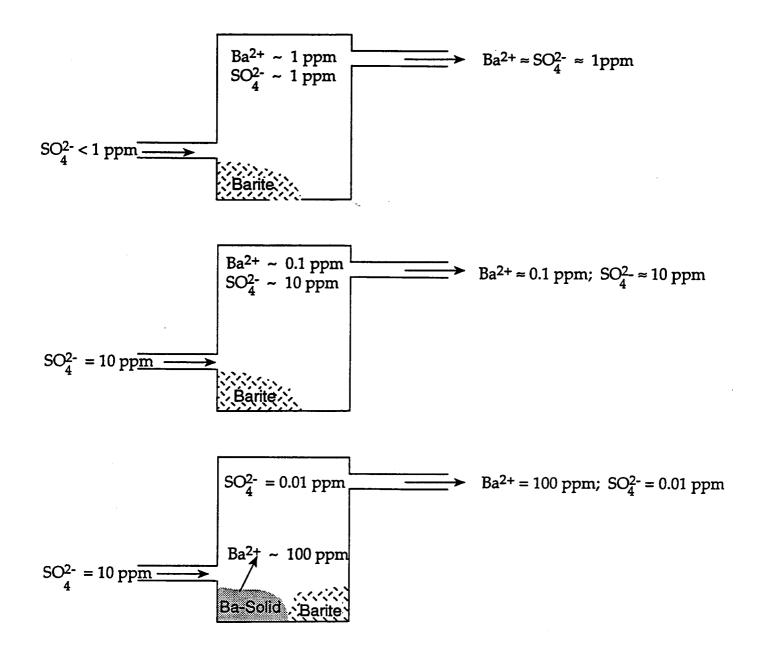
How does mineral equilibrium affect barium mobility?

## Barite (BaSO4) Equilibrium Constraint on Barium Mobility

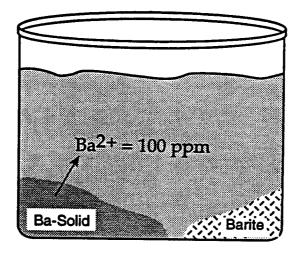


 $BaSO_4(s) = Ba^{2+} + SO_4^{2-}$ 

## **Barium Mobility**



# **Barite Solubility Limit on Sulfate Concentration**



$$BaSO_4 = Ba^{2+} + SO_4^{2-} K = 10^{-9.98}$$

At equilibrium

$$a_{Ba}^{2+} a_{SO_4^{2-}} = 10^{-9.98}$$

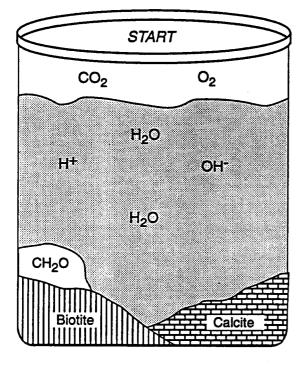
If  $a_{Ba}^{2+} \approx m_{Ba}^{2+} = 100 \text{ ppm} = 10^{-3.14} \text{ molal}$ 

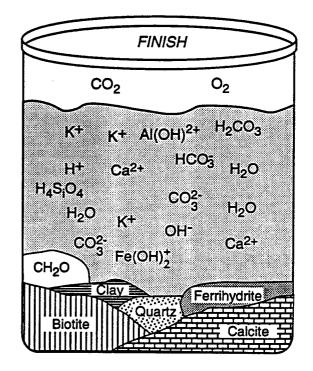
then  $a_{SO_4^{2-}} = \frac{K_{Barite}}{a_{Ba}^{2+}} = \frac{10^{-9.98}}{10^{-3.14}} = 10^{-6.84}$ 

$$a_{SO_4^{2-}} = 10^{-6.84} \approx m_{SO^{2-}} = 0.01 \text{ ppm}$$

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## Aquifer Mineral Equilibria





### **Mineral Equilibria**

- Complete equilibrium between groundwater and aquifer minerals is the exception, not the rule
- Total equilibrium is not achieved because the reaction rates for some minerals are slow compared to the groundwater residence time
- Partial equilibrium between groundwater and some of the aquifer minerals is common

weathering products, clays

 Aquifer minerals present in minor, and trace quantities often play a major role in determining groundwater chemistry

#### **Reactive Minerals**

#### **CARBONATES**

Calcite (CaCO<sub>3</sub>) Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub> Siderite (FeCO<sub>3</sub>) Rhodocrosite (MnCO<sub>3</sub>) Magnesian Calcite (Ca<sub>1-x</sub>Mg<sub>x</sub>CO<sub>3</sub>)

#### OXIDES/HYDROXIDES

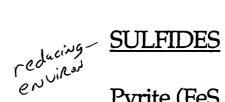
Fe(OH)<sub>3</sub> Goethite (FeOOH) Al(OH)<sub>3</sub> MnO<sub>2</sub>

#### **SULFATES**

Gypsum (Ca<sub>SO4</sub>  $\bullet$  2H<sub>2</sub>O) KFe (SO<sub>4</sub>)<sub>2</sub> Al (OH)SO<sub>4</sub>

#### SILICA (SiO<sub>2</sub>)

Cristobalite Chalcedony Amorphous SiO,



Pyrite (FeS<sub>2</sub>) FeS As, Se, Mo

#### **SILICATES**

Clays Zeolites

## **Typical Solution Compositions (mg/L)**

(from Snoeyink & Jenkins, 1980, Water Chemistry)

1970 **-** 1987 - 1987

Component	Rain	River Water	Groundwater
SO (HSO)		10(10)	
$SiO_2$ (H <sub>4</sub> SiO <sub>4</sub> )	0.3 (0.48)	1.2 (1.9)	10 (16)
Fe (III)	-	0.02	0.09
Ca <sup>2+</sup>	0.8	36) due to Calcite	92 due to culcite
Mg <sup>2+</sup>	1.2	8.1	34
Na <sup>+</sup>	9.4	6.5	8.2 - Mayberdue to cation exchange
K⁺	_	1.2	1.4
HCO <sub>3</sub> (CO <sub>3</sub> <sup>2-</sup> )	4 (3.9)	(119 (117))	(339)(333)
SO <sub>4</sub> <sup>2-</sup>	7.6	22	<b>84</b> )
CI-		13	9.6
NO <sub>3</sub>	_	0.1	13
pH (estimated)	6.0	6.0	8.4
TDS	38	165	434 )
L	L		
due to f	Centilizer		
prob. due to f but postible, e possible, en vitrati	sources	14	Idrover is consumed
poss witrati produ	e UNS	( 17	large is consumed pH goes up
produ	<i>zri</i> L	and	pli goes up

# Saturation Indices for Minerals Calculated for Typical Solution Compositions

SATURATION INDICES		
<u>Rain</u>	<u>River Water</u>	<u>Groundwater</u>
-5.3	-2.2	(1.3)
-10.2	-4.9	2.5
-1.3	-0.7	/ 0.2
-2.6	-1.9	-1.1
	14.4	18.4
-	0.3	2.3
-15.6	-12.1	0.18
-46.3	-34.4	(9.6)
-8.3	-8.6	-8.7
	had nother	Hie
wrong	(too high pir or	ue to
	Rain -5.3 -10.2 -1.3 -2.6 - -15.6 -46.3 -8.3 -8.3	RainRiver Water $-5.3$ $-2.2$ $-10.2$ $-4.9$ $-1.3$ $-0.7$ $-2.6$ $-1.9$ $ 14.4$ $ 0.3$ $-15.6$ $-12.1$ $-46.3$ $-34.4$

#### Summary

- Mineral equilibria of a solution is determined by comparing the equilibrium constant of the minerals with the ion activity product of the components of the minerals
- Partial equilibrium normally exists in aquifers between groundwater and reactive minerals
- Equilibrium solubility calculations are an important component in the evaluation of the mobility of many inorganic compounds

if metal is adsorbed to Ferric Hydropike, then mobility will depend on the mobility of the Ferric Hydropide Section 5

# Oxidation and Reduction Reactions

Lecture by: Patrick Longmire Los Alamos National Laboratory

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#### **OXIDATION AND REDUCTION CHEMISTRY**

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### The Kinetics of Fe(II) Oxidation and Well Screen Encrustation

by Kenneth R. Applin and Naiyu Zhao<sup>a</sup>

#### ABSTRACT

The unconsolidated sediments which border the Missouri River constitute an important ground-water aquifer that has been developed for municipal and industrial water supplies. The hydraulic efficiency of wells in these sediments decreases with time because of well screen encrustation caused by the oxidation of dissolved ferrous iron to insoluble ferric oxyhydroxides. The kinetics of ferrous iron oxidation are strongly dependent upon the solution pH and to a lesser extent the dissolved oxygen content. Chemical analyses of the well water including pH, Eh, dissolved oxygen, and dissolved iron indicate that at least one-half time for ferrous iron oxidation occurs prior to ground water entering the wells. As ground-water velocity increases near a pumping well, shallow, oxygen-bearing ground water may mix with deeper, reduced water by mechanical dispersion and turbulent flow and facilitate the oxidation of dissolved ferrous iron. Although little can be done to prevent well screen encrustation, the rate of encrustation may be slowed by regulated pumping and avoidance of shutdowns.

### INTRODUCTION

The unconsolidated alluvial sediments bordering the Missouri River constitute an important ground-water aquifer that is capable of supplying abundant water of reasonably good quality. Within Missouri, several communities including the metropolitan areas of Independence, New Franklin, St. Peters, St. Charles, and Columbia rely upon this aquifer for their public water supply.

The pumping of ground water from the alluvium is preferred over direct withdrawals from the Missouri River because it eliminates the costs of suspended sediment removal and disposal. However, the alluvial waters generally contain high amounts of dissolved iron, and reports of reduced well

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yields or shutdowns due to well screen encrustation by iron mineralization are common. Although the encrustation can be remedied by costly acidizing treatments, the problem is commonly recurrent. A better understanding of the processes leading to encrustation, however, could provide the basis for improved pumping operations or well costruction which might reduce the frequency of such treatments.

Although previous studies (e.g., Hem, 1967) have dealt with the problem of encrustation by applying solution-mineral equilibria concepts, this study focuses on the kinetics of ferrous iron oxid. tion in an attempt to determine the ratedetermining factors which affect well screen encrustation.

### **GEOLOGIC SETTING**

The study was performed along a segment of the Missouri River floodplain shown in Figure 1. The study area is bounded by a bow-shaped meander of the Missouri River on the west and by Perche Creek on the east. The alluvial sediments

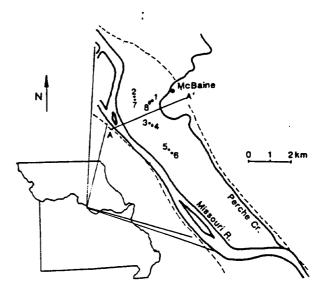


Fig. 1. Map of study area showing locations of wells.

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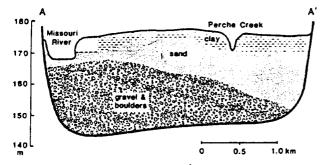


Fig. 2. Geologic cross section (A-A') of alluvial deposits at the McBaine area. (After De Moraes, 1969).

which comprise the floodplain fill a large, Ushaped channel which has been incised in Mississippian carbonate bedrock (Figure 2).

The alluvium is comprised of three, welldefined units (De Moreas, 1969). The lowest unit in contact with bedrock consists of boulders, gravel, and coarse to medium sand. The thickness varies from a few meters to about 30 meters (m). The central unit, which varies in thickness from a few to 18 m, is dominated by coarse to fine sand. This unit exhibits elongated lenses, cut-and-fill structures, and abrupt changes in particle size that are characteristic of a rapidly aggrading stream. The upper unit grades from clayey silt to silt and fine sand at depth. It is generally less than 5 m thick. The total thickness of the alluvium varies from about 24 m near the valley walls to about 30 m or more near the central part of the channel.

Mansur and Kaufman (1956) and Dahl (1961) have suggested that the three-unit sequence of sedimentation is related to Pleistocene glaciation and involves a two-stage process. First, the braided glacial outwash streams deposited cobble, gravel, and sand that comprise the substratum. Later, as the continental glaciers retreated and sea level rose, the river began to meander and finer, floodplain sediments were deposited.

The composition of the alluvial sediments is not well-documented. For samples taken to a depth of about 10 m, Goydan (1971) found that the composition varied with size. The coarse fraction consisted mainly of chert, granite, and carbonates with lesser amounts of mafic igneous rocks, metamorphic rocks, shale, and sandstone. The finer fractions were predominantly quartz. Iron oxide stains were observed on all size fractions.

Samples of alluvium associated with Perche Creek taken from an excavation site approximately 5 km north of the well field shown in Figure 1 clearly show the presence of early siderite cement (Gorday, 1982). As will be discussed later, the dissolved iron content of the alluvial ground waters appears to be controlled by the solubility of siderite.

The main water supply for the City of Columbia consists of eight wells located within the segment of alluvium shown in Figure 1. All wells have been drilled to bedrock and vary in depth between 30 and 34 m. Each well is screened at the base over a length of 10.6 m. Thus, each well is screened at the lowermost and coarsest fraction of the alluvium. Pump tests performed on well number 1 yielded an overall hydraulic conductivity of the alluvium in the range of 187 to 217 m/d and storage coefficients of about .12 to .22 (Foreman, 1979). Numerical modeling of the aquifer assuming a three-unit composition as described above vielded hydraulic conductivities of about 285-628 m/d for the lowest unit, 114-342 m/d for the middle unit, and 3 m/d for the upper, clay-rich unit (Foreman, 1979).

As shown in Figures 1 and 2, the wells are grouped in pairs with the distance between each pair less than about 150 m. During periods of low demand, the operation of the well field involves the alternate pumping of one well of each pair. Generally, wells 2, 4, and 5 are operated for about three to four days and then wells 3, 6, and 7 are pumped for a few days. Well 1 is used to augment supplies when needed. During periods of high demand, all the wells may be pumped. Well 8 was completed after this study.

### **METHODS AND PROCEDURES**

Water samples were collected from each of the seven wells in operation at the time of the study. Samples of Missouri River and Perche Creek water were taken at locations adjacent to the segment of alluvium in which the well field is located. All wells had been pumped continuously for at least one day prior to sampling.

At each well site, measurements of temperature, pH, Eh (oxidation potential), and dissolved oxygen (DO) were made prior to collecting samples. The pH of the well water was measured to within  $\pm 0.05$  pH units using a portable pH/mv meter and glass combination electrode which were calibrated with buffers of pH 7 and 8.3. During the measurement, the flow of well water was temporarily stopped to avoid streaming potentials.

Eh measurements were made in a vertically held glass tube approximately 4 cm in diameter by 25 cm in length. A calomel reference electrode was stoppered at the top of the tube and a platinum electrode was stoppered at the bottom. Ports in each stopper allowed for the inflow and outflow of water through the tube. A continuous flow of

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							Perche		Missouri	Well/River	
	1	2	3	4	5	б	7	avg	Cr.	River	ratio
Τ (°C)	17	16	17	18	17	18	17	17	27	28	0.6
рН	7.2	6.2	6.8	7.2	7.3	7.2	7.1	7.0	6.1	7.7	0.9
Eh (mv)	325	374	338	347	360	350	356	350	371	395	0.9
DO (mg/l)	0.8	1.2	1.4	2.0	2.2	1.4	1.2	1.5	9.2	5.8	0.3
Ca	100	89	124	107	60	62	100	92	66	61	1.5
Mg	24	18	27	23	14	14	23	20	12	18	1.1
Na	8.0	35	30	36	41	42	34	32	26	37	0.9
к	2.0	4.4	6.5	6.4	5.4	6.5	5.5	5.2	8.6	9.2	0.6
SiO2	29	23	27	26	20	17	27	24	12	14	1.7
HCO3	<del>4</del> 24	340	484	394	212	212	408	353	222	204	1.7
SO₄	28	106	104	134	130	138	88	104	40	185	0.6
Cl	7.2	20	18	20	18	19	16	17	30	16	1.0
Fe	<.02	.13	4.1	.05	3.1	3.9	5.4	2.4	<.02	.04	60.0
Mn	.20	.16	.98	.97	.27	.46	.29	.48	.78	.01	48.0

Table 1. Well and Surface Water Data (Chemical Data are in mg/l)

water was directed through the tube from bottom to top to eliminate air during operation. The flow was temporarily stopped during the Eh reading. All Eh measurements were corrected for the calomel reference potential (Wood, 1976). Prior to each reading, the meter and electrodes were checked against Zobell's solution. Comparison of the measured and theoretical Eh of Zobell's solution indicated an accuracy of about ±5 mv.

Dissolved oxygen was measured using a portable meter and membrane-type probe. Measurements were made in an open container through which water was continuously pumped. Values of DO were taken as the lowest stable readings and have an estimated accuracy of  $\pm 0.1$  mg/l.

Following the field measurements, two 500-ml samples were taken. Both samples were filtered through a 0.45- $\mu$ m membrane filter. One sample was treated for cation analyses by acidifying to pH < 2 with nitric acid. The other sample remained nonacidified and was used to perform anion analyses. The concentrations of dissolved Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> were determined in the lab according to the methods of Brown *et al.* (1970) within 24 hours after sample collection. Cation analyses were performed later using an ICP emission spectrometer.

### RESULTS

### Ground-Water Chemistry

The chemical and related data obtained for each well, Perche Creek, and the Missouri River are listed in Table 1. Although the waters were analyzed for several minor dissolved elements, only those that exhibited detectable concentrations are listed in Table 1. All of the waters are of the calcium-bicarbonate type, which reflects the influence of the limestone bedrock and carbonatebearing sediments of the area.

To compare the chemical compositions of the alluvial and river waters, ratios of the average con-. centrations of major dissolved species in well waters to the concentrations in Missouri River water were computed and are shown in Table 1. The ratios show that the alluvial waters are more concentrated than the river water with respect to all major dissolved species except Na, K, and  $SO_4^{2^2}$ . The concentrations of iron and manganese are notably higher in the alluvial waters and reflect the greater solubility of iron and manganese minerals under the more reducing conditions of the alluvial waters. The well to river water chloride ratio is unity which is expected if the alluvium is recharged mainly by the Missouri River and chloride is conserved. Well waters from adjacent bedrock are about two to three times higher in dissolved chloride which suggests that the ground water contribution from bedrock to the alluvium is negligible

If the Missouri River is the main source of recharge for the alluvium, the removal of dissolved oxygen and the subsequent lowering of the oxidation potential appear to be the major processes contributing to the observed difference between the river and alluvial water chemistry. As river water flows into the alluvium, the removal of dissolved oxygen may occur by the oxidation of organic matter within the riverbed or adjacent sediments as illustrated by reaction (1), in which  $CH_2O$ represents all organic matter.

$$CH_2O + O_2 = CO_2 + H_2O$$
 (1)

Reaction (1) should also increase the  $CO_2$ content and lower the pH of the alluvial waters. As shown in Table 1, the average pH of the well waters is about 0.7 units lower than that of the Missouri River water. The depletion of dissolved  $O_2$  by reaction (1) lowers the redox potential of the alluvial waters.

The increase in dissolved iron between the river and alluvial waters can be explained by the reduction of ferric to ferrous iron. The concentrations of dissolved Fe(II) appear to be limited by the solubility of siderite, FeCO<sub>3</sub> (Singer and Stumm, 1970). The state of saturation of the well waters with respect to siderite was evaluated using a modified version of the WATEQ computer program (Truesdell and Jones, 1974). The results indicate that only wells 3 and 7 contain dissolved Fe(II) at levels that approach siderite saturation. All other wells are undersaturated by various degrees with respect to siderite. The undersaturation may reflect the partial oxidation of Fe(II) to Fe(III) as waters are drawn toward the wells.

The possibility that iron bacteria may mediate the oxidation of dissolved ferrous iron at or near the well screens was also considered. However, tests performed on the well water by the City of Columbia prior to this study indicated negligible concentrations of iron bacteria.

### **Eh-pH Relationships**

The equilibria among various dissolved and solid forms of Fe(II) and Fe(III) as a function of Eh and pH are shown in the Eh-pH diagrams of Figure 3. The on-site Eh and pH values are plotted on each diagram. As shown in Figure 3(a), the measured Eh and pH data plot on the boundary between  $Fe^{2+}$  and  $Fe(OH)_3^\circ$  which suggests that the ground water contains approximately equal amounts of dissolved ferrous and ferric iron. A limited number of on-site ferrous and total iron analyses were performed later using a Hach kit. The results indicated that the well waters contained about equal amounts of dissolved Fe(II) and Fe(III). The measured Eh, therefore, is considered to be a reliable indicator of the redox state of the dissolved iron species.

As shown in Table 1, the well water also contains measureable amounts of dissolved oxygen, which suggests that there is a potential for further oxidation of Fe(II) to Fe(III) beyond that measured at the time of sampling. Given the half reaction which expresses the equilibrium between water and oxygen (reaction 2), the Eh of water can be calculated from the Nernst expression [equation (3)], in which  $E^{\circ}$  is 1.23 volts, R is the gas constant, T is absolute temperature, n is the moles of electrons, and F is the Faraday constant.

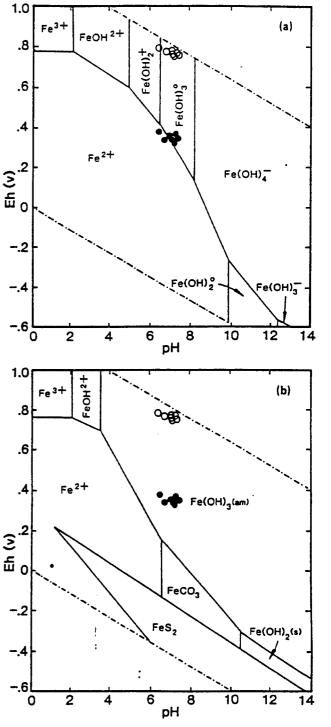


Fig. 3. Eh-pH relations among (a) aqueous iron species only and (b) aqueous and selected mineral species of iron drawn for  $\Sigma Fe = 2.5 \text{ mg/l}$ ,  $\Sigma CO_3 = 350 \text{ mg/l}$ , and  $\Sigma SO_4 = 100 \text{ mg/l}$ , the average well water values reported in Table 1. Measured Eh and pH values of the well water samples are plotted as closed circles. Values computed from DO measurements and equation (3) are plotted as open circles.

$$Eh = E^{\circ} + \frac{RT}{nF} \ln [H^{*}]^{2} P_{O_{2}}$$
(3)

Eh values computed using the dissolved oxygen contents of the well waters are also shown in Figure 3 and plot significantly higher than the

$$H_2O = 2H^2 + \frac{1}{2}O_2 + 2e^2$$

(2)

measured Eh values near the upper stability limit of water. The difference between the two sets of Eh values suggests a kinetic constraint on the oxidation of dissolved Fe(II). As the Fe(III)/Fe(II) ratio increases with further oxidation, however, the measured Eh should begin to correspond to the Eh values computed from dissolved oxygen values.

The disequilibrium condition which exists between the dissolved Fe (III)/Fe (II) ratio and the dissolved oxygen concentration arises because of the introduction of dissolved oxygen prior to the time the ground waters reach a pumping well. As discussed below, the time at which  $O_2$  enters the waters can be evaluated by examining the kinetics of ferrous iron oxidation.

A comparison of Figures 3(a) and 3(b) indicates that whereas the concentrations of Fe(II) and Fe(III) are nearly equal, the waters are supersaturated with respect to amorphous Fe(OH)<sub>3</sub>. However, in sample bottles that were filled to the brim and tightly capped, precipitation is not observed until about an hour after sample collection. Apparently, additional oxidation of Fe(II) to Fe(III) leading to higher degrees of supersaturation are required to initiate the nucleation and precipitation of Fe(OH)<sub>3</sub> (e.g., Nielson, 1964; Berner, 1980).

### The Kinetics of Fe(II) Oxidation

From the foregoing discussion, it is obvious that the oxidation of dissolved Fe(II) and subsequent precipitation of amorphous Fe(OH)<sub>3</sub> is at least a three-step process. The first step involves electron transfer of the ferrous ion as shown by reaction (4).

$$Fe^{2^{+}} = Fe^{3^{+}} + e^{-}$$
 (4)

This reaction is rapid at circumneutral pH and is immediately followed by deprotonation of the waters of hydration (reaction 5).

$$Fe^{3^{+}} + 3H_2O = Fe(OH)_3^{\circ} + 3H^{+}$$
 (5)

As oxidation continues, the concentration of  $Fe(OH)_3^\circ$  increases. The water becomes supersaturated with respect to amorphous  $Fe(OH)_3$  which facilitates its nucleation and growth (reaction 6).

$$Fe(OH)_{3}^{\circ} = Fe(OH)_{3}(am)$$
(6)

Reaction (6) is presumably the slowest of the three steps and is therefore the rate-limiting step for precipitation.

The kinetics of ferrous iron oxidation has been studied extensively (Tamura *et al.*, 1976; Sung and Morgan, 1980; Davidson and Seed, 1983; Millero *et al.*, 1987). The general rate law is given by equation (7), in which k is the rate constant in  $M^{-2} atm^{-1} min^{-1}$ , Fe(II) is the total ferrous iron concentration,  $P_{O_2}$  is the partial pressure of oxygen in atmospheres, and [OH<sup>-</sup>] is the hydroxyl ion concentration.

$$-\frac{dFe(II)}{dT} = k[Fe(II)] P_{O_2} [OH^-]^2$$
(7)

The rate constants determined by different workers generally lie in the range of  $1-6 \times 10^{13} \text{ M}^{-2}$ atm<sup>-1</sup> min<sup>-1</sup>. Based on a comprehensive survey of available data, Davison and Seed (1983) suggest an average value of  $2 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  for natural fresh waters at pH 6.5-7.4.

Tamura et al. (1976) showed that ferric hydroxide has an autocatalytic effect on the oxidation of ferrous iron and that at pH 6.2, the rate constant for ferrous iron oxidation increases linearly with the amount of ferric hydroxide. Furthermore, they found that adsorption of  $Fe^{2^+}$ onto ferric hydroxide was rapid and increased linearly with increasing pH. Thus, when the precipitation of iron occurs either at the well screen or within the sediments surrounding the well screen, the rates of oxidation should increase beyond those predicted by equation (7).

Equation (7) shows that the oxidation rate is dependent upon the ferrous iron concentration and  $P_{O_2}$  but is mostly sensitive to pH. Integration of equation (7) allows one to compute the half-time for oxidation [equation (8)].

$$t_{\frac{1}{2}} = \frac{0.693}{kP_{O_2} [OH^-]^2}$$
(8)

The half-time dependence on  $P_{O_2}$  at various pH values is plotted in Figure 4. Because the halftime is inversely proportional to  $[OH^-]^2$ , the halftime decreases by two orders of magnitude with each unit increase in pH. Factors that raise the pH of ground waters at or near the well sites, such as  $CO_2$  degassing, will significantly increase ferrous iron oxidation rates. The addition of  $O_2$  to ground waters will also increase the oxidation rates but to a lesser extent than pH.

#### Well Screen Encrustation

The Eh-pH data and limited ferrous and total dissolved iron analyses indicate that the dissolved iron is about equally divided between Fe(II) and Fe(III). Therefore, by the time the waters are pumped from the wells about one half-time for ferrous iron oxidation has occurred. Using the average DO content of 1.5 mg/l and average pH of 7.0, equation (8) predicts a half-time for oxidation of about 74 minutes.

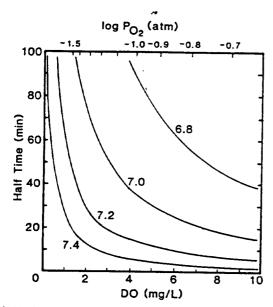


Fig. 4. Half-times for oxidation of Fe(II) to Fe(III) as a function of dissolved oxygen for pH 6.8-7.4 computed from equation (8).

The residence time of the water in the well varies inversely with the pumping rate and can be calculated by dividing the volume of water in the well (in gals) by the pumping rate (in gpm). A 26inch diameter well with a pumping water level of 100 feet contains about 2,760 gallons of water. At maximum efficiency, the wells can be pumped at a rate of about 2500 gpm which yields a residence time of 1.1 minutes. At a relatively slow pumping rate of 500 gpm, the residence time is 5.5 minutes. Thus, the introduction of oxygen and the initiation of ferrous iron oxidation must occur prior to the time the ground waters reach the wells, because even at low pumping rates the water does not reside in the wells long enough for a significant amount of oxidation to occur.

.. In a free aquifer such as the Missouri River alluvium, the upper layers of the ground water are likely to contain some dissolved oxygen that enters via meteoric recharge and by gaseous diffusion through the unsaturated zone. Hence, the oxidation potential of the ground waters may grade from high to low with depth. Iron in shallow ground water is oxidized and precipitated as amorphous  $Fe(OH)_3$ , as evidenced by the reddishorange iron staining observed on shallow alluvial sediments (Gorday, 1982). Iron is mobile only in the deeper ground water as Fe(II).

As noted above, about half of the dissolved Fe(II) in the deep ground water has oxidized by the time the ground water reaches a pumping well. For a homogeneous, isotropic aquifer, the radial distance from the well, r, at which oxidation of Fe(II) is initiated can be estimated from equation

(9), in which V is the volume of water pumped from the well,  $\phi$  is the sediment porosity, and L is the saturated thickness of the sediment.

$$r = \left(\frac{V}{\phi \pi L}\right)^{\frac{1}{2}} \tag{9}$$

à

V is computed by multiplying the pumping rate (2500 gpm or  $0.16 \text{ m}^3 \text{ sec}^{-1}$ ) times the halftime for oxidation (74 min.). For a saturated thickness of 24-30 meters, which is the approximate range of the pumping and nonpumping water depths measured in the wells, equation (9) yields distances of 5.4 to 6.1 meters. Assuming that O<sub>2</sub> is added to the upper layers of alluvial ground water through rainfall or diffusion, a mechanism must be invoked for mixing shallow, oxygenated ground water with deeper, Fe(II)-bearing water within these computed radii.

The velocity of water flowing to the wells increases markedly within the 5-6 meter range (Figure 5). Mechanical dispersion, which is directly dependent upon velocity, should become an increasingly effective mechanism for the vertical mixing of ground water flowing to a pumping well. Mixing may also be facilitated by a strong component of vertical flow within the cone of depression and by a change from laminar to turbulent flow close to the well bore.

Although ferrous iron may begin oxidizing at some time prior to the ground waters reaching the wells, the precipitation of amorphous  $Fe(OH)_3$ probably does not occur until sometime after the waters are pumped from the well. As noted above, no precipitate is visible within water samples taken at the well head until about one hour after sampling. This means that nearly an additional half-time for oxidation is required for precipitation.

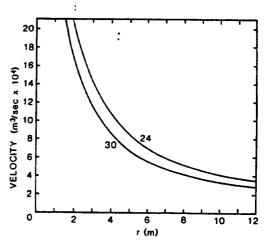


Fig. 5. Velocity of ground-water flow versus radial distance from a pumping well computed for a discharge of 0.16 m<sup>3</sup> sec<sup>-1</sup>, sediment porosity of 0.25, and saturated thicknesses of 24 and 30 meters. Drawdown is assumed to be negligible.

Therefore, significant precipitation of  $Fe(OH)_3(am)$ is likely to occur within the immediate vicinity of the well screens only under very slow pumping rates or when the pumps are shut down.

When pumping is stopped, the reduced iron that remains within the column of water within the well has sufficient time to oxidize and encrust the well screen and casing. Multiple shutdowns could significantly increase the rate of encrustation. In this respect, it is interesting to note that among the City of Columbia water wells, well number 1 is the oldest and most frequently operated. It became inoperative because of encrusted well screens shortly after the completion of this study. Continuous pumping, therefore, may minimize the rate at which encrustation occurs provided the pumping rate yields a residence time for well water which does not exceed about two half-times for oxidation.

### CONCLUSIONS

The results of this study suggest that for wells situated within the Missouri River alluvium the rate of well screen encrustation by iron mineralization could be substantially reduced by maintaining pumping rates and avoiding unnecessary shutdowns. The minimum pumping rates required to avoid the precipitation of iron at the well screens can be estimated by comparing the half-time of iron oxidation for the pH and DO content of the alluvial waters with the residence time of the waters in the well. The greatest rate of iron oxidation will occur when pumping is stopped and the water that remains in the well gradually becomes oxygenated after exposure to atmospheric  $O_2$ . The available kinetic data suggest that when nucleation of oxidized iron begins to occur at well screens, the precipitation will continue until Fe(OH)<sub>3</sub> production ceases.

The problems associated with encrustation might also be alleviated by constructing wells in a manner that would reduce drawdown. In this regard, a larger casing diameter or modifications in the positioning or lengths of screens may be helpful.

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### Thermodynamic Framework for Evaluating PAH Degradation in the Subsurface

by Michael J. McFarland and Ronald C. Sims<sup>a</sup>

#### Abstract

A method is presented to evaluate the influence of redox conditions and pH on mineralization of polycyclic aromatic hydrocarbons (PAH) in subsurface environments. Microbial yields based on the free energy liberated from heterotrophic PAH metabolism are estimated under various environmental conditions using a simple bioenergetic growth model. The types and chemical forms of electron acceptors addressed in this paper include oxygen, nitrate, sulfate, carbon dioxide, iron (Fe<sup>+3</sup> and FeOOH), and manganese (Mn<sup>+4</sup> and MnO<sub>2</sub>). PAHs addressed include naphthalene (2-fused aromatic rings), anthracene (3-fused aromatic rings), and pyrene (4-fused aromatic rings).

Calculated free energy changes demonstrated that sequential utilization of electron acceptors will follow the order  $Mn^{4}$ ,  $O_2$ ,  $NO_3^{-1}$ ,  $Fe^{-3}$ ,  $MnO_2$ , FeOOH,  $SO_4^{-2}$ , and  $CO_2$ . The behavior in microbial growth yield predictions were found to mimic the change in free energy liberated with the use of different electron acceptors. Despite release of free energy under all conditions evaluated, the small energy liberated during PAH mineralization under sulfate-reducing and methanogenic conditions suggests that heterotrophic degradation of PAH compounds under these conditions is unlikely to occur.

The large microbial growth yields associated with reduction of free metal species (Mn<sup>\*4</sup>, Fe<sup>\*3</sup>) during PAH oxidation suggest a selective advantage for microbes that can tolerate acid conditions and/or participate in metal chelation processes.

### Introduction

Characterization of contaminated sites often include an assessment of biological degradation in making decisions regarding site remediation/management strategies (Keely, 1987; Thomas et al., 1987; Lee et al., 1988; U.S. EPA, 1989a, b). Under certain conditions, an organic contaminant may serve as the primary carbon and energy source for microbial growth. This particular mechanism of biological removal of contaminants is an example of heterotrophic biodegradation. The role of heterotrophic biological reactions in influencing the fate and behavior of organic chemicals in subsurface environments is generally considered to be significant. In addition, biologically mediated reactions may be amenable to management and engineering strategies to accomplish site remediation. A framework for evaluating biodegradation at a contaminated site consists of characterization of the environment to determine: (1) type and

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amount of electron acceptors present, (2) chemical form(s) of electron acceptor(s); and (3) the free energy change(s) associated with electron transfer from a PAH compound to the electron acceptor(s).

The type, occurrence, and management of subsurface biological reactions to achieve decontamination objectives have been the focus of several recent scientific meetings, conferences, reports, and journal articles (Castro et al., 1985; DeWeerd et al., 1986: Gibson and Suflita, 1986: Borden and Bedient, 1987; Vogel et al., 1987; Wilson and Ward, 1987; Engineering Foundation, 1988; Lee et al., 1988; McCarty, 1988; Omenn. 1988; Park et al., 1988; Ross et al., 1988; Sims et al., 1988; AWMA/EPA, 1989; Genthner et al., 1989; Keck et al., 1989: Park et al., 1989; Roberts et al., 1989; Suflita, 1989; Thomas and Ward, 1989; U.S. EPA, 1989a, b). Biodegradation is often quantified by measuring a decrease in chemical concentration in a solvent extract of a subsurface sample over time. The biodegradation reaction rate may be described by a power-law kinetic rate model whose form will depend on whether or not the chemical is utilized by microorganisms as food and energy substrates (heterotrophic growth) or degraded through the process of cooxidation (Bulman et al., 1985; Sims et al., 1988; Keck et al., 1989; Loehr, 1989; Park et al., 1989). Biological reaction stoichiometry and rate, measured in laboratory and/or field stud-

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ies, have been used as input to mathematical models for predicting the influence of biodegradation on the fate of chemicals in subsurface environments (Short, 1986; McLean et al., 1988; Symons et al., 1988; U.S. EPA, 1988; Rifai et al., 1989; Stevens et al., 1989).

In subsurface soil and ground-water environments, oxygen may be limiting as a result of its rapid consumption by aerobic microorganisms and its slow rate of atmospheric recharge. Under these conditions, heterotrophic mineralization of organic chemicals will depend upon microbial utilization of electron acceptors other than molecular oxygen. Although the mineralization of four and five fused ring PAH compounds under aerobic conditions has been reported (Bauer and Capone, 1985; Heitkamp et al., 1987; Keck et al., 1989), in anoxic environments, only two and three fused ringed PAH compounds (e.g., naphthalene, anthracene, and phenanthrene) have been reported to mineralize (Scheunert et al., 1987; Mihelcic and Luthy, 1988).

Demonstration of the presence of requisite microorganisms in the subsurface and the absence of microbial toxicity is necessary, but not sufficient, to evaluate whether biodegradation activity is potentially important at a site. Specific additional information that can be obtained as part of a site characterization include: (1) identification of the electron acceptor(s) present: (2) quantity of electron acceptor(s); and (3) pH. This information can be used in thermodynamic calculations to estimate the potential for heterotrophic biodegradation of organic compounds.

Microorganisms in subsurface environments gain energy to meet metabolic needs through mediating energy yielding (i.e., exergonic) redox reactions. From a macroscopic view, subsurface microorganisms, whether as a single organism or as consortia, cannot survive by catalyzing thermodynamically unfavorable (i.e., endergonic) reactions. Moreover, the net energy yield must be sufficient to meet microbial cell maintenance requirements. These fundamental principles can be used to illustrate under what sitespecific conditions heterotrophic microbial mineralization of organic chemicals may occur. Redox conditions under which heterotrophic mineralization could occur can be estimated by estimating the free energy changes associated with the presence of specific electron acceptors and contaminant organic chemicals at a specific site.

To demonstrate the application of the framework described, results are presented for four chemicals in the semivolatile chemical class of compounds known as the polycyclic aromatic hydrocarbons (PAHs). PAH compounds are a group of hazardous organic substances of critical public health and environmental concern due to the following characteristics: (1) chronic health effects (e.g., carcinogenicity); (2) microbial recalcitrance; (3) high bioaccumulation potential: and (4) low removal efficiency in traditional waste treatment processes (Herbes and Schwall, 1978). PAH compounds have been identified in many types of industrial wastes but have been associated particularly with oily wastes, such as wastes from the petroleum refining, wood preserving, and electric power industries (Aprill et al., 1990).

This paper discusses important parameters that can be

obtained in a site characterization that can assist in evaluating the potential for heterotrophic biological mineralization of PAH compounds at a specific site. The thermodynamic framework presented provides a rational basis for an assessment of potential mechanisms influencing biodegradation at a contaminated site. In addition, it provides a focus for the design of treatability studies to determine rates of reaction and management options for stimulating biodegradation.

#### Background

Due to the slow diffusion of oxygen from the atmosphere into the subsurface, oxygen can be depleted in environments in which there is significant microbial activity. In natural environments, the depth of the oxygenated zone will depend on the input of biodegradable organic matter together with rate of oxygen recharge into the subsurface. Once oxygen becomes limiting, a variety of anoxic oxidation processes will follow in sequence. This sequence is determined by the electron affinity of the electron acceptors (Zehnder and Stumm, 1988).

Biochemical oxidation/reduction or redox reactions may be defined in terms of electron transfer. An organic chemical is oxidized if it undergoes a net loss of electrons; it is reduced if it undergoes a net gain of electrons. Organic compounds present at a contaminated site represent potential electron donors to support heterotrophic microbial metabolism. Potential electron acceptors include, but are not limited to, oxygen. nitrate, sulfate, carbonate, manganese, iron, and chlorinated organics that may undergo reductive dehalogenation.

The redox potential of an aqueous environment (pe) is related to the electric potential  $E_h$  that would be generated at an inert conducting electrode immersed in the aqueous solution and coupled with a standard hydrogen electrode. The relationship between pe and  $E_h$  is given by the following equation:

$$E_{\rm h} = pe(2.3 \ {\rm RT}/{\rm F})$$

where  $E_h = redox$  potential, volts;  $pe = negative \log of$ electron activity (i.e., redox potential); R = gas constant, 0.001987 KCal/mole-°K; T = temperature, °K; and F = Faraday constant, 23.06 kcal/Vg equivalent. Thus,

$$pe = 16.9(E_h) (at 25^{\circ}C)$$

 $E_h$ -pH diagrams are often used to illustrate the predominant dissolved and mineral species at equilibrium as functions of the  $E_h$  and pH values for a system. For example, with iron, in well-aerated soils with pH above 4, hydrous ferric oxide minerals and coatings are considered to be the soil minerals controlling equilibrium aqueous Fe<sup>+3</sup> concentrations. As the system becomes more reduced (lower  $E_h$ values), Fe<sup>+2</sup> may be expected to predominate up to pH 8.

 $E_h$  measurements may be used to evaluate systems for which the concentration of all species are known. Conversely, knowledge of the equilibrium  $E_h$  (or pe) of an environment permits determination of the activities of all redox species.

Although there is presently no fundamentally accept-

able method for directly measuring redox potential, a redox level in the subsurface may be estimated by determining relative concentrations of one of the redox couples in the system and applying electrochemical relations in reverse (Stumm and Morgan, 1981). Comparison of two redox couples should yield the same  $E_h$  (or pe) if the system is at thermodynamic equilibrium. Although subsurface systems are not normally at thermodynamic equilibrium, thermodynamic calculations can be used to predict the equilibrium state to which the system is approaching.

Bower and Cobb (1987) demonstrated the sequential use of electron acceptors during the biotransformation of organic matter in a model aquifer environment. Under nonlimiting electron donor conditions, oxygen utilization preceded denitrification after which followed sulfate reduction and finally methanogenesis. The sequential utilization of electron acceptors  $(O_2, NO_3^{-1}, SO_4^{-2}, CO_2)$  can be predicted by evaluating the free energy change associated with the use of each of these species. Bower and Cobb (1987) neglected microbial reactions involving the oxidation of iron and manganese because of the lack of information regarding their importance in organic contaminant biotransformation processes although ferric chloride (FeCl<sub>3</sub>) was included as part of the microbial nutrient solution.

Recent reports indicate that iron and manganese are not only important microbial electron acceptors in natural subsurface environments, but may effectively outcompete sulfate and carbon dioxide for electron equivalents (Lovely and Phillips, 1988; Lovely et al., 1989). The concentrations of iron and manganese in subsurface environments may be significant with concentrations ranging from 20 to 3000 ppm for manganese and 3800 to 5100 ppm for iron in most soils (Lindsay, 1979). In saturated neutral environments (pH of 6 to 9), reduced manganese (IV) and iron (III) normally exist as the insoluble salts MnO<sub>2</sub> and FeOOH, respectively. However, under saturated acidic conditions, a significant amount of the metal species may be biologically available as free cations (Brock and Gustafson, 1976).

Microbial chelation of Mn<sup>44</sup> and Fe<sup>43</sup> is also important in evaluating the availability of metal species to serve as electron acceptors during biological oxidation of organic matter. For example, some microbes secrete acidic organic materials (e.g., hydroxamic acids) which help maintain soluble Fe<sup>43</sup> concentrations at nonlimiting levels (Brock, 1981). Other naturally occurring organic materials (e.g., polyhydroxamic acids) are known to form soluble manganese complexes in the acidic environment (Stumm and Morgan, 1981). Due to the variability of subsurface environments impacted by organic contamination, free metal ions together with insoluble iron and manganese oxides were evaluated as electron acceptors in the present study.

#### Approach

This paper presents a thermodynamic framework that was developed for assessing the potential for heterotrophic biodegradation at a contaminated site. The approach consists of: (1) characterization of a site to determine type and amount of electron acceptors present; (2) determination of chemical form(s) of electron acceptor(s); and (3) calculation of free energy change(s) associated with electron transfer from a PAH compound to the electron acceptor(s) during heterotrophic microbial growth. The relevance of free energy on the microbial yield coefficient is evaluated in a simple bioenergetic growth model developed by McCarty (1971).

### Characterization of a Site to Determine Type and Amount of Electron Acceptors Present

Electron acceptors commonly found at waste sites were considered. These include oxygen, nitrate, sulfate, carbon dioxide, manganese, and iron. Electron acceptors were considered to be present in nonlimiting amounts and in reactive forms.

Two chemical forms of iron, Fe<sup>+3</sup> and FeOOH, and two chemical forms of manganese, Mn<sup>+4</sup> and MnO<sub>2</sub>, were considered. The effects of pH in determining the chemical form of the electron acceptor(s) at equilibrium are related by thermodynamic principles (Stumm and Morgan, 1981).

#### Calculation of Free Energy Change(s) Associated with Electron Transfer

PAHs selected include naphthalene (2-fused aromatic rings), anthracene (3-fused aromatic rings), phenanthrene (3-fused aromatic rings), and pyrene (4-fused aromatic rings). The method proposed to estimate the influence of redox conditions on PAH heterotrophic mineralization involves comparing the free energy change associated with electron transfer from the PAH compound to electron acceptor(s).

Due to differences in energy content of PAH compounds, comparison of free energy changes should be evaluated on an electron equivalent basis. Free energy liberated per mole of electrons transferred provides a rational basis with which to compare each mineralization reaction.

The general electron donor oxidation half cell reaction that describes the transfer of one mole of electrons during PAH mineralization under aqueous conditions is given by the following equation (modified from Stumm and Morgan, 1981):

$$\frac{1}{(4a+b)} C_{a} H_{b} + \frac{2a}{(4a+b)} H_{2} O - \frac{a}{(4a+b)} CO_{2} + H^{*} + e^{-}$$
(1)

where a and b are stoichiometric coefficients. Using the above relationship, the equation describing the overall complete hydrolysis (mineralization) of one electron equivalent of naphthalene is given as follows:

$$1/48(C_{10}H_8) - 20/48(H_2O) - 10/48(CO_2) + H^* + e^-$$
  
....(2)

Free energies associated with the mineralization of naphthalene, anthracene, phenanthrene, and pyrene were estimated from free energy of formation calculations. The procedure is illustrated in Example 1 using phenanthrene as an example.

### Example 1. Free Energy Change Associated with the Mineralization of Phenanthrene Under Aqueous Conditions

Using equation (1), the following equation illustrates the half cell reaction for the mineralization of phenanthrene  $(C_{14} H_{10})$  under aqueous conditions:

$$(1/66) C_{14} H_{16} + (28/66) H_2 O - (14/66) CO_2 + H^2 + e^2$$
  
....(3)

.....

The free energy liberated from this reaction can be estimated by subtracting the free energy of formation of reactants from that of products.

$$G(W) = \Sigma \partial \Delta G_{f(\text{products})} - \Sigma \partial \Delta G_{f(\text{reactants})}$$
(4)

where  $\partial =$  stoichiometric coefficients, and  $\Delta G_f =$  free energy of formation. For phenanthrene, equation (4) becomes:

$$\Delta G (W) = [(14/66) \Delta G_{f(CO2)} + \Delta G_{f(H^*)} + \Delta G_{f(e^*)}] - [(1/66) \Delta G_{f(C14|H10)} + (28/66) \Delta G_{f(H20)}]$$
(5)

By convention, the Gibbs free energy of formation for the electron is zero whereas that of the proton is -9.67kcal/mole for a pH of 7. Therefore, equation (5) reduces to the following:

$$\Delta G_{(C_{14}H_{10})}(W) = [(14/66) \Delta G_{((C_{2})} + \Delta G_{((H^*)}] - [(1/66) \Delta G_{((C_{14}H_{10})} + (28/66) \Delta G_{((U_{20})}]$$
(6)

The Gibbs free energy of formation of carbon dioxide and water are -94.22 kcal/mole and -56.67 kcal/mole at  $25^{\circ}$ C, respectively (Stumm and Morgan, 1981). The Gibbs free energy of formation for phenanthrene under *aqueous* conditions was not found in the literature, but could be estimated from other thermodynamic parameters such as the Gibbs free energy of formation in the solid phase, the vapor pressure, and Henry's Law Constant at the temperature of interest using equilibrium partitioning chemistry. The following are the steps involved in estimating the free energy of formation of PAH compounds under aqueous conditions from thermodynamic data.

### Estimation of Free Energy of Formation of Phenanthrene $\Delta G_{I(C_{14}H_{10})}$ Under Aqueous Condition

Phenanthrene (Thermodynamic Data)

1. Gibbs free energy of formation (solid phase = 60.0 kcal/mole [data from Lange's Handbook of Chemistry (1985)].

2. Vapor pressure (atm) =  $8.9 \times 10^{-7}$  [Sims and Overcash (1983)].

3. Henry's Law Constant (atm-liter/mole) = 0.1225 [Sims and Overcash (1983)].

4. Universal gas constant (R) 0.082057 liter-atm/ mole-°K) or (R) 1.987 calorie/(mole-°K).

Step 1

The first step is to determine the free energy of formation of the compound in its gaseous state from solid state data using the following equilibrium relationship

$$C_{14}H_{10}(solid) < = > C_{14}H_{10}(gas)$$
 (7)

The equilibrium constant K, that describes this reaction, is given by the following equation:

$$K = \frac{\{C_{14} H_{10}(g)\}}{\{C_{14} H_{10}(s)\}}$$
(8)

By convention, the activity of the solid is unity while the activity of a gas over a pure solid is its vapor pressure. Thus, the equilibrium constant K is equal to  $8.9 \times 10^{-7}$ . The free energy change in going from the solid to gas is given by the following relationship:

$$\Delta G_{\text{(reaction)}} = -RT \ln K = \Delta G_{f(C_{14} H_{10})(\text{pas})} - \Delta G_{f(C_{14} H_{10})(\text{solid})}$$
..., (9)

where R is the universal gas constant (1.987 cal/mole- $^{\circ}$ K), and T = absolute temperature (Kelvin). Making the numerical substitutions results in the following free energy of formation of phenanthrene in the gaseous phase:

$$\Delta G_{f(C_{14}H_{10})(gas)} = 68.25 \text{ kcal/mole} (at 25^{\circ}C) \qquad (10)$$

Step 2

The free energy of formation in the gas phase can be related to the free energy of formation in the aqueous phase:

$$C_{14} H_{10}(aqueous) < = > C_{14} H_{10}(gas)$$
 (11)

The equilibrium constant K, that describes this reaction, is given by the following equation:

$$K = \frac{\{C_{14}H_{10}(gas)\}}{\{C_{14}H_{10}(aqueous)\}}$$
(12)

Using Henry's Law and the Ideal Gas Law permits transformation of equation (11) to a more suitable form. Henry's Law is given by the following:

$$P_{C_{14}H_{10}} = H_{C} \{ C_{14} H_{10} (aqueous) \}$$
(13)

where  $P_{C_{14}H_{10}}$  is the partial pressure of phenanthrene (atm);  $H_C$  is the Henry's Law Constant (atm-liter/mole); and  $C_{14}H_{10}$  (aqueous) is the concentration of phenanthrene (mole/liter). Using the Ideal Gas Law, the following relationship is found:

 $\{C_{14}H_{10}(gas)\} = n/V = total no. of moles/volume of gas$ 

$$= P_{C_{14}H_{10}}/RT$$
 (14)

Substituting the ideal gas relationship into equation (11) results in the following:

$$K = \frac{\{C_{14} H_{10} (gas)\}}{\{C_{14} H_{10} (aqueous)\}} = \frac{P_{C_{14} H_{10}}}{RT\{C_{14} H_{10} (aqueous)\}}$$
$$= \frac{H_c \{C_{14} H_{10} (aqueous)\}}{RT\{C_{14} H_{10} (aqueous)\}}$$
(15)

$$K = \frac{H_c}{RT}$$
(16)

The free energy of formation under aqueous conditions may be determined using the following relationship:

Table 1. Stoichiometry and Free Energy Change	e in the Half Cell Mineralization Reaction of
Naphthalene, Anthracene, Phenanthrene	e, and Pyrene (at 25°C and pH of 7)*

	ΔG°(W) kcal/ <del>ce</del> q
<b>1. Naphthalene:</b> $(1/48) C_{10} H_8 + (20/48) H_2 O - (10/48) CO_2 + H^+ + e^-$	-6.75
2. Anthracene: $(1/66) C_{14} H_{10} + (28/66) H_2 O - (14/66) CO_2 + H^* + e^-$	-6.70
3. Phenanthrene: $(1/66) C_{14} H_{10} + (28/66) H_2 O - (14/66) CO_2 + H^* + e^-$	-6.60
4. Pyrene: $(1/74) C_{16} H_{10} + (32/74) H_2 O - (16/74) CO_2 + H^* + e^-$	-6.49

\* The Standard states are one molar concentrations for reactants and products at 25°C.

Table 2. Free Energy Change in the Reduction of Electron Accepting Species (at 25°C and pH of 7)
(Data taken from Zehnder and Stumm, 1988)

	ΔG°(W) kcal/eeq
<b>1. Oxygen</b> $1/4 O_2 + H^* + e^ 1/2 H_2O$	-18.675
2. Nitrate $1/5 \text{ NO}_3 + 6/5 \text{ H}^2 + e^2 - 1/10 \text{ N}_2 + 3/5 \text{ H}_2\text{O}$	-17.128
3. Manganese (oxide and soluble species) 1/2 MnO <sub>2</sub> + 1/2 HCO <sub>3</sub> <sup>-</sup> + 3/2 H <sup>-</sup> + e <sup>-</sup> - 1/2 MnCO <sub>3</sub> + H <sub>2</sub> O (insoluble oxide form)	-12.130*
$1/2 \text{ Mn}^{-4} + e^{-} \rightarrow 1/2 \text{ Mn}^{-2}$ (soluble Mn <sup>-4</sup> )	-28.32**
4. Ferric iron (oxide and soluble species) FeOOH + HCO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + e <sup>-</sup> - FeCO <sub>3</sub> + 2H <sub>2</sub> O (iron oxide)	1.091*
$Fe^{+3} + e^ Fe^{-2}$ (soluble iron)	-17.78**
5. Sulfate $1/8 \text{ SO}_4^{-2} + 19/16 \text{ H}^* + e^ 1/16 \text{ H}_2\text{S} + 1/16 \text{ HS}^* + 1/2 \text{ H}_2\text{O}$	5.085
6. Carbon dioxide 1/8 CO <sub>2</sub> + H <sup>+</sup> + e <sup>-</sup> - 1/8 CH <sub>4</sub> + 1/4 H <sub>2</sub> O	5.763

\* Assumes a bicarbonate concentration of 10<sup>-3</sup> M, which is more typical of aquatic environments.

\*\* Assumes a soluble species is available at neutral pH.

 $\Delta G_{(reaction)} = -RTinK$ 

$$= (\Delta G_{f(C_{14}H_{10})(gas)} - \Delta G_{f(C_{14}H_{10})(aqueous)})$$
(17)

Making the necessary substitutions and solving for  $\Delta G_{flC_{14}H_{10}}$  (squeous) gives a free energy of formation of +65.12 kcal/mole for phenanthrene. [Note: the equilibrium constant K in equation (16) was estimated using a value of 0.082057 liter-atm/mole – °K for the universal gas constant – R]. Substituting the numerical values into equation (6), the free energy of the half cell mineralization reaction of phenanthrene under aqueous conditions at pH = 7 ([H<sup>\*</sup>] = 10<sup>-7</sup>) is calculated as follows:

$$\Delta G_{(C_{14}H_{10})}(W) = -[(14/66)(-94.22 \text{ kcal/mole}) +$$

$$(-9.67 \text{ kcal/mole})] - [(1/66)(+65.12 \text{ kcal/mole}) +$$

$$(28/66)(-56.67 \text{ kcal/mole})]$$
 (18)

 $\Delta G_{(C_{14}H_{10})}(W) = -6.60$  kcal/mole of electrons transferred. Therefore, equation (3) becomes:

$$(1/66) C_{14} H_{10} + (28/66) H_2 O - (14/66) CO_2 + H^* + e^-$$
  
= -6.60  $\Delta G^{\circ}(W)$  kcal/eeg

The half cell reactions for the other PAH compounds can be found using similar calculations (Table 1). When the half cell

oxidation reactions are coupled with the half cell reduction reactions, then overall energy yield can be estimated (Tables 3 and 4).

Table I summarizes free energy estimations of half cell reactions of the four PAH compounds. Values for free energy presented in Table 1 indicate that half cell hydrolysis reactions of the four PAH compounds are energy releasing (i.e., exergonic) at 25°C and a pH of 7. These half cell reactions must be coupled to reduction reactions that will result in an overall negative free energy change for the reactions to be thermodynamically possible. In groundwater systems, reactions that may couple with PAH oxidation reactions include oxygen, nitrate, carbon dioxide, iron, and manganese reductions. Table 2 summarizes the free energy changes associated with the reduction of electron acceptors.

Free energy changes associated with electron acceptor reduction reactions can be combined with free energy changes associated with the oxidation of PAHs to generate stoichiometrically balanced reactions and an overall free energy change for each electron donor (PAH) and electron acceptor combination. Results are presented in Table 3 for the mineralization of naphthalene under different redox conditions by combining the equations in Tables 1 and 2.

By performing similar calculations for the other three PAH compounds, free energy changes associated with heterotrophic mineralization of each PAH can be estimated (Table 4).

### Results

Results presented in Table 4 indicate that free manganese reduction resulted in a much higher free energy change than aerobic mineralization of naphthalene. This greater free energy yield associated with free manganese reduction is not unreasonable since there are reports of microorganisms that will preferentially utilize manganese as an electron acceptor under strictly aerobic conditions (DeVrind et al., 1986; Ehrlich, 1981; Ghiorse, 1988). Therefore, even in aerobic aquifers, if acidity is high, oxygen may not be utilized until free manganese becomes limiting.

The free energy changes associated with heterotrophic PAH mineralization at a system pH of 4 and 9 are given in Tables 5 and 6, respectively. The net effect of the change in proton activity on the overall free energy change was particularly significant when the electron acceptor was a free metal species.

The capture of free energy by cells is not 100% efficient, and only a portion of the free energy released by mineralization reactions is available for cell use. The fraction of free energy released that is available to a microorganism depends on the PAH compound (substrate), environmental conditions, and species and age of biological populations.

Although free energy calculations provide a general basis for evaluating whether or not heterotrophic mineralization is possible, the reaction must result in releasing sufficient energy to support microbial growth and cellular maintenance requirements if the PAH compound is to serve as the primary carbon and energy source. McCarty (1971) developed an energetic model that has been successful in estimating the heterotrophic growth of microorganisms in waste treatment operations and in subsurface biofilms (Luthy. 1980; Bower and Cobb, 1987).

The following example describes the bioenergetic model together with an application of the model to predict microbial growth when pyrene is utilized as the sole carbon and energy source by denitrifying microorganisms.

## Example 2. Bioenergetic Model for Prediction of Microbial Yields

In heterotrophic microbial utilization of organic matter, a portion of the electron donor is used for energy production while a portion is utilized in biosynthetic reactions. The following is an approach developed by McCarty (1971) to estimate microbial yields from free energy calculations for heterotrophic metabolism. The model is based on the following schematic illustration:

 Table 3. Stoichiometry and Standard Free Energy Changes During the Heterotrophic Mineralization of

 Naphthalene Under Various Redox Conditions (at 25°C and pH of 7)

	∆G°(W) kcal/eeq
1. $1/48 \operatorname{C_{10}H_8} + 20/48 \operatorname{H_2O} + 1/2 \operatorname{Mn}^{*4} - 10.48 \operatorname{CO}_2 + 1/2 \operatorname{Mn}^{*2} + \operatorname{H^*}$	-35.07
2. $1/48 C_{10}H_8 + 1/4 O_2 - 10/48 CO_2 + 1/12 H_2O$ 3. $1/48 C_{10}H_8 + 20/48 H_2O + Fe^{*3} - 10/48 CO_2 + Fe^{*2} + H^*$	-25.43
4. $1/48 \ C_{10}H_8 + 1/5 \ NO_5^{-} + 1/5 \ H^{-} - 10 \ 48 \ CO_2 + 1/10 \ N_2 + 11/60 \ H_2O$	-24.53**
5. $1/48$ CmHz + $1/3$ MnO <sub>2</sub> (z) + $1/3$ H = 10.48 CO <sub>2</sub> + $1/10$ N <sub>2</sub> + $11/60$ H <sub>2</sub> O	-23.88
5. $1/48 C_{10}H_8 + 1/2 MnO_2(s) + 1/2 HCO_3 + 1/2 H^2 - 10/48 CO_2 + 1/2 MnCO_3 + 7/12 H_2O$ 6. $1/48 C_{10}H_8 + FeOOH(s) + HCO_3 + H^2 - 10/48 CO_2 + FeCO_3 + 76/48 H_2O$	-18.88*
7. $1/48 C_{10}H_8 + 1/8 SO_4^{-2} + 3/16 H^2 - 10/48 CO_2 + 1/16 H_2 S + 1/16 HS^2 + 1/12 H_2 O$	-5.66*
8. $1/48 C_{10}H_8 + 1/4 H_2O - 4/48 CO_2 + 1/8 CH_4$	-1.67
	-0.99

\* Assumes a bicarbonate concentration of 10<sup>-3</sup> M, which is more typical of aquatic environments.

\*\* Assumes a soluble species is available at neutral pH.

Table 4. Free Energy Change [△G°(W)] Associated with Hel	terotrophic PAH Mineralization Under
Various Oxidation-Reduction Conditions (a	at 25°C and pH of 7)

Electron acceptor	Naphthalene	Anthracene	Phenanthrene	Pyrene
Nonmetal:				
O2	-25.43	-25,38	-25.28	
NO3 <sup>-1</sup>	-23.88	-24.28		-25.17
SO4 <sup>-2</sup>	-1.67		-23.73	-23.62
CO <sub>2</sub>		-1.61	-1.51	-1.40
	-0.99	-0.94	-0.84	-0.73
Metal:				0.75
Mn <sup>+4</sup>	-35.07	-35.02	24.02	
Fe <sup>+3</sup>	-24.53		-34.92	-34.81
MnO <sub>2</sub>		-24.48	-24.38	-24.27
-	-18.88	-18.83	-18.73	-18.62
FeOOH	-5.66	-5.61	-5.51	-5.40
				-2.40

Electron acceptor	Naphthalene	Anthracene	Phenanthrene	Pyrene
Nonmetal:				
Oz	-25.42	-25.37	-25.27	-25.16
NO <sub>3</sub> <sup>-1</sup>	-24.71	-24.66	-24.56	-24.45
SO4 <sup>-2</sup>	-2.46	-2.41	-2.31	-2.20
CO <sub>2</sub>	-0.99	-0.94	-0.84	-0.73
Metal:				
Mn**	-30.86	-30.81	-30.71	-30.60
Fe <sup>+3</sup>	-20.32	-20.27	-20.17	-20.06
MnO <sub>2</sub>	-15.43	-15.38	-15.28	-15.17
FeOOH	-6.73	-6.68	-6.58	-6.47

 Table 5. Free Energy Change [△G°(W)] Associated with Heterotrophic PAH Mineralization Under Various Oxidation-Reduction Conditions (at 25°C and a pH of 4.0)

 
 Table 6. Free Energy Change [△G°(W)] Associated with Heterotrophic PAH Mineralization Under Various Oxidation-Reduction Conditions (at 25°C and a pH of 9.0)

Electron acceptor	Naphthalene	Anthracene	Phenanthrene	Pyrene
Nonmetal:				
O <sub>2</sub>	-25.42	-25.37	-25.27	-25.16
NO <sub>3</sub> <sup>-1</sup>	-23.35	-23.30	-23.20	-23.09
SO <sup>1</sup> -:	-1.18	-1.13	-1.03	-0.92
CO:	-0.99	-0.94	-0.84	-0.73
Metal:				
Mn <sup>-1</sup>	-37.68	-37.63	-37.53	-37.42
Fe*	-27.14	-27.09	-26.99	-26.88
MnO <sub>2</sub>	-17.59	-17.54	-17.44	-17.33
FeOOH	-3.05	-3.00	-2.90	-2.79

Respiration Reaction (Energy Reaction)

#### Microbial Synthesis

(Electron Donor) +  $NH_4^* - - C_5 H_7 O_2 N$  (New Cells)

In order to use the model, the following definitions are made:  $\Delta G_r$  = free energy released per electron equivalent of substrate converted for energy (i.e., respiration);  $\Delta G_s$  = free energy required to synthesize one electron equivalent of microbial cells (including energy losses);  $\Delta G_p$  = free energy change in transforming the electron donor to pyruvate (which is assumed to be the redox state at which carbon enters the biosynthetic pathway);  $\Delta G_n =$ free energy of converting nitrogen source to ammonium (which is assumed to be the redox state at which nitrogen enters the biosynthetic pathway);  $\Delta G_c =$  free energy in converting pyruvate plus ammonium to one electron equivalent of microbial cells;  $\beta =$  efficiency of transferring energy from electron donor to ADP (adenosine diphosphate) to form ATP (adenosine triphosphate) (assumed to be 0.6 by McCarty, 1971); and A = electron equivalent of electron donor converted to energy per electron equivalent of cells synthesized (note: we neglect energy required for maintenance); this term is noted in some texts as  $f_e/f_s$  where  $f_e$  is the fraction of electron donor that goes to energy reactions, and  $f_s$  is the fraction of electron donor that goes to biosynthesis reactions.

Using these definitions, an energy balance for production of new cells can be estimated. The amount of energy available after the respiration of one electron equivalent of electron donor-including losses =  $\beta A \Delta G_r$ . The amount of energy required for synthesis of one electron equivalent of new cells =  $\Delta G_s$ .

Neglecting maintenance energy, we have the following energy balance equation:

or

$$A = -(\Delta G_s)/\beta \Delta G_r$$

 $\beta A \Delta G_r + \Delta G_s = 0$ 

 $\Delta G_s$  has three components ( $\Delta G_p$ ,  $\Delta G_n$ ,  $\Delta G_c$ ). The equation that describes the biosynthesis reaction is given as follows:

$$\Delta G_{s} = \Delta G_{p} / \beta^{m} + \Delta G_{c} + \Delta G_{n} / \beta$$

where m = -1 if  $\Delta G_p > 0$ , and m = -1 if  $\Delta G_p < 0$ . The coefficient m takes into account the energy state of the electron donor relative to that of pyruvate.  $\Delta G_c = 7.5$  kcal/electron equivalent of cells produced from pyruvate, plus ammonium, is assumed constant [McCarty (1971) assumes all cells have the same energy capture efficiency].  $\Delta G_n = 4.17$  kcal/mole if nitrate is the nitrogen source and 0

kcal/mole if the nitrogen source is ammonium.

The microbial yield (Y) can be defined in terms of the given definitions as the following:

$$Y = 1/(1 + A)$$

Y = electron equivalent of cells formed/electron equivalent of electron donor used.

This expression of microbial yield although theoretically correct, is inconvenient for many practical applications. A more convenient expression for microbial yield is gms Volatile Solids/gm COD (chemical oxygen demand). The present definition of microbial yield (Y) can be converted to the more convenient expression by invoking the following relationship for the half reaction of microbial cell oxidation:

$$C_5H_7O_2N + 9H_2O -$$

$$4CO_2 + HCO_3 + NH_4 + 20 H^2 + 20 e^2$$

(microbial cells = 113 gms/mole.)

Since 20 moles of electrons are released per mole of microbial cells oxidized, one electron equivalent of cells is equal to 1/20 mole of  $C_5H_7O_2N$ . In other words, one electron equivalent of microbial cells is equal to 5.65 grams of  $C_5H_7O_2N$  (i.e., 113/20). Invoking the relationship that one electron equivalent is equal to 8.0 grams of chemical oxygen demand (COD) (McCarty, 1972), the convenient form of the microbial yield can be expressed as the following:

$$Y = (5.65)/8(1 + A)$$

where Y now has the dimensions of gm Volatile Solids per gram Chemical Oxygen Demand.

Use of this model for prediction of microbial yield is demonstrated by the following example in which pyrene is utilized as the electron donor and nitrate as the electron acceptor at 25°C and a pH of 7.0.

**Pyrene:**  $(1/74) C_{16} H_{10} + (32/74) H_2 O -$ 

 $(16/74) CO_2 + H^* + e^- = -6.490 \Delta G^{\circ}(W) \text{ kcal/eeq}$ 

Nitrate:  $1/5 \text{ NO}_3^- + 6/5 \text{ H}^+ + e^- - -$ 

$$1/10 N_2 + 3/5 H_2O = -17.128 \Delta G^{\circ}(W) \text{ kcal/eeq}$$

 $\Delta G_r = -23.618$  kcal/eeq of electron donor oxidized (-6.490 + -17.128);  $\Delta G_n = 4.17$  kcal/eeq of cells produced; and  $\Delta G_c = 7.5$  kcal/eeq of cells produced.

The following can be used to estimate the free energy change of converting the electron donor to pyruvate  $\Delta G_p$ :

**Pyrene:** 
$$(1/74) C_{16} H_{10} + (32/74) H_2 O -$$

$$(16/74) CO_2 + H^* + e^- = -6.490 \Delta G^{\circ}(W) \text{ kcal/eeq}$$

**Pyruvate:**  $(1/5) CO_2 + (1/10) HCO_3 + H^* + e^- -$ 

(1/10) CH<sub>3</sub>COCOO<sup>-</sup> + (2/5) H<sub>2</sub>O = +8.545 
$$\Delta$$
G°(W)  
kcal/eeg

Therefore,  $\Delta G_p = 2.055$  kcal/eeq of electron donor (i.e., pyrene) converted to pyruvate.

The free energy required per eeq of cells synthesized can now be evaluated ( $\beta = 0.6$ , m = +1):

$$\Delta G_{s} = \Delta G_{p} / \beta^{m} + \Delta G_{c} + \Delta G_{n} / \beta$$

 $\Delta G_s = 17.875$  kcal required/eeq of cells produced.

The coefficient A can be calculated using the following expression:

$$A = -(\Delta G_s)/\beta \Delta G_r$$

A = 1.261 eeq of electron donor to energy/eeq of electron donor to synthesis.

The microbial coefficient Y can be calculated using the following expression:

$$Y = (5.65)/8(1 + A)$$

Y = 0.31 gms Volatile Solids/gm COD (as pyrene).

Using this same technique, microbial yields for all of the PAH compounds under various redox conditions can be estimated. Results from this model are given in Table 7 in which the microbial yields for glucose, methanol, and benzoate are estimated for comparison.

Table 7 presents the results of the bioenergetic model applied to the four PAH compounds together with estimated microbial yields using glucose, methanol, and benzoate for comparison.

#### Discussion

The advantage of a chemical energetics approach in evaluating the potential for heterotrophic mineralization of PAH compounds is that knowledge of competition among different anoxic microbial species for the PAH compound is unnecessary.

From Table 4, the low energy yield associated with sulfate and carbon dioxide reduction confirms the experimental results observed by Mihelcic and Luthy (1988) in which naphthalene mineralization was observed under aerobic and nitrate reducing conditions but not under carbon dioxide reducing (methanogenic) conditions.

These results are important when considering the fate of PAH compounds in subsurface anoxic environments including unsaturated and saturated zones. In environments in which sulfate or carbon dioxide are the principal electron acceptors, heterotrophic biodegradation of PAH compounds is unlikely since the energy liberated from these reactions may be too low to support microbial maintenance requirements. Mineralization will occur only by changing the redox state of the environment (i.e., introducing alternative electron acceptors with greater electron affinities).

One possible approach for inducing heterotrophic mineralization of PAH compounds in an environment in which there is a significant concentration of insoluble metal oxide would be to take advantage of the favorable energetics associated with free metal reduction. Increasing the solubility of metals may be accomplished by decreasing the pH of the environment that results in shifting more of the insoluble metal into its more mobile (i.e., free) form. It should be noted that despite the reduction in free energy change due to the decrease in pH [equation (1)], the formation of free metal species results in an overall increase in free energy liberated during the mineralization reaction.

	•		•	• •			
Electron acceptor	Naphthalene	Anthracene	Phenanthrene	Pyrene	Glucose	Methanol	Benzoate
Nonmetais:							
O2	0.33	0.33	0.33	0.32	0.40	0.38	0.33
NO3 <sup>-1</sup>	0.32	0.32	0.31	0.31	0.39	0.37	0.32
SQ4 <sup>-2</sup>	0.06	0.06	0.06	0.05	0.22	0.17	0.07
CO <sub>2</sub>	0.04	0.04	0.03	0.03	0.20	0.15	0.04
Metals:							
Mn⁺⁴	0.39	0.39	0.38	0.38	0.44	0.43	0.39
MnO <sub>2</sub>	0.28	0.28	0.27	0.27	0.35	0.33	0.28
FeOOH	0.12	0.11	0.11	0.11	0.20	0.18	0.12
FeOOH**	0.17	0.17	0.17	0.16	0.32	0.28	0.18
Fe <sup>+1</sup>	0.32	0.32	0.32	0.32	0.39	0.37	0.33
Fe <sup>*3</sup> **	0.41	0.41	0.41	0.40	0.51	0.49	0.42

Table 7. Estimated Microbial Yield from Heterotrophic PAH Mineralization*
(gm Volatile Solids/gm Chemical Oxygen Demand)

Assumes pH of 7.0 at 25°C.

\*\* Assumes ammonium (NH<sub>4</sub><sup>\*</sup>) is the nitrogen source [in all other cases, nitrate (NO<sub>3</sub><sup>-</sup>) is the nitrogen source].

In the absence of oxygen and under neutral or alkaline pH. insoluble metal oxide species will be the predominant electron acceptors in the subsurface environment. An important factor in evaluating the availability of insoluble metal oxides as electron acceptors is the extent of microbial adhesion to the oxide surface. Utilization of an insoluble metal species as an electron acceptor requires that the microbial electron transport system be in intimate contact with the oxide surface for metal reduction to occur. In addition to microbial adhesion, the form of solid metal oxides also will affect their reduction rates. It has been reported that the more amorphous the metal oxide, the more easily it is reduced (Lovely et al., 1989). This is not surprising since the free energy change is a function of the randomness (or entropy) of the chemical environment.

In oxygen depleted acidic environments, nitrate and sulfate are often the predominant electron acceptors. In cases where there are noniimiting concentrations of free manganese and iron, the free manganese ions would be used preferentially followed by nitrate, free iron, then sulfate according to free energy calculations (Table 4).

The free energy estimations are consistent with the results reported by Lovely and Phillips (1988), who demonstrated that  $Fe^{+3}$  reduction will outcompete methanogens (carbon dioxide reducers) for organic matter. MnO<sub>2</sub> has been found to competitively inhibit iron reduction, which is not surprising since the energetics for manganese reduction are more favorable compared to iron (Table 4).

Free energy calculations of reaction only indicate the potential for a reaction to occur at a particular set of environmental conditions. Favorable kinetic conditions must also exist for the reaction to proceed at measurable time scales. Temperature and reaction activation energy are important considerations in evaluating kinetic conditions. In the present study, only the potential of a reaction to occur (e.g. free energy) is evaluated.

From microbial yield estimates, the utilization of free manganese (Mn<sup>44</sup>) as an electron acceptor during hetero-

trophic biodegradation of PAH compounds resulted in the largest microbial growth yield, followed by oxygen, nitrate, free iron ( $Fe^{-3}$ ). MnO<sub>2</sub>. FeOOH, sulfate, and carbon dioxide (Table 7). In regards to the electron donor, naphthalene mineralization resulted in the largest microbial yield relative to the three other PAH compounds evaluated. However, the microbial yield for naphthalene was consistently lower than that obtained during the mineralization of either glucose or methanol. Only benzoate (monoaromatic acid) resulted in microbial yields comparable to those found for PAH compounds.

Although the free energy change associated with anaerobic mineralization (CO2 as the electron acceptor) was negative and microbial yield estimations indicated potential heterotrophic growth using PAH compounds under anaerobic conditions, experimental evidence of PAH mineralization under anaerobic conditions has not been reported. Explanations for the difference between theoretical and experimental results can be found in evaluating the assumptions of the bioenergetic model. The bioenergetic model assumes that the energy transfer efficiency is 60% for all microorganisms evaluated. This is certainly not the case for all species, and a reduction of transfer efficiency to 20 or 30% results in a significant change in microbial yield estimations. The bioenergetic model assumes also that the microbial population is actively growing and, thus, maintenance energy can be neglected. Neglecting maintenance energy for aerobic systems may not result in a significant change in microbial yield estimates, but under anaerobic conditions, where most of the electron donor is released as methane (CH4), maintenance energy represents a significant portion of the energy captured by the cell.

Little is known regarding the maintenance energy requirements of anaerobic microorganisms. However, like all microbes, some minimal amount of energy is required to maintain osmotic regulation, regeneration of proteins and nucleic acids, molecular transport, etc. The absence of PAH mineralization under anaerobic conditions (Mihelcic and Luthy, 1988) suggests that the energy available from these bioreactions is insufficient to support microbial maintenance requirements.

#### Conclusions

An important aspect of site characterization for evaluation of bioremediation factors, in addition to identifying chemical pollutants present (potential electron donors), involves the evaluation of the: (1) type and amount of electron acceptors present, (2) chemical form(s) of the electron acceptors, and (3) free energy changes associated with electron transfer from electron donor to electron acceptor. A thermodynamic framework for evaluating the potential for heterotrophic PAH biodegradation in aerobic, anoxic, and methanogenic subsurface environments has been presented. Thermodynamically favorable conditions were shown to exist for the biodegradation of the PAHs under all redox conditions evaluated. The difference in free energy liberated during PAH degradation in the presence of oxygen, nitrate, and carbon dioxide supported experimental observations of Mihelcic and Luthy (1988). Microbial yield models predicted larger growth under conditions of higher energy yield. The use of aliphatic carbon sources (e.g., glucose and methanol) as electron donors led to a significantly greater microbial yield than the aromatic acid (e.g., benzoate) or PAH compounds.

Although microbial growth was predicted during heterotrophic PAH mineralization under sulfate reducing and methanogenic conditions, no experimental evidence has been reported to support this finding. Energy liberated from these reactions is not likely to be sufficient to support minimal microbial maintenance requirements. More study is required to quantify anaerobic microbial maintenance energy and to confirm its importance in microbial yield estimations. The thermodynamic framework presented for evaluating PAH degradation in subsurface environments provides a rational basis for site characterization activities and for assessment of potential mechanisms influencing biodegradation at a contaminated site.

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## LECTURE ILLUSTRATIONS

## OXIDATION — REDUCTION CHEMISTRY

- Introduction
- The electrochemical cell
- Measurement of Eh
- Eh-pH and pe-pH diagrams
- Oxidation and reduction conditions in natural waters
- Case history
- Summary

### NWWA

### **OXIDATION AND REDUCTION REACTIONS**

The chemical elements, C, N, O, S, Mn, and Fe undergo important oxidation-reduction, or redox reactions, in the subsurface. Other elements including Cr, Cu, As, Ag, Hg, Mo, Se, and U are influenced by redox reactions in contaminated soils and geologic strata. Sposito (1983) suggested that there are two ways in which redox reactions can influence the chemical forms of environmentally significant trace metals in the soils; first, through a direct change in the oxidation state of the trace metal itself. An example of this redox process is the oxidation of Cr(III) to Cr(VI) (Sposito, 1983). A second way in which redox reactions indirectly influence trace metals is through a change in the oxidation state of a different element contained in a ligand that can form chemical bonds with the metal. This redox effect is represented by the oxidation of C(II) to C(IV) in an organic ligand that can form a soluble complex with a trace metal cation in solution (Sposito, 1983).

Redox reactions generally are slow reactions in soil, because oxidation and reduction half-reactions do not couple well to one another (Sposito, 1983). Catalysis of redox reactions is mediated by microbial organisms, which increases the reaction rate of a redox reaction.

### **EXAMPLES OF OXIDATION AND REACTION REACTIONS**

### CARBON

 $CH_4 + 3H_2O = H_2CO_3 + 8H^+ + 8e^-$ 

 $CH_4 + 3H_2O = HCO_3 + 9H^+ + 8e^-$ 

 $CH_4 + 3H_2O = CO_3^{2-} + 10H^+ + 8e^-$ 

### HYDROGEN

 $2H_2O = O_2(g) + 4H^+ + 4e^-$ 

 $2H_2O = 2H_2(g) + O_2(g)$ 

 $H_2(g) = 2H^+ + 2e^-$ 

IRON

 $Fe^{2+} = Fe^{3+} + e^{-}$ 

 $Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + e^-$ 

 $FeCO_3 + 3H_2O = Fe(OH)_3 + HCO_3 + 2H^+ + e^-$ 

## **INTRODUCTION**

### **PURPOSE**

To provide an overview of oxidation-reduction (*redox*) equilibria as it may apply to natural waters.

Oxidation-reduction reactions control solubility of minerals or solid phases, influence adsorption processes, and control fate and transport of organic and inorganic species.

**EXAMPLES:** 

 $Cr^{3+} + 4H_2O = CrO_4^{2-} + 8H^+ + 3e^-$ 

 $Cr(III) \rightarrow Cr(VI)$ 

**Benzene Oxidation** 

 $C_6H_6 + 6O_2(aq) = 6CO_2(g) + 6H^+ + 6e^-$ 

 $C(-I) \rightarrow C(IV)$ 

## **OXIDATION-REDUCTION REACTIONS**

An *oxidation-reduction* (or *redox*) reaction is a chemical reaction in which electrons are transferred completely from one species to another.

The chemical species that loses electrons in this charge transfer process is called *oxidized*.

The chemical species receiving electrons is called *reduced*.

**EXAMPLE**: reduction half reaction

 $4FeOOH(s) + 12H^{+}(aq) + 4e^{-}(aq) = 4Fe^{2+} + 8H_{2}O$ 

Goethite-oxidized

Fe<sup>2+</sup>(aq)-reduced

### **COUPLED REDOX REACTION**

1. Oxidation half-reaction

**EXAMPLE:** 

 $CH_2O(aq) + 2H_2O = HCO_3^{-}(aq) + 5H^{+} + 4e^{-}(aq)$ 

CH<sub>2</sub>O(aq) -[C(0)]

 $HCO_3^{-}(aq) - [C(IV)]$ 

2. Reduction half-reaction

EXAMPLE:

 $4FeOOH(s) + 12H^{+}(aq) + 4e^{-}(aq) = 4Fe^{2+} + 8H_{2}O$ 

### **COUPLED REDOX REACTION**

 $4FeOOH(s) + 7H^{+}(aq) + CH_{2}O(aq) = 4Fe^{2+}(aq) + 6H_{2}O + HCO_{3}^{-}(aq)$ 

## **BALANCING REDOX REACTIONS**

For a monoatomic species, the oxidation state equals the valence.

### EXAMPLES:

K(I), Ca(II), Mg(II), O(-II), H(I), Ra(II), CI(-I)

For a molecule, the sum of the oxidation numbers of the constituent atoms equals the net charge expressed in units of protonic charge.

**EXAMPLES:** 

FeOOH(s); 3 + 2(-2) + 1 = 0

```
SO_4^{2-}(aq); 6 + 4(-2) = -2
```

 $H_2O(aq); 2(1) + -2 = 0$ 

OH<sup>-</sup>(aq); -2 + +1 = -1

## **BALANCING REDOX REACTIONS**

For a chemical bond in a molecule, the shareable, bonding electrons are assigned entirely to the more electronegative atom. If no difference in electronegativity exists, each atom receives half the bonding electrons.

**EXAMPLES:** 

 $C_6H_{12}O_6(aq); 6(O) + 12(1) + 6(-2) = 0$ 

N<sub>2</sub>(aq); 0

### **OXIDATION OF FORSTERITE**

### **OXIDATION REACTION**

 $(Mg, Fe)_2SiO_4 = 6e^- + 2Fe^{3+} + 2Mg^{2+} + SiO_4^{4-}$ 

### **REDUCTION REACTION**

 $6e^{-} + 1.5O_2(g) + 6H^+ = 3H_2O$ 

# COUPLED REACTION $(Mg, Fe)_2SiO_4 + 1.5O_2(g) + 6H^+$ $= 2Fe^{3+} + 2Mg^{2+} + SiO_4^{4-} + 3H_2O$ or,

$$(Mg, Fe)_2 SiO_4 + 1.5O_2(g) + 3H_2O + 4H^+$$
  
= 2Fe(OH)<sub>3</sub> + 2Mg<sup>2+</sup> + Si(OH)<sub>4</sub><sup>0</sup>

### **CLASS EXERCISE**

BALANCE THE FOLLOWING OXIDIZING-HALF REACTIONS [hint Fe(II,III)]:

- 1.  $FeCl_2(aq) = Fe + Cl^+ e^-$
- 2.  $Fe^{2+} + H_2O = Fe(OH)$  (s)  $+ H^+ + e^-$
- 3.  $CH_4(g) + H_2O = HCO_3^{-} + H^+ + e^{-}$

BALANCE THE FOLLOWING REDUCING-HALF REACTIONS [hint S(-II,VI)]:

- 4.  $HSO_4^- + H^+ + e^- = H_2S^0(aq) + 4H_2O$
- 5.  $SO_4^{2-} + \__H^+ + \__e^- = S^-(aq) + 4H_2O$

EXTRA CREDIT COMBINE REACTION 2 WITH REACTION 5 AND WRITE A COUPLED REDOX REACTION.

		pe <sup>o</sup> = log K
HYDROGEN		
	$H^* + e^- = \frac{1}{2}H_2(g)$	0
OXYGEN		
	$\frac{1}{2}O_3(g) + H^* + e^- = \frac{1}{2}O_2(g) + \frac{1}{2}H_2O$	+35.1
	$\frac{1}{4}O_2(g) + H^* + e^- = \frac{1}{2}H_2O$	+20.75
	$\frac{1}{2}H_2O_2 + H^* + e^- = H_2O$	+ 30.0
	(Note also $HO_2^- + H^* = H_2O$ ; log $K = 11.6$ )	
NITROGEN		
	$NO_3^- + 2H^+ + e^- = \frac{1}{2}N_2O_4(g) + H_2O$	+13.6
	(Note: $N_2O_4(g) = 2NO_2(g)$ ; log $K = -0.47$ )	
	$\frac{1}{2}$ NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> + e <sup>-</sup> = $\frac{1}{2}$ NO <sub>2</sub> <sup>-</sup> + $\frac{1}{2}$ H <sub>2</sub> O	+14.15
	(Note $NO_2^- + H^+ = HNO_2$ ; log $K = 3.35$ )	
	$\frac{1}{3}NO_{3}^{-} + \frac{4}{3}H^{+} + e^{-} = \frac{1}{3}NO(g) + \frac{2}{3}H_{2}O$	+ 16.15
	$\frac{1}{4}$ NO <sub>3</sub> <sup>-</sup> + $\frac{3}{4}$ H <sup>+</sup> + $e^- = \frac{1}{6}$ N <sub>2</sub> O(g) + $\frac{5}{6}$ H <sub>2</sub> O	+ 18.9
	$\frac{1}{5}$ NO <sub>3</sub> <sup>-</sup> + $\frac{6}{5}$ H <sup>+</sup> + $e^- = \frac{1}{10}$ N <sub>2</sub> (g) + $\frac{3}{5}$ H <sub>2</sub> O	+21.05
	$\frac{1}{8}NO_{3}^{-} + \frac{5}{4}H^{+} + e^{-} = \frac{1}{8}NH_{4}^{+} + \frac{3}{8}H_{2}O$	+14.9
SULFUR		
	$\frac{1}{2}$ SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> + e <sup>-</sup> = $\frac{1}{2}$ SO <sub>5</sub> <sup>2-</sup> + $\frac{1}{2}$ H <sub>2</sub> O	-1.65
	[Note also $(SO_3^2 + H^* = HSO_3^2; \log K \cong 7)$ ]	
	$\frac{1}{4}$ SO <sup>2-</sup> <sub>4</sub> + $\frac{5}{4}$ H <sup>*</sup> + $e^- = \frac{1}{8}$ S <sub>2</sub> O <sup>2-</sup> <sub>3</sub> + $\frac{5}{8}$ H <sub>2</sub> O	+4.85
	$\frac{1}{6}$ SO <sub>4</sub> <sup>2-</sup> + $\frac{4}{3}$ H <sup>*</sup> + $e^- = \frac{1}{46}$ S <sup>0</sup> <sub>8</sub> (s. ort.) + $\frac{2}{3}$ H <sub>2</sub> O	+6.03
	[Note also $\frac{1}{8}S_8^0(s. \text{ ort.}) = \frac{1}{8}S_8^0(s. \text{ col.}); \log K = -0.6$ ]	
	$\frac{3}{19}$ SO <sub>4</sub> <sup>2-</sup> + $\frac{24}{19}$ H <sup>*</sup> + $e^- = \frac{1}{38}$ S <sub>6</sub> <sup>2-</sup> + $\frac{12}{19}$ H <sub>2</sub> O	+5.41
	$\frac{5}{32}$ SO <sub>4</sub> <sup>2-</sup> + $\frac{5}{4}$ H <sup>+</sup> + $e^- = \frac{1}{32}$ S <sub>5</sub> <sup>2-</sup> + $\frac{5}{8}$ H <sub>2</sub> O	+5.29
	(Note also $S_5^{2^-} + H^* = HS_5; \log K = 6.1$ )	
	$\frac{2}{13}SO_4^{2-} + \frac{16}{13}H^* + e^- = \frac{1}{26}S_4^{2-} + \frac{8}{13}H_2O$	+5.12
	(Note also $S_4^{2^-} + H^* = HS_4$ ; log $K = 7.0$ )	
	$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^4 + e^- = \frac{1}{8}H_2S(aq) + \frac{1}{2}H_2O$	+5.13
	(Note also $H_2S(g) = H_2S(aq)$ ; log $K_h = 1.0$ , and other	
	acid-base, coordination, and precipitation reactions)	
TRACE METALS		
Cr	$\frac{1}{3}\text{HCrO}_{4}^{-} + \frac{7}{3}\text{H}^{*} + e^{-} = \frac{1}{3}\text{Cr}^{3*} + \frac{4}{3}\text{H}_{2}\text{O}$	+20.2
	(Note HCrO <sub>4</sub> <sup>-</sup> = H <sup>*</sup> + $\frac{1}{2}$ Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + $\frac{1}{2}$ H <sub>2</sub> O, log K = -15;	
	$HCrO_4^- = H^+ + CrO_4^{2-}$ , log $K = -6.5$ ; and various Cr(III)	
Ma	precipitation and coordination reactions)	
Min	$\frac{1}{5}MnO_4^- + \frac{8}{5}H^+ + e^- = \frac{1}{5}Mn^{2+} + \frac{4}{5}H_2O$	+25.5
	$\frac{1}{2}$ MnO <sub>2</sub> (s) + 2H <sup>+</sup> + $e^{-} = \frac{1}{2}$ Mn <sup>2+</sup> + H <sub>2</sub> O	+20.8

### Some important half redox reactions\*

- el -e-

(Continued)

		pe° = log K
TRACE METALS (cont.)		
Fc	$Fc^{3*} + e^- = Fc^{2*}$	+13.0
	$\frac{1}{2}$ Fc <sup>2+</sup> + $e^- = \frac{1}{2}$ Fc(s)	-7.5
	$\frac{1}{2}$ Fe <sub>3</sub> O <sub>4</sub> (s) + 4H <sup>•</sup> + $e^{-} = \frac{3}{2}$ Fe <sup>2•</sup> + 2H <sub>2</sub> O	+ 16.6
Со	$Co(OH)_3(s) + 3H^2 + e^2 = Co^{2^2} + 3H_2O$	+29.5
	$\frac{1}{2}$ Co <sub>3</sub> O <sub>4</sub> (s) + 4H <sup>*</sup> + $e^{-} = \frac{3}{2}$ Co <sup>2*</sup> + 2H <sub>2</sub> O	+31.4
Cu	$\mathrm{Cu}^{2*} + e^{-} = \mathrm{Cu}^{*}$	+2.6
	$\frac{1}{2}Cu^{2*} + e^{-} = Cu(s)$	-5.7
Se	$\frac{1}{2}$ SeO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup> + $e^- = \frac{1}{2}$ H <sub>2</sub> SeO <sub>3</sub> + $\frac{1}{2}$ H <sub>2</sub> O	+ 19.4
	$\frac{1}{4}$ H <sub>2</sub> SeO <sub>3</sub> + H <sup>+</sup> + $e^- = \frac{1}{4}$ Se(s) + $\frac{3}{4}$ H <sub>2</sub> O	+12.5
	$\frac{1}{2}$ Se(s) + H <sup>*</sup> + $e^- = \frac{1}{2}$ H <sub>2</sub> Se	-6.7
	(Note also $H_2Se = H^* + HSe^-$ , log $K = -3.9$ ; $H_2SeO_3 = H^*$ + HSeO <sub>5</sub> , log $K = -2.4$ ; HSeO <sub>5</sub> = H <sup>*</sup> + SeO <sub>5</sub> <sup>2-</sup> , log $K = -7.9$ ; SeO <sub>4</sub> <sup>2-</sup> + H <sup>*</sup> = HSeO <sub>4</sub> <sup>2</sup> , log $K = +1.7$ )	
Ag	$AgCl(s) + e^{-} = Ag(s) + Cl$	+3.76
	$Ag^* + e^- = Ag(s)$	-13.5
Hg	$\frac{1}{2} Hg^{2^{*}} + e^{-} = Hg(1)$	-14.4
	$Hg^{2*} + e^{-} = \frac{1}{2}Hg_2^{2*}$	+15.4
РЪ	$\frac{1}{2} PbO_2 + 2H^* + e^- = \frac{1}{2} Pb^{2*} + H_2O$ (Note many other reactions for Mn, Fe, Co, Cu, Se, Ag, Hg, Pb)	+24.6

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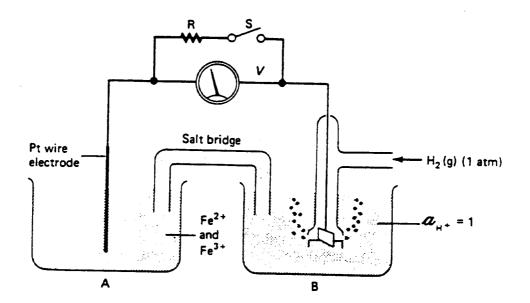
.

Element and		
oxidate state in brackets	Example	
C(+IV)	HCO <sup>-</sup> <sub>3</sub> , CO <sup>2-</sup>	
C(O) C(-IV)	CH₂O, C CH₄	
S( 1)		
Cr(+IV)	$CrO_4^{2-}, Cr_2O_7^{2-}$	
Cr(+III)	Cr <sup>3+</sup> , Cr(OII) <sub>3</sub>	
Fe(+III)	Fe <sup>3+</sup> , Fe(OH) <sub>3</sub>	
Fe(+II)	Fe <sup>2+</sup>	
N(+V)	NO; very	mobile
N(+III)	NO;	
N(O)	N	
N(-III)	NH <sup>+</sup> , NH <sub>3</sub>	
S(+VI)	SO <sub>4</sub> -	
S(+V)	S <sub>2</sub> O <sub>6</sub> <sup>2-</sup>	
S(+II)	$S_2O_3^{2-}$	
S(-II)	H <sub>2</sub> S, HS <sup>-</sup>	

Some elements found with more than one oxidation state and examples of ions or solids formed from those elements\*

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All redox reactions transfer electrons and involve elements with more than one oxidation number. Listed in the table are some of the more important of these elements, their typical oxidation states, and some of the ions and solids that form. A host of trace metals not included in the table also have variable oxidation numbers. APPENDIX



# THE ELECTROCHEMICAL CELL

- Two half-cells A and B connected by a saltbridge
- Half-cell A platinum wire acts as an inert means of transferring electrons to or from solution
- Electrode reaction:  $Fe^{2+} = Fe^{3+} + e^{-1}$
- Overall reaction:  $Fe^{3+} + \frac{1}{2}H_2 = Fe^{2+} + H^+$

pe and Eh

Eh refers to: Potential of the electrode in halfcell and potential is measured relative to she

Electron activity can be expressed as

pe ( =  $-\log_{10} a_{e}^{-}$ )

By analogy with

 $pH(-\log_{10}a_{H^{+}})$ 

$$pe = \frac{F}{2.303 \text{ RT}} \text{ Eh}$$

### Where

- F = Faraday's constant (23.06 kcal/volt-gram equivalent)
- R = Gas constant (1.987 cal/deg mol)
- T = Absolute temperature

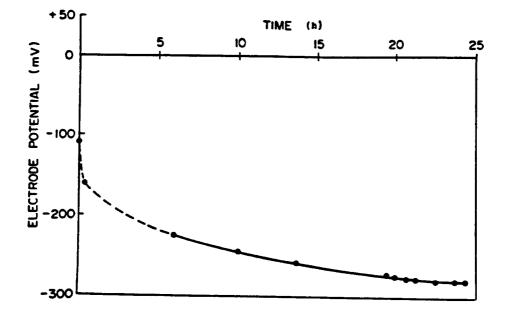
2.303 conversion from natural to base 10 logarithms

At 25C PE = 16.9 Eh Eh = 0.0592 pe

NWWA

## **MEASUREMENT OF Eh**

- Combination platinum and reference electrode
- The reference electrode is usually calomel (Hg<sub>2</sub> Cl<sub>2</sub>) or Ag/AgCl
- The Eh measurement is usually that of a mixed potential composed of more than one redox couple



Variation of electrode potential with time for an undisturbed clayey sample from the Sarnia Landfill, Ontario, Canada (Yanful, et al., 1988).

Reducing conditions exist beneath the landfill, which are probably the result of microbial activity.

# Eh — pH DIAGRAMS

Eh — pH diagrams are a convenient way of displaying stability relationships where equilibrium redox reactions are involved.

It must be remembered that departures from equilibrium are common in natural waters.

#### **Systems to Consider**

Water Iron Carbon

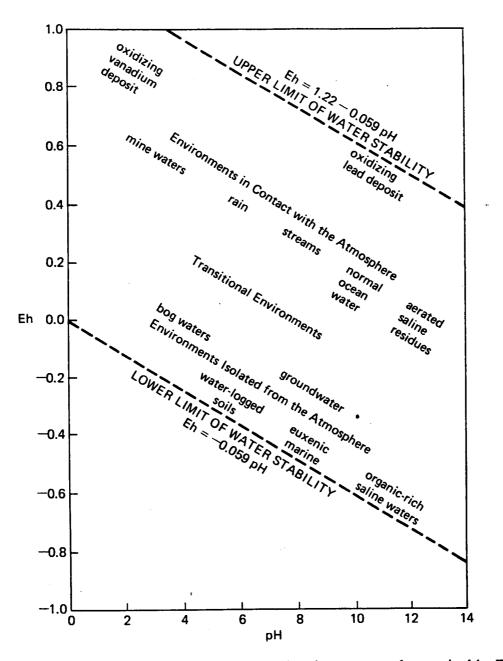
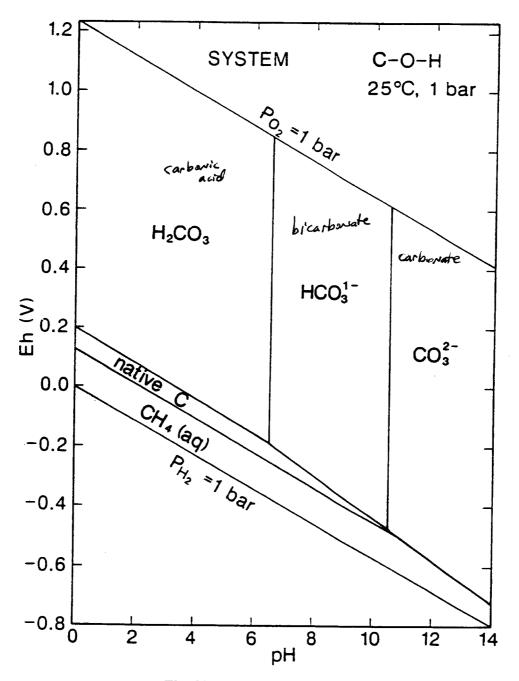


Figure 4-3 Approximate position of some natural environments as characterized by Eh and pH. (After Garrels and Christ, Solutions, Minerals, and Equilibria, Freeman-Cooper, San Francisco, p. 381.)



Eh-pH diagram for part of the system C-O-H. The assumed activity of dissolved  $C = 10^{-3}$ .

Valence states for carbon include -4, -3, -2, -1, 0, 1, 2, and 4. The valence states of carbon in methane (CH<sub>4</sub>) is -4, in CH<sub>2</sub>O = 0, and H<sub>2</sub>CO<sub>3</sub>O, HCO<sub>3</sub>, and CO<sub>3</sub><sup>2-</sup> = + 4. Methane is stable under relatively reducing conditions and H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub>, and CO<sub>3</sub><sup>2-</sup> are stable under relatively oxidizing conditions. (Brookins, 1988).

#### OXIDATION - REDUCTION REACTIONS OF ORGANIC COMPOUNDS

The concept of chemical oxidation - reduction (redox) is more easily understood for simple inorganic: reactions than for redox reactions involving organics. In soil, redox reactions involving both inorganic and organic species are important. Organic oxidation reactions frequently involve a gain of oxygen and a loss of hydrogen atoms. The reverse is true for reduction reactions.

The table below provides a summary of the relative oxidation states of several functional groups. Conversion of a functional group into one in a higher oxidation state category characterizes oxidation of the original group. Reduction is defined by the conversion to a group in a lower oxidation state.

#### RELATIVE OXIDATION STATES

LEAST OXIDIZED			MOST OXIDIZED	
RH	ROH	RC (O) R	RCOOH	∞ <sub>2</sub>
	RCl	(R) 20012	RC (O) NH <sub>2</sub>	ccl <sub>4</sub>
	RNH <sub>2</sub>	- C ≡ C -	RCC13	
	Cl = C + H	H C Cl		Cl C = C H
	benzene			<sup>CO</sup> 2
	toluene	various intermediates		co <sub>2</sub> .
	xylene	°°2		

#### INCREASING OXIDATION STATES

SOURCE: March (1977).

An oxidation cannot occur without a reduction. In complex organic reactions, the mechanism involves the exchange of an equal amount or number of electrons. For example, the oxidation of benzene to carbon dioxide and  $H_2O$  by oxygen can be written as:

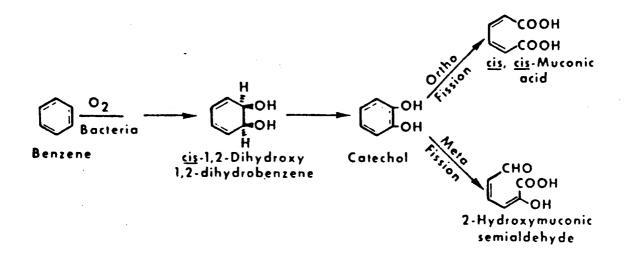
$$C_6 H_6 + 12 H_2 O = 6CO_2 + 30H^+ + 30e^-$$
 an oxidation  
 $7.50_2 + 30H^+ 30e^- = 15 H_2 O$  a reduction  
 $C_6 H_6 + 7.50_2 = 6CO_2 + 3H_2 O$ 

In many cases, half reactions can be written that do not describe the real mechanism but are only a convenient "bookkeeping" method to correctly balance the net reaction as is the case for the oxidation of benzene shown above.

Evidence for the existence of redox reactions in soil come from the identification of reaction products that are characteristic of redox reactions. Very little is known, however, about the oxidants and reductants or reaction mechanisms and kinetics of importance in soil. Oxygen  $(O_2)$  is probably the most important oxidant in soils. Atmospheric and soil oxygen are capable of directly oxidizing many organic and inorganic compounds. The rate of oxidation, however, is usually slow.

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A more detailed reaction path for benzene oxidation in presence of bacteria (Pseudomonas putida 39/D) is given below. Carbon dioxide is the final compound produced via <u>cis</u>, <u>cis</u>-Muconic acid and 2-Hydroxymuconic semialdehyde.



As organic compounds such as aromatic hydrocarbons become oxidized, the electrons that are lost by the organics can be gained by minerals. The minerals that can undergo chemical reduction (gain of electrons) include iron oxyhydroxides and manganese oxyhydroxides. Organic oxidation products can in addition complex or bind on the mineral surface, which causes the solubility of the mineral to increase. The mineral begins to undergo dissolution caused by chemical reduction. An example of an organic and inorganic oxidation - reduction reaction is:

 $L + soil Fe(OH)_3 + H^+ + e^- = Fe(II)L + 3H_2O$ 

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where L = catechol (an oxidation product of benzene); soil  $Fe(OH)_{3}^{=}$ soild compound; Fe(II)L = iron-organic complex. The  $Log_{10}$  K (stability constant) for the above reaction is 23.87. Reduction of soil  $Fe(OH)_{3}$ without organic compounds is:

soil  $Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$ 

and the  $\log_{10}$  K (equilibrium constant) for this reaction is 15.92. Organic complexation can increase solubility of Fe(OH)<sub>3</sub> by approximately eight orders of magnitude according to the above reactions. Such reactions may explain why concentrations of iron are elevated above background within dissolved hydrocarbon plumes.

# REDOX REACTIONS OF ORGANIC COMPOUNDS

OXIDATION REACTIONS WITH ORGANIC COMPOUNDS FREQUENTLY INVOLVE A GAIN OF OXYGEN ATOMS AND A LOSS OF HYDROGEN ATOMS (PROTONS).

**EXAMPLE OF BENZENE OXIDATION** 

 $C_6H_6 + O_2 + BACTERIA \rightarrow C_6H_8O_2$  (CIS-1,2 - DIHYDROXY 1, 2 - DIHYROBENZENE) +

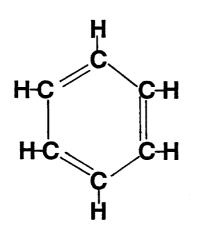
 $C_6H_6O_2$  (CATECHOL)  $\rightarrow$   $C_6H_6O_4$  (<u>CIS</u>, <u>CIS</u> - MUCONIC ACID)

**OVERALL REDOX REACTION** 

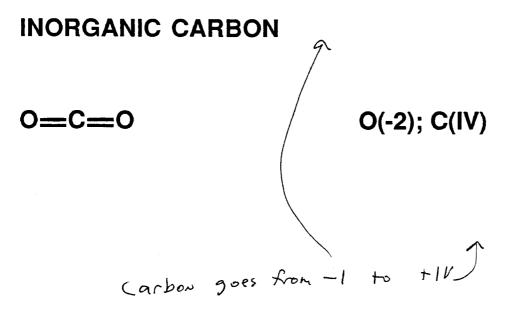
 $C_6H_6 + 7.5O_2 + BACTERIA = 6CO_2 + 3H_2O$  $\int \int ben rent end$ 

### OXIDATION STATES OF CARBON IN SELECTED ORGANIC COMPOUNDS

BENZENE



C(-I); H(I)



# REDOX REACTIONS OF ORGANIC COMPOUNDS

REDUCTION REACTIONS WITH ORGANIC COMPOUNDS FREQUENTLY INVOLVE A LOSS OF OXYGEN AND HALOGEN (CI, Br) ATOMS AND A GAIN OF HYDROGEN ATOMS.

#### EXAMPLES OF REDUCTIVE DEHALOGENATION REACTIONS WITH TETRACHLOROETHENE

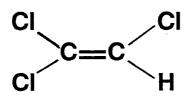
tetradbroetheve

LOSS OF CHLORINE ATOMS

GAIN OF HYDROGEN ATOMS

# OXIDATION STATES OF CARBON IN SELECTED ORGANIC COMPOUNDS

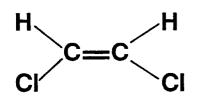
#### TRICHLOROETHENE



C(II); C(0)

CI(-I); H(I)

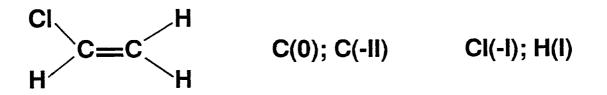
#### 1,2 CIS - DICHLOROETHENE



C(0); C(0)

Cl(-l); H(l)

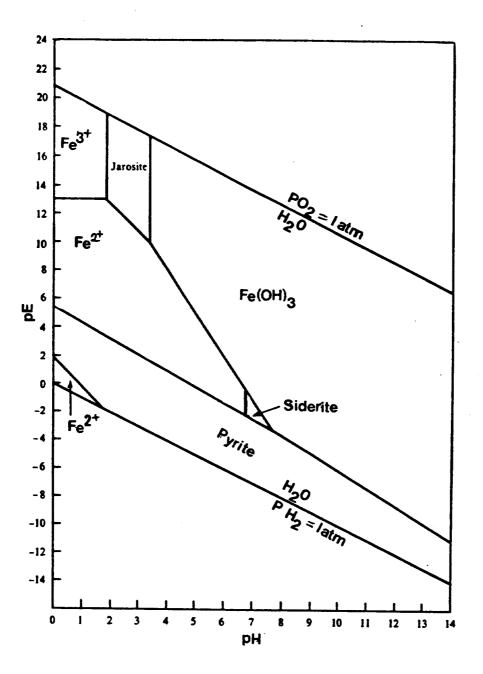
#### **VINYL CHLORIDE**



### SOME REDOX PROCESSES THAT CONSUME ORGANIC MATTER AND REDUCE INORGANIC COMPOUNDS IN GROUND WATER

Process	Equation*		
Denitrification <sup>†</sup>	$CH_2O + \frac{4}{5}NO_{\bar{3}} = \frac{2}{5}N_2(g) + HCO_{\bar{3}} + \frac{1}{5}H^+ + \frac{2}{5}H_2O$		
Manganese (IV) reduction $CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3 + 2H_2O$			
Iron(III) reduction	$CH_{2}O + 4Fe(OH)_{3}(s) + 7H^{+} = 4Fe^{2+} + HCO_{\bar{3}} + 10H_{2}O$		
Sulfate reduction	$CH_2O + \frac{1}{2}SO_4^{2-} = \frac{1}{2}HS^- + HCO_{\bar{3}} + \frac{1}{2}H^+$		
Methane fermentation	$CH_2O + \frac{1}{2}H_2O = \frac{1}{2}CH_4 + \frac{1}{2}HCO_{\bar{3}} + \frac{1}{2}H^+$		

\*(g), gaseous or dissolved form; (s), solid
 †CH<sub>2</sub>O represents organic matter; other organic compounds can also be oxidized
 SOURCE: Freeze and Cherry, 1979



A pE-pH diagram for selected iron minerals at 25°C, assuming activites of  $10^{-4}$  for dissolved iron,  $10^{-4}$  for dissolved potassium, and  $10^{-2}$  for dissolved sulfur, and assuming  $P_{CO2} = 10^{-2atm}$ .

Oxidation of pyrite generates high concentrations of Fe and an acidic pH. Reactions describing pyrite oxidation are:

$$FeS_{2} + 3.50_{2} + H_{2}O = Fe^{2+} + 2SO_{4}^{2-} + 2H^{+}$$
$$Fe^{2+} + 0.250_{2} + 2.5H_{2}O = Fe (OH)_{3} + 2H^{+}$$

Acidification of water samples for metal analysis puts all the metals in solution, for example Fe (Fe<sup>2+</sup> and Fe<sup>3+</sup>), to prevent precipitation of metals.

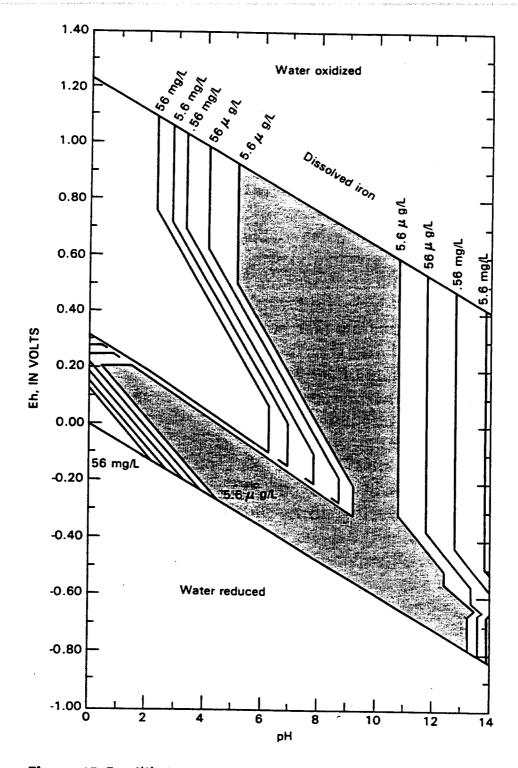


Figure 15. Equilibrium activity of dissolved iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as  $SO_4^2$ , and carbon dioxide species 61 mg/L as  $HCO_3^2$ .

THIS FIGURE SHOWS VARIATION OF IRON CONCENTRA-TIONS WITH RESPECT TO STABILITY FIELDS OF IRON SOLIDS (Fe(OH)<sub>3</sub>, FeO, FeS<sub>2</sub>, and FeS). INCREASING CONCENTRA-TIONS OF DISSOLVED IRON RESULT IN EXPANSION OF STABILITY FIELDS FOR SOLID PHASES.

## EXAMPLE OF WATER QUALITY ANALYSES

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Species/Parameter	Concentration (mg/L)	
Silica	<u> </u>	
Iron	10	
Manganese		
Calcium	8.8	
Magnesium	8.4	
Sodium	34	
Potassium	2.9	
Bicarbonate	65	
Sulfate	71	
Chloride	2.0	
Dissolved Solids	187	
pH	6.4	

Location: Marysville, Tennessee

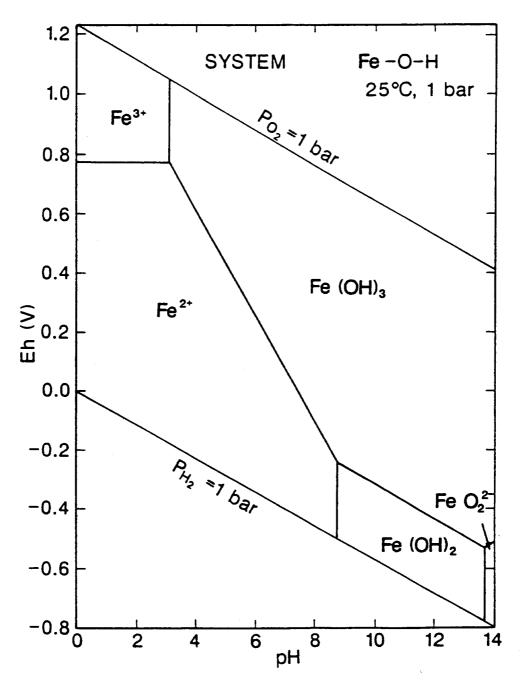
THIS ANALYSIS TYPIFIES IRON-CONTAINING GROUND WATER WHERE A PYRITE-OXIDATION MECHANISM IS PLAUSIBLE. AS OXIDATION OF PYRITE OCCURS, HYDROGEN IONS ARE RELEASED TO SOLUTION, AS WELL AS FERRIC IRON WHICH MAY RESULT IN AN ACIDIC PH.

#### EXAMPLE OF WATER QUALITY ANALYSES

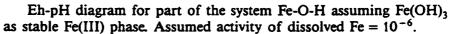
Species/Parameter	Concentration (mg/L)
Silica	30
Iron is being Manganasa	reduced t 56
Manganese	3.4
Calcium	101
Magnesium	20
Sodium	223
Potassium	12
Bicarbonate	869
Sulfate	131 "
Chloride	98
<b>Dissolved Solids</b>	1540
рН	7.14
Eh (mV) - reducing env.	<del></del>

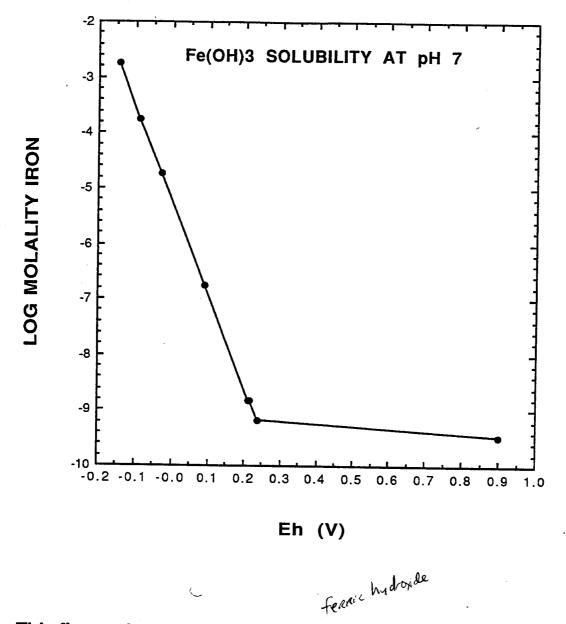
#### Location: Albuquerque, New Mexico

THE ABOVE ANALYSIS IS FROM A GROUND WATER SAMPLE FROM AN ALLUVIAL AQUIFER CONTAMINATED FROM UNLEADED GASOLINE. CHEMICAL REDUCTION OF HYDROUS IRON OXIDES BY OXIDATION (BIODEGRADATION) OF ORGANIC COMPOUNDS HAS OCCURRED. FERROUS IRON (Fe<sup>2+</sup>) IS MOBILE UNDER RELATIVELY REDUCING CONDITIONS IN THE ABSENCE OF SULFIDE AND AT LOW CONCENTRATIONS OF BICARBONATE. ŝ.



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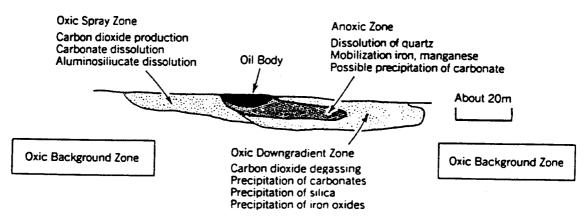




This figure shows the solubility of  $Fe(OH)_3$  as a function of Eh at pH 7. The solubility curve was calculated using the geochemical computer code, PHREEQE with the following dissolution reaction:

 $Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O;$  Log K = 15.70.

This reaction helps quantify dissolution of  $Fe(OH)_3$  under reducing conditions. For example, below Eh values of 0.2 V, at pH 7, concentrations of Fe are predicted to increase 63 times per 0.1 V decrease in Eh. Precipitation of  $Fe(OH)_2$  occurs at pH 8.6 according to the previous Eh-pH diagram.



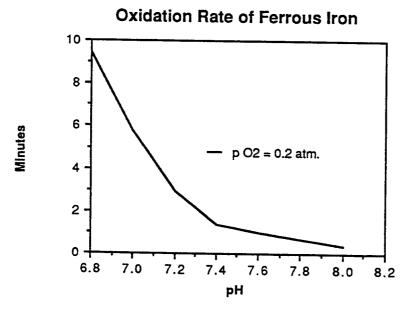
Redox environments related to a crude oil spill at Bemidji, Minnesota (from Siegel, 1987).

Based on detailed studies of major ions, some trace elements. pH, Eh, and dissolved oxygen, Siegel (1987) defined four redox environments related to a pipeline spill at Benidji, Minnesota. These processes are shown in the above figure. This study shows the importance of characterizing aquifer materials as well as the water chemistry, including inorganic and organic solutes. Microbial degradation was shown to be dominant process for removing organic contaminants from solution.

Iron concentrations in ground water containing dissolved petroleum products can be substantially increased by chemical reduction involving ferric oxyhydroxides and complexation reactions with organic ligands. Modeling of the chemical reactions along the ground-water flow path was attempted by determining the equilibrium state of ground water by using the geochemical code, WATEQFC. The saturation indices (S.I. =  $Log_{10}$  activity product/solubility product) of waters with respect to calcite, ferric hydroxide, and PCO<sub>2</sub> are given below. Iron concentrations may be controlled by ferric hydroxide upgradient from a gasoline station in Albuquerque, New Mexico. The SI for ferric hydroxide calculated from an upgradient water sample is 0.28, which implies that equilibrium may occur. Ferric hydroxide, however becomes progressively unstable along the ground-water flow path in response to a declining Eh. The PCO<sub>2</sub> increases downgradient due to the oxidation of organic compounds (benzene, toluene, xylenes). Reduction of ferric hydroxide in the presence of organic-rich (gasoline contaminated) ground water is given by:

 $11H^+ + CH_2 + 6Fe(OH)_3 = 6Fe^{2+} + 15H_2O + HCO3^-$ .

Parameter and Species	Upgradient	Source Area	Downgradient	
рН	7.40	7.14	7.22	
Eh (mV)	-115	-150	-120	
Fe (OH) <sub>3</sub>	0.28	-1.07	0.38	
Calcite	0.35	0.41	-0.19	
Total Fe (mg/L)	0.3	56	34	
Log <sub>10</sub> PCO <sub>2</sub> (atm)	-1.88	-1.26	-2.01	



This figure shows that the oxidation rate of ferrous iron is much faster at higher pH values. Aeration caused by sampling methods will cause less chemical alteration at a pH of 6.8 than a pH of 7.3.

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# SUMMARY OF CARBON REDOX CHEMISTRY

Carbon (IV) species ( $H_2CO_3^0$ ,  $HCO_3^-$ , and  $CO_3^{2-}$ ) are stable under oxidizing conditions, whereas carbon (-IV, -III, -II, -I, 0, I, II, III) species (CH<sub>4</sub>(aq), trichloroethene, and benzene) are stable under reducing conditions conditions.

As aromatic species, such as benzene, become oxidized or degraded to  $CO_2(g)$ , dissolved oxygen becomes reduced to  $H_2O$ . The aqueous solution then becomes depleted in dissolved oxygen and reducing conditions can prevail.

Microbes often mediate or control reaction rates for redox processes involving carbon.

**Occurrences** 

Hydrocarbon plumes

Landfills

**Chlorinated solvent plumes** 

# SUMMARY OF IRON REDOX CHEMISTRY

Iron (III) species  $(Fe(OH)_3(s), Fe^{3+}, and Fe(OH)_4^-)$ are stable under oxidizing conditions, whereas Fe(II) species (FeSO<sub>4</sub>(aq), FeS<sub>2</sub>(s), FeCO<sub>3</sub>(s)) are stable under reducing conditions.

Oxidation of pyrite results in acidic conditions and Fe(II) oxidizes to Fe(III) aqueous and solid phases.

As iron-bearing solids such as  $Fe(OH)_3(s)$  become reduced to Fe(II) species, the solid dissolves and concentrations of iron increase under reducing conditions.

Ferrous iron (Fe<sup>2+</sup>) tends to be mobile under reducing conditions in the absence of hydrogen sulfide.

Microbes often mediate or control reaction rates for redox processes involving iron.

# SUMMARY OF IRON REDOX CHEMISTRY

**Occurrences of elevated iron concentrations** 

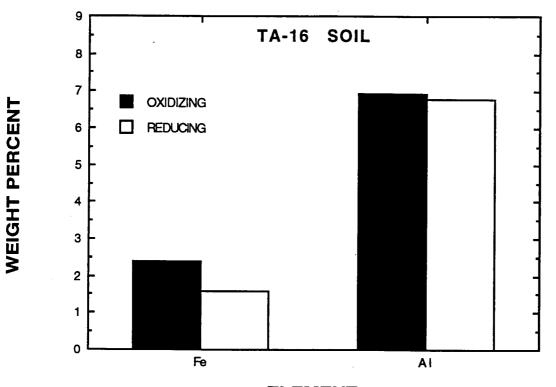
Hydrocarbon plumes

Landfills

**Chlorinated solvent plumes** 

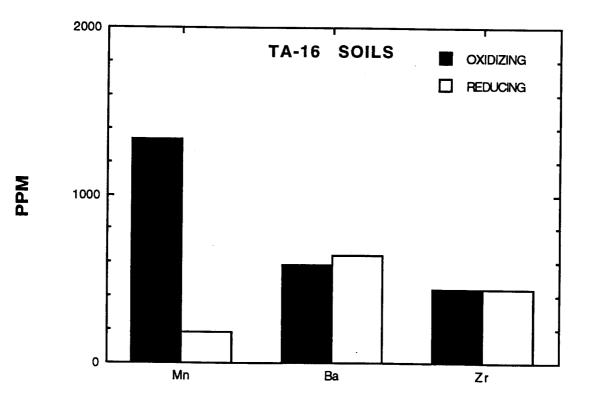
Acid-mine drainage

Natural organic-rich environments



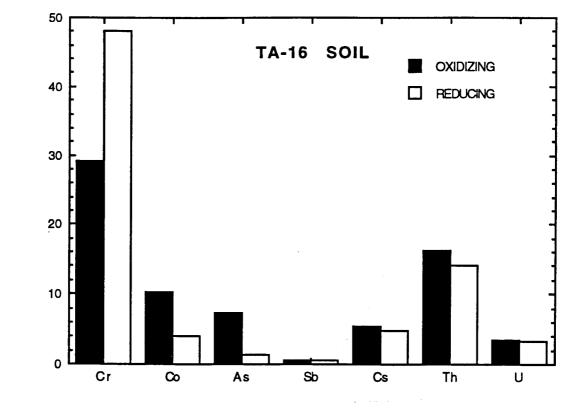
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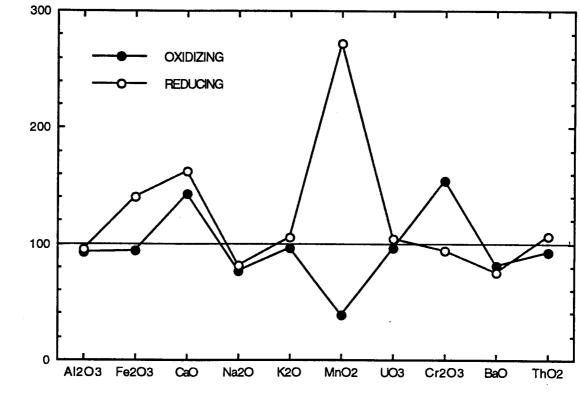


#### ELEMENT

5-62A



**ELEMENT** GAIN-LOSS DIAGRAM FOR REDOX ZONE, TA-16 SOIL



МЧЧ

% OXIDE, BASE COLLUVIUM)/ % OXIDE, REDOX ZONE) X 100

₩T ₩T

OXIDE

5-62B

# OXIDATION AND REDUCTION CONDITIONS IN NATURAL WATERS

**Redox Buffering** 

Buffering refers to the ability of a system to maintain a particular condition when it is perturbed

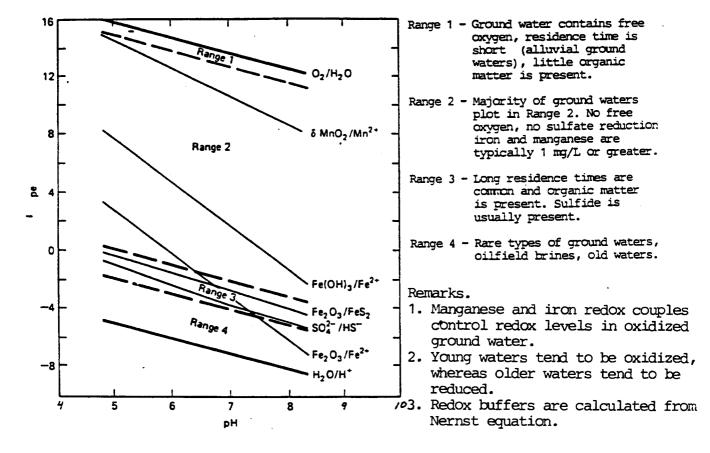
Example:  $NH_4^+ / NO_3^-$  redox couple

 $NH_4^+ + 3H_2O = NO_3^- + 8e^- + 10 H^+$ 

Log K = -119.1

at pH 7

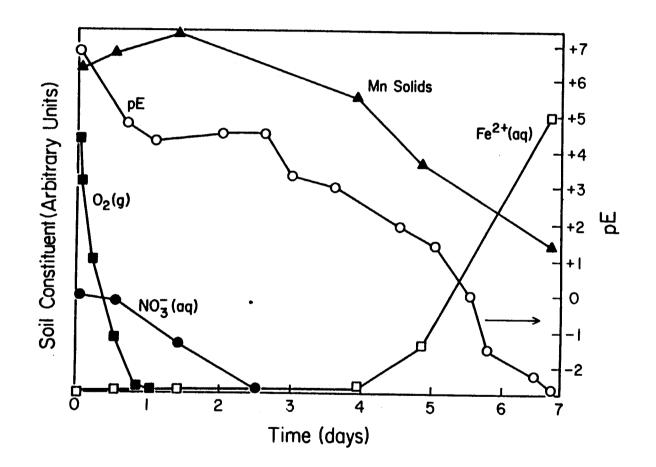
```
Eh = 0.36 V
pe = 6.1
```



Positions of redox ranges discussed in the text (Drever, 1982)

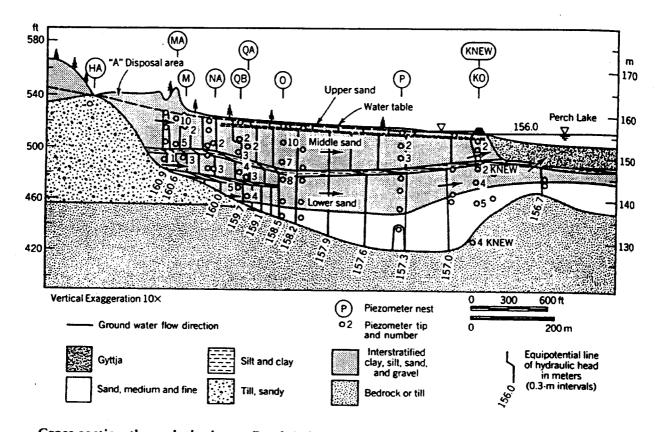
Some possible redox buffers in a groundwater system. Solid/solution boundaries are drawn for activity of solute =  $10^{-6}$ .

**FIG. 6.3** Relative changes in  $O_2$ ,  $NO_3^-$ , Mn(IV), and Mn(III) solid phases, and Fe(II) content of a soil with time elapsed after flooding. Changes in pE are also shown and labeled on the right side. [Data from F. T. Turner and W. H. Patrick, Chemical changes in waterlogged soils as a result of oxygen depletion, *Trans. IX Congress, Int. Soil Sci. Soc.* (Adelaide, Australia) 4:53-65 (1968).]

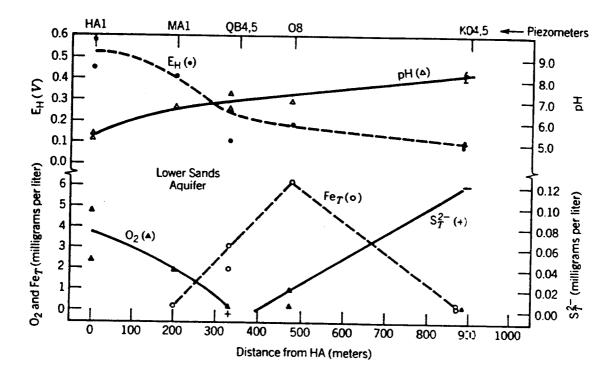


# IMPORTANT VARIABLES CONTROLLING REDOX

- The oxygen content of recharge water
- The distribution and reactivity of organic matter and other potential reductants
- The distribution of potential redox buffers (MnO<sub>2</sub>, Fe<sub>2</sub> O<sub>3</sub>, Fe(OH)<sub>3</sub>)
- The circulation rate of ground water



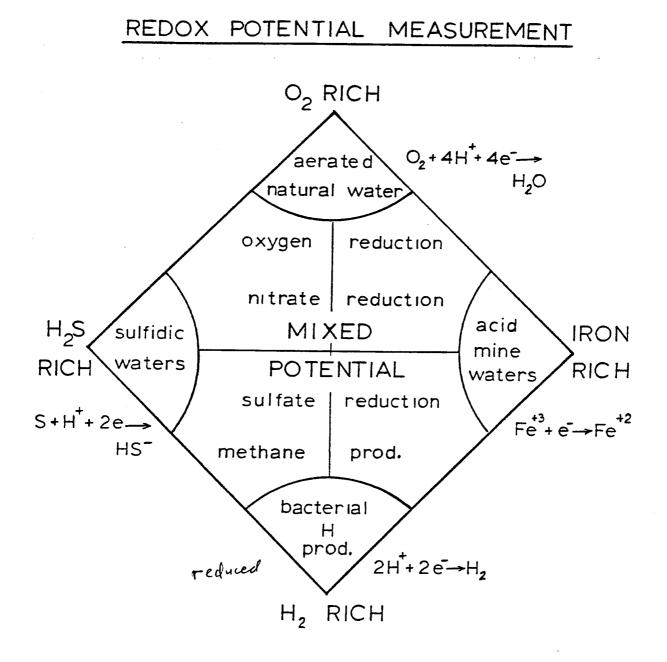
Cross section through the lower Perch Lake basin aquifer at Chalk River Nuclear Laboratories, Canada, showing equipotential lines, piezometer tips, and the position of the water table. Hydraulic head measurements averaged over the period of 1973–1975 (from Jackson and Patterson). Water Resources Res., v. 18, p. 1255–1268, 1982.



The pH,  $E_H$ ,  $O_2$ , and total dissolved iron and sulfide values for the deep, confined Lower Sands aquifer. The piezometer numbers are shown on the top abscissa (from Jackson and Patterson). Water Resources Res., v. 18, p. 1255–1268, 1982. Copyright by American Geophysical Union.  $5^{-1}67$ 

#### Hydrogeochemical Studies at Chalk River Nuclear Laboratories

Jackson and Peterson (1982) studied hydrogeochemical conditions, specifically the redox conditions along the ground water flow path, at Chalk River Nuclear Laboratories near Ottawa, Canada. By careful measurements of pH, Eh, dissolved oxygen, and concentrations of trace elements, including iron and sulfur, they defined three redox zones. The main geological units of interest include two fluvial sand aquifers shown in the above figure. Ground water flows southward from the upland area toward Perch Lake. The lower aquifer in the recharge area contains dissolved oxygen and has an Eh of approximately 0.55 V. Dissolved concentrations of Mn<sup>2+</sup> and Fe<sup>2+</sup> are low and sulfide is below detection limits. Depletion of oxygen within the deep flow system coincides with declining Eh values. High concentrations of iron and manganese, however, decrease further downgradient due to precipitation of ferrous sulfides.



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# GENERAL CHARACTERISTICS OF OXIDIZING GROUND WATER-AQUIFER MATERIAL

#### **MINERALS OR SOLID PHASES**

Goethite (FeOOH) Fe(III)-Silicates

Fe(OH)<sub>3</sub> Fe(III)-Clay Minerals

MnOOH

MnO<sub>2</sub>

#### WATER CHEMISTRY

Fe<sup>2+</sup> > 5 mg/L (acidic conditions)

Mn<sup>2+</sup> >1 mg/L (acidic conditions)

NO3- > 5 mg/L  $SO_4^{2-}$  > 5-100 mg/L (variable)

Fe<sup>2+</sup> < 1 mg/L Mn<sup>2+</sup> < 0.5 mg/L

**Positive or High Eh Value** 

Dissolved Oxygen > 1 mg/L

# GENERAL CHARACTERISTICS OF REDUCING GROUND WATER-AQUIFER MATERIAL

#### **MINERALS OR SOLID PHASES**

Pyrite (FeS<sub>2</sub>)

Fe(II)-Silicates

Siderite (FeCO<sub>3</sub>)

Fe(II)-Clay Minerals

Solid Organic Matter

Metal Sulfides

#### WATER CHEMISTRY

 $Fe^{2+} > 5 mg/L$  (absence of  $H_2S(g, aq)$  or HS-)

 $Mn^{2+} > 1 mg/L$  (absence of  $H_2S(g, aq)$  or HS-)

 $NH_4$ + > 5 mg/L  $H_2$ S or HS- > 1mg/L

Organic Species- CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>Cl<sub>3</sub>H

**Negative or Low Eh Value** 

Dissolved Oxygen < 0.1-1 mg/L

# NON-EQUILIBRIUM CONSIDERATIONS

From equations for Eh (and pe) and measured analytical data

Fe<sup>3+</sup> / Fe<sup>2+</sup>

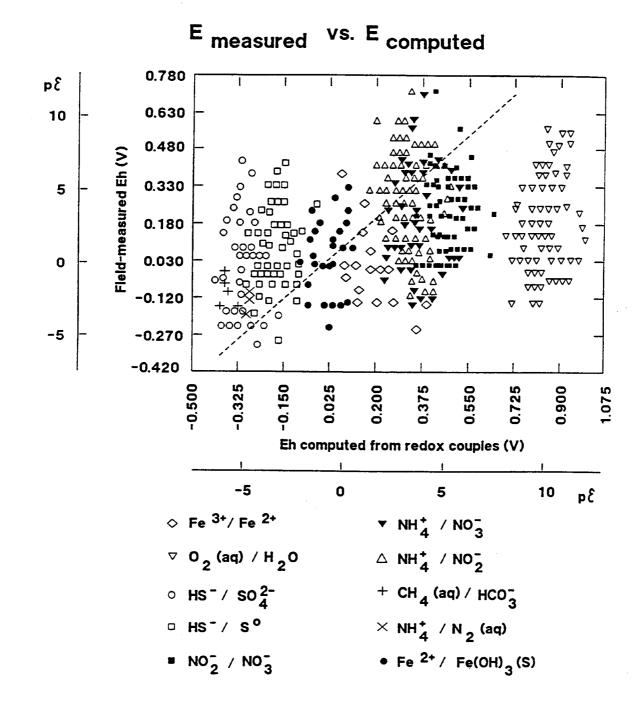
SO42- / HS-

As<sup>5+</sup> / As<sup>3+</sup>

an Eh value can be calculated.

If the solution is in electrochemical equilibrium, the calculated Eh should be the same as the measured Eh.

### Disequilibrium Prevails in Most Natural Systems



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#### **SUMMARY**

Eh-pH (OR pe-pH) DIAGRAMS ARE A USEFUL WAY TO ILLUSTRATE OXIDATION-REDUCTION REACTIONS.

CARBON, IRON, MAGANESE, NITROGEN, AND SULFUR ARE ELEMENTS THAT CONTROL REDOX STATES IN NATURAL WATERS.

NATURAL WATERS ARE IN DISEQUILIBRIUM WITH RESPECT TO OXIDATION-REDUCTION PROCESSES.

Trow Redox Couple Trow Redox Couple is 5000 one to look at

BALANCE THE FOLLOWING OXIDIZING-HALF REACTIONS [hint Fe(II,III)]:

1. 
$$\text{FeCl}_2(\text{aq}) = \text{Fe}^{3+} + 2\text{Cl}^- + 1\text{e}^-$$
  
2.  $\text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + 1\text{e}^-$   
3.  $\text{CH}_4(\text{g}) + 3\text{H}_2\text{O} = \text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^-$ 

BALANCE THE FOLLOWING REDUCING-HALF REACTIONS [hint S(-II,VI)]:

4.  $HSO_4^- + 9H^+ + 8e^- = H_2S^0(aq) + 4H_2O$ 5.  $SO_4^{2-} + 8H^+ + 8e^- = S^{2-}(aq) + 4H_2O$ 

**COUPLED REDOX REACTION (NOS. 3 AND 5)** 

 $0.25SO_4^{2-} + 2Fe^{2+} + 5H_2O =$ 

 $2Fe(OH)_3(s) + 4H^+ + 0.25S^{2-}(aq)$ 

1. Calculate the slope of the line representing the  $Fe^{2+}/Fe(OH)_3$  redox buffer with the following information. (HINT - look at section on oxidation and reduction conditions in natural waters). The activity of  $Fe = 10^{-4}$ , and the equation for the redox buffer is  $Fe^{2+} + 3H_2^0 = Fe(OH)_3 + 3H^+ + e^-$ .

 $\Delta G$  reaction =  $\Delta G$  products -  $\Delta G$  reactants

Species/solid	▲ G(kcal/mole)
Fe <sup>2+</sup>	-18.85
Fe(OH) <sub>3</sub>	-166.50
H <sub>2</sub> 0.	-56.69
H <sup>+</sup>	0
e	0

$$\Delta^{G}_{r} = nFE^{O} \text{ (first calculate } \Delta_{G_{r}}, \text{ then calculate } E^{O}\text{)}$$

$$n = number \text{ of electrons}$$

$$F = Faraday's \text{ Constant (23.06 kcal per volt gram eqv.)}$$

$$E^{O} = \text{standard electrode potential}$$

$$Eh = E^{O} + \frac{0.0592}{n} \qquad (activity product of oxidized species)$$

$$PH = - \log a H^{+}$$

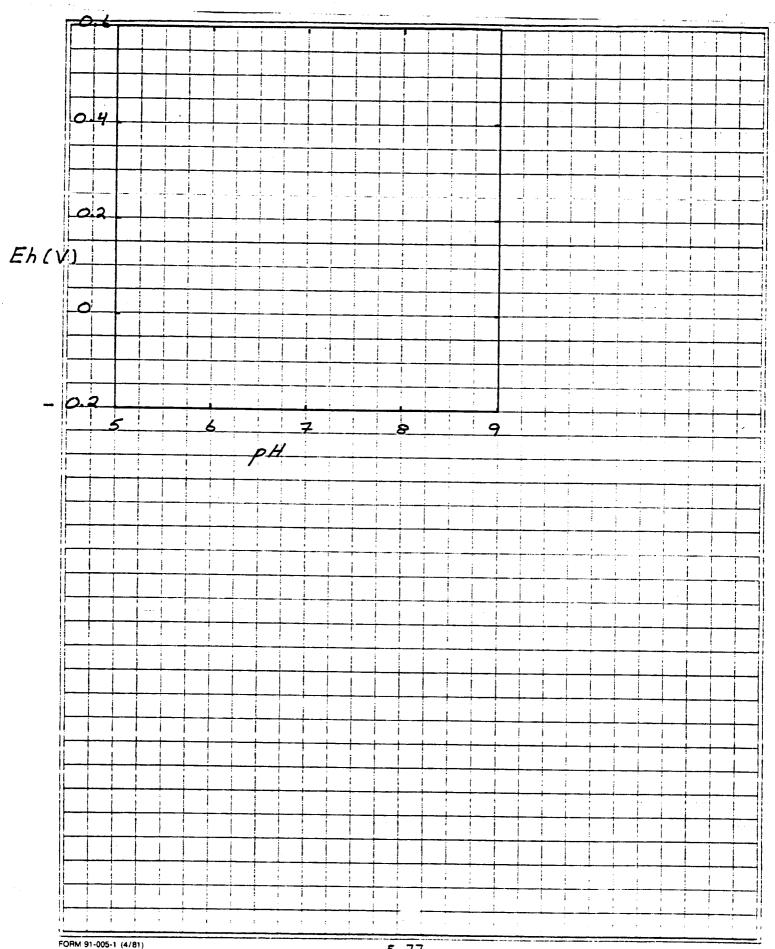
$$(activity product of reduced species)$$

Plot the slope of the redox buffer on the graph provided.

Plot the following data on the graph provided.

. . . . .

Eh(V)	PH	Eh(v)	рH
0.28 0.23 0.22 0.16 0.02 0.00	5.25 5.35 5.70 5.80 6.50 6.85	-0.05 -0.07 -0.09 -0.15 -0.17	7.00 7.15 7.25 7.73 8.00



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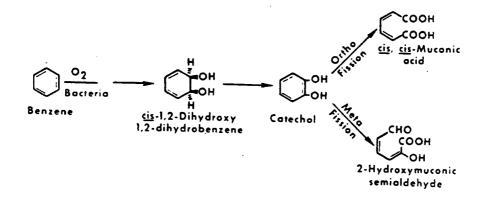
÷.,

The data that you have now plotted are from an acid mine drainage site in Colorado. Answer the following questions.

1. Do equilibria conditions exist between Fe<sup>2+</sup> and Fe(OH)<sub>3</sub>? Justify your answer.

2. Is this redox couple useful, and if so, under what geochemical conditions would the Fe<sup>2+</sup>/Fe(OH)<sub>3</sub> redox apply?

3. The oxidation of benzene by bacteria present under relatively oxidizing conditions is shown below. What are the oxidation states of carbon in the different compounds shown below? (HINT - the oxidation state of H is +1 and Oxygen is -2)



Write the oxidation reaction (half reaction) of toluene  $(C_7 H_8)$ oxidizing to  $CO_2$ . How many electrons and protons are required for this reaction to occur? Then write the reduction reaction (half reaction) of  $O_2$  reducing to water. Combine the two half reactions. How many moles of oxygen are consumed in the oxidation of toluene? Is this amount of oxygen typically found in ground water? Justify your answer. This redox buffer is important for groundwaters characterized by relatively oxidizing, acidic conditions such as acid mine drainage. Surface waters are also included.

Source: Drever, 1982

Steps:

1. Write redox reaction, activity of Fe =  $10^{-4}$ 

$$Fe^{2+} + 3H_2^0 = Fe(OH)_3 + 3H^+ + e^-$$

2. Calculate  $\Delta G_r$ 

Species/solid	$\Delta G_r$ (kcal/mole)	
Fe <sup>2+</sup>	-18.85	
<sup>H</sup> 2 <sup>0</sup>	-56.69	
Fe(OH) <sub>3</sub>	-166.50	
H <sup>+</sup>	0	
e	0	

$$\Delta G_{r} = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

$$\Delta G_{r} = \Delta G (\text{Fe}(\text{OH})_{3}) - 3 \Delta G (\text{H}_{2}0) - \Delta G (\text{Fe}^{2+})$$

$$\Delta G_{r} = -166.50 - (3) (-56.69) - (-18.85)$$

$$\Delta G_{r} = 22.42 \text{ kcal}$$

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3. Calculate  $E^{O}$  and Eh

~ 1

 $\Delta G = nFE^{O}$  where n = number of electrons , F = Faraday's constant (23.06 kcal per volt gram equilvent), and  $E^{O}$  = standard electrode potential

$$E^{O} = \frac{\Delta G}{nF} = \frac{22.42 \text{ kcal}, E^{O} = 0.972v}{(1)(23.06)}$$

$$\frac{\text{kcal per volt}}{\text{gram equivalent}}$$

$$Eh = E^{O} + \frac{0.0592}{n} \log \frac{(\text{activity product of oxidized species})}{(\text{activity product of reduced species})}$$

$$Eh = E^{O} + \frac{0.0592}{1} \log \left( \frac{[H^+]^3}{[Fe^{2+}]} \right), \text{ the activities of Fe(OH)}_3 \text{ and } H_2^0 = 1$$

now, pH =  $-\log_{H}^{+}$ 

Eh = 
$$0.972 - \frac{3(0.0592)}{1}$$
 pH  $-\frac{(0.0592)}{1}$  log [Fe<sup>2+</sup>], aFe<sup>2+</sup> =  $10^{-4}$   
Eh =  $0.972 - 0.178$ pH  $-\frac{(0.0592)}{1}$  log [ $10^{-4}$ ]

Eh = 1.21 - 0.178 pH

This equation is the slope of the line representing the  ${\rm Fe}^{2+}/{\rm Fe\,(OH)}_3$  redox buffer.

PLOTTING SLOPE OF Fe<sup>2+</sup>/Fe(OH) 3 REDOX BUFFER

At pH = 5

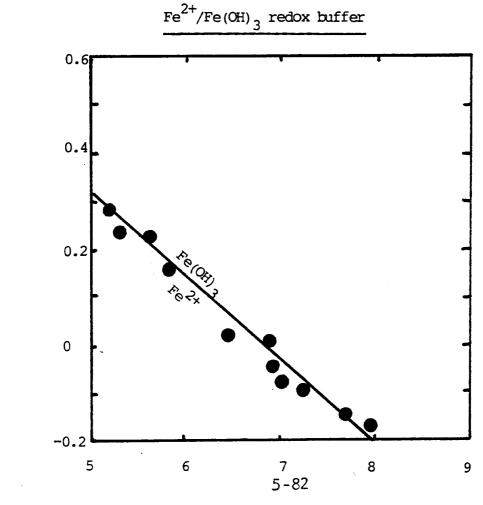
Eh = 1.21 - 0.178(5)Eh = 0.32vEh = -0.04v

At pH = 7

At 
$$ph = 6$$
At  $pH = 8$ Eh = 1.21 - 0.178(6)Eh = 1.21 - 0.178(8)Eh = 0.14vEh = -0.21v

Now plot the Eh values at different pH values.

Eh values calculated from the  $Fe^{2+}/Fe(OH)_3$  redox couple versus pH are plotted below. If field measured Eh values on the line, then  $Fe^{2+}/Fe(OH)_3$  couple is important.



Eh (volt)

## THE NERNST EQUATION

$$\Delta G_{r}^{\overline{o}}$$
 is  $\Delta G_{r}^{o}$  = nFE<sup>o</sup>

n = number of electrons

$$E^{\circ} = \frac{\Delta G_{r}^{\circ}}{nF}$$

 $E^{o}$  = Standard electrode potential

 $Eh = E^{o} + \frac{RT}{nF} \ln \left( \frac{Activity prod. oxidized species}{Activity prod. reduced species} \right)$ 

# THE NERNST EQUATION

For Iron, At 25 C  $Fe^{2+} = Fe^{3+} + e^{-}$  $Eh = E^{0} + \frac{0.0592}{1} \log \left(\frac{a Fe^{3+}}{a Fe^{2+}}\right)$ 

1.1

# LIST HALF REDOX REACTIONS IN ORDER OF DECREASING OXIDATION.

REACTION	log K
$H_{+} e_{-} = 1/2H_{2}(g)$	0
1/8NO3- + 5/4H+ + e- = 1/8NH4+ + 3/5H2O	14.9
1/3HCrO4 <sup>-</sup> + 7/3H+ + e <sup>-</sup> = 1/3Cr <sup>3+</sup> + 4/3H <sub>2</sub> O	20.2
1/4 <b>O<sub>2</sub>(g) + H+ + e<sup>-</sup> =</b> 1/2 <b>H2O</b>	20.75
$1/8SO_4^{2-} + 5/4H^+ + e^- = 1/8H_2S + 1/2H_2O$	5.13
Fe <sup>3+</sup> + e <sup>-</sup> = Fe <sup>2+</sup>	13.0
1/2 <b>Se(s) + H+ + e<sup>-</sup> =</b> 1/2 <b>HSe</b>	-6.7
1/2MnO <sub>2</sub> (s) + 2H+ + e- = 1/2Mn2+ + H <sub>2</sub> O	20.8

LIST SEVERAL REDOX COUPLES THAT COULD BE USED TO DEFINE A RANGE OF Eh VALUES FOR A GIVEN GROUND WATER SAMPLE.

DISCUSS POTENTIAL LIMITATIONS IN USING ONLY ONE EN VALUE AS INPUT FOR GEOCHEMICAL MODELING.

LIST SEVERAL CHARACTERISTICS (WATER CHEMISTRY, MINERALOGY) OF OXIDIZING AND REDUCING GROUND WATER. <u>OXIDIZING</u> REDUCING

WHY IS GROUND WATER CONTAMINATED FROM GASOLINE REDUCING NEAR THE SOURCE?

WRITE A COUPLED REDOX REACTION FOR THE OXIDATION OF BENZENE  $(C_6H_6)$  TO BICARBONATE. (HINT, BALANCE NUMBER OF ELECTRONS IN BOTH HALF RACTIONS.)

WHAT GROUNDWATER TRACERS WOULD YOU USE TO DETERMINE THE EXTENT OF A HYDROCARBON PLUME CONSISTING OF A MIXTURE OF GASOLINE AND DIESEL FUEL?

# LIST HALF REDOX REACTIONS IN ORDER OF DECREASING OXIDATION.

REACTION	log K
$H_{+} e_{-} = \frac{1}{2}H_{2}(g)$	0
1/8NO3 <sup>-</sup> + 5/4H+ + e <sup>-</sup> = 1/8NH4+ + 3/5H2O	14.9
1/3HCrO4- + 7/3H+ + e- = 1/3Cr3+ + 4/3H2O	20.2
1/4 <b>O<sub>2</sub>(g) + H+ + e<sup>-</sup> =</b> 1/2H <sub>2</sub> O	20.75
1/8SO4 <sup>2-</sup> + 5/4H+ +e <sup>-</sup> = 1/8H <sub>2</sub> S + 1/2H <sub>2</sub> O	5.13
Fe <sup>3+</sup> + e <sup>-</sup> = Fe <sup>2+</sup>	13.0
1/2 <b>Se(s) + H+ + e<sup>-</sup> =</b> 1/2 <b>HSe</b>	-6.7
1/2MnO <sub>2</sub> (s) + 2H+ + e- = 1/2Mn <sup>2</sup> + + H <sub>2</sub> O	20.8

# **REACTION NUMBERS (DECREASING OXIDATION):** 8 > 4 > 3 > 2 > 6 > 5 > 1 > 7

LIST SEVERAL REDOX COUPLES THAT COULD BE USED TO DEFINE A RANGE OF Eh VALUES FOR A GIVEN GROUND WATER SAMPLE.

 $O_2/H_2O$ , Fe<sup>3+</sup>/Fe<sup>2+</sup>, Fe(OH)<sub>3</sub>/Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>/H<sub>2</sub>S, NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>

DISCUSS POTENTIAL LIMITATIONS IN USING ONLY ONE EN VALUE AS INPUT FOR GEOCHEMICAL MODELING.

Natural waters do not have one master Eh value due to disequilibrium between redox couples. A range of calculated/measured Eh values is required to bound the redox potential of the aqueous solution.

LIST SEVERAL CHARACTERISTICS (WATER CHEMISTRY, MINERALOGY) OF OXIDIZING AND REDUCING GROUND WATER.

#### **OXIDIZING**

low concentrations of Fe, Mn,  $H_2S$ dissolved oxygen  $NO_3$ -,  $SO_4^2$ -Fe(OH)<sub>3</sub>, MnO<sub>2</sub>

#### REDUCING

detectable amounts of Fe, Mn, H<sub>2</sub>S, NH<sub>4</sub>+ metal sulfides Fe (II) silicates

WHY IS GROUND WATER CONTAMINATED FROM GASOLINE REDUCING NEAR THE SOURCE?

Oxidation of benzene and other organic species results in depletion of  $O_2$  and the ground water becomes reducing. Solubilities of  $Fe(OH)_3$  and  $MnO_2$  increase under these reducing conditions and subsequently dissolved concentrations of Fe and Mn increase.

WRITE A COUPLED REDOX REACTION FOR THE OXIDATION OF BENZENE  $(C_6H_6)$  TO BICARBONATE. (HINT, BALANCE NUMBER OF ELECTRONS IN BOTH HALF RACTIONS.)

 $C_6H_6 + 18H_2O = 6HCO_3 + 36H + 30e^{-1}$ 

 $30H^+ + 30e^- + 7.5O_2 = 15H_2O$ 

 $C_6H_6 + 3H_2O + 7.5O_2 = 6HCO_3 + 6H +$ 

WHAT GROUNDWATER TRACERS WOULD YOU USE TO DETERMINE THE EXTENT OF A HYDROCARBON PLUME CONSISTING OF A MIXTURE OF GASOLINE AND DIESEL FUEL?

Dissolved oxygen, Fe, Mn, Benzene, and MTBE could be used as chemical tracers for hydrocarbon-contaminated ground water.

Write the oxidation reaction (half reaction) of toluene ( $C_7H_8$ ) oxidizing to  $CO_2$  gas. How many electrons and protons are required for this reaction to occur? Then write the reduction (half reaction) of  $O_2$  reducing to water. Combine the two half reactions. (Hint, balance number of electrons in both half reactions.) How many moles of  $O_2$  are consumed in the oxidation of toluene? Concentrations of dissolved oxygen ( $O_2$ ) in surface water in equilibrium with the atmosphere are typically 8 ppm (10-3.6 molar). What processes are required to enhance oxidation of aromatic species in ground water with lower concentrations of dissolved oxygen?

#### **OXIDIZING REACTION**

 $C_7H_8 + 14H_2O = 7CO_2 + 36H^+ + 36e^-$ 

#### **REDUCING REACTION**

 $9O_2 + 36H^+ + 36e^- = 18H_2O$ 

#### **COUPLED REACTION**

 $C_7H_8 + 9O_2 = 7CO_2 + 4H_2O$ 

Soil microbes (for example, Pseudomonas putida 39/D) catalyze redox reactions involving organic and many inorganic species. Sufficient concentrations of oxygen, however, are required to enhance oxidation of aromatic species.

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Yanful, E.K., Nesbitt, H.W., and Quigley, R.M., 1988. Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada - 1. Thermodynamic Assessment and Chemical Interpretations: Applied Geochemistry, Vol. 3, pp. 523-533.

Yanful, E.K., Quigley, R.M., and Nesbitt, H.W., 1988. Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada - 2. Metal Partitioning and Geotechnical Implications: Applied Geochemistry, Vol. 3, pp. 623-629. Section 6

## Introduction to Organic Chemistry I - Structure and Nomenclature

Lecture by: Richard Meyerhein New Mexico Scientific Laboratory Division

## SECTION CONTENTS

Additional References:

Montgomery, J.M., 1985. Water Treatment Principles and Design, Chapter 16, Organics.

#### **6**-/ INTRODUCTION TO ORGANIC CHEMISTRY STRUCTURE AND NOMENCLATURE by Richard Meyerhein N.M. SCIENTIFIC LABORATORY DIVISION

#### ORGANIC CLASSIFICATIONS AND NOMENCLATURE

It must be understood possible "organic contaminants" comprises a very large, complex, and diverse group of compounds. Organic contaminants range from natural gas to complex biochemical compounds such as proteins and deoxyribonucleic acids (DNA). While there are over seven million known and characterized organic compounds, these comprise only a small fraction of the total possible organic compounds. The intent here is to describe some of the organic chemicals found in ground water and/or specified for analysis in ground water by the Environmental Protection Agency (EPA).

There are gasses, liquids and solids. Some are water soluble while others are oil soluble. Some are extremely similar chemically and physically. For example, there are at least 53 possible halogenated (containing chlorine, bromine, iodine, or fluorine) compounds with one carbon atom. This can make it very difficult to separate and identify one of these compounds that might be a contaminant in water, soil, etc.

Organic compounds can generally be grouped into large classes based on their chemical structure, physical or chemical properties, and/or their use in society. For practical reasons in the analytical laboratory all of the above categories are used in grouping chemicals.

Some of the more common categories based on chemical structure used are:

- <u>Aliphatic compounds</u> contain mainly carbon and hydrogen in straight and branched chains, and rings. However, the nature of an aliphatic compound can be changed greatly by the addition of one or more functional groups with oxygen, nitrogen or other atom capable of chemical reactions. These functional groups create many more classes of organic compounds. Some of these classes, along with their structures are listed below:
  - <u>Acyclic Hydrocarbons</u> (chains containing carbon and hydrogen only) <u>Alkanes</u> have the general formula  $H(CH_2)_n H$  where n is the number of carbon atoms in the molecule. Fossil fuels such as gasoline, diesel fuel, motor oils, etc. are comprised mainly of complex mixtures of aliphatic hydrocarbons. These hydrocarbons

Organic Introduction

are commercially fractionated by their boiling points to give the following products:

USE AND BOILIN	G RANGE OF MAJOR A	LKANE FRACTIONS
Principal Alkanes		Boiling Range
Number of Carbons	Product	(°C)
C 1-2	Natural Gas	Gas at 25°C
C 3-4	Liquid Petroleum gas	Gas at 25°C
C 4-6	Petroleum ether	20-60
C 5-7	Petroleum Benzin	40-90
C 6-8	Petroleum naphtha	65-120
C 5-10	Gasoline	36-210
C 7-9	Mineral spirits	150-210
C 7-12	Stoddard solvent	160-210
C 9-16	Kerosene	170-300
C 5-16	Jet and turbo fuels	40-300
C 17 and higher	Lubricating oils	300-700
C 20 and higher	Waxes	204-750

Aliphatic hydrocarbons with more than six carbons are not very soluble in water. Generally these compounds will be found floating on top of the water and/or bound to clays.

Aliphatic hydrocarbon chains are named as follows where n indicates the number of carbon atoms:

<u>n Name</u>	0	Name
1 Methane	12	Dodecane
2 Ethane	13	Tridecane
3 Propane	14	Tetradecane
4. Butane	15	Pentadecane
5 Pentane	16	Hexadecane
6 Hexane	17	Heptadecane
7 Heptane	18	Octadecane
8 Octane	19	Nonadecane
9 Nonane	20	Eicosane
10 Decane	21	Heneicosane
11 Undecane	30	Triacontane

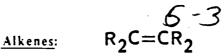
As aliphatic hydrocarbons lose hydrogen (become more oxidized) they form "Unsaturated" (having bonds to which other atoms can add) aliphatic compounds such as alkenes and alkynes. These compounds are much less stable in the environment and tend to be further oxidized to alcohols, aldehydes, ketones, and acids. The classes of aliphatic compounds are indicated below:

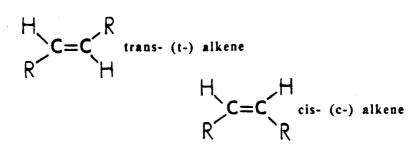
R- = Aliphatic chain

<u>Alkanes:</u>  $R-CH_3$  Primary (1°) or "straight chain"  $R-CH_2-R$  Secondary (2°) or "branched"  $R_3CH$  Tertiary (3°) or "branched"

**Organic Introduction** 

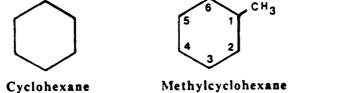
6-2





R-C≡C-R Alkynes:

Cyclic Aliphatics - Aliphatic hydrocarbons can also form rings as shown below:



Cyclopentane

Whenever one of the Carbon (C) atoms or Hydrogen (H) atoms is replaced with a different atom it changes the character of the molecule and creates a different class of compounds. There are literally hundreds of classes of organic compounds. Most aerobic bacteria will use hydrocarbons as an energy source when necessary and will tend to oxidize these compounds to alcohols, ketones, acids and eventually to carbon dioxide. These intermediate oxidized compounds are more soluble in water than the aliphatic hydrocarbon. This type of compound is also frequently used in industrial processes. A few of the more common oxygen, sulfur and nitrogen classes are listed below:

O = Oxygen; S = Sulfur; N = Nitrogen

**R-O-R** 

// R-C-H

Alcohols: R-O-H

Aldehydes:

Ethers:

Ketones:

Acids:

Esters:

Organic Introduction

R-C-OH

:

R-C-R

#### Functional Groups:

Halides: Chlorine (Cl); Bromine (Br); Fluorine (F); Iodine (l) <u>Thiols:</u> R-S-H

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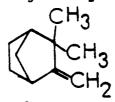
Sulfides: R-S-R

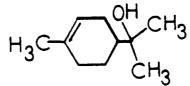
<u>Amines</u>:  $R-\dot{N}H_2$  (1°)  $R_2\dot{N}H$  (2°)  $R_3\ddot{N}$  (3°)

Nitroso: -N=O

Nitro: -NO2

<u>Bicyclic compounds</u> - Many natural products are bicyclic in structure such as terpines. Often naturally occurring products from plants contain 10 or 15 carbons because they are synthesized from the 5 carbon isoprene unit  $(CH_2=C(CH_2)CH=CH_2)$ .

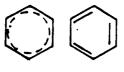


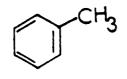


Camphene

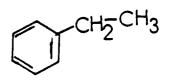
alpha-Terpineol

<u>Aromatic compounds</u> - contain at least one aromatic ring. Crude oil contains an appreciable percentage of aromatic compounds. While the percentage of aromatic compounds is not high it is significant in that aromatic compounds are much more soluble in water than their saturated analogs. For instance in the case of an underground gasoline leak it is difficult to find any saturated hydrocarbons dissolved in the water while Benzene, Toluene, and Xylenes (BTX) can be found at the mg/l (PPM) levels. Generally hydrocarbon fuels higher boiling than gasoline do not contain the BTX compounds.





Toluene

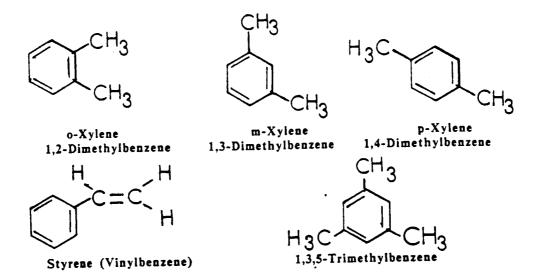


Benzeue

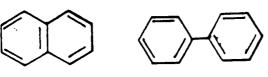
Ethylbenzene

Organic Introduction

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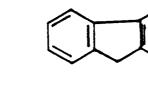
Polycyclic Aromatic Hydrocarbons (PNA's or PAH's): generally when 2 or more aromatic rings are fused together they form a class of compounds called the polynuclear aromatic hydrocarbons. These compounds are important because many have been found to be carcinogenic. These compounds are found in crude oil and are produced during the combustion of hydrocarbon fuels. A few of the possible ring systems are shown below:



Naphthalene

Acenaphthalene

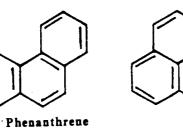
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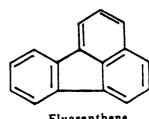


Fluorene

Pyrene

Biphenyl





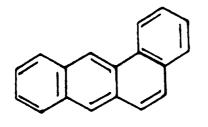
Anthracene

Acenaphthene

Fluoranthene

Organic Introduction

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Benzo(a)anthracene

Benzo(a)pyrene

Halogenated compounds - contain at least one fluorine, chlorine, bromine or iodine atom. Many of the industrial solvents used today are chlorinated compounds. Because of their common usage and relatively high water solubility this class of compounds is the one most frequently found contaminating ground water. Some of the halogenated compounds (trihalomethanes) are generated by the chlorination of drinking water. A few of these compounds halogenated are shown below:



Cl<sub>3</sub>C-CH<sub>3</sub>

Cl<sub>2</sub>C=CHCI

Cl<sub>2</sub>HC-CHCl<sub>2</sub>

1,1,1-Trichloroethane Trie

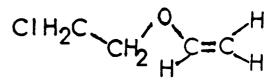
Trichloroethene

1,1,2,2-Tetrachloroethane

There are too many other possible organic compounds to try to cover here, but below are some representative names and structures of compounds on the EPA Priority Pollutant list:

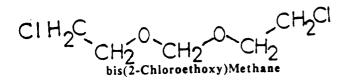
CH3

2-Hexanone



2-Chloroethylvinylether

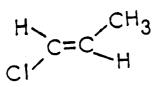
Organic Introduction



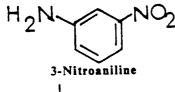
· 1

(Pr)2 N-N=0

N-Nitroso-Di-n-Propylamine



trans-1,3-Dichloropropene

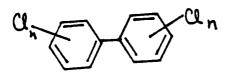




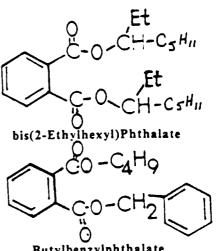
Isopherone

(CH3)3C-0-CH3

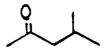
t-Butylmethylether

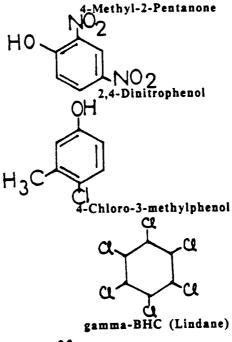


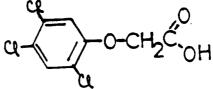
PCB (Arochlor-1254 isomer) (Mixture of PCB's with 54% chlorine)



Butylbenzylphthalate







2,4,5-Trichlorophenoxyacetic acid (A chlorophenoxy acid herbicide, Silvex)

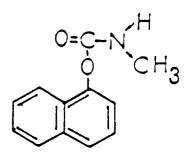
Organic Introduction

5 - 1

5-8

E+ \" E+ \"P-2

Parathion (An Organophosphate Pesticide)



Carbaryl (Sevin) (A Carbamate Pesticide)

Organic Introduction



#### REFERENCES

Clayton, G.D. and Clayton, F.E., 1981 (Third Ed.), Patty's Industrial Hygiene and Toxicology, John Wiley & Sons, N Y

(Excellent reference for information on uses and toxicology of industrial type compounds.)

Meister, Richard T., 1987, Farm Chemicals Handbook, Meister Publishing Company, Willoughby, OH.

> (Excellent reference for pesticides and agricultural chemicals. Includes information on chemical and common names, chemical properties, toxicity, and application. Well indexed with addresses and phone numbers of emergency response persons for many agricultural manufacturing companies.)

Montgomery, James M., Consulting Engineers, 1985, Water Treatment Principles and Design, John Wiley & Sons, N.Y.

(Chapter 16 gives a good introduction on organics in ground water.)

Verschueren, Karl, 1983 (Second Ed.), Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Co. Ltd., NY.

(Excellent reference for many organic chemicals. Gives information on properties, biological effects, water and air pollution factors.)

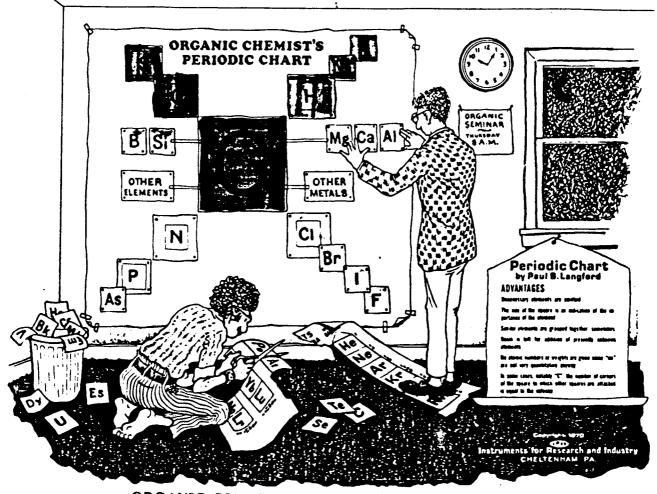
Weast, Robert C., 1984, CRC Handbook Of Chemistry and Physics, CRC Press, Inc., Boca Raton Florida.

> (Useful handbook with physical and chemical properties of organic and inorganic compounds published yearly)

Windholz, Martha, 1983 (Tenth Ed.), THE MERCK INDEX, Merck & Co., Inc., Rahway, N.J.

(An encyclopedia of chemicals, drugs and biologicals)

**Organic Introduction** 



ORGANIC COMPOUNDS ARE BASED ON CARBON (C)

# INTRODUCTION TO ORGANIC CHEMISTRY

### **TOPICS**

- STRUCTURE OF ORGANIC COMPOUNDS
- PHYSICAL PROPERTIES
- CHEMICAL PROPERTIES
- ORGANIC NOMENCLATURE
- COMMON CLASSES OF ORGANIC COMPOUNDS
  - » HYDROCARBONS
    - ♦ ALIPHATIC
    - AROMATIC
    - POLYNUCLEAR AROMATIC
  - » HALOGENATED
  - » OXYGEN CONTAINING
    - ALCOHOLS
    - ♦ KETONES
    - ESTERS
    - ACIDS



### **ENVIRONMENTAL CLASSIFICATION**

#### ♦ INDUSTRIAL

- Fuels
- Solvents
- Products and By-products

#### ♦ AGRICULTURAL

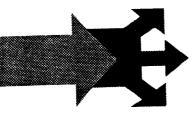
- Pesticides
- Herbicides
- Nutrients

#### LANDFILLS AND DUMPS

- Everything

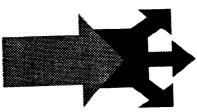
### NOT ALWAYS A SIMPLE CORRELATION

◆ PESTICIDE



♦ HERBICIDE

1



ORGANOCHLORINE ORGANOPHOSPHATE CARBAMATES CHLOROPHENOXY ACIDS

TRIAZINES

**GLYPHOSATE** 

### **ANALYTICAL CLASSIFICATION**

5-14

#### ♦ PHYSICAL PROPERTIES

- Water Solubility
- Volatility
- Acidic/Basic Character

#### CHEMICAL PROPERTIES

- Electronic configuration
- Containing Specific Elements: Cl, Br, P, N, S



6-15

### **HELP IS AVAILABLE!**

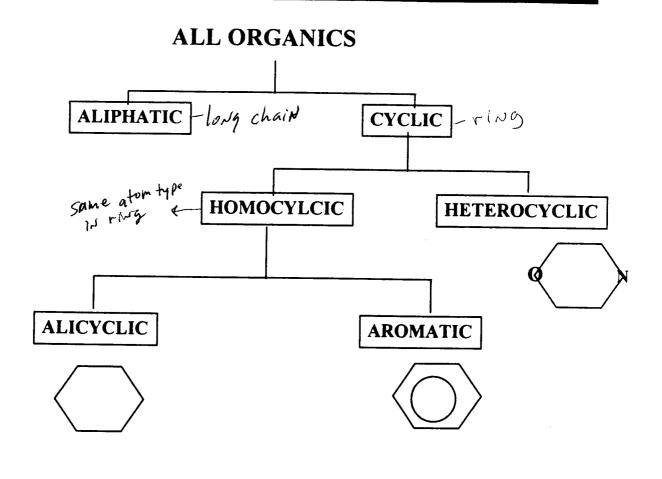
#### ◆ Talk with Chemists

- Develop a personal relationship with lab
- Learn from the facility
- Use literature resources

- Handbook of Environmental Data Verschueren
   Handbook of Environmental Data Verschueren
   The Merck Index
- Patty's Industrial Hygiene and Toxicology
- Farm Chemicals Handbook
- Laboratory Chemical Catalogs (free from manu factures)

Chas CAS#

### **ORGANIZATION OF ALL ORGANICS**

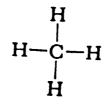


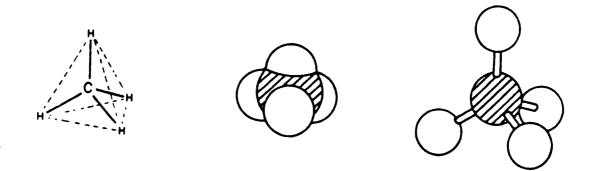
polynuclear = more than one aromatic ring



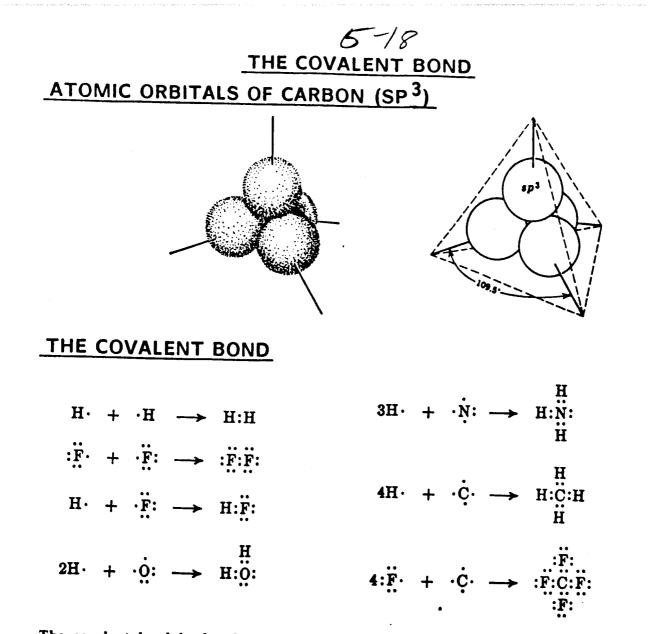
#### THE SIMPLEST ORGANIC COMPOUND

#### METHANE

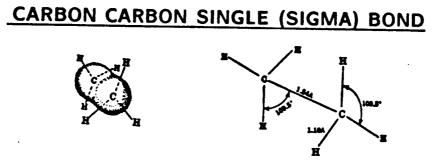




Covalent bonds tend to stay together Carbos has 4 electrinos to share Atoms are most stable with 8 electrons por outer shellmethave - carbor shares its 4 electrons with the 4 electrons from 4 Hydroger atoms



The covalent bond is the sharing of two electrons by two atoms. This bond is typical of compounds of carbon and is very important to understanding the structure and properties of organic compounds.



The C-C single bond is a strong bond and is not easily broken. This bond will not break or dissociate under normal environmental conditions.

VALENCE OR OXIDATION STATE

#### • General Assumptions for Organic Compounds

- H- (+1) Gives up 1 electron
- O- (-2) Accepts two electrons
- Cl- (-1) Accepts 1 electron
- C- (-4 to +4) depending on attached atoms
- Bonds between identical atoms (C-C) assumed to equally share electrons (Valence = 0)

#### • Bonds in Organic Molecules are Covalent

- Share electrons
- Not ionic
- Not easily broken

#### NAMES OF NORMAL ALKANES

Number of carbon atoms	Name	Structurel formule	Molecular Jormula
1	Methane	н  - н-С-н  - н	сн,
2	Ethane	Н Н     H-C-C-H     H Н	С,ң
3	Propane (prō' pān)	Н Н Н       H-C-C-C-H       Н Н Н	C₃H∎
4	Butane (bū' tān)	Н Н Н Н         H-C-C-C-C-H         H Н Н Н	C <sub>4</sub> H <sub>10</sub>
5	Pentane (pēn' tān)	Н Н Н Н Н           H-C-C-C-C-C-H           Н Н Н Н Н	C <sub>5</sub> H <sub>12</sub>
6	Hexane (hēx ān)	Н Н Н Н Н Н           H-C-C-C-C-C-C-H             Н Н Н Н Н Н	C <sub>6</sub> H <sub>14</sub>
7	Heptane (hëp tän)	Н Н Н Н Н Н Н               H-C-C-C-C-C-C-C-H                 Н Н Н Н Н Н	C <sub>7</sub> H <sub>16</sub>
8	Octane (öc' tān)	Н Н Н Н Н Н Н Н                 H-C-C-C-C-C-C-C-C-H                 Н Н Н Н Н Н Н Н	C <sub>e</sub> H <sub>ia</sub>
9	Nonane (nō' nān)	Н Н Н Н Н Н Н Н Н                 H-C-C-C-C-C-C-C-C-C-H                   Н Н Н Н Н Н Н Н Н	C <sub>s</sub> H <sub>20</sub>
- 10	Decane (dë cān)	Н Н Н Н Н Н Н Н Н Н Н                   H-C-C-C-C-C-C-C-C-C-C-H                       H Н Н Н Н Н Н Н Н Н Н	C10Hz

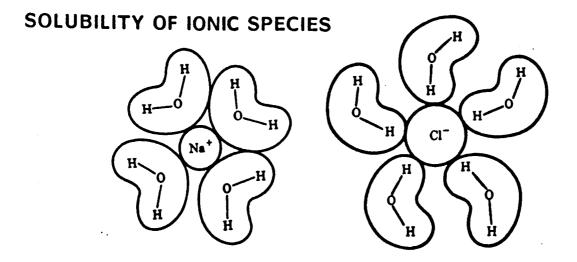
5-21

### COMPOSITION AND USE OF COMMON HYDROCARBON FUEL FRACTIONS

No. of CarbonsProductBoiling Pt. (C)UseClass CompoundC1-2Natural Gas-76Fuel ChemicalMethane, E ChemicalC3-4Liquefied or Bottled Gas-45.4Synthesis FuelParaffi Paraffins CC4-5Petroleum Ether20 - 60SolventsParaffins C Motor FuelC5-10Gasolines32 - 149Aviation/ Motor FuelParaffins C AromatC5-11VM&P naphtha95 - 160ThinnersParaffins C VolumeC6-12Mineral Spirits150 - 200ThinnersParaffins Aromat Olefins Aro Olefins Aro SolventC7-12Stoddard Solvent160 - 210Cleaning Fluids SolventsParaffins Aromat AlkylbenzC5-16Kerosines40 - 300Heating/ JetParaffins	ithanes ns ns ilefins ics ns
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Bottled Gas     Fuel       C4-5     Petroleum Ether     20 - 60     Solvents     Paraffins C       C5-10     Gasolines     32 - 149     Aviation/     Paraffins C       C5-11     VM&P naphtha     95 - 160     Thinners     Paraffin       C5-12     Mineral Spirits     150 - 200     Thinners     Paraffin       C6-12     Mineral Spirits     160 - 210     Cleaning     Paraffin       C7-12     Stoddard     160 - 210     Cleaning     Paraffin       Solvent     Solvents     Alkylbenz     Alkylbenz	ns Vefins ics
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Motor Fuel     Aromat       C5-11     VM&P naphtha     95 - 160     Thinners     Paraffii       C6-12     Mineral Spirits     150 - 200     Thinners     Paraffii       C6-12     Mineral Spirits     150 - 200     Thinners     Paraffii       C7-12     Stoddard     160 - 210     Cleaning     Paraffii       Solvent     Solvent     Solvents     Alkylbenz	ics 1s
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C6-12     Mineral Spirits     150 - 200     Thinners     Paraffie       C7-12     Stoddard     160 - 210     Cleaning     Paraffie       Solvent     Fluids     Cyclopara       Solvents     Alkylbenz	-
C6-12     Mineral Spirits     150 - 200     Thinners     Paraffit       C6-12     Mineral Spirits     150 - 200     Thinners     Paraffit       Naphthale     Olefins Aro       C7-12     Stoddard     160 - 210     Cleaning     Paraffit       Solvent     Fluids     Cyclopara       Solvents     Alkylbenz	
C6-12       Mineral Spirits       150 - 200       Thinners       Paraffil         Naphthale       Naphthale       Olefins Aro         C7-12       Stoddard       160 - 210       Cleaning       Paraffil         Solvent       Fluids       Cyclopara         Solvents       Alkylbenz	
C7-12 Stoddard 160 - 210 Cleaning Paraffit Solvent Fluids Cyclopara Solvents Alkylbenz	
C7-12     Stoddard     160 - 210     Cleaning     Paraffit       Solvent     Fluids     Cyclopara       Solvents     Alkylbenz	
C7-12 Stoddard 160 - 210 Cleaning Paraffi Solvent Fluids Cyclopara Solvents Alkylbenz	1
Solvent Fluids Cyclopara Solvents Alkylbenz	
Solvents Alkylbenz	
Fuels Cyclopara	-
Alkylbenz	
C11-18 Diesel/Gas Oil 177 - 400 Fuel, Heating Paraffins, C	
Oil Cyclopara	
Alkylbenz	
PAH	
C17-higher Lubricating 204 - 400 Lubricating Stock	-
Oils ar	
Greas	-
Cyclopara	
Alkylbenz	
PAH	
C1-50+ Crude Oil <0 - >1000 Fuel Stock Paraffins, C	
Aromatics,	lefins.
paraffins, f	
Aspha	Cyclo-

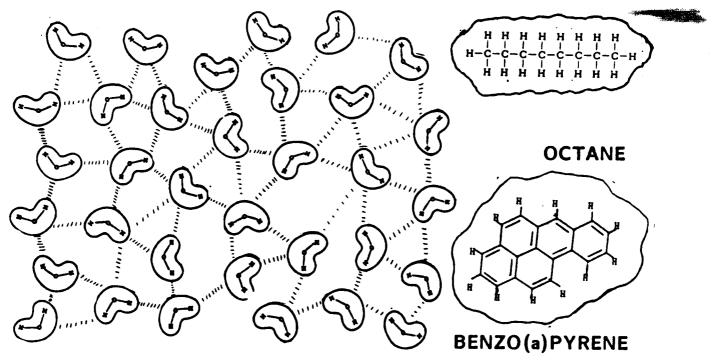
#### STRUCTURE-PROPERTY RELATIONSHIPS

6-22



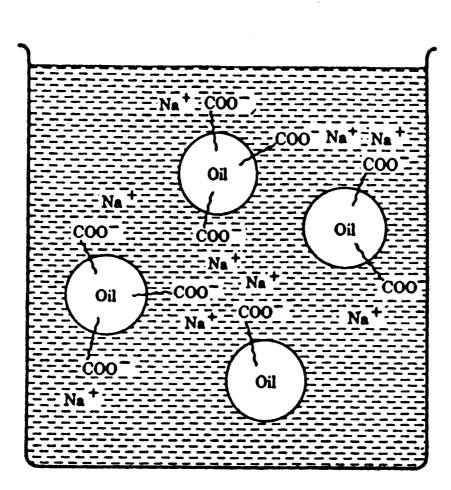
ION-DIPOLE Interactions keep the Na<sup>+</sup> and Cl<sup>-</sup> ions hydrated and thus in solution

#### **NON-POLAR ORGANICS**



The non-polar organic molecules generally have very small dipole moments and thus would have to disrupt some of the dipole interactions of the water to stay in solution. This requires more energy than if the organic molecules were excluded from the water.

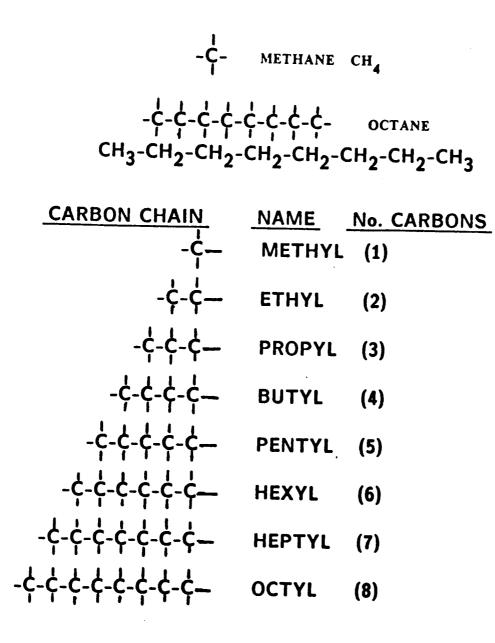
Bonds must be broken to make organic compound Soluable. The larger molecules take more energy to put them into Solution.



**CO-SOLVENCY** 

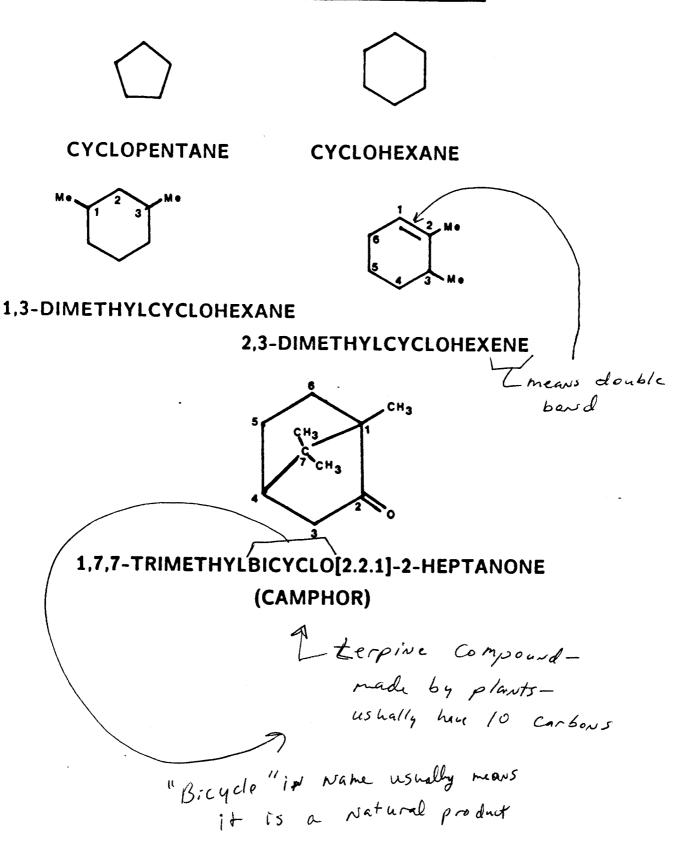
Polar and/or ionic substituents increase solubility.

Once an organic molecule has become "soluble" in water it has created a "hole" in the water "structure" which means that it will take less energy (break fewer dipoledipole water bonds) when an additional molecule is added to that hole. Non-polar organic molecules have little or no attraction for one another, but are "forced" together (excluded from the water) by the hydrogen bonding of the water. This cosolvency is generally a greater factor when one of the organic molecules has a polar and a non-polar "end". That way the polar end can help to create the "hole" in the water while the non-polar end can make an environment where other organics can exist without disturbing many more hydrogen bonds. 5-24THE "CHAIN" OF CARBON ATOMS IS THE BASIS OF ORGANIC COMPOUNDS



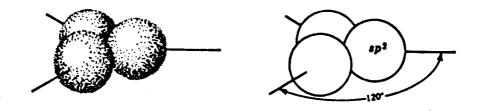
5-25

#### NAMING CYCLIC HYDROCARBONS

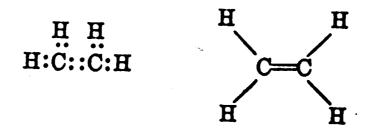




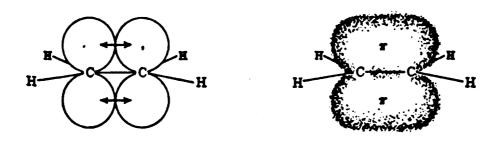
ATOMIC ORBITALS FOR PI BONDS (SP<sup>2</sup> ORBITALS)



ETHENE (ETHYLENE) AN ALKENE - More soluable than alkaves



THE PI BOND



Since the SP<sup>2</sup> orbitals are planar, the atoms associated with a pi bond are also planar. Also, since there is not free rotation about a pi bond, there can be two different isomers for alkenes when there are different groups attached to the pi bond. These isomers are called "cis-" (or sometimes Z- for zusammen) for together/same side, and "trans-" (or sometimes E- for entgegen) meaning across from/opposite sides.

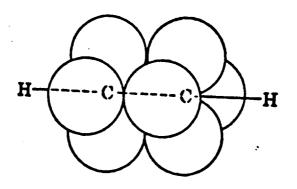
5-27

#### THE TRIPLE BOND

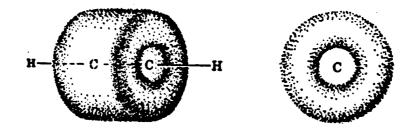
#### ACETYLENE MOLECULE (SP ORBITALS)

ı

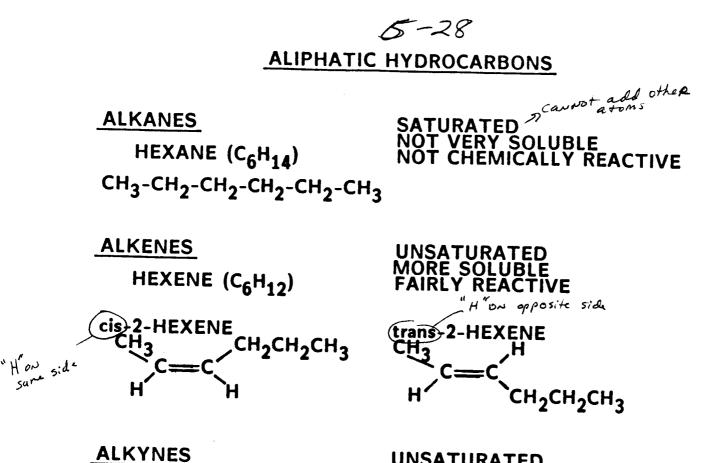
can forem Salts



The triple bond is made by two carbons sharing six electrons (two each p orbitals and one each sp orbital. This is like a sigma (single) bond and two pi (double) bonds. Triple bonds are linear bonds.



The pi cloud forms a cylindrical sheath. The triple bond has a total bond strength of 123 kcai. It is stronger than a C-C double bond (100 kcal) or the single C-C bond (83 kcal). Generally Alkynes are much more reactive (chemically) than alkenes or alkanes.



2-HEXYNE CH<sub>3</sub>C=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> UNSATURATED EVEN MORE SOLUBLE VERY REACTIVE

### 5-29 NAMING SUBSTITUTED ALKANES

- 1

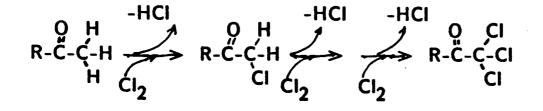
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CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<su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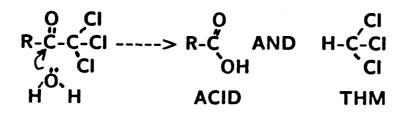
CH<sub>3</sub> CH<sub>3</sub>-CH<sub>2</sub>-CH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> 3-METHYLNONANE

### **RULES FOR ORGANIC NOMENCLATURE**

- Name compound as longest chain or largest ring
- List substituents and side groups in alphabetical order
  - Disregard prefixes: ortho-, meta-, para-, alpha-, beta-, gamma-, sec-, tert-, sym-, as-, uns-, cis-, trans-, d-, l-, dl-, n-, N-, and all numbers
  - Use Prefixes: iso-, di-, tri-, bi-, bis-, cyclo-, bio-, neo-, pseudo-
- Number groups from end of longest chain or position on ring to give the lowest numbers

TRIHALOMETHANES (THM's) CI replaces H







Cl / H-C-Br \ Cl

5-31 chloringtion 2

CHLOROFORM

BROMODICHLOROMETHANE



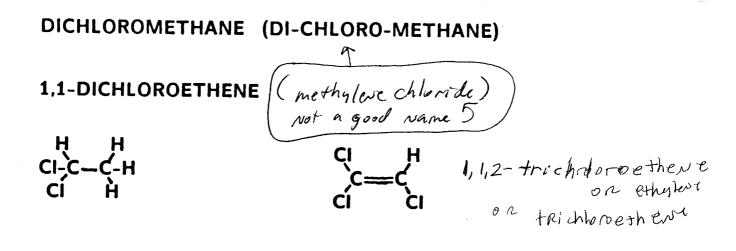


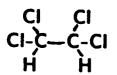
DIBROMOCHLOROMETHANE

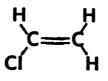
BROMOFORM

bromoform is not used alot - can be used as Specific gravity Separation

#### 6-32 OTHER HALOCARBONS







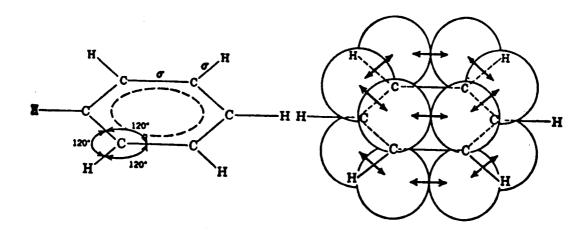
1, 1, 2, 2, tetra chloro ethave

Chloroethene (uingl chloride) bad name

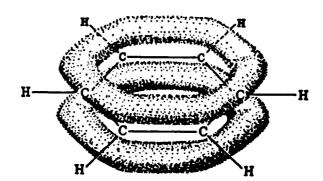
ethene -> double boud

### 6-33 AROMATIC COMPOUNDS

#### BENZENE: THE SIMPLEST AROMATIC COMPOOUND



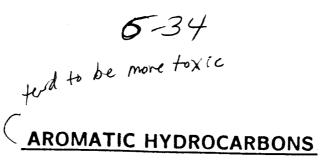
COMPLETE OVERLAPPING OF "PI" (SP<sup>2</sup>) ORBITALS

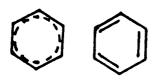


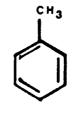
#### "PI CLOUD" ABOVE AND BELOW PLANE OF RING

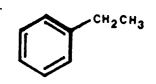
The aromatic nature of compounds cannot be accurately represented by drawing alternating single and double bonds. The pi cloud of electrons above and below the ring give the molecule a considerably lower energy state which makes the ring much more stable, and thus much less reactive chemically. Normally aromatic compounds are stable in the environment with the exception of bio-degredation. However, the pi cloud of electrons makes aromatic compounds more water soluble than aliphatic hydrocarbons of the same "size".

extra electrons in pi cloud make it more soluquie + more stable





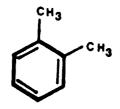


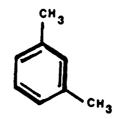


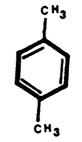
BENZENE

TOLUENE

**ETHYLBENZENE** 







o-XYLENE

**m-XYLENE** 

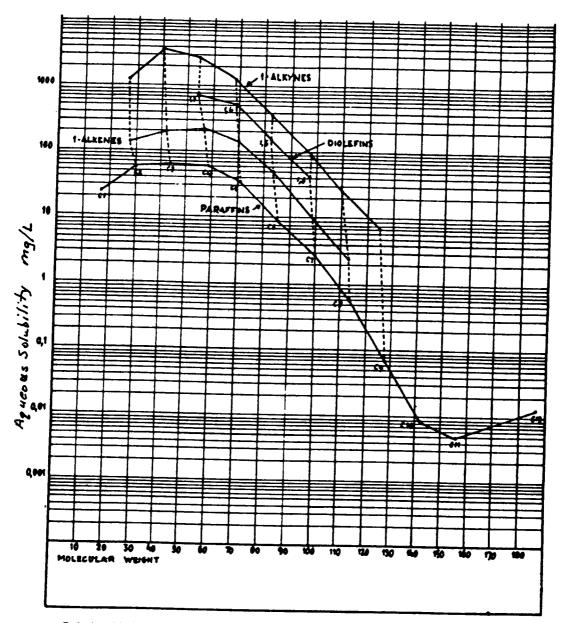
**p-XYLENE** 

1,2-DIMETHYLBENZENE 1,3-DIMETHYLBENZENE 1,4-DIMETHYLBENZENE

## DOUBLE (Pi) BONDS INCREASE SOLUBILITY

	13 mg/L	n-Hexane aliphatic are less soluable
	50 mg/L	1-Hexene
$\bigcirc$	55 mg/L	Cyclohexane
$\langle \rangle$	200 mg/L	Cyclohexene
	700 mg/L	Cyclohexadiene
	1880 mg/L	Benzene (Aromatic)

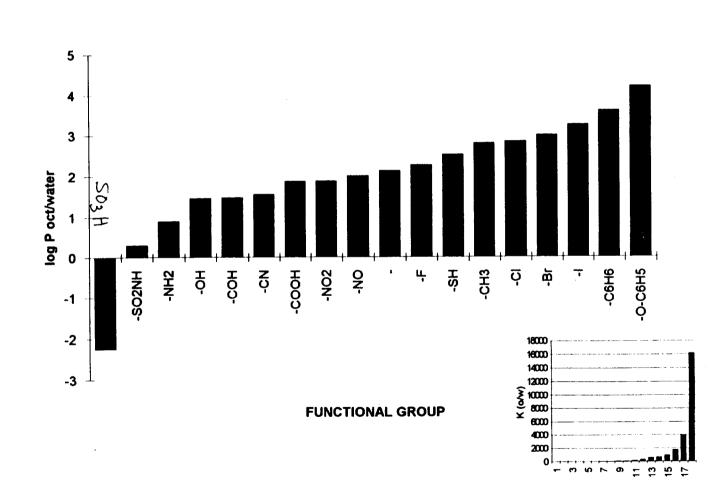
### **SOLUBILITY OF HYDROCARBONS**

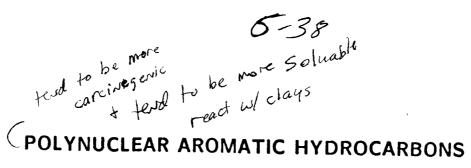


Relationship between aqueous solubility and molecular weight for saturated and unsaturated straight-chain hydrocarbons.

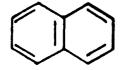
FROM: HANDBOOK OF ENVIRONMENTAL DATA ON ORGANIC CHEMICALS

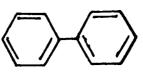
### Influence of Functional Groups on n-Octanol/Water Partition Coefficient of Benzene Derivatives





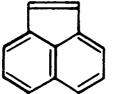
(PAH's or PNA's)



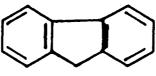


Naphthalene





Acenaphthalene

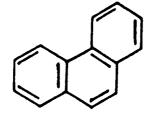


Fluorene

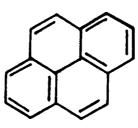


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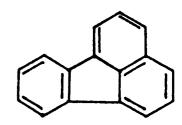
Anthracene



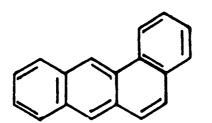
Phenanthrene



Pyrene



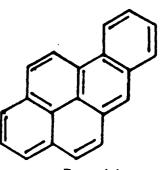
Fluoranthene



•

Benzo(a)anthracene

.



Benzo(a)pyrene

#### 6-39 OXYGEN COMPOUNDS

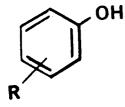
R R-C-OH Ŕ ALCOHOLS: METHANOL ETHANOL R3C-C, Peachive **ALDEHYDES:** FORMALDEHYDE PROPANAL  $R_2C=0$ **KETONES:** ACETONE BUTANONE R-C 0-R' **ESTERS**: ETHYL ACETATE DIOCTYLPHTHALATE R-CO ionic at low OH pHs (4-5) ACIDS:

BUTYRIC ACID



(AROMATIC RING)-OH

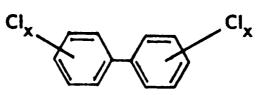
ACIDIC VERY WATER SOLUBLE VERY LOW TASTE/ODOR THRESHOLD



PHENOL 2,4-DIMETHYL<u>PHENOL</u> CRES<u>OL</u>

5-41

#### POLYCHLORINATED BIPHENYLS (PCB's)



relatively insoluable unless there is a Cosolvent

.

AROCHLORS	PERCENT CHLORINE
1221	21 %
1016	42 %
1242	42 %
1248	48 %
1254	54 %
1260	60 %

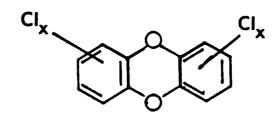
.

4

5-42

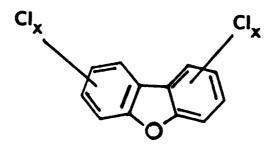
very toxic

DIOXINS



byproduct formed when man a facturing pesticules

Very toxic DIBENZOFURANS



high temp. fire with PCB's Lill form dibenzofuran

## ODOR THRESHOLDS FOR ORGANIC CHEMICALS

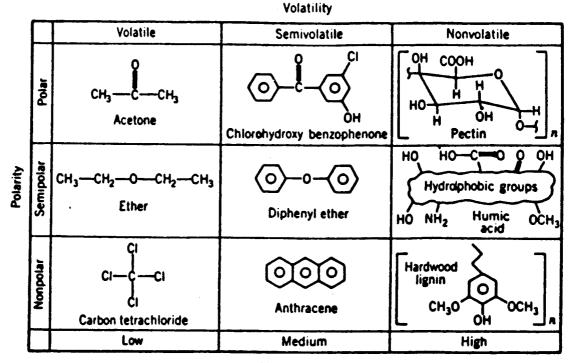
		MOL.	ODOR	100% ODOR
CHEMICAL	FORMULA	WT.	INDEX	RECOGNITION
AROMATICS (BETEX)				
BENZENE	C6H6	78	300	300 ppm
TOLUENE	C6H5-CH3	92	720	40 ppm
XYLENES	C6H5(CH3)2	106	360-18,200	0.4-20 ppm
1,2,3,5-TETRAMETHYLBENZENE	C6H5(CH3)4	134	136,000	2 ррb
		<u></u>		
ESTERS	CH3COOC2H5	88	1,900	50 ppm
ETHYLACETATE	C3H7COOC2H5	116	1,982,000	7 ppb
ETHYLBUTYRATE	CSHICOUCZHS			
KETONES	СНЗСОСНЗ	58	720	300 ppm
ACETONE		72	3,800	30 ppm
BUTANONE (MEK)	CH3COC2H5	114	171,000	20 ppb
2-HEPTANONE	CH3COC5H11		4	250 ppm
2-OCTANONE	CH3COC6H13	128		
SULFUR COMPOUNDS			000 000 000	2 ppb
ETHYLMERCAPTAN	C2H5SH	62	289,000,000	
BUTYLMERCAPTAN	C4H9SH	90	49,000,000	
ISOPROPYLMERCAPTAN	(CH3)2CHSH	76	1,052,000,000	
HYDROGEN SULFIDE	H2S	34	17,000,000	1 ppm

ODOR INDEX: O=VP/100% RECOGNITION ODOR

FROM: Handbook of Environmental Data on Organic Compounds

6-43





Molecular weight

FIGURE 16-3. Example compounds in classification schematic. (Reprinted from JAWWA, Vol. 70, No. 11 (November 1978) by permission. Copyright 1978, The American Water Works Association.)

Montgomery, James M., Consulting Engineers, 1985, Water Treatment Principles and Design, Chapter 16 "Organics"



ГТ	Volatile	Semivolatile	Nonvolatile
Polar	Alcohols Ketones Carboxylic acids	Alcohols Ketones Carboxylic acids Phenols	Polyelectrolytes Carbohydrates Fulvic acids
Semipolar	Ethers Esters Aldehydes	Ethers Esters Aldehydes Epoxides Heterocyclics	Proteins Carbohydrates Humic acids
Nonpolar	Aliphatic hydrocarbons Aromatic hydrocarbons	Aliphatics Aromatics Alicyclics Arenes	Nonionic polymers Lignins Hymatomelanic acid
}	Low	Medium	High

#### Volatility

#### Molecular weight

FIGURE 16-2. Schematic classification of organic compounds found in water. (Reprinted from JAWWA, Vol. 70, No. 11 (November 1978) by permission. Copyright 1978, The American Water Works Association.)

Montgomery, James M., Consulting Engineers, 1985, Water Treatment Principles and Design, Chapter 16 "Organics"



# Carbonate System

Lecture by: William Deutsch Woodward-Clyde Consultants

# SECTION CONTENTS

1

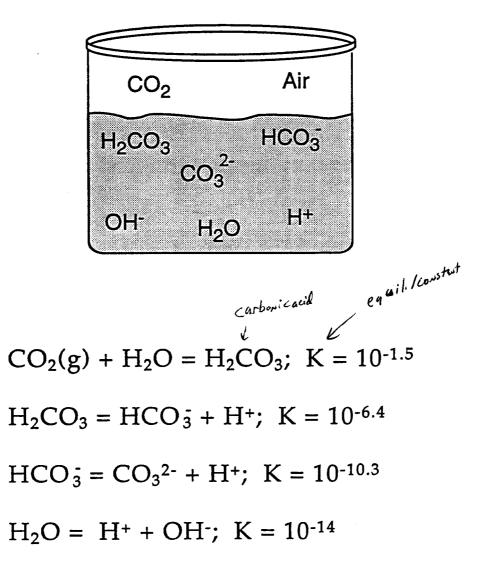
#### **The Carbonate System**

- It is the most important acid/base system in natural water
- Can act to neutralize strong acids or bases added to a system
- Tends to buffer the pH within a particular range
- CO, is important in biological processes
- Carbonate ions form strong complexes with cations
- Carbonate minerals are common in many rock types and these minerals are reactive with groundwater

#### Topics

- Carbonate speciation
- Open/closed systems with respect to CO<sub>2</sub> gas
- Carbonate mineral solubility
- pH buffers
- Alkalinity

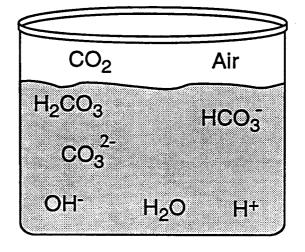
#### CO<sub>2</sub> (gas) and Water Equilibrium



#### Carbonate Species Concentrations in Open Systems

- Carbonate species are in equilibrium with CO<sub>2</sub> gas in the atmosphere above the solution
- Common condition for the soil and vadose zone
- The atmosphere acts as an unlimited source of carbon
- The total amount of dissolved carbon will change with the pH
- The dominant carbonate species will also change with pH

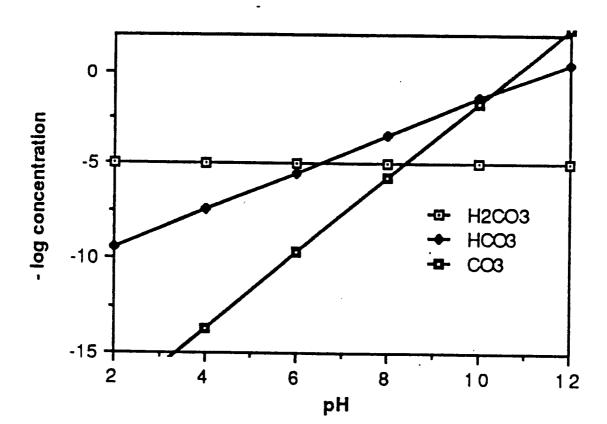
#### System Open to CO<sub>2</sub> Gas



# Use equilibrium constants to calculate concentration and distribution of species

## **Carbonate Species in an Open System**

in atmospheric conditions

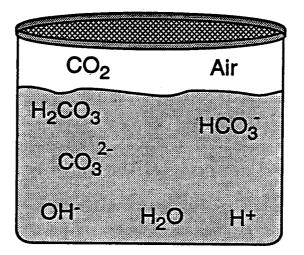


7-6

#### Carbonate Species Concentrations in Closed Systems

- No external source of carbon such as CO<sub>2</sub> gas
- Typical situation for groundwater
- Total dissolved carbon will remain constant as pH changes
- Dominant carbonate species will change in response to pH changes

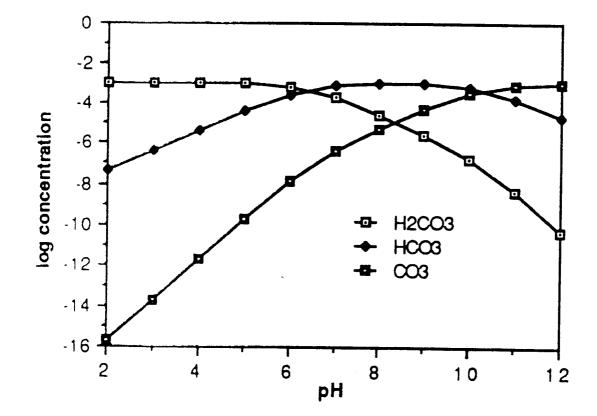
## System Closed to CO<sub>2</sub> Gas



Total carbonate in system is constant

 $Ct = Constant = m_{H_2CO_3} + m_{HCO_3} + m_{CO_3}^2 + m_{CO_3}^2$ 

### **Carbonate Species in a Closed System**

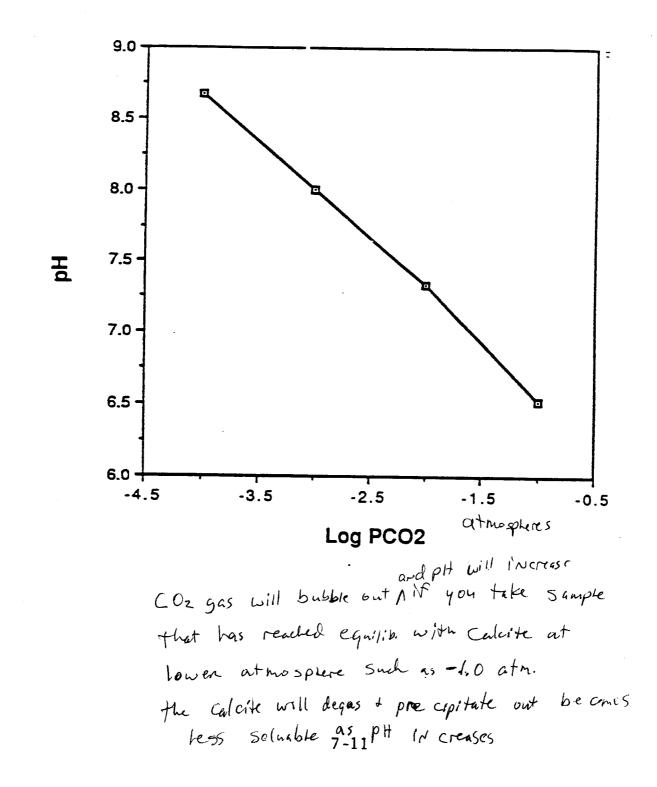


7-9

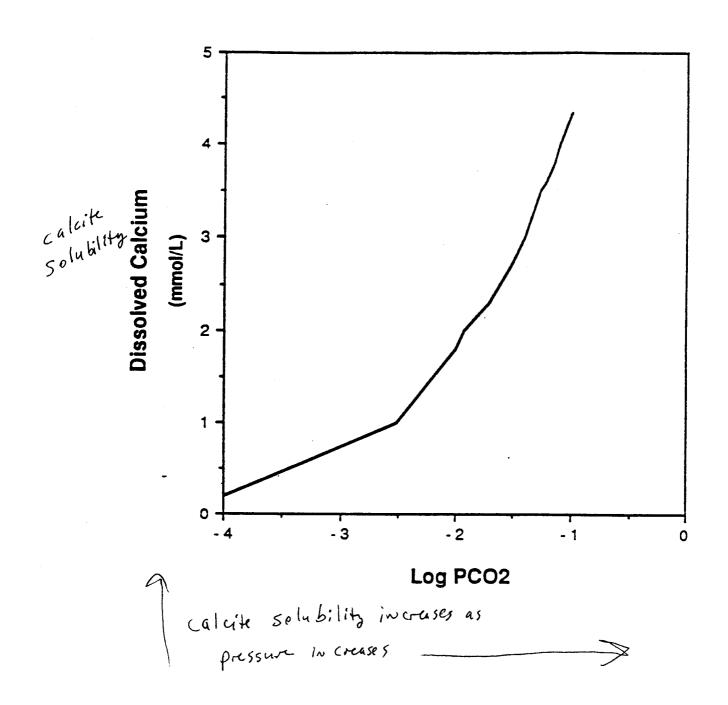
#### Solubility of Calcite in Open and Closed Systems

- CO<sub>2</sub> gas produces carbonic acid which increases the solubility of calcite
- Calcite is more soluble in a system open to CO<sub>2</sub> than a closed system
- In recharge zones, groundwater may be open to CO<sub>2</sub> gas exchange whereas downgradient it may be closed
- The amount of calcite dissolved will depend on whether equilibration with the mineral occurred under open or closed conditions

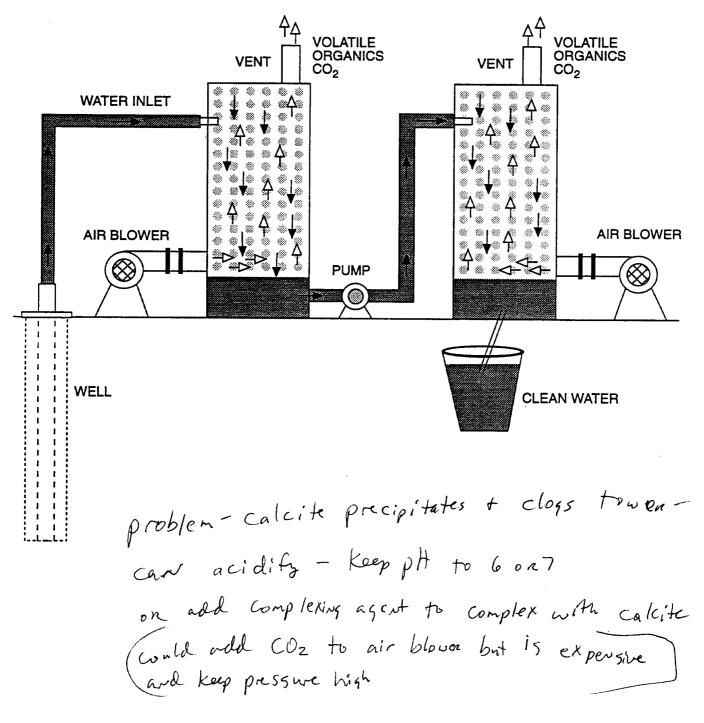
# pH and Log pCO<sub>2</sub> in Solution in Equilibrium with Calcite



#### Concentration of Dissolved Calcium in Water in Equilibrium with Calcite as a Function of pCO<sub>2</sub>



#### Packed Tower Air Strippers



#### pH Buffers

- Buffered solutions are capable of maintaining their pH as considerable amounts of acid or base are added
- pH buffering in groundwater is mainly a consequence of carbonate equilibria

#### **Calculation of Buffering Capacity**

1. Starting solution:

 $H_2CO_3 = 0.01$  moles/liter  $HCO_3^- = 0.01$  moles/liter

pH = ?

2. Add enough acid to change  $H_2CO_3/HCO_3$  ratio from 1 to 2 (3 ml of 1 molar HCI to a 1 liter solution)

pH = ?

Without buffering the pH would equal 2.5 if this amount of acid was added to pure water

#### **Calculation of Buffering Capacity (continued)**

If a base were added instead of an acid the reaction would be:

 $H_2CO_3 + OH^- = HCO_3^- + H_2O$ 

The presence of a carbonate solid can also buffer a solution according to the reactions:

 $CaCO_{3} + H^{+} = Ca^{2+} + HCO_{3}^{-}$ 

 $Ca^{2+} + HCO_3^{-} + OH^{-} = CaCO_3 + H_2O$ 

#### **Alkalinity**

• Alkalinity is a measure of the acid neutralizing dour to capacity of a solution

Total alkalinity =  $m_{HCO_3}^2 + 2m_{CO_3}^2 + m_{B(OH)_4}^2 + (equiv./L)$ 

 $m_{H_3SiO_4} + m_{HS} + m_{organic anions} + ... + m_{OH} - m_{H^+}$ 

- An alkalinity titration is generally perfomed on water samples to obtain the inorganic carbon concentration
- This assumes the other constituents are present in very small concentrations compared to inorganic carbon

#### Alkalinity (continued)

- The alkalinity titration is performed by adding small increments of dilute acid to the sample and measuring the resulting change in pH
- The reactions that occur are:

$$OH^{-} + H^{+} = H_{2}O$$

 $CO_{3}^{2-} + H^{+} = HCO_{3}^{--}$ 

$$HCO_{3}^{-} + H^{+} = H_{2}CO_{3}^{-}$$

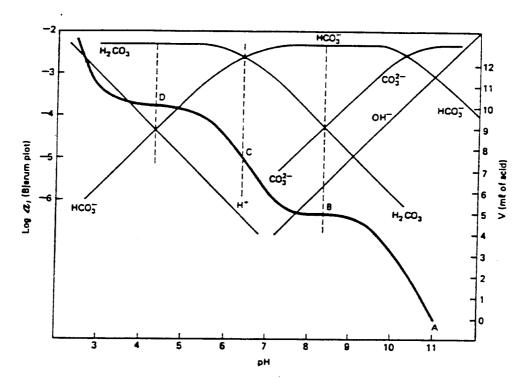


Figure 3-2 Titration curve (heavy line ABCD) for  $5 \times 10^{-3}$  m Na<sub>5</sub>CO<sub>5</sub> with acid, and Bjerrum plot for  $\Sigma CO_5 = 5 \times 10^{-5}$ . B is carbonate end-point, C is region of strong buffering, and D is bicarbonate end-point.

### Alkalinity (continued)

 Alkalinity is generally reported as mg/L CaCO<sub>3</sub>. This is not a normal concentration value. Alkalinity must be converted to concentration of the carbonate species

Alkalinity conversion:

Alkalinity (mg/L CaCO<sub>3</sub>) x 61 = "mg/L HCO<sub>3</sub>-"  

$$\begin{pmatrix} 1 + 2 \times 10^{-10.3} \\ [H^+] \end{pmatrix}$$
 x 50

 $\frac{\text{Alkalinity (mg/L CaCO_3) x 60} = "mg/L CO_3^{2-"}}{\binom{2 + [H^+]}{10^{-10.3}} \times 50}$ 

#### Alkalinity (continued)

Alkalinity Conversion Example:

Alkalinity measured at 100 mg/L CaCO<sub>3</sub>; pH = 8.5

HCO3:	$\frac{100}{(1 + 2x \ 10^{-10.3}) \times 50}$ [ 10 <sup>-8.5</sup> ]	x 61 = 118 mg/L
CO <sub>3</sub> <sup>2</sup> :	$\frac{100}{(2 + [10^{-8.5}]) \times 50}$	x 60 = 1.8  mg/L

#### Summary

- Dominant inorganic carbon species are strongly pHsensitive over the natural pH range of groundwater
- pCO<sub>2</sub> gas pressure influences the solubility of carbonate minerals
- Dissolved inorganic carbon species provide pH buffering capacity to water
- Alkalinity is a measure of a solution's acid neutralizing capacity and can be used to determine inorganic carbon species concentrations



C

# Chemical Evolution of Ground Water

Lecture by: William Deutsch Woodward-Clyde Consultants

# SECTION CONTENTS

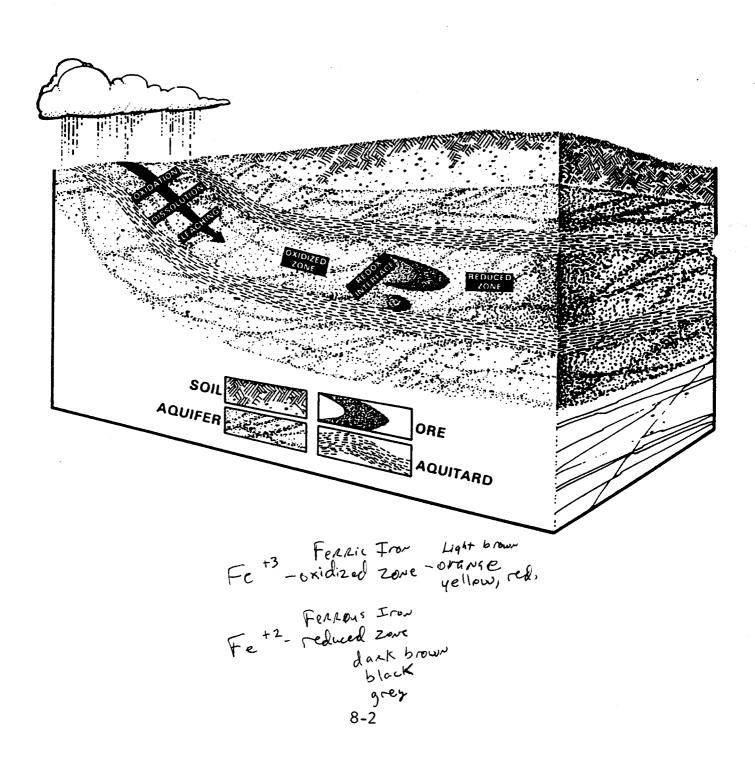
Additional References:

Champ, D.R., J. Gulens and R.E. Jackson, 1979. Oxidation-Reduction Sequences in Ground Water Flow Systems, *Canadian Journal of Earth Sciences*, Vol. 16, pp. 12-23.

## **The Chemical Evolution of Groundwater**

- Important water/rock processes
- General evolutionary sequences
- Examples

#### Aquifer Geochemical Processes and Redox Zones



#### **Important Chemical Processes**

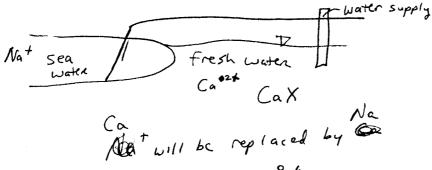
- Cation exchange
- Specific adsorption
- Calcite and gypsum equilibrium
- Dolomite equilibrium
- Oxidation of iron minerals and organic matter
- Reduction of manganese and iron oxides
- Reduction of dissolved sulfate
- Alteration of silicate minerals

# Cation Exchange - clay minerals

• Reactions of the type:

 $CaX + 2Na^+ = Na_2X + Ca^{2+}$ 

- Relatively fast equilibration compared to groundwater flow rates
- More important for major cations (Ca, Mg, Na, K) than for minor or trace constituents
- Required data:
  - 1. Distribution of cation exchange capacity in the aquifer
  - 2. Composition of exchangeable cations in the aquifer
  - 3. Equilibrium constants for ion exchange reactions



8-4

#### **Specific Adsorption**

• Direct complexation of aqueous species with the solid surface

 $Ag^{+} + XOH = [XO^{-} - Ag^{+}] + H^{+}$ 

where XO is the adsorption site

- Very important influence on the mobility of trace elements because they are strongly adsorbed into iron and manganese oxide and hydroxide solids
- Required data:
  - 1. Distribution and concentration of solids that adsorb solutes
  - 2. Initial composition of adsorbed solutes
  - 3. Equilibrium constants for the adsorption reactions  $K = \alpha_{Na_2^+} \times \alpha_{Ca^{2+}}$

8-5

Q C.a QNA

# Dissolution and Precipitation of Calcite and Gypsum (and any other soluble salts)

- Assumed to be rapid compared to groundwater flow rate
- Requires information on the distribution of soluble salts in the aquifer

#### **Dissolution and Precipitation of Dolomite**

- Slow to equilibrate
- May be affected by incongruent dissolution, i.e.,

 $CaMg (CO_3)_2 = CaCO_3 + Mg^{2+} + CO_3^{2-}$ 

• Need data on the presence of dolomite and rate equations for dissolution and precipitation

## Oxidation of Pyrite, Organic Matter, Ferrous Iron Silicates and Carbonates

• Consumes dissolved oxygen  

$$\rho_{H^{ri}}^{tc}$$
  
 $2 \operatorname{FeS}_{2} + 7.5 \operatorname{O}_{2} + 7 \operatorname{H}_{2}\operatorname{O} =$   
 $\operatorname{Fexacc} hydrowide \int_{1}^{SulfBife} dvidte for the formula of the fore$ 

$$O_2 \longrightarrow 2O^{2-}$$

#### Oxidation of Pyrite, Organic Matter, Ferrous Iron Silicates and Carbonates (continued)

- Lowers the redox potential  $(E_{H})$  of the solution
- Required data:
  - 1. Oxygen content of recharge water
  - 2. Distribution of pyrite and other ferrous minerals
  - 3. Distribution and reactivity of organic matter
  - 4. Rate equations that are available for pyrite but not for most of the organics

# Reduction of Manganese Oxides Followed by Reduction of Reactive Iron Oxides

- Critical in predicting trace element distribution because of the strong adsorption of trace elements on these solids
- Required data:
  - 1. Distribution of iron and manganese oxides
  - 2. Distribution of reactive organic matter (the reducing agent)

#### Reduction of Sulfate to Sulfide by Reactive Organic Matter

 $SO_4^{2-} + CH_2O = S^{2-} + 2CO_2 + 2H_2O$ 

- Great influence on both major and trace element chemistry
- Sulfide forms very insoluble solids with most heavy metals under reducing conditions
- Increased carbonate concentration may lower the solubility of calcite and increase degree of carbonate complexation
- Requires data on distribution of organic matter and rate constants

### **Alteration of Silicate Minerals**

- Feldspars and mafic minerals (biotite, hornblende, pyroxenes) more reactive than quartz
- Possible equilibrium of groundwater with secondary minerals (clays and zeolites) produced by chemical weathering

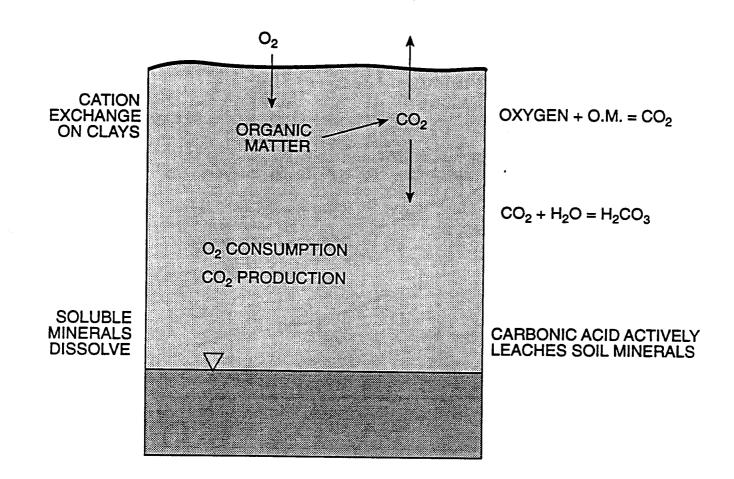
### Nonchemical Processes that Affect the Composition of Groundwater

- Hydrodynamic dispersion
- Diffusion
- Evolution/transport of gases from deep sedimentary aquifers (e.g., CH<sub>4</sub> and H<sub>2</sub>S)

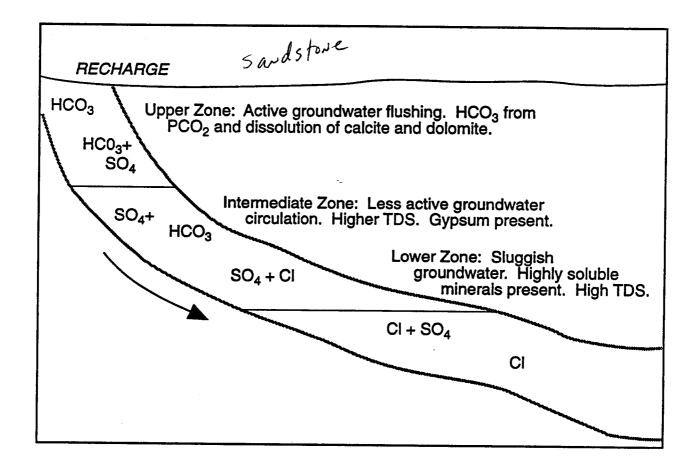
### The Soil and Vadose Zones

- Water flows through these chemically-active zones on its way to the water table
- Reactivity is mainly due to the presence of:
  - organic matter
  - gases  $(O_2 \text{ and } CO_2)$
  - clay minerals
  - soluble minerals
- The occurrence and concentration of these reactive phases may vary greatly with the seasons and topography

### **Processes in the Soil and Vadose Zones**



### **Anion Evolution Sequence (Chebotarev)**



- This sequence is understandable in terms of mineral availability and solubility
- Reversals may occur (e.g., reduction of sulfate and production of bicarbonate by anaerobic decay)

### **Cation Evolution**

- Variations in dominant cations are also observed in groundwater systems
- No general trend has been established because cation exchange on clays often causes alterations or reversals in the sequence

### **Redox Evolution**

• As the redox potential decreases the following sequence is possible in groundwater

 $O_2/H_2O \longrightarrow NO_3/N_2 \longrightarrow SO_4^{2-}/H_2S \longrightarrow$ 

 $CO_2/CH_4 \longrightarrow H_2O/H_2$ 

- Reactions must be biologically catalyzed
- Sequence rarely proceeds past the nitrogen couple

### Chemical Evolution of Groundwater - Case Study - Acid Mill Tailings

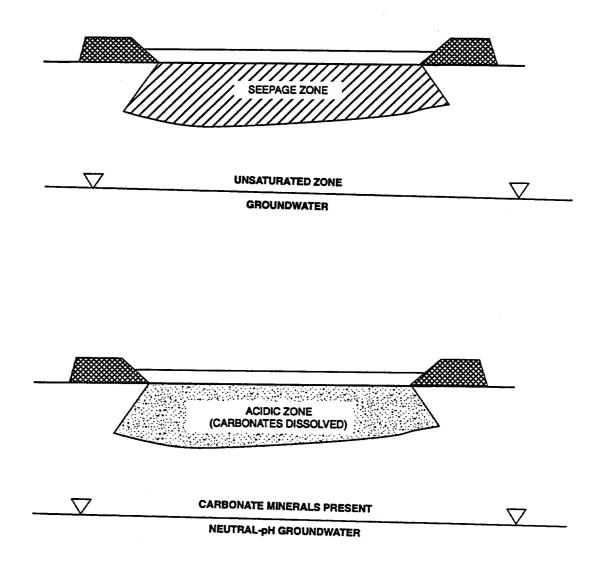
Concentrations of Selected Constituents in Acid Tailings Solutions (milligrams/liter)

	Mexican Hat, Utah	Gunnison, Colorado
pН	4.37	1.62
U	3.3	0.4
Fe	1,070	35,400
Мо	< 0.01	9.5
SO4	7,800	130,000

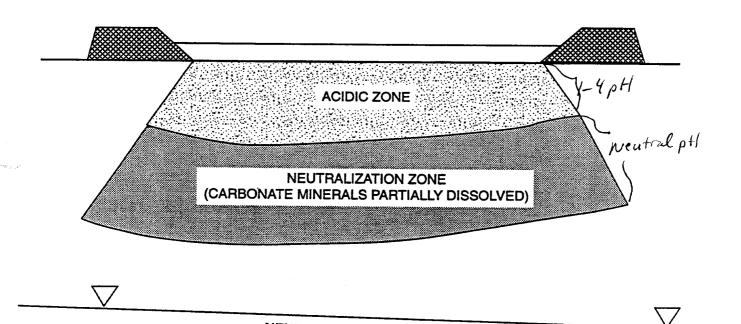
Sulphuric acid was used to

leach the ore

# Seepage Movement Below a Tailings Pile

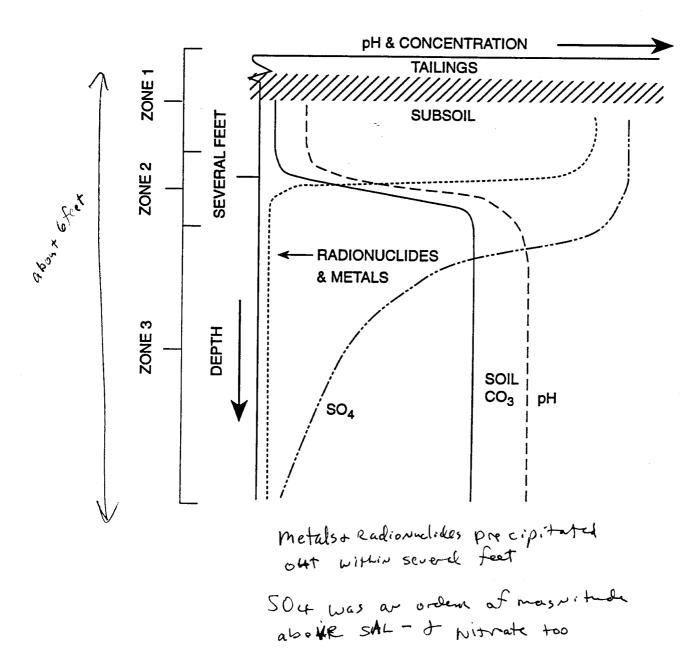


### Seepage Movement Below a Tailings Pile

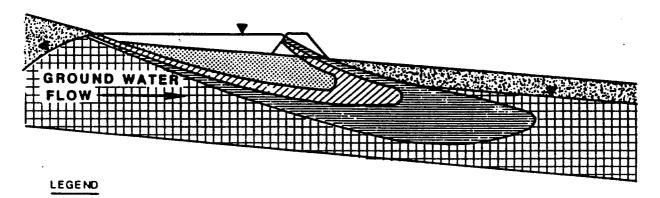


#### NEUTRAL-pH GROUNDWATER

### Distribution of Indicator Parameters in Foundation Material



### Contaminant Plume Characteristics at Uranium Mill Tailings Site



ACID ZONE

NEUTRALIZATION ZONE

NEUTRAL PH ZONE

### Chemical Evolution of Groundwater-Summary

- The principle types of chemical reactions are well established
- The minerals that affect major ion chemistry have been identified
- Reaction rates for many of the important minerals are not known
- The soil and vadose zones in recharge areas can play a major role in removing oxygen from infiltrating water and adding carbon dioxide

### Chemical Evolution of Groundwater-Summary (continued)

- The anion evolutionary sequence is well established, but reversals do occur
- A cation evolutionary sequence does not normally exist
- Redox evolution requires bacterial mediation
- Changes in groundwater chemistry can occur over short distances if there is significant disequilibrium

## Adsorption of Solutes

Lecture by: Patrick Longmire Los Alamos National Laboratory

### SECTION CONTENTS

Section	Outline	9-1
		•
Lecture	Illustrations	

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Additional References:

Benjamin, M.M., 1983. Adsorption and Surface Precipitation of Metals on Amorphous Iron Oxyhydroxide, *Environmental Science and Technology*, Vol. 17, No. 11, pp. 686-692.

Brownawll, B.J., H. Chen, J.M. Collier and J.C. Westall, 1990. Adsorption of Organic Cations to Natural Materials, *Environmental Science and Technology*, Vol. 24, No. 8, pp. 1234-1241.

- Davis, J.A. and J.O. Leckie, November 1978. Effect of Adsorbed Complexing Ligands on Trace Metal Uptake by Hydrous Oxides, *Environmental Science and Technology*, Vol. 12, No. 12, pp. 1309-1315.
- Holsen, T.M., E.R. Taylor, Yong-Chan Seo and P.R. Anderson, 1991. Removal of Sparingly Soluble Organic Chemicals from Aqueous Solutions with Surfactant-Coated Ferrihydrite, *Environmental Science and Technology*, Vol. 25, No. 9, pp. 1585-1589.

Penrose, W.R., W.L. Poizer, E.H. Essington, D.M. Nelson and K.A. Orlandini, 1990. Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region, *Environmental Science and Technology*, Vol. 24, No. 2, pp. 228-234.

Weber, W.J., Jr., P.M. McGinley and L.E. Katz, 1991. Sorption Phenonmena in Subsurface Systems: Concepts, Models and Effects on Contaminant Fate and Transport, *Water Resources Research*, Vol. 25, No. 5, pp. 499-528.

### **ADSORPTION OF SOLUTES**

#### I. INTRODUCTION

- II. THE SORPTION PROCESS A. Physical Adsorption B. Electrostatic Adsorption C. Specific Adsorption
- iii. THE Kd CONCEPT

#### IV. MULTI-PARAMETER SORPTION MODELS A. Isotherm Models

- **1. Freundlich Model**
- 2. Langmuir Model
- **B. Mass Action Models** 
  - 1. Single-Binary Ion Exchange
  - 2. Multi-Site Models
- C. Electrical Double Layer Model
  - 1. Surface Area
  - 2. Surface Charge
  - 3. Adsorption Edge Plots
- D. Effects of Organics on Adsorption
- V. SUMMARY
- VI. PROBLEM SET

### **ADSORPTION OF SOLUTES**

- Introduction
- The sorption process
- The Kd concept
- Multi-parameter sorption models
- Effects of organics on adsorption
- Practical examples of adsorption
- Summary

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### INTRODUCTION

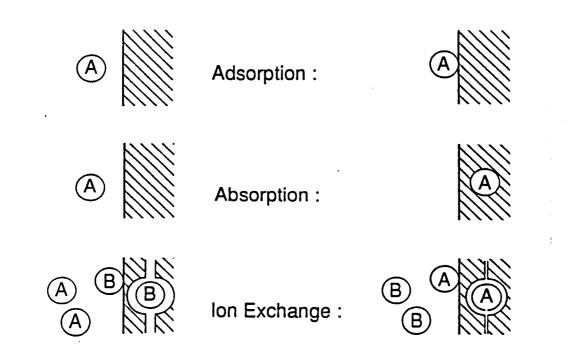
DISSOLVED SUBSTANCES HAVE A TENDENCY TO PARTITION THEMSELVES BETWEEN THE SOLUTION AND SURFACES OF SOLIDS.

SORPTION INCLUDES:

ADSORPTION ABSORPTION

#### ADSORPTION - CONTROLS SOLUTE TRANSPORT AT ALL CONCENTRATIONS BELOW MINERAL SATURATION, AND BECOMES MOST IMPORTANT AT THE LOWEST SOLUTE CONCENTRATIONS.

Adsorption is a process for separating inorganic and organic contaminants from waters and waste waters. The most common environmental applications of this process are used in ion exchange (inorganic solutes) and activated carbon systems (organic solutes). During the mid-1970s, interest in adsorption as a process for removal of organics from drinking water heightened as the public became increasingly concerned about water sources contaminated by industrial wastes, agricultural chemicals, and sewage discharges. Adsorption is the physical and/or chemical process in which a substance is accumulated at an interface between phases. The adsorbate is the substance being removed from the liquid phase to the interface. The adsorbent is the solid phase onto which the accumulation occurs.



#### DEPENDENCE OF TYPES OF ADSORPTION ON ENVIRONMENTAL PHYSICO-CHEMICAL PARAMETERS

	Phy sical adsorption	Electro- static adsorption	Specific adsorption
рН	variable	appreciable	appreciable
Eh	variable	large	large
Temperature	small	appreciable	appreciable
Speciation of sorbate	large	large	large
Concentration of sorbate	small	large	large
Concentration of complexing or competing solutes	large	large	large
lonic strength	small	large	variable
Properties of the sorbent	small	large	large
Time	small ( <i>Fas</i> t)	small	variable

Physical adsorption includes non-ionized organic compounds; electrostatic adsorption includes cation exchange by clay minerals; and specific adsorption of cations and anions by metal oxides. The sensitivity of each type of sorption to changes in the physical-chemical environment is summarized in this table. All three types of adsorption are strongly influenced by the speciated form of the adsorbate. Other parameters including Eh, pH, and concentration of competing and complexing species influence adsorption by controlling speciation of the adsorbate.

### THE Kd CONCEPT

A measure of the ratio of the amount of the element bound to the solid phase relative to the amount that is in solution has been used to this effect

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- Empirical value measured in laboratory experiment
- Does not imply reversibility or equilibrium
- Adsorption mechanism is not known Rd has the units of  $L^3 \times M^{-1}$

The distribution coefficient (Kd) indicates the extent to which adsorption takes place for a particular ion. The Kd is the ratio of the mass of an element adsorbed onto the solid phase per unit weight of solid to the mass of an element remaining in solution per unit volume of liquid:

(g of sorbed element/g of solid) Kd (ml/g) = -----

(g of element remaining in solution/ml of solution)

The Kd for  $CrO_4^{-2}$  on amorphous iron hydroxide (Fe<sub>2</sub>O<sub>3</sub> ·H <sub>2</sub>O) (am)) varies strongly with both pH and ion composition of the bulk solution. The distribution coefficient fails as an invariant predictor of attenuation, because it depends on both aqueous and solid phase properties.

### COMPARISON OF Kd FOR $CrO_4^{-2}$ ON Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O IN DIFFERENT SOLUTIONS

	,	Kd (ml/g)
Solution pH		$\overline{Na}$ , $\overline{NO}_3$ , $\overline{SO}_4$ , $\overline{Ca}$ , $\overline{CO}_2$
5.65	478,630	18,621
6.53	281,838	11,482
6.94	112,202	5,370
7.50	10,471	1,413
7.80	6,607	132

#### SOURCE: EPRI, 1985

. . .

Kd is related to the transport velocity of the trace element to that of the water by determining the retardation factor R.

The retardation equation:

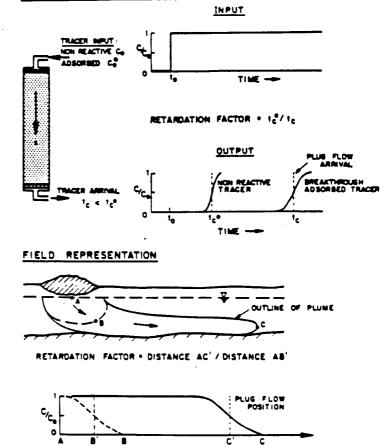
$$R = 1 + \frac{pKd}{\phi}$$
  
higher the R, the slower it moves  
$$R = 10, \text{ then moves } \frac{1}{10} \text{ of the Velocity of water}$$
  
Where

P = Bulk density (M/L<sup>3</sup>)

 $\phi$  = Effective Porosity (L<sup>3</sup>/L<sup>3</sup>)

The Kd is measured experimentally, either by batch or column methods. Because Kd varies with the experimental conditions, experiments must be carefully controlled. The solution composition must have the same composition as natural ground water in equilibrium with the rock type used in the experiment. For modeling contaminant migration, the retardation factor is used. When there is no adsorption, Kd equals zero, and R is equal to one (its minimum value). A major problem in estimating the retardation factor is the dependence of Kd on the laboratory conditions under which it is measured.

#### LABORATORY REPRESENTATION



Schematic illustration of the retardation concept: the ideal laboratory case and a hypothetical field case (Cherry, et.al., 1984)

The retardation concept is illustrated in this figure for laboratory conditions and for a hypothetical field situation. For the field sample, the groundwater velocity is assumed to have little spatial or temperal variability.

### RETARDATION FACTORS FOR SOME RADIONUCLIDES IN ROCK MATERIALS BEING CONSIDERED FOR REPOSITORY SITING

ELEMENT	GRANITE	BASALT	TUFF	SHALE	SALT
Sr	20-4000	50-3000	100-100000	100-100000	10-50
Cs	200-100000	200-100000	500-100000	200-100000	40-100
Тс	1-40	1-100	1-100	1-40	1-10
U	40-500	100-500	40-400	100-2000	20-100
1	1	1	1	1	1
Pu	20-2000	20-10000	20-5000	50-100000	200-2000
Am	500-10000	100-1000	100-1000	500-100000	200-2000
Ra	50-500	50-500	100-1000	100-200	20-50

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SOURCE: Krauskopf, 1986

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1.	cupacity

Table 0-5. Ranges of s		L Cop
Element	Devitrified Tuff	Zeolitized Tuff
Cs, Sorption	150-870	8600-29,000
Cs, Desorption	310-630	13,000-33,000
Sr, Sorption	53-190	1800-20,000
Sr, Desorption	56-200	2700–20,000
Ba, Sorption	430-1500	15,000-130,000
Ba, Desorption	440-1300	34,000–190,000
Ce, Sorption	80-15,000	550-2000
Ce, Desorption	400-15,000	1200-13,000
Eu, Sorption	90–7500	1200-2500
Eu, Desorption	800-7300	2100-8700
Am, Sorption	130	180
Am, Desorption	2200	1100
Pu, Sorption	110	120
Pu, Desorption	1100	340
Tc (air), Sorption	0.3	0.2
Tc (air), Desorption	1.2	2.0
Tc $(N_2)$ , Sorption	8–26	13
Tc $(N_2)$ , Desorption	18–79	118
U (air), Sorption	1.6-2.2	2.3-5.1
U (air), Desorption	6–13	15
$U(N_2)$ , Sorption	0.5-1.5	15
$U(N_2)$ , Desorption	2–14	57
I, Sorption	0	0

Table 6-5. Ranges of sorption ratios (mL/g).

Source: From Wolfsberg (1980).

Wolfsberg, K. 1980. Sorptive properties of tuff and nuclide transport and retardation. In: J.K. Johnstone and K. Wolfsberg, Eds., Evaluation of Tuff as a Medium for Nuclear Waste Repository: Interum Status Report on the Properties of Tuff. Sandia National Laboratory Report SAND80-1464, p. 39-48.

Element	Salt	Basalt	Tuff	Granite
Tc	2 <sup><i>a</i></sup>	20, <sup><i>b</i></sup> O	10, <sup><i>b</i></sup> O	4 <sup>a</sup>
Pu	500, <sup>b</sup> 50	$200,^{b} 100$	500, <sup>b</sup> 40	500, <sup>b</sup> 100
Np	30, <sup>b</sup> 7	50, <sup>b</sup> 3	50, <sup>b</sup> 3	50, <sup>b</sup> 1
Ι	0	0	Ó	0
U	1a	6 <i>a</i>	<b>4</b> <i>a</i>	4 <sup>a</sup>
Cs	1,800	300	100	300
Ra	5	50	200	50
Sr	5	100	100	12
С	0	0	0	0
Am	300	50	50	200
Sn	1, <sup><i>b</i></sup> , 50	10, <sup>b</sup> 100	50, <sup>b</sup> 500	10, <sup>b</sup> 500
Ni	6	50	50	10
Se	20; 100, <sup>b</sup> 20	20, <sup>b</sup> 5	2	2
Cm	300	50	50	200
Zr	500	500	500	500
Sm	50	50	50	100
Pd	3	50	50	10
Th	50, 100	500	500	500
Nb	50	100	100	100
Eu	50	50	50	100
Pa	50	100	100	100
РЬ	2	25	25	5
Мо	0, 5, <sup>b</sup> 1	10, <sup>b</sup> 4	10, <sup>b</sup> 4	5, <sup>b</sup> 1

**Table 7-7.** Empirically derived  $R_d$  (ml/g) values from batch experiments at 25°C. 0.1 MPa for selected radionuclides in order of ranking.

<sup>a</sup>No significant difference beween value measured in oxidizing and reducing Eh's.

 $^{b}$ Reducing conditions, second-value oxidizing conditions. First value for dome salt, second for bedded salt.

Johnstone, J.K., and K. Wolfsberg, Eds. 1980, Evaluation of Tuff as a Medium for Nuclear Waste Repository: Interim Status Report on the Properties of Tuff. Sandia National Laboratory Report SAND80-1464.

#### 9-100

#### **RELATIONSHIP BETWEEN Kd AND RETARDATION**

- Not Simple
- Cannot assume a single Kd value for an element along the flow path considered
- Assumes that the entire mass of solid is equilibrated with solution

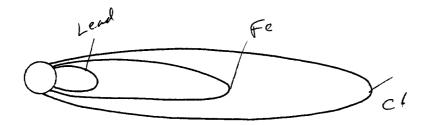
Most Kd measurements involve crushed rock or soil equilibrated with trace amounts of solutes in solution. The measured Kd depends on the particle size of the sample, the pH, the time of equilibration, and the temperature. In addition, it is not known how Kd values measured in static experiments related to the retardation factors in ground water, which may flow interstitially, along grain boundaries, or through fractures.

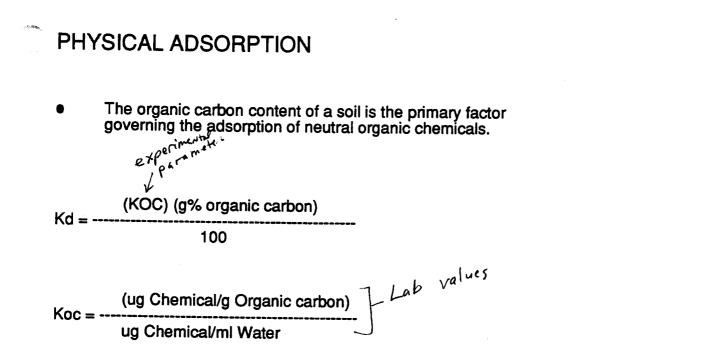
### **CLASS EXERCISE**

GIVEN THAT Rd = 1 + <u>pKd</u>, where n Rd = RETARDATION FACTOR, p = DENSITY (g/cm<sup>3</sup>), n = POROSITY, AND Kd = DISTRIBUTION COEFFICIENT (ml/g) CALCULATE Rd FOR THE FOLLOWING:

SPECIES	Kd(ml/g)	p/n	Rd
CI	0	8	1
Fe	10	8	81
Pb	50	8	401

BELOW IS AN ISOCONCENTRATION MAP FOR A HYPOTHETICAL WASTE SITE WITH GROUND WATER CONTAMINATION. LABEL ISOCONCENTRATION LINES WITH APPROPRIATE SPECIES BASED ON Rd.





The degree that a neutral organic chemical (benzene, toluene, xylene, and carbon tetrachloride) partitions between water and soil is a measurement of the magnitude of the Kd or Koc.

This table is a proposed classification scheme for the mobility of anthropogenic organic contaminants. Organic contaminant mobility is related to partitioning of contaminants into solid organic matter or humic substances. When partitioning into solid organic matter increation (high KOC values), the mobility of the organic contaminant decreases.

### High KOC = Low Mobility

SOLVENT	Кос	MOBILITY CLASS
methanol, acetone, methyl ethyl ketone, pyridine, ethyl acetate, isobutyl alcohol, diethyl ether, cyclohexanone, n-butyl alcohol, o-cresol, p-cresol, methyl isobutyl ketone, methylene chloride		Very Highly Mobile
m-cresol, carbon disulfide, benzene	100	Highly Mobile
trichloroethylene, 1,1,1-trichloroethane		
carbon tetrachloride toluene	200	-
tetrachioroethylene chlorobenzene	300	_ Medium Mobility
o-xylene	400	-
	500	
p-xylene		
m-xylene	600	 
ethyl benzene		
	700	Low Mobility
	800	  -
o-dichlorobenzene	900	  -
SOURCE: Utah Water Research Laboratory		

### **RETARDATION FACTORS FOR ORGANIC SOLUTES**

 $R = 1 + 3.2 \text{ffoc (kow)}^{0.72} \text{p } (1 - N_t) / N_t$ 

where

f = fraction of material  $< 125 \mu m$ 

foc = fraction organic carbon on  $< 125 \mu m$  material

 $p = bulk density (g/cm^3)$ 

 $N_t$  = total porosity

kow = octanol/water partition coefficient

The parameters f, foc, p,  $N_t$ , and kow are measured experimentally. The above equation is empirical based on the work of Schwarzenbach, et al. (1983). Retardation factors calculated from this equation are valid only at sorption equilibria. This equation is useful for predicting the magnitude of the velocity at which a specific hydrophobic (water disliking) organic compound is transported in a given aquifer.

### **CLASS EXERCISE**

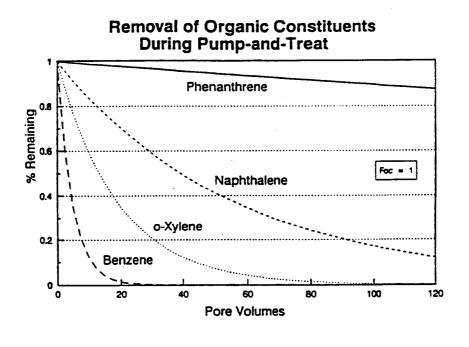
GIVEN THAT Rd = 1 + <u>pKd</u>, where n Rd = RETARDATION FACTOR, p = DENSITY (g/cm<sup>3</sup>), n = POROSITY, AND Kd = DISTRIBUTION COEFFICIENT (ml/g) CALCULATE Kd AND Rd FOR THE FOLLOWING:

<b>SPECIES</b>	KOC	00	Kd	p/n	Rd
BENZENE	100	0.01		8	
TOLUENE	200	0.01		8	
<b>M-XYLENE</b>	600	0.01		8	
	1/00			-	

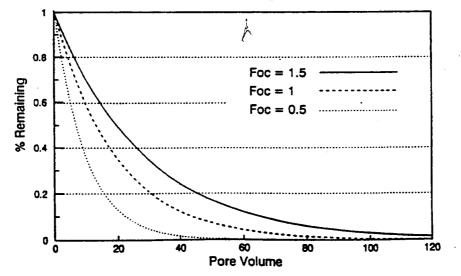
*Note: Kd* = *KOC x Organic Carbon Content.* 

BELOW IS AN ISOCONCENTRATION MAP FOR A HYPOTHETICAL WASTE SITE WITH GROUND WATER CONTAMINATION. LABEL ISOCONCENTRATION LINES WITH APPROPRIATE SPECIES BASED ON Rd.









The upper figure illustrates the change in the concentration of benzene, o-xylene, naphthalene, and phenanthrene after 100 pore volumes of solution have been extracted. Benzene is the most mobile (greatest removal) of the four organic compounds listed in the upper figure. The lower figure shows the difference in o-xylene removal as a function of the solid-organic carbon content of the soil. These estimation techniques predict much greater removal efficiencies when the solid-organic carbon content is low. These relationships are probably not valid when the solid organic carbon content is below 0.5 percent.

### MULTI-PARAMETER SORPTION MODELS

### ADSORPTION EQUATIONS

Adsorption of a single solute species by a solid can be evaluated mathematically by several different types of equations. An adsorption isotherm is a mathematical equation for relating concentrations of adsorbed and free adsorbate at a surface at a constant temperature.

For the adsorption of a solute X from solution by a mass of solid, m, the Freundlich isotherm is:

x -- = K [C]<sup>l/n</sup>

where X is mass of solute adsorbed, K is the distribution coefficient, [C] is the active concentration of C in the solution, and n is a constant. For most systems, K is constant only over a limited concentration range, when the quantity x/m is a simple mass ratio.

A more realistic representation of the adsorbed fraction is to use units for M that express the adsorption capacity of the active solid surface. This is done by using surface area or the number of available adsorption or charged sites per unit area on the active surface. This concept of finite adsorption capacity enters into the Langmuir isotherm.

x		b[C]	
-	=		
xm		1 + b[C]	

where x/xm is the fraction of the adsorption capacity that is occupied by x, and b is a constant.

## **FREUNDLICH EQUATION**

The simplest of the isotherm equations is the Freundlich equation

 $x/m = KC^{1/n}$ 

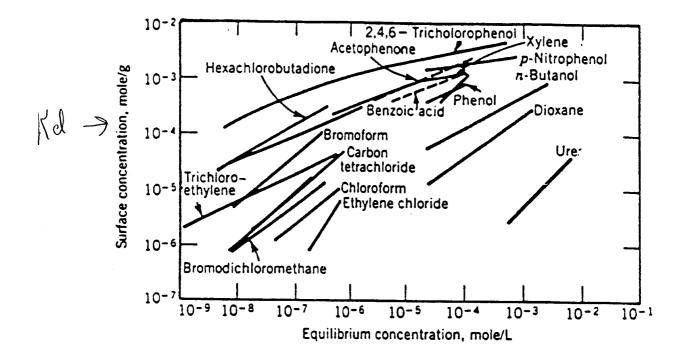
or in logarithmic terms

LOG x/m = LOG k + 1/n LOG C

x/m = The weight of sorbate divided by weight of sorbent (μg/g or mg/g)

C = The dissolved concentration of the sorbate

k and n = Constants



This figure shows some Freundlich isotherms graphically. All these compounds are adsorbed on granular activated carbon (GAC) to different degrees; substituted phenols (common odorcausing industrial contaminants) are generally more readily adsorbed than halogenated methanes and ethylenes. The greater the amount of adsorption, the higher Kf is, that is, t' adsorption constant. The slope of the isotherm is the parameter 1/n. Readily adsorb, organics onto GAC include aromatic solvents (benzene, toluene), chlorinated aromatics (PCBs, chlorobenzne), phenols and chlorophenols, polynuclear aromatics, pesticides and herbicides, chlorinated non aromatics (carbon tetrachloride), and high MW hydrocarbons (gasoline, humic substances). Alcohols, ketones, aldehydes, colloidal organics, and low MW aliphatics are poor adsorbates with GAC.

. .

## LANGMUIR EQUATION

Developed to describe the adsorption of gas molecules onto the surface of homogeneous solids

$$\frac{X}{XM} = \frac{bC}{1+bC}$$

X = Amount of solute adsorbed per mass of solid

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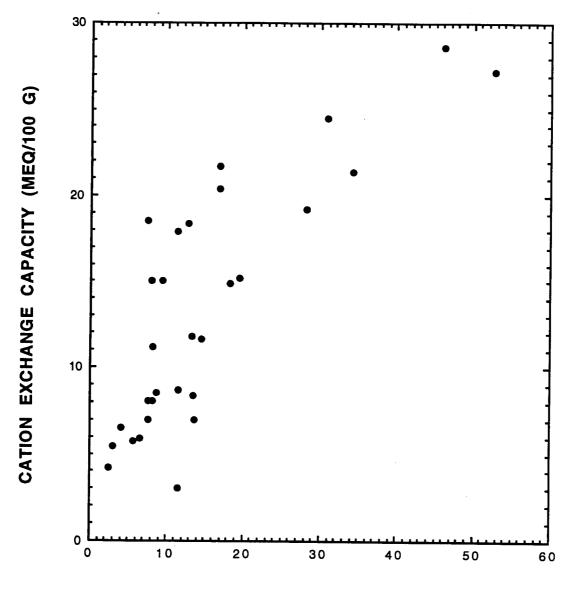
- Xm = Maximum amount which can be adsorbed by the solid
- C = Equilibrium solute concentration of sorbate
- b = Constant related to the energy of adsorption

### MASS ACTION MODELS

Mass action models include ideal ion exchange (exchange of cesium or strontium on a singlesite aluminosilicate) and multi-site exchange. These models describe ion exchange with alkaline earth (magnesium, calcium, barium, etc.) and alkaline metals (sodium, potassium, cesium, etc.). The adsorbents (usually clay minerals) have a constant cation exchange capacity, and the sorbate ions are not complexed.

### ELECTRICAL DOUBLE-LAYER MODELS

A theoretical model of the cation adsorption process can be developed from electrostatic considerations. The surface of a mineral or an amorphous solid immersed in a solution typically has a net negative electrostatic charge that attracts cations from the solution to maintain electroneutrality. The charge tends to immobilize a "fixed layer" of cations at the solid surface.

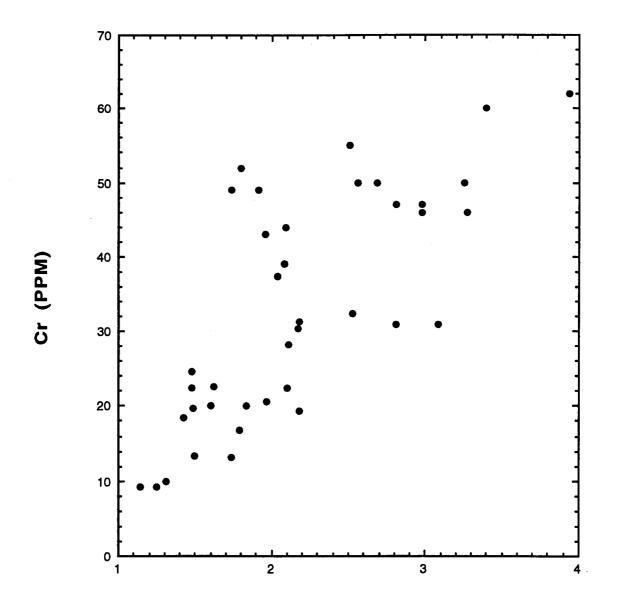


SOILS, LOS ALAMOS, NEW MEXICO

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WT % CLAY-SIZE MATERIAL

SOIL SERIES, LOS ALAMOS, NEW MEXICO





9-22B

## CATION EXCHANGE CAPACITIES FOR VARIOUS MATERIALS

Material	Approximate Cation Exchange Capacity (meq/100g)	
Organic matter	150-500	
Kaolinite	3–15	
Illite	10–40	
Smectite	80–150	
Feldspars	1-2	
Quartz	1–2	
Basalt	1–3	
Zeolites	230-620	

Source: Birkeland (1984)

This table summarizes the cation exchange capacities (CEC) for different materials. The CEC varies with the material and it is expressed in milliequivalents (meq) per dry weight of the material. One meq is defined as 1 mg of H<sup>+</sup> or the amount of any other cation that will displace it. For example, if the CEC is 1 meq/100g, 1 mg of H<sup>+</sup> is adsorbed. If Ca<sup>2+</sup> displaced the H<sup>+</sup>, the amount of Ca<sup>2+</sup> has to be equivalent to 1 meq of H<sup>+</sup>. The amount of Ca<sup>2+</sup> required to displace 1 meq of H<sup>+</sup> is 40/2 (atomic weight/valence), or 20 mg, the weight of 1 meq of Ca<sup>2+</sup>.

### IMPORTANT PROPERTIES OF A SORBENT

- Surface Area
- Surface Charge
- Effects of Solution Species on Surface Charge
- Properties of Electrical Double Layer

The important properties of a sorbent are given above. The surface area is experimentally determined and varies between different minerals and amorphous solids, ranging from 2 meter squared per gram ( $m^2/g$ ) for hematite (Fe<sub>2</sub>O<sub>3</sub>) to over 1000 m<sup>2</sup>/g for solid organic matter, known as humic substances. The net surface charge is usually negative above a certain pH called the zero point of charge (ZPC). The speciated form of the adsorbate also influences adsorption. Generally, under highly acidic conditions, anions can be adsorbed because the net surface charge of the adsorbent is positive below the ZPC.

## SURFACE AREA OF SELECTED SOLIDS

Solid Phase	Surface Area (m²/gm)
Kaolinite	10–20
Montmorillonite	600-800
Attapulgite	70-120
Fe (OH) <sub>3</sub> (am)	306
γ–FeOOH	45
Fe <sub>2</sub> O <sub>3</sub>	1.8

- dominant sorbing phase at Los Almos

### ZERO POINT OF CHARGE

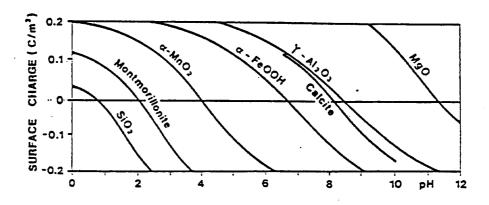
- At some intermediate pH, the number of net positive and negative surface sites will be equal
- The solid surface has no net surface charge at a given pH called zero point of charge (ZPC)
- At pH values below ZPC a mineral will be positively charged, and can adsorb anions, whereas at higher pH's they become cation exchanger

### ZERO POINT OF CHARGE<sup>e</sup>

Material	pHzpc
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	9.1
$\alpha$ -Al(OH) <sub>3</sub>	5.0
y-AlOOH	8.2
CuO	9.5
Fe <sub>3</sub> O <sub>4</sub>	6.5
α-FeOOH	7.8
γ-Fe <sub>2</sub> O <sub>3</sub>	6.7
"Fe(OH) <sub>3</sub> "(amorph)	8.5
MgO	12.4
$\delta$ -MnO <sub>2</sub>	2.8
$\beta$ -MnO <sub>2</sub>	7.2
SiO <sub>2</sub>	2.0
ZrSiO <sub>4</sub>	5
Feldspars	2-2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Chrysotile	>12

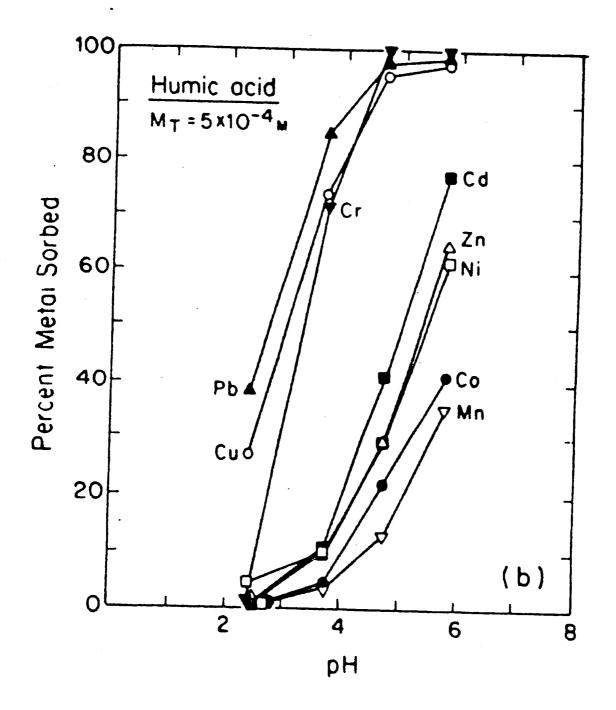
<sup>a</sup> The values are from different investigators who have used different methods and are not necessarily comparable. They are given here for illustration.

SOURCE: Stumm and Morgan, 1981

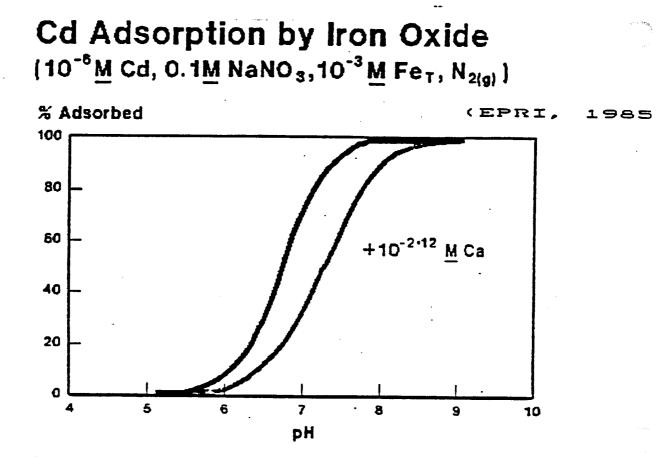


Effect of pH on surface of inorganic particles (Stumm and Morgan, 1981, p. 613)

This figure shows that many suspended and colloidal solids found in aquifer materials have surface charge, and that the charge may be strongly affected by pH. The above minerals can adsorb anions when the net surface charge is positive and conversely, they can adsorb cations when the net surface charge is negative. Surface charge can originate from chemical reactions at the surface, by isomorphous replacement within the lattice, and by adsorption of a surfactant ion.



This figure shows the effect of pH on adsorption of metals onto coagulated humic acid (Kerndorff and Schnitzer, 1980). The curves show that an increase in pH, or an increase in  $OH^-$  activity, increases the extent of trace metal adsorption. Hydrolysis reactions with trace metals enhance adsorption onto humic acid.



Of the main anionic and cationic constituents commonly present in ground water and leachate, Ca exerts the strongest influence on Cd adsorption by amorphous iron oxide. Calcium displaces the adsorption edge to the right, which represents a decrease in adsorption. Calcium will compete with Cd for available surface sites in soil and aquifer materials and increase Cd desorption. Anions (e.g.  $SO_4^{2-}$ ,  $H_4SiO_4CO_3$ ,  $HCO_3$ ) have little influence on Cd adsorption.

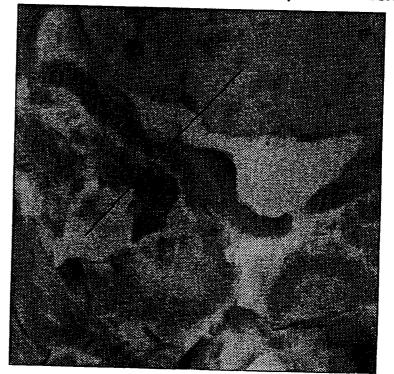
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## SUMMARY OF LEACHING TESTS ON OXIDIZED STEEL CASING

TRACE		
ELEMENT	pH 1 (μg/g)	pH 5 (μg/g)
As	12.57	0.20
Ba	<13.5	<4.0
Cd	0.13	0.4
Cr	43.65	<0.20
Pb	1.08	<0.29
Se	<0.68	<0.20
Mn	1276.0	6.4
Al	93.24	<10.0
U	22.43	<0.2
V	8.51	<0.40
Co	10.81	<0.40
Ni	16.22	2.08
Zn	9.46	<2.0
Мо	1.35	<0.40

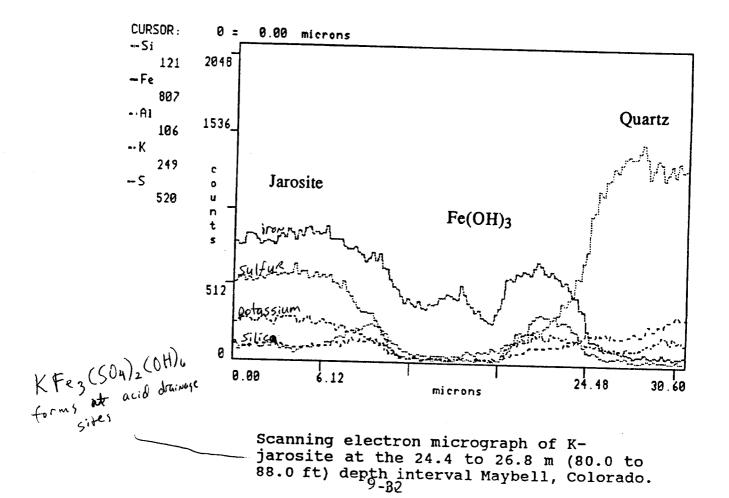
Leaching tests were performed at pH 1 (nitric acid) and pH 5 (acetic acid) on oxidized steel monitor well casing. The oxidized iron was in contact with a high TDS ground water (TDS is approximately 19,200 mg/L) with a pH value of 6.8. Arsenic, selenium, uranium, and possibly other metals are desorbed from the oxidized iron. What is the long-term integrity of steel casing in contact with high TDS solutions when adsorption of contaminants onto the steel casing is occurring?

Browns Park Fm 80-88', Fe Phases

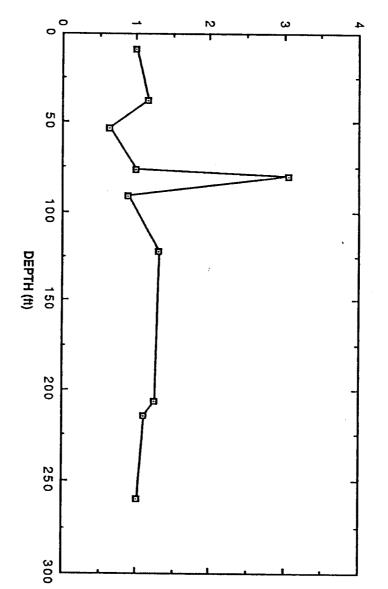


20 MICRONS

Magnification = 3940 Image Size = 512 by 512

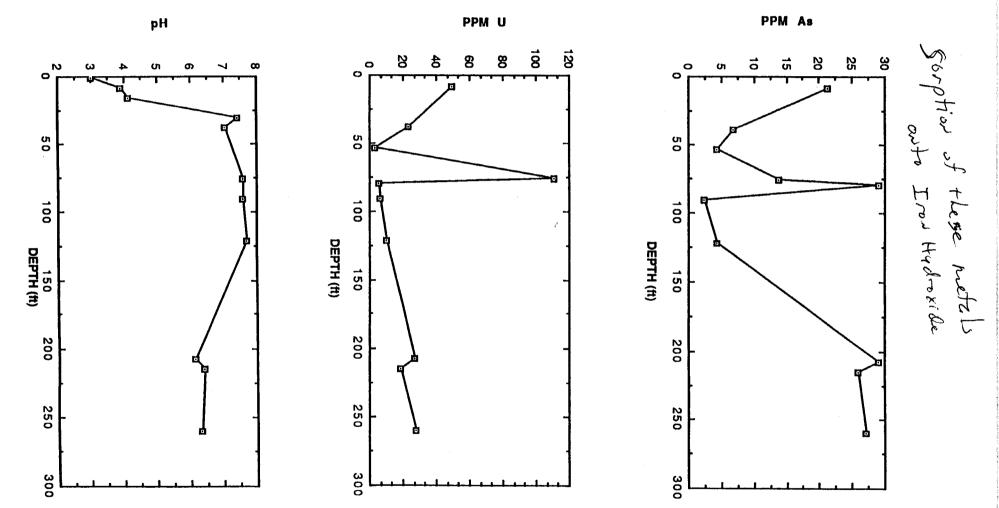


Concentrations of Fe versus depth, Maybell Colorado determined by INAA. Error bars for first standard deviation for Fe range between  $\pm$  300 to  $\pm$  1600 ppm.



WEIGHT PERCENT Fe

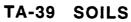
Concentration of U versus depth, Maybell, Colorado determined by DNAA. Error bars for first standard deviation for U range between  $\pm$  0.1 to  $\pm$  4.0 ppm.

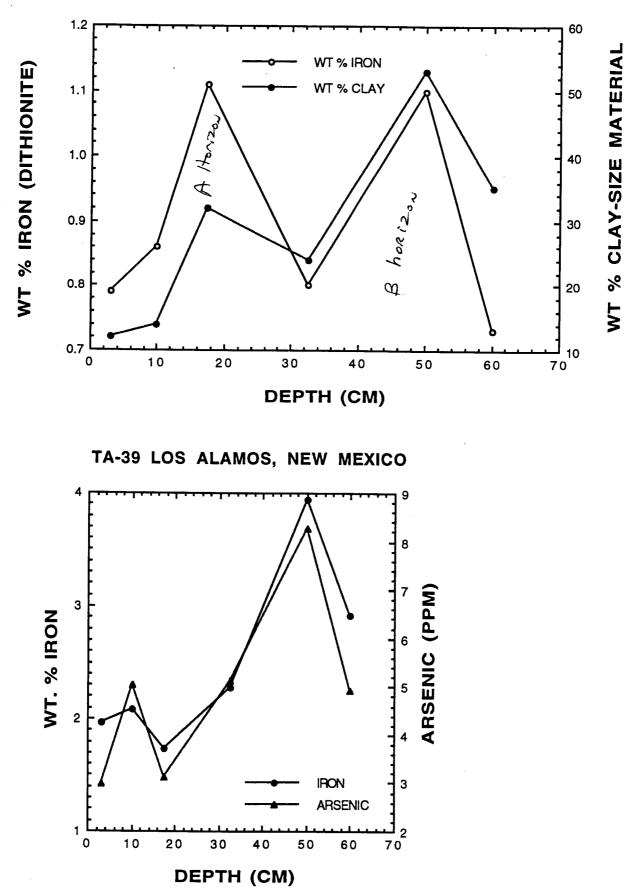


pH versus depth for tailings impoundment, tailings subsoil, and Browns Park Formation. pH was measured with 1:1 paste using sediments and deionized water.

Concentration of As versus depth, Maybell, Colorado determined by INAA. Error bars for first standard deviation for As range between  $\pm$  0.3 to  $\pm$  3.0 ppm.

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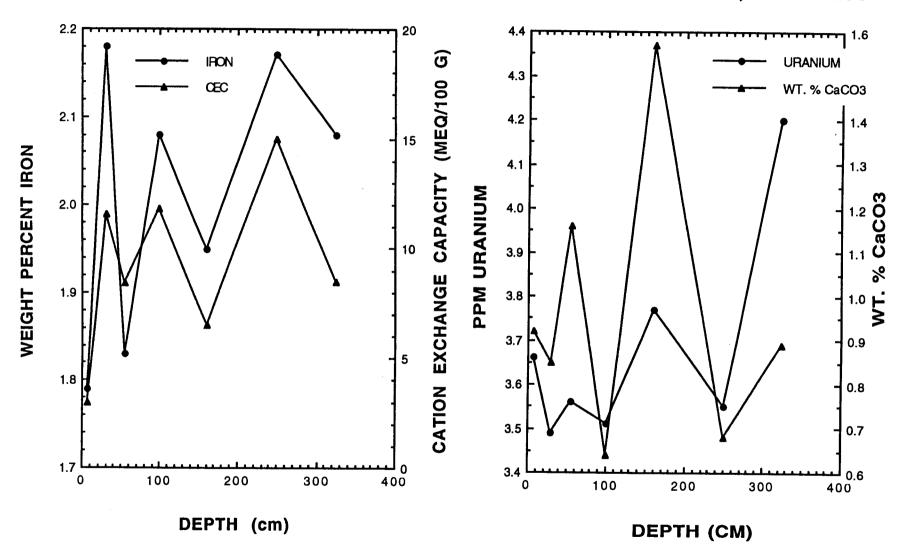




9-34A

TOWNSITE SOIL (EG&G SITE)

EG&G SOIL, LOS ALAMOS, NEW MEXICO

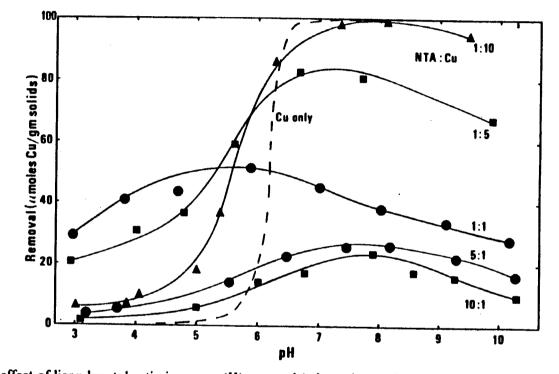


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### EFFECTS OF ORGANICS ON ADSORPTION

- Organic ligands increase the solubility of adsorbing metals
- Organic-metal complexes are not significantly adsorbed by hydrous metal oxides and clay minerals

Torganics T solubility of adsorbin, metals A mobility of metals



The effect of ligand:metal ratio in copper(11) removal (adsorption and/or precipitation). Concentrations of copper, y-Al<sub>2</sub>O<sub>3</sub> and ionic strength are 10<sup>-4</sup> M, g/liter, and 0.025 M, respectively. Ligand (NTA) concentration is variable. The dashed line represents the typical removal pattern of Cu(II) alone due mainly to precipitation (Elliott and Huang, 1979)

The effect of ligand to metal ratio is shown in this figure, where NTA denotes nitrilotriacetic acid. When  $Cu^{2+}$  is in excess to NTA, hydrolysis reactions dominate; however, when NTA: Cu>1.0, it is clear that an increase in ligand concentration results in a decrease of  $Cu^{2+}$  adsorption. Conceptually, this effect can be visualized as a competition for surface site between the CuNTA<sup>-</sup> complex and the free NTA ligand. Nitrilotriacetic acid occurs naturally in humic substances.

## **SUMMARY**

ADSORPTION IS AN IMPORTANT ATTENUATION MECHANISM.

FACTORS THAT INFLUENCE ADSORPTION INCLUDE:

SORBING SPECIES

SORBENT CHARACTERISTICS SURFACE AREA SURFACE CHARGE

SOLUTION PROPERTIES pH Eh IONIC STRENGTH ORGANIC LIGANDS COMPLEXING LIGANDS

#### **REFERENCES FOR ADSORPTION OF SOLUTES**

Birkeland, P.W., 1984. Soils and Geomorphology: Oxford University Press. New York, 372 p.

Cherry, J.A. Gillham, R.W., and Barker, J.F., 1984. <u>Contaminants in Groundwater: Chemical</u> <u>Processes in Studies in Geophysics</u>, National Academy of Sciences.

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Elliott, H.A. and Huang, C.P., 1979. The adsorption characteristics of Cu (11) in the presence of cheuluting agents, <u>Journal of Colloid Interface Science</u>, Vol. 70, pp. 29-45.

EPRI (Electric Power Research Institute), 1984. <u>Solute Migration in Ground Water at Utility</u> <u>Waste Disposal Sites</u>.

Hsi, D. and Langmuir D., 1985. Adsorption of Uranyl onto Ferric Oxyhydroxides: Application of the surface complexation site-binding model, <u>Geochimica et Cosmochimica Acta</u>, Vol. 49, No. 9, pp. 1931-1341.

Kerndoff, H. and Schnitzer, M., 1980. Sorption of metals on humic acid. <u>Geochimica et</u> <u>Cosmochimica Acta</u>, Vol. 44, pp. 1701-1708.

Krauskopf K., 1986. Aqueous Geochemistry of Radioactive Waste Disposal, <u>Applied</u> <u>Geochemistry</u>, Vol. 1, pp. 15-23.

Montgomery, J.M., 1985. Water Treatment Principles and Design, John Wiley and Sons, New York.

Schwarzenbach, R.P., Giger, W., Hoehn, E., and Schneider, J.K., 1983. Behavior of Organic Compounds during Infiltration of River Water to Groundwater. <u>Field Studies: Environmental</u> <u>Science and Technology</u>, Vol. 17, No. 8, pp. 472-479.

Sigworth, E.A. and Smith, S.B., 1972. Adsorption of Inorganic Compounds by Activated Carbon. Journal of American Water Works Association, pp. 386-391.

Stumm, W. and Morgan, J.J., 1981. Aquatic Chemistry, Wiley-Interscience, New York, 780 p.

#### PROBLEMS FOR ADSORPTION LECTURE

Calculation of retardation factors for  $CrO_4^{2-}$  at different pH values. Calculate retardation factors (R<sub>d</sub>) for  $CrO_4^{2-}$  with the data provided. Retardation Equation:

Rd = 1 + p/n Kd (Freeze and Cherry, 1979)

where

 $p = bulk density (m/L^3)$ 

n = porosity

Kd = distribution coefficient (L<sup>3</sup>/m)

Kd data for  $CrO_4^{2-}$  on  $Fe_2O_3 \cdot H_2O$ 

Solution pH	<u>Kd (ml/gm)</u> Na, NO <sub>3</sub>
5.65 6.94 7.80	478,630 112,202 6,607

assume that  $pb = 2.32 \text{ g/cm}^3$  and n = 0.20

Calculate Rd at different pH values using the above equation.

рН	Kd	Rd
6.65	478,630	5,548,977
6.94	112,202	1,301,544
7.80	6,607	76,642
	وجوا والا و والا و و و و و و و و و و و و و	

Questions:

Why does Rd decrease with increasing pH for  $CrO_4^{2-2}$ ?

What are some limitations using Kd values to calculate adsorption constants?

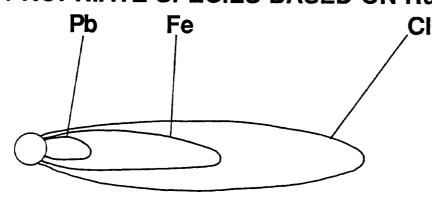
How do Eh, solution composition, and ionic strength affect Rd and Kd values?

## SOLUTION TO CLASS EXERCISE

GIVEN THAT Rd = 1 + <u>pKd</u>, where n Rd = RETARDATION FACTOR, p = DENSITY (g/cm<sup>3</sup>), n = POROSITY, AND Kd = DISTRIBUTION COEFFICIENT (ml/g) CALCULATE Rd FOR THE FOLLOWING:

SPECIES	Kd(ml/g)	p/n	Rd
CI	0	8	1
Fe	10	8	81
Pb	50	8	401

BELOW IS AN ISOCONCENTRATION MAP FOR A HYPOTHETICAL WASTE SITE WITH GROUND WATER CONTAMINATION. LABEL ISOCONCENTRATION LINES WITH APPROPRIATE SPECIES BASED ON Rd.



9-40

## SOLUTION TO CLASS EXERCISE

GIVEN THAT Rd = 1 + pKd, where n

Rd = RETARDATION FACTOR, p = DENSITY (g/cm<sup>3</sup>), n = POROSITY, AND Kd = DISTRIBUTION COEFFICIENT (ml/g) CALCULATE Kd AND Rd FOR THE FOLLOWING:

<b>SPECIES</b>	KOC	<u> </u>	Kd	p/n	Rd
BENZENE	100	0.01	1	8	9
TOLUENE	200	0.01	2	8	17
M-XYLENE	600	0.01	6	8	49
<b></b>		_			

*Note: Kd* = *KOC x Organic Carbon Content.* 

BELOW IS AN ISOCONCENTRATION MAP FOR A HYPOTHETICAL WASTE SITE WITH GROUND WATER CONTAMINATION. LABEL ISOCONCENTRATION LINES WITH APPROPRIATE SPECIES BASED ON Rd. M-XYLENE TOLUENE BENZENE

### CALCULATION OF RETARDATION FACTORS FOR SEVERAL ORGANIC SOLUTES

Given that the retardation equation is,

 $Rd = 1 + 3.2 ffoc (kow)^{0.72} p (1 - Nt)/Nt$  Schwarzenbach et.al., (1983)

where

f = fraction of material < 125 um

foc = fraction organic carbon on < 125-um materal

 $p = bulk density (g/cm^3)$ 

Nt = total porosity

kow = octanol/water partition coefficient

Calculate the relative mobilities of organic solutes and assume

f = 0.05; foc = 0.001; p = 2.60 g/cm<sup>3</sup>; and Nt = 0.20.

Species	kow	Rd
Acetone Benzene Ethylbenzene tetrachloroethylene trichloroethylene DDT MTBE	0.58 135 1413 759 0.02 2 x 10 <sup>6</sup> 1.66	

Questions:

Which of the above organic solutes are mobile in ground water?

Are these Rd values realistic and reasonable?

What effects do other organic solutes have on the solubilities of the above compounds?

Section 10

# Analytical Organic Methods and Instrumentation

Lecture by: Richard Meyerhein New Mexico Scientific Laboratory Division

## SECTION CONTENTS

()-1

#### INTRODUCTION TO ORGANIC CHEMISTRY LABORATORY METHODS FOR ORGANIC COMPOUNDS by Richard Meyerhein N.M. SCIENTIFIC LABORATORY DIVISION

#### ANALYTICAL AND SAMPLING TECHNIQUES

Since compound classifications can be based on chemical properties, physical properties, and/or their use in society, it is often difficult for a person desiring an analysis for several compounds to know what analysis to request. Even different laboratories will list compounds under different analysis groupings. In most cases the field person will be looking for a group of chemicals based on their usage.

For field personnel, most analytical requests are based on environmental usage or impact. Examples of frequently requested analyses are "Pesticides", "Solvents", "Hydrocarbon fuels", and "Poisons". For instance one might be interested in "pesticides" if he suspected water contamination from a nursery. However, for the laboratory, "pesticides" would mean chlorinated hydrocarbon pesticides, organophosphate pesticides, carbamate pesticides, chlorophenoxyacid herbicides, triazine herbicides, etc. Because of the nature of analytical methods, the chemist can only "screen" for a relatively small class of compounds at one time. This class is based on their physical and/or chemical properties so that they can all be extracted from the matrix (water, soil, etc.), separated from one another for identification, and then detected at very low concentrations. Often the compounds and classes of compounds that a laboratory will detect depends on the equipment available to the laboratory.

Contrary to popular belief and wishful thinking, there is <u>no</u> "black box" which can analyze a sample for anything and/or everything that it contains. To get the "best" results when analyzing a sample it is necessary that the field personnel and the lab

 $10^{-2}$ personnel work closely together to plan what to look for and how to look for it. Organic analyses are not inexpensive and it is very easy to spend a lot of money for an analysis and still not get an answer to your question. To a great extent, it is up to the person requesting the analysis to become aware of the analytical methodology so that he can "talk" with the laboratory. Below are listed some of the more common analytical classes of compounds used by most laboratories today:

- <u>Volatiles (purgeables)</u> those compounds which have a low enough boiling point that they can be purged out of water with nitrogen or helium gas at room temperature. Examples would be the trihalomethanes, low molecular weight halogenated or aromatic solvents, and gasoline.
- <u>Extractable (Semivolatile) compounds</u> Those compounds (generally nonpolar and/or hydrophobic) which can be extracted from water with an organic solvent. Extractables are generally divided into three groups:
  - <u>Acidic fraction</u> compounds which are soluble in a basic (pH > 7) solution of water. Examples of compounds from the acid fraction would be phenols, chlorophenoxy acid herbicides, and organic acids.
  - <u>Basic fraction</u> Compounds which are soluble in an acidic (pH < 7) solution of water. This group would include most organic compounds containing a basic nitrogen such as amines.
  - <u>Neutral fraction</u> compounds which are nonpolar, nonionic and do not carry an electric charge. This class of compounds is not very soluble in either an acidic or basic solution of water. Examples would be hydrocarbom fuels, many chlorinated pesticides, and polynuclear aromatic hydrocarbons.

Often the basic and neutral fractions are extracted together and are called the Base/Neutral (B/N) fraction. Sometimes the acid fraction is added back into the B/N fraction and it is analyzed as the B/N/A fraction.

### /Q-3

#### II STEPS IN THE ANALYTICAL ANALYSIS

The laboratories are capable of detecting organic contaminants at a level of a part per billion (PPB) or less. To perform an analysis generally it is necessary to go through the following steps:

- (a) Decide what to look for;
- (b) Separate the compound class in question (remove impurities);
- (c) Concentrate the compounds;
- (d) Separate the compounds within that class;
- (e) Detect, identify, and determine the amount of the compound;
- (f) Confirm the identity of the compound

Often this must be done with less compound than can be seen. Without the magic black box which says that a sample has "poisons" or "poilutants" the laboratory must depend on the physical and chemical properties of the compound for which it is analyzing.

#### **GROUP EXTRACTION/SEPARATION:**

For the separation step of the analysis some of the more common techniques used at most laboratories are:

- EXTRACTION separation of a class of compounds based on their solubility in acids, bases and organic solvents. Used in pesticide, basic, neutral, and acidic fraction analyses.
- DISTILLATION Separation of a class of compounds based on their boiling points (vapor pressure). Used in ethylene dibromide (EDB) analysis in food.
- <u>PURGE AND TRAP</u> Purging of a the class of compounds from the sample and trapping them on a small column prior to analysis by gas chromatography. This is the technique used in the analysis of most water samples for volatiles.
- <u>COLUMN CHROMATOGRAPHY</u> Passing a sample through a column of adsorbent material using solvents of various polarities and collecting the fraction of interest.



#### SEPARATION OF COMPOUNDS WITHIN A GROUP:

Once a group (volatiles, acid extractables, etc.) of organics has been isolated, then further separation of that group is required to detect and identify any individual compounds within that group. The most common methods used at the laboratory are gas liquid chromatography (GC or GLC), high performance liquid chromatography (HPLC), and thin layer chromatography (TLC).

- <u>Gas chromatography</u> is used extensively to detect and identify many organic pollutants. With gas chromatography a concentrated extract of the sample is vaporized at a high temperature, and this vapor is pushed by an inert gas through a column coated with a very thin film of a very high boiling liquid. Each compound will pass through the column in a consistent and somewhat unique period of time. From the length of time it takes a compound to pass through the columa, it is sometimes possible to identify the compound. The laboratory will use about 10 different types of columns to separate the different classes of compounds. If the chemist were to use an aromatic volatile column for a pesticide analysis he could wrongly assume that there was no pesticide in the sample, because the pesticide would not quickly come through that column.
- <u>High Performance Liquid Chromatography</u> uses a similar principle except that:
  1) the sample extract is dissolved in a solvent and not vaporized; and
  2) the compounds are pushed through the column with a liquid under high pressure rather than with a gas.

High Performance Liquid Chromatography is used whenever a compound is not stable enough to be vaporized or it has too high a boiling point to be vaporized.

<u>Thin layer chromatography</u> separates compounds based on their solubility in a solvent and their attraction to a finely divided adsorbent solid. TLC is used extensively in laboratories for the analysis of drugs.

### DETECTION/IDENTIFICATION:

Detection of a compound after it has been separated by a chromatographic method is one of the more challenging aspects of the analysis. Some of the different detectors used by laboratories are:

### 10-5

#### GAS CHROMATOGRAPHIC DETECTORS

<u>PHOTOIONIZATION DETECTOR</u> - uses a high energy light to ionize compounds with a double bond, an aromatic ring, or an easily ionizable electron. This detector would not "see" a halogenated or aliphatic compound.

#### HALL ELECTROLYTIC CONDUCTIVITY AND COULSON

<u>DETECTORS</u> - will only see compounds with a halogen in them. The Hall detector reduces all organic compounds with hydrogen gas at high temperature and measures the electrical conductivity of the products in solution. The Hall detector can also be made specific for Nitrogen or Sulfur rather than halogens.

- FLAME IONIZATION DETECTOR burns the compounds and detects ionized products from the combustion. This is a very general detector which will detect almost any compound which will burn. It is non-specific and not as sensitive as the most other detectors.
- <u>NITROGEN-PHOSPHOROUS DETECTOR</u> detects certain products which are formed on the surface of a special bead. This detector is very sensitive to compounds containing either nitrogen or phosphorous. It is relatively insensitive to other elements.
- FLAME PHOTOMETRIC DETECTOR burns the compound and detects the amount of light of a specific wave length which is produced in the flame. This detector can be made specific for either sulfur or phosphorous containing compounds.
- <u>ELECTRON CAPTURE DETECTOR</u> detects compounds which "capture" low energy electrons given off from a radioactive foil. An extremely sensitive detector for compounds which contain a halogen such as chlorinated pesticides. It is relatively insensitive to aliphatic compounds.
- MASS SPECTROMETER this detector measures the mass fragmentation pattern of compounds after they have been "hit" by high energy electrons. The mass spectrometer gives considerable information about the structure and/or identity of the compound. However Mass Spectrometers are complicated and expensive to buy and keep up.

Laboratory Methods

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### HIGH PERFORMANCE LIQUID CHROMATOGRAPHY DETECTORS

- <u>ULTRA-VIOLET / VISIBLE DETECTOR</u> This detector determines the amount of light of a given wave length that a compound absorbs. This can give some information about the identity of a compound.
- FLUORESCENCE DETECTOR This detector determines the amount of light given off by a compound after it has been "excited" by a high energy light. It also can be used to give some information about the identity of a compound.

To be sure that the analyst looks for all of the types of compounds which the field collector requires, the analyst might have to analyze the sample on several different columns. With a possibility of 10 different columns, 7 different detectors, and at least 3 different temperature conditions, there are over 200 possible gas chromatographic conditions to detect most of the possible organics which can be gas chromatographed. With each gas chromatographic analysis taking about an hour, that would mean over a month of analytical chromatographic time per sample.

### III REQUESTING ANALYSES FROM THE LABORATORY

When requesting analyses from the iaboratory, it is essential that the field personnel provide as much information as possible regarding the compound(s) to be analyzed for and background about the sample. This gives the chemist the necessary information to plan the analysis so that the compounds of concern will not be missed. It is possible to say that a certain compound is not in the sample but it is impossible to say that there were "no poisons or pesticides" in the sample.

The vast majority of analyses involve gas or liquid chromatography. With these procedures, if the "right" column, the "right" detector, the right conditions, etc. are chosen then the only indication that there is something in the sample is a "peak" on a chart which occurs at a consistent time after the sample was injected. This time is characteristic of, but not necessarily unique for, any given compound. With over seven million organic compounds it is not always easy to match that peak a with the correct compound without any additional background information to help.

10-7

Since the sample cleanup sometimes extracts impurities from the sample along with the compounds of interest (i.e. pesticides), it is very difficult to try to identify all of the peaks observed. If one is only interested in pesticides or a small number of pesticides it is very helpful to list them. That way the analyst can be sure to look specifically for those pesticides and be sure that they are or are not in the sample. Perhaps it isn't important that there are 10 parts per billion (PPB) of phthalates from the plastic pipe in the sample. In general if an unidentified compound, which is felt to be significant, is seen in the sample the submitter would be informed. Many laboratories use what is called "target compound analysis." That is they look for only the compounds which they list in a analysis class. If other compounds are present they will not be reported - even if they are detected.

Remember that while it is not possible to say that "there is nothing in the sample", if the analyst is screening for a compound or class of compounds he will see similar compounds and will generally report them. Often a certain analytical methodology is required by the State or Federal Government in order to comply with their regulations. Most regulations require or accept the EPA methodologies listed in "Test Methods for Evaluating Solid Wastes" (SW-846) for RCRA analyses, or the 500 series analyses (for drinking water) or the 600 series analyses (for ground water pollution). Most of the analyses are quite similar analytically.

Some of the more common screens Performed by laboratories are:

### EPA Methods (Drinking Water, Ground Water, Waste)

502.1	601	8010	Volatile Halocarbons - up to about 3 carbons
503.1	602	8020	Volatile Aromatics - benzene, toluene, xylenes, etc.
	603	8030	Acrolein and Acrylonitrile
	604	8040	Phenols
	605		Benzidine
	60 <b>6</b>	8060	Phthalate Esters
	607		Nitrosamines
	60 <b>8</b>	8080	Pesticides and PCB's
	609	8090	Nitroaromatics and Isophorone
	610	8100	Polynuclear Aromatic Hydrocarbons
	611		Haloethers
	612	8120	Chlorinated Hydrocarbons
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EPA Methods (continued)

613 8280 2,3,7,8-Tetrachlorodibenzo-p-dloxin 524.1 624 8240 8250 Volatiles (by Mass Spectrometry) (Equivalent to 601 plus 602) 625 8270 Base/Neutrals, Acids, and Pesticides (Equivalent to methods 604 plus 606-612)

There are many other classes of compounds and specific compounds which it might be necessary to analyze for, and which could be analyzed for if the laboratory is aware to check for the compound(s) required. Some of the classes are listed below:

- a) Aliphatic Hydrocarbons (Fossil fuels)
- b) Carbamate pesticides
- c) Chlorophenoxyacid herbicides
- d) Natural gas
- e) Triazine herbicides

#### Screening (Indicating) Tests

Considerable attention has been given to trying to develop a simple screening test or finding a simple parameter which would indicate that there is or is  $n_{c.}$  "contamination" in ground water.

Total Organic Halide (TOX) and Total Organic Carbon (TOC) have been used to test for "any" halogen which might be in the water and for excessive amounts of organic material. Ultra-violet absorption scans have been made to search for "any" aromatic compounds which might be in the sample. Generally, such tests have not proven too useful because of lack of sensitivity and/or specificity and because of insufficient background information.

However, work done by Plum and Pitchford indicates that of all of the indicator tests tested, the ground water volatiles (purgeables) screen gave the best indication of contamination. Not only were volatiles detected more frequently than any other class of compound, but also it was unlikely to find non-volatiles without the presence of volatiles. It has also been my experience that ground water contamination is most likely to be caused by volatile compounds because of their relatively high water solubility and mobility in soil.

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## APPENDIX A

# ORGANIC SAMPLE COLLECTION GUIDE

### ANALYTICAL METBODS, REQUIRED CONTAINERS, PRESERVATION TECHNIQUES AND MAXIMUM BOLDING TIMES FOR ENVIRONMENTAL ANALYSIS

PRIORITY POLLUTANTS - Groundwater and Wastewater Organics Analysis (Federal Register Vol. 49, No. 209, October 1984)

PARAMETER	VOLUME REQUIRED	CONTAINER	PRESERVATION	Maximum Holding Time	METHOD FOR ANALYSIS	
Purgeable Halocarbons	40 ml (2)	Glass, Teflon- lined Septum, 40 ml capacity	Cool, 4°C, if there is presence of residual chlorine, then preserve with 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	14 days	Nethod 601, GC/Hall or Method 624, GC/MS	
Pesticides (Organochlorine Pesticides)	l liter (2)	Same as Below	Cool, 4°C, pre-rinse with Sample 3X	Extract within 7 days and analyze within 40 days	Method 608, GC or Method 625, GC/MS	
Base/Neutrals and Acids	1 liter (3)	Amber glass, Teflon-lined Septum, 1 liter or 1 gal. capacity	Cool, 4°C, if there is presence of residual chlorine, then preserve with 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Same as above	Method 625, GC/MS	
Chlorinated Herbicides (i.e., 2,4-D, 2,4,5-T	Approx. 1 liter for liquid sample (2)	Glass, Teflon- lined Septum	Cool, 4°C	Extract within 7 days and completely analyze within 30 days	Method 615, Extraction/ Esterification/ GC/ECD	

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### ANALTTICAL METHODS, REQUIRED CONTAINERS, PRESERVATION TECHNIQUES AND MAXIMUM BOLDING TIMES FOR ENVIRONMENTAL ANALYSIS

SOLID WASTE EVALUATION - ORGANICS ANALYSIS (Test Nethods for Evaluating Solid Waste, EPA, 1982) - continued

PARAMETER	volume Required	CONTAINER	PRESERVATION	MAXIMUM Holding Time	METHOD FOR ANALYSIS	
Chlorinated Herbicides (i.e., 2,4-D, 2,4,5-T	Approx. 1Glass, Teflon-liter forlined Septumliquid(2)sample.Approx. 100.grams for.sludge or.solid.	Cool, 4°C	Extracted within 7 days and completely analyzed within 30 days	Method 8150, Extraction/ Esterification/ GC/ECD		
Volatile Organics (VOA's)	40 ml (2)	Glass, Teflon- lined Septum, 40 ml capacity	Iced or refrigerated, protected from light	14 days	Method 8240, Purge and Trap GC/MS Method	
Semivolatile Organics	Approx. 1 liter for liquid sample (2) Approx. 100 grams for sludge or solid sample	lined Septum	Cool, 4*C	Extracted within 14 days and completely analyzed within 40 days	Nethod 8250, Packed column/ GC-MS	
					Method 8270, Capilliary Column/GC-MS	

10-12

#### REFERENCES

- EPA Test Methods for Evaluating Solid Wastes (SW-846), 1986, Office of Solid Waste and Emergency Response, Washington, DC, Third Edition, Volume 1B: Laboratory Manual Physical/Chemical Methods.
- EPA, 1981, The Determination of Halogenated Chemicals in Water by the Purge and Trap Method: Method 502.1, EPA# 600/4-81-059, US Government Printing Office.
- EPA, 1981, Ed. Rev. 1986, Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography Method 503.1, Us Government Printing Office.
- EPA, Rev. 1985, Method 524.1 Volatile Organic Compounds in Water by Purge and Trap Gas Chromatography/Mass Spectrometry, US Government Printing Office.
- EPA, 1982, Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (Methods 601 to 625), US Government Printing Office.

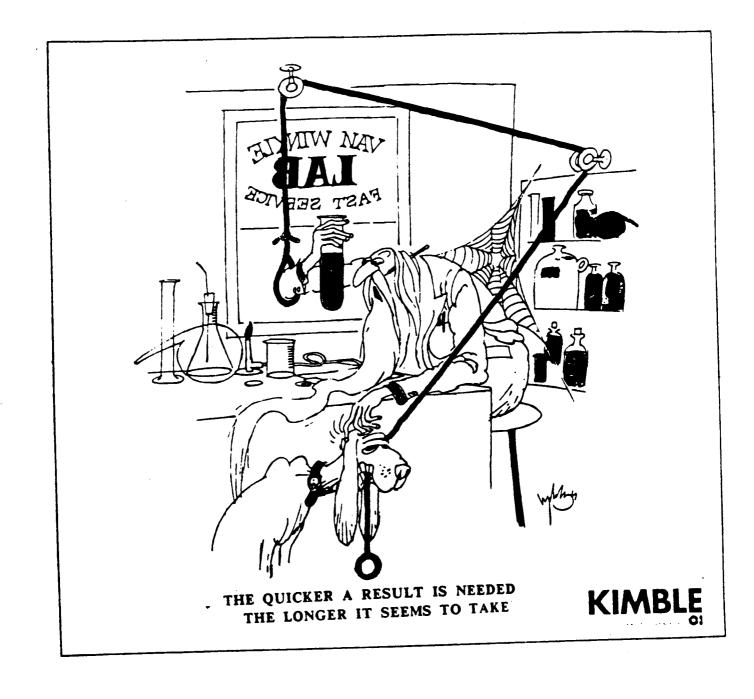
(The above EPA references have summaries for all methods which give a brief description of the method, interferences, and compounds definitely detected. It could be very useful to read this 1-2 page summary.)

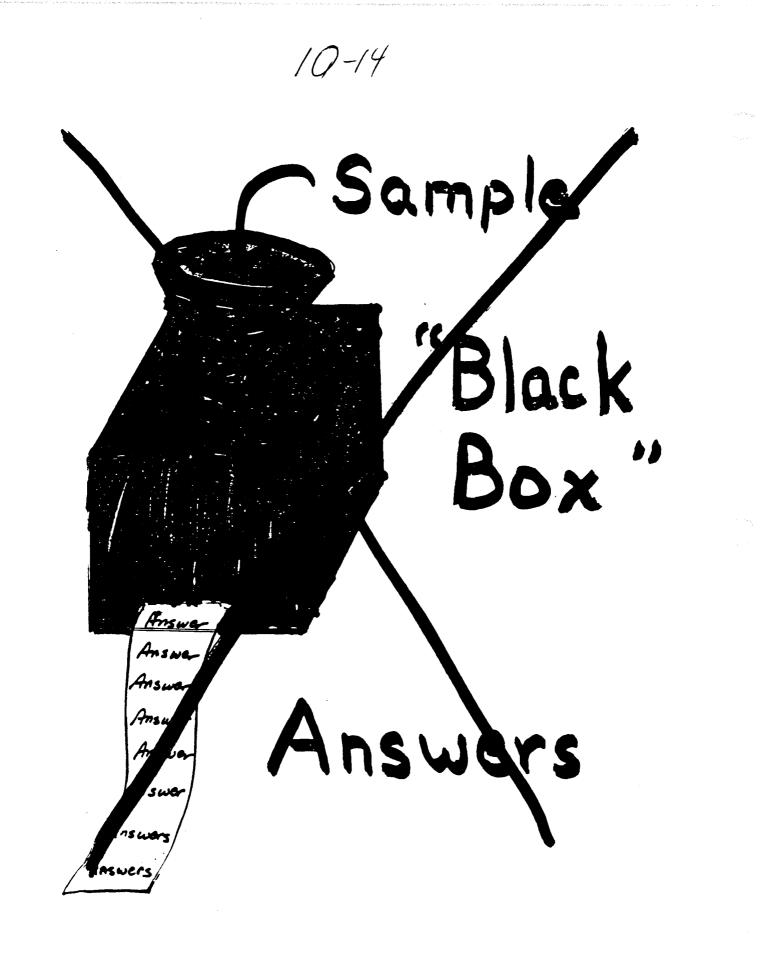
Montgomery, James M., Consulting Engineers, 1985, Water Treatment Principles and Design, John Wiley & Sons, N.Y.

(Chapter 16 gives a good introduction on organics in ground water.)

Plumb, R. H., Jr. and Pitchford, A, M. 1986. VOLATILE ORGANIC SCANS: IMPLICATIONS FOR GROUND WATER MONITORING. NWWA/AIP Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection and Restoration (Houston, Texas), Proc., 207-222.

10-13





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# Information Found in EPA Analytical Methods

### **•** SCOPE AND APPLICATION

- Applicability (program, matrix, etc.)
- List of Compounds Detected
- SUMMARY OF METHOD
  - Type of Instrumentation
  - Methods of conformation
- DEFINITIONS
- INTERFERENCES
  - -Common Contaminants
  - Factors Causing High/Low Results

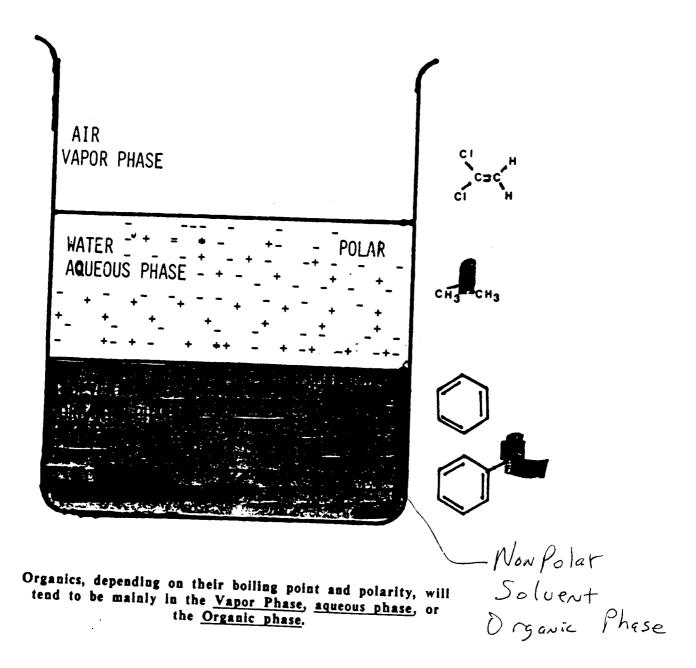
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## STEPS IN THE ANALYTICAL PROCEDURE

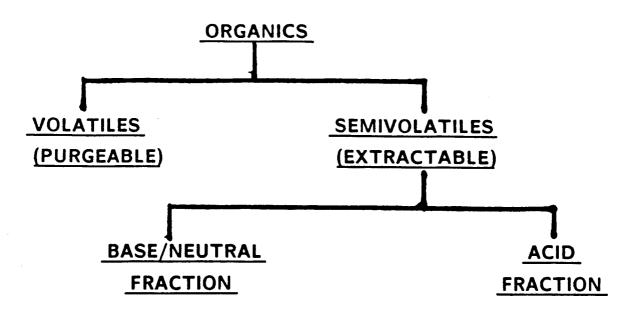
1. DECIDE WHAT TO LOOK FOR; - Concentration 2

- 2. SEPARATE COMPOUND(S) FROM IMPURITIES;
- 3. CONCENTRATE THE COMPOUND(S);
- 4. SEPARATE THE COMPOUNDS WITHIN THE CLASS;
- 5. DETECT A GIVEN COMPOUND;
- 6. IDENTIFY THE COMPOUND;
- 7. DETERMINE THE AMOUNT;
- 8. CONFIRM THE IDENTITY;
- 9. REPORT THE RESULTS.

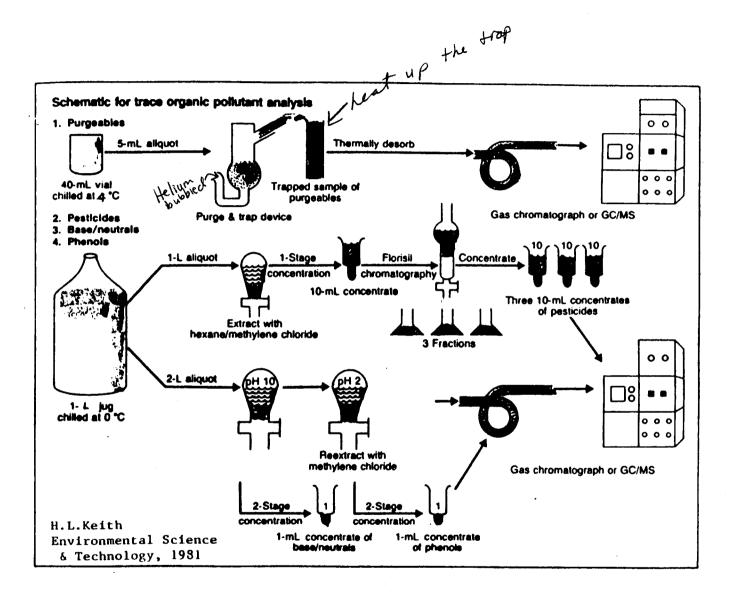
# USING EQUILIBRIUM TO PURIFY COMPOUNDS



EXTRACTION SCHEME FOR ORGANICS /0-18



# ORGANIC COMPOUNDS CAN BE DIVIDED INTO 3 MAJOR ANALYTICAL GROUPS



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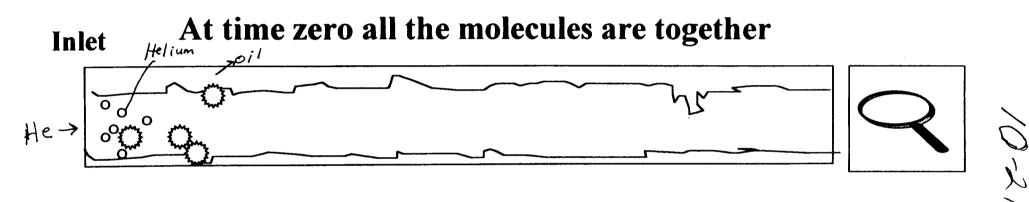
# **Boat Chromatography**

At the start of a boat race all boats are together At a later time:



220

# **Gas Chromatography**

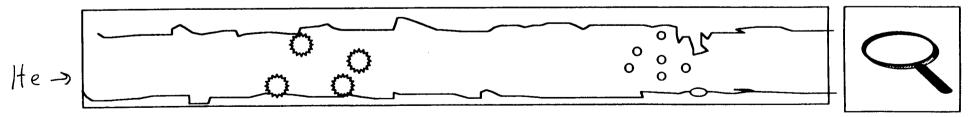


Chromatography

Column

Detector

At a later time the molecules have separated according to their vapor pressure in the column.



He Gas carries the molecules through the column whenever they are in the gas phase.

1-22

## GAS CHROMATOGRAPHY DETECTORS

### DETECTOR

- 1. PHOTOIONIZATION
- 2. HALL
- 3. FLAME IONIZATION
- 4. N-P
- 5. FLAME PHOTOMETRIC
- 6. ELECTRON CAPTURE

# COMPOUNDS/ELEMENTS DETECTED

UNSATURATED AND AROMATIC

HALOGENATED OR NITROGEN chloring on

bromine

CARBON CONTAINING

NITROGEN & PHOSPHORUS

SULPHER OR PHOSPHORUS

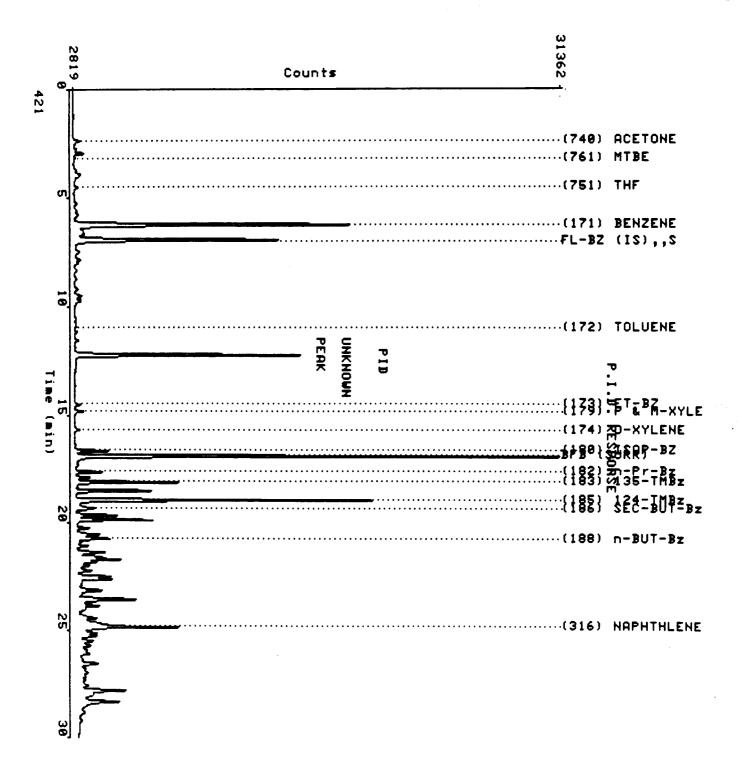
ELECTRONEGATIVE ELEMENTS

(CI > 0 >> C)

- 7. THERMAL CONDUCTIVITY ALL (LOW SENSITIVITY)
- 8. MASS SPECTROMETER

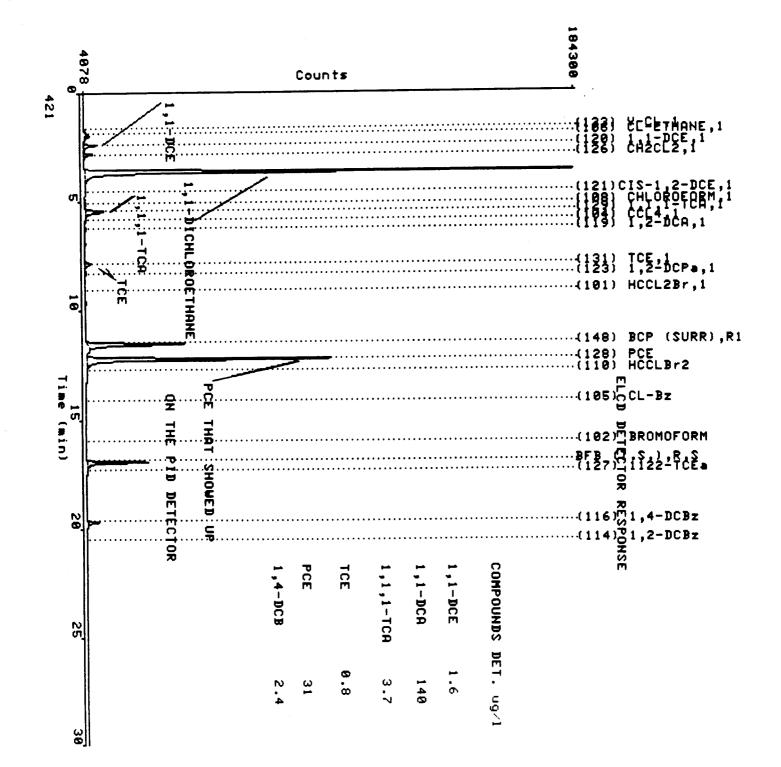
ALL COMPOUNDS

EACH GAS CHROMATOGRAPH DETECTOR IS DESIGINED TO WORK BEST FOR A CER-TYPE OF COMPOUND. THE ELECTRON CAPTURE DETECTOR, WHICH CAN "SEE" PICOGRAMS OF A CHLORINATED PESTICIDE, CAN'T "SEE" A THOUSAND TIMES THAT MUCH OF A HYDROCARBON. Data file:USER\$DIA1:[DATA.ODIN]73A93004Report:NoneAcquired:19-MAR-1993 12:27:29Time range:0.00-29.98Vert. scale/offset:1.0/0

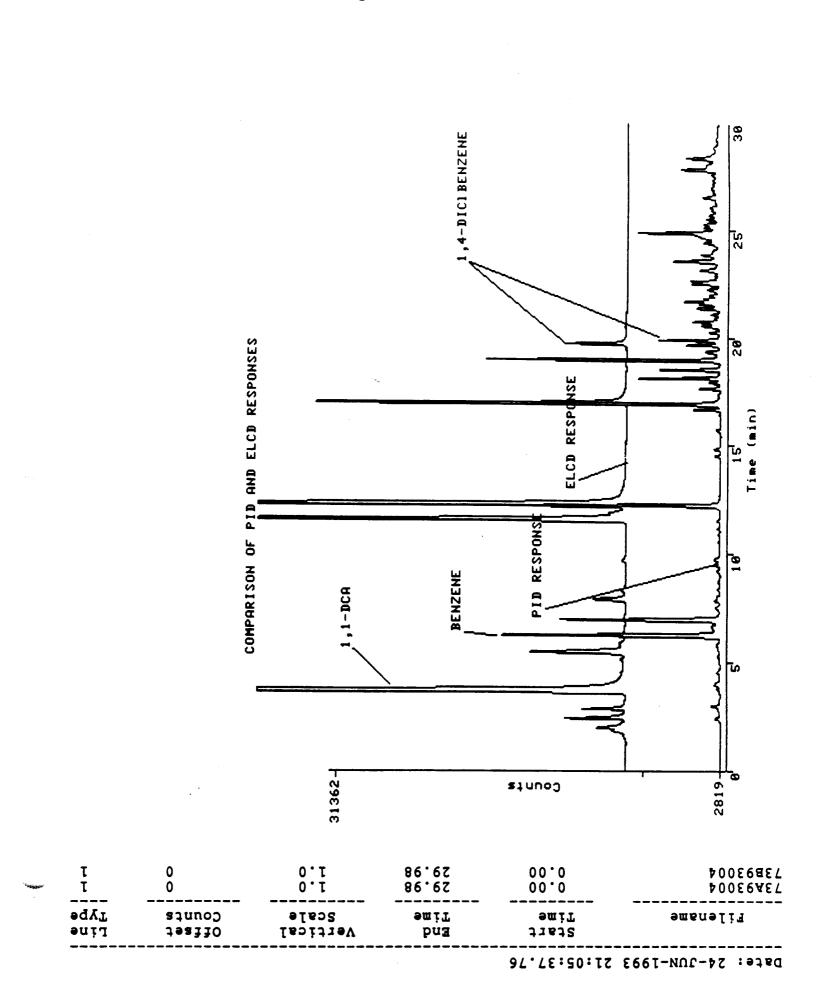


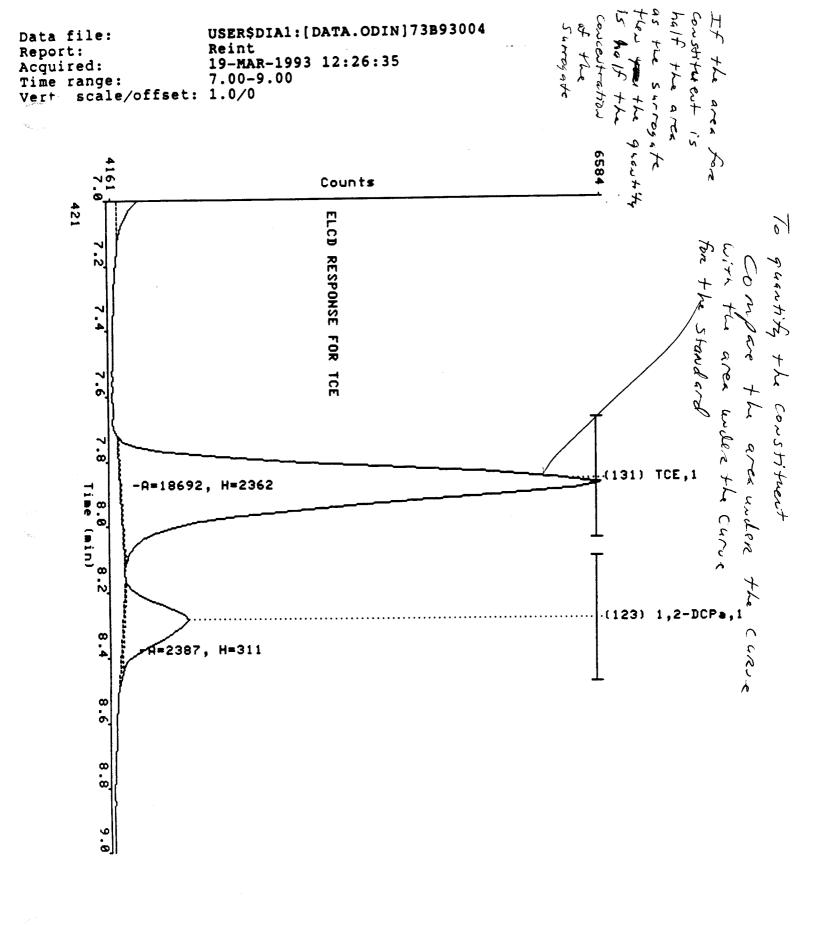
52-01

Data file:USER\$DIA1:[DATA.ODIN]73B93004Report:ReintAcquired:19-MAR-1993 12:26:35Time range:0.00-29.98Vert scale/offset:1.0/0



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# ORGANIC ANALYSES FOR VOLATILES

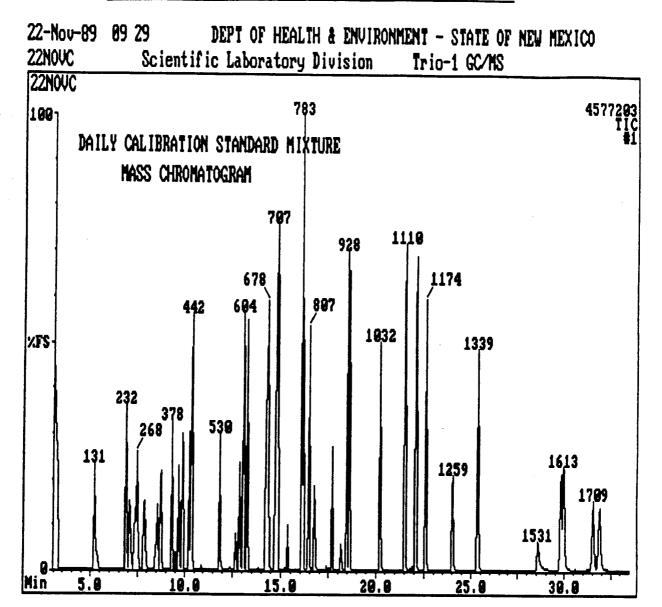
TYPE OF ANALYSIS	EPA METHODS			METHOD/		
	DW	GW	SW	DETECTOR		
AROMATIC COMPOUNDS	503.1	602	8020	GC/PID	1	
HALOGENATED COMPOUNDS	502.2	601	8010	GC/ELCD -	→ Hall	
ACROLIEN, ACRYLONITRILE		603	8030	GC/FID		
MASS SPECTROMETER	524.2	624	8240/50	GC/MS		

### ORGANIC BASE/NEUTRAL/ACID ANALYSES

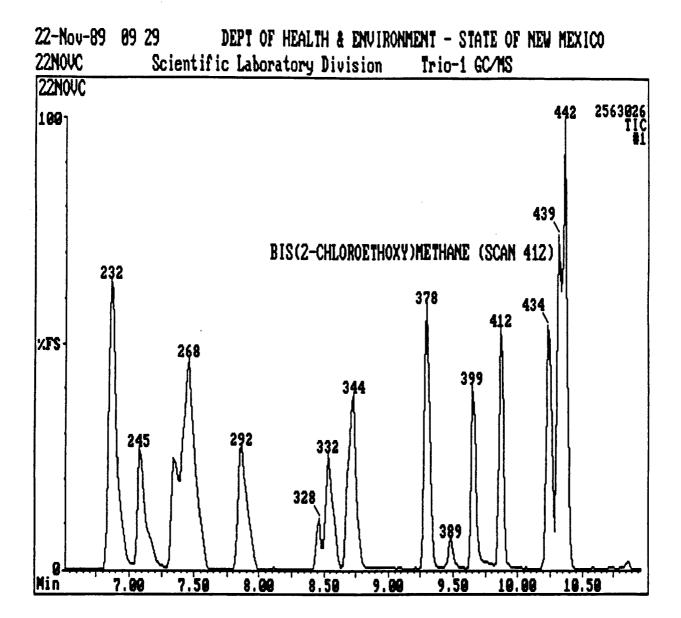
TYPE OF ANALYSIS	EPA METHODS		METHOD/			
BASE/NEUTRAL EXTRACTABLES	DW	GW	SW	DETECTOR		
BENZIDINE		605		HPLC/EC		
DIOXINS	1613	613	8280	GC/HRMS		
CHLORINATED HYDROCARBONS		612	8120	GC/ECD		
HALOETHERS		611		GC/ELCD		
NITRO AROMATICS		609	8090	GC/ECD/FID		
NITROSAMINES		607		CG/NPD		
ORGANOCHLORINE PESTICIDES	508	609	8080	GC/ECD		
ORGANOPHOSPHORUS PEST.	507		8140	GC/NPD		
PHTHALATE ESTERS		606	8060	GC/ECD		
POLYNUCLEAR AROMATICS	550.1	610	8100	HPLC/UV/F		
GC/MS SEMIVOLATILES	525	625	8270	GC/MS		
ACID EXTRACTABLES						
PHENOLS		604	8040	GC/FID		

10-28

### CHROMATOGRAM OF DAILY STANDARD

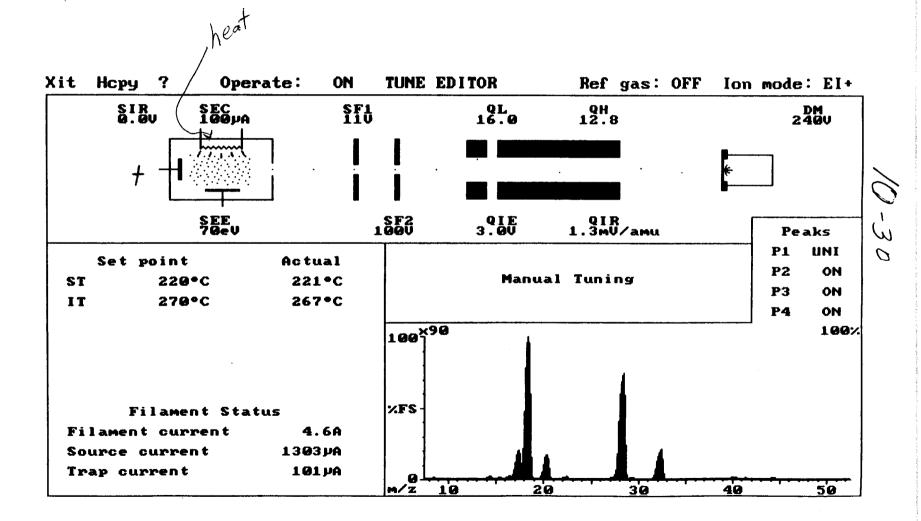


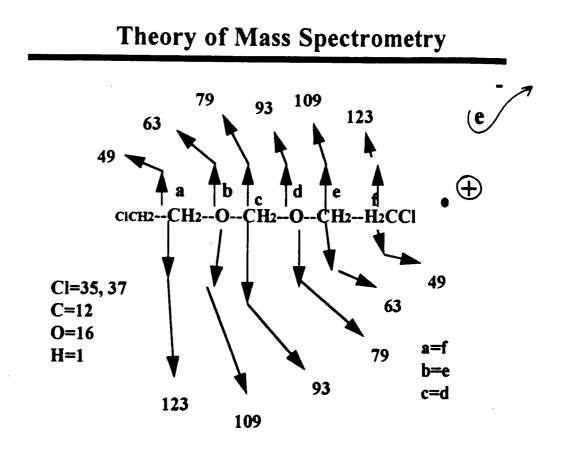
The chromatogram itself only indicates that a compound is comming off of the column at a certain time. While this is a good indication that a certain compound might be present, it is not conclusive proof. Generally, if a peak is detected for a certain compound on two dissimilar columns, it is assumed that the compound has been identified. This "proof" would probably not hold up under a rigerous attack.

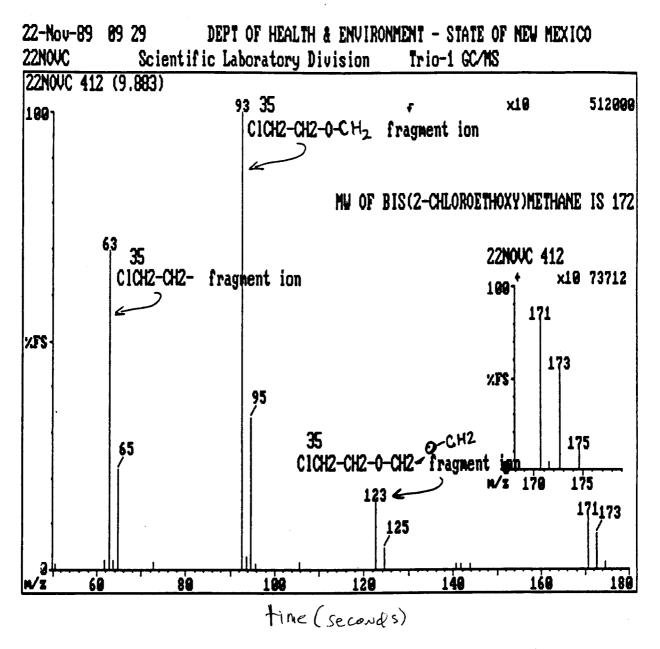


Above, the scale has been expanded to give a better view of some of the peaks detected in the daily calibration standard. It is expected, based on retention time, that the peak at scan 412 is Bis(2-chloroethoxy)methane. However, without additional information it is impossible to be certain that the peak at scan 412 is due to Bis(2-chloroethoxy)methane.

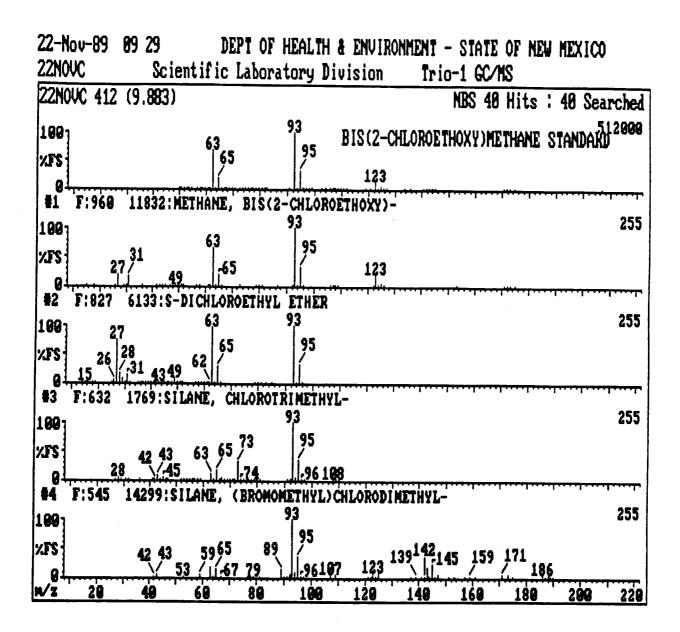
10-29



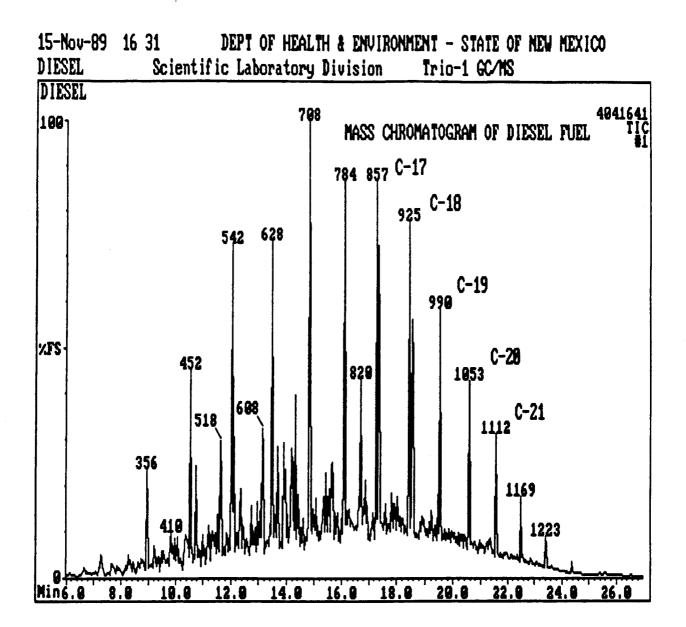




Above is a mass spectrum of the peak at scan 412. One can see major mass fragment ions at m/z 63, 93, and 123. These masses agree with fragments from Bis(2-chloroethoxy)methane as follows: 63:  $Cl^{35}CH_2-CH_2^+$ ; 93:  $Cl^{35}CH_2-CH_2-O^+$ ; and 123:  $Cl^{35}CH_2-CH_2-O-CH_2^+$ . The ions at those masses plus 2 are due to the chlorine<sup>37</sup> isotope. One can also see that there is not an ion for the molecular ion (MW=172). Apparently the molecule looses a Hydrogen very easily so that the parent ion (moleculer weight) is not seen. The ions at m/z 173 and 175 are also due to the chlorine<sup>37</sup> isotope.

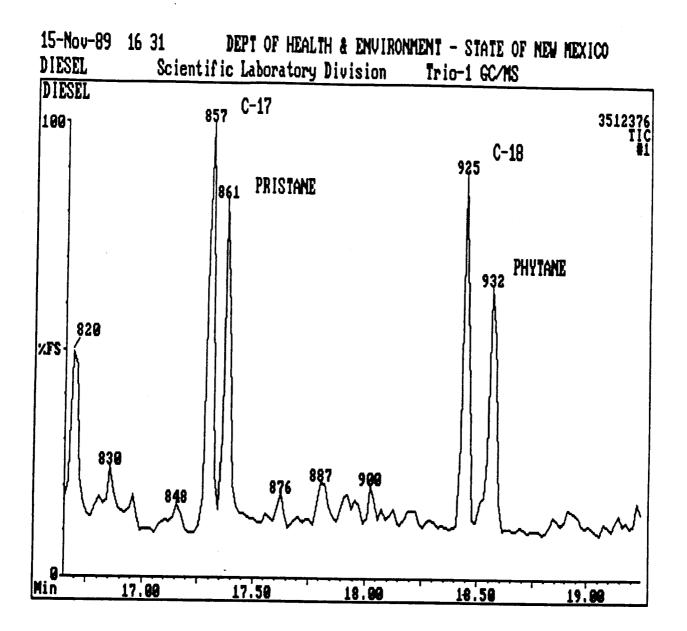


It is possible for most mass spectrometers to search a large (about 40,000 entry) data base to find the closest matches to the mass spectrum obtained. In this case the first choice was Bis(2-chloroethoxy)methane with a "fit" of 960 out of 1000. The second choice was s-dichloroethylether (a very similar compound) with a fit of 827. The fit's (a measure of the probability of the match being correct) for the other matches drop off rapidly indicating that either the first or second compound are the correct matches or the compound spectrum is not in the library.



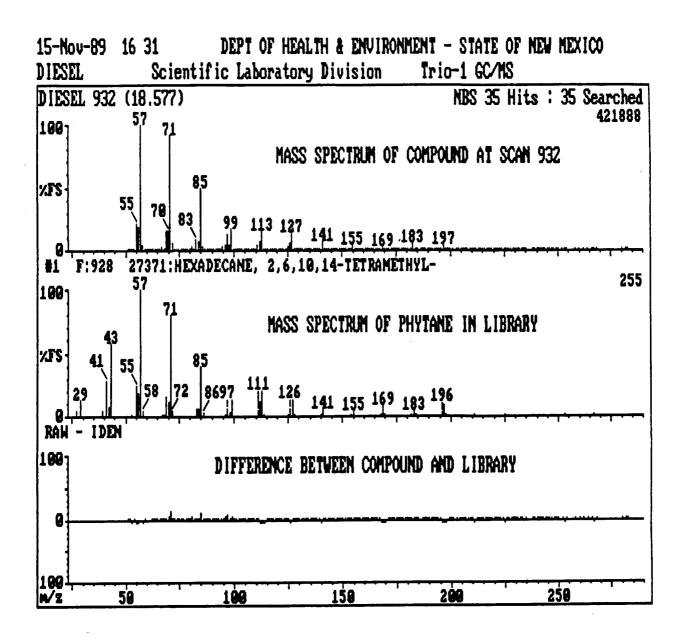
Above is a mass chromatogram of diesel fuel. It is obvious that there are a number of different compounds in diesel fuel. The more abundant compounds that are evenly spaced throughout the chromatogram are "normal" (straight chain) hydrocarbons. The smaller peaks between them are mostly branched chain hydrocarbons and PNA's.

10 - 34

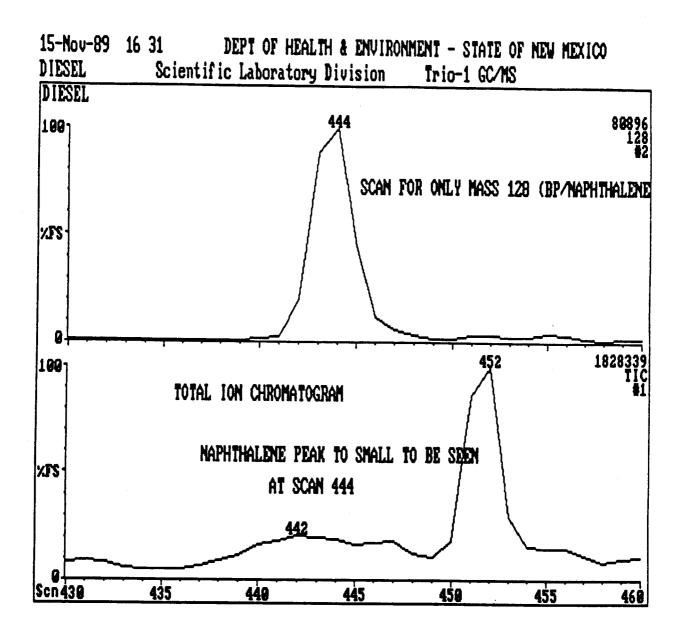


When the scale on the chromatogram is expanded, one can easily see large peaks after the  $C_{17}$  and the  $C_{18}$  normal hydrocarbons. These compounds are Pristane and phytane which are  $C_{19}$  and the  $C_{20}$  branched chain hydrocarbons.

10-36

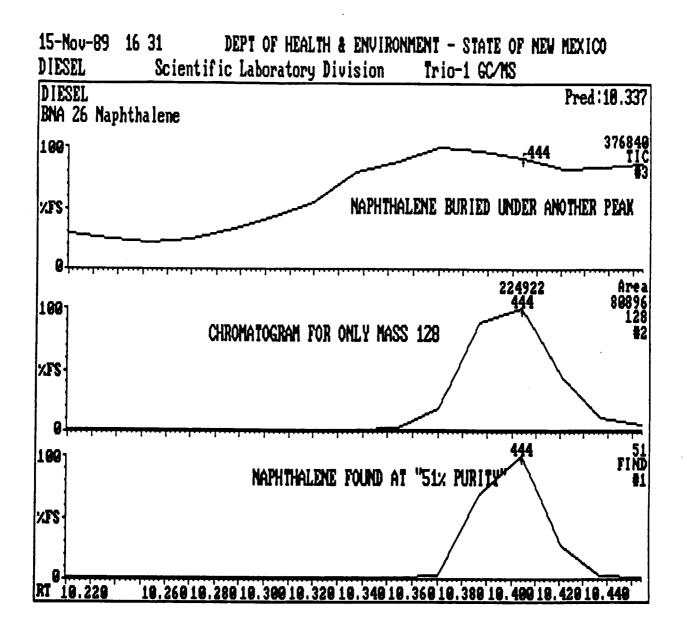


The plot above shows a method of comparing an unknown spectrum with a library spectrum. As can be seen in the lower plot, the match between the unknown and library was very good. The ions below m/z 50 are not included because the unknown spectrum did not scan below m/z 50. The "fit" is 928/100 or an agreement of about 93%.

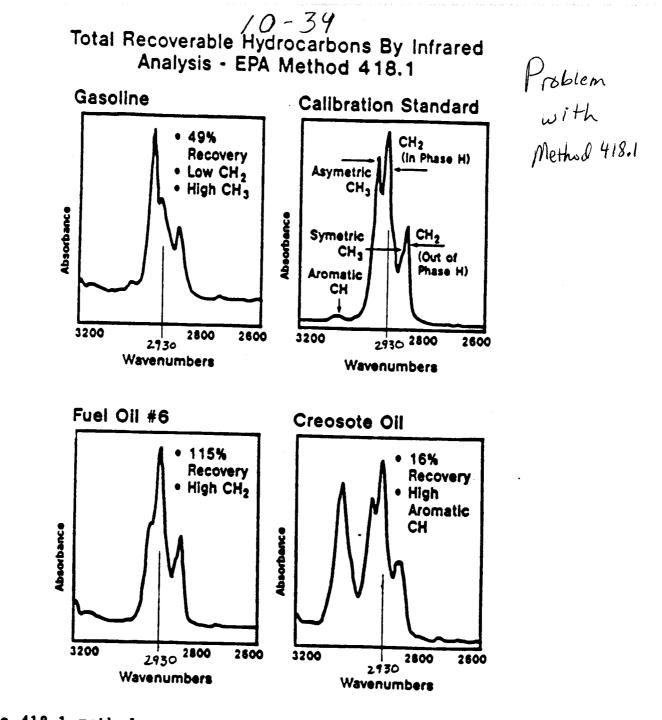


Often, many compounds would be missed if only the larger peaks were examined. In the above expanded chromatogram of the diesel fuel, a plot of only mass 128 indicates that there might be a small amount of naphthalene (BP=128) buried under another peak. Often this method is used to find compounds suspected of being in the sample.

10-38

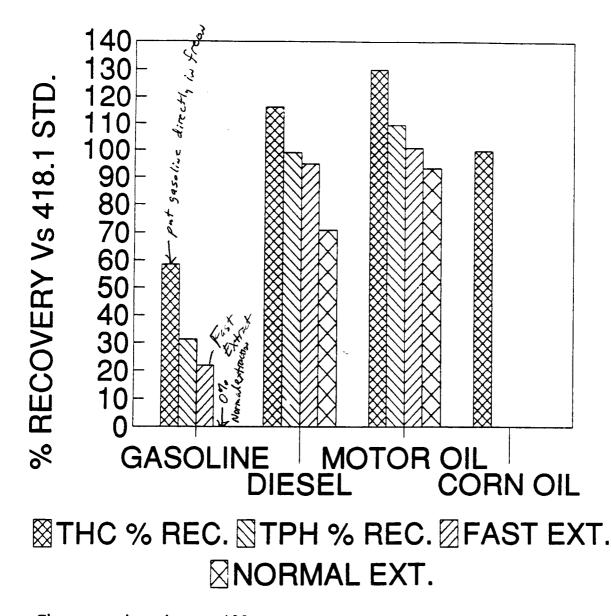


Most mass spectrometers have a method of searching for specific compounds. In the above plots the program indicates that naphthalene is present in the sample. The top plot is the total ion chromatogram centered around the time when naphthalene is supposed to elute. The middle plot shows that a m/z 128 ion is eluting around scan 444. The lower plot shows that at scan 444 the "purity" for naphhalene is 51%. Most contract labs use this method to look for desired (EPA) compounds. This is called "Target Compound Analysis". The disadvantage to Target Compound Analysis is that it is easy to ignore large peaks (compounds) and look only at the computer printer report.



The 418.1 method measures the concentration of "hydrocarbons" by measuring the amount of Carbon Hydrogen bond stretching. The problem is that the stretching frequency which is measured is more specific for methylene  $(-CH_2-)$  stretching and does not measure methyl  $(-CH_3)$  or Aromatic (=CH) stretching. Thus mixtures that have a high percentage of methyl or aromatic hydrogen (i.e. Gasoline) methylene hydrogen than the standard tend to give high results. For any analysis it is important to know exactly what you are

# 10-40 PERCENT BIAS FOR TPH USING 418.1



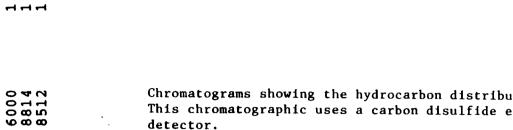
The graph above illustrates the percent recoveries (Vs a gravimetric standard) for various types of hydrocarbon mixtures using the 418.1 method. The <u>THC % REC.</u> shows the analytical bias of the 418.1 method due only to the difference due to their percent of methylene carbons. <u>TPH % REC.</u> shows the results after the freon extract has been treated with silica gel to "remove non petroleum hydrocarbons". (Now gasoline is down to about 30% of the true value.) The <u>FAST EXT.</u> shows the results when a spiked dirt sample is extracted by a modified method used at the Scientific Laboratory System to reduce as much as possible the evaporation of the sample during preparation. (Gasoline is about 20% of the true value.) The <u>NORMAL EXT.</u> shows the results when the sample is extracted according to the EPA protocol. (Gasoline at 100 mg/1 was not detected - 0% recovery.)

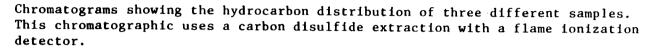
take methanol in sample bottle to field + put soil in bottle for VOC analyses - to preserve + prevent loss of volatiles use carbon disulfide for hydro carbon contan. spillesp gaso hire)

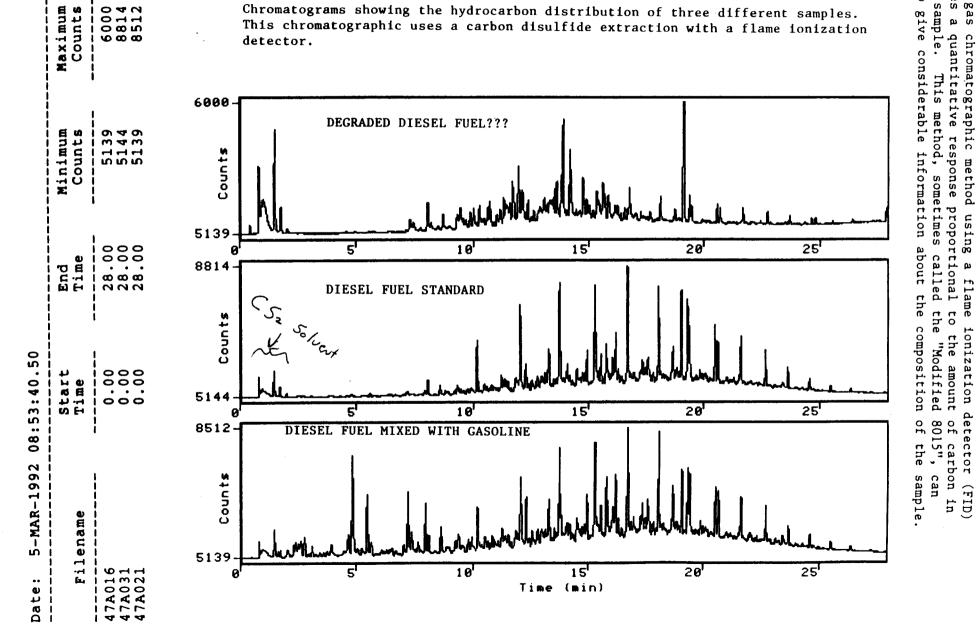


Line Type

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using

a flame ionization

detector

(FID)

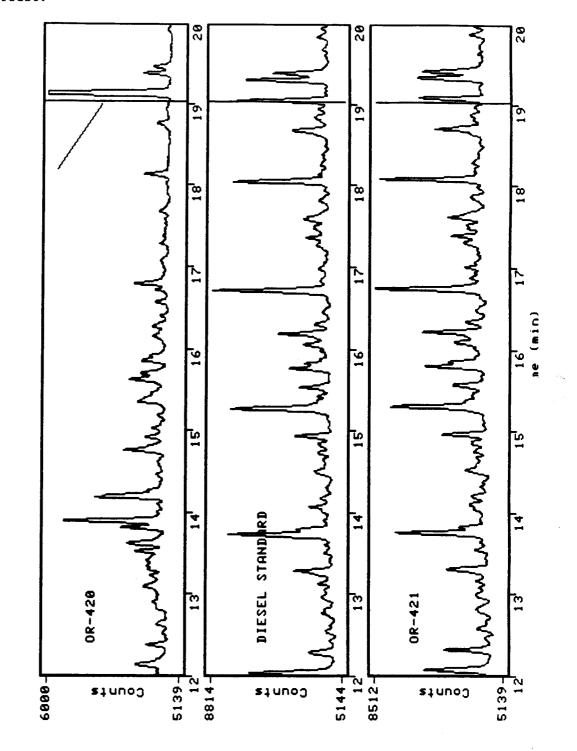
gives a quar the sample.

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gas

also

10-42Expanded view of the previous chromatograms showing how in some cases it is possible to show a 1 to 1 correspondence between a sample and a standard. In other cases weathering may cause some compounds to "disappear" while others seem to persist.



T T 12.00 2128 6273 20.00 120474 00.21 12.00 20.00 1188 7744 IEUI τ 0009 6213 S 523 TYpe əmiT Filename sjunoj sjunoj əmiT euil mumixem wnwyuyw pug 72872

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S/I

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UAZARROUG WARES FOR A	DETECTION	MAXIMUM	AVERAGE
HAZARDOUS WASTE DISPOSAL	FREQUENCY	CONC.	DETECTABLE
SITE CONTAMINANT	%	(mg/l)	(ug/l)
1. TRICHLOROETHENE (V)	51.3	790	3,816
2 TETRACHLOROETHENE (V)	36.0	21 <b>,750</b>	9,676
3. 1,2-t-DICHLOROETHENE (V)	29.1	75	
4. CHLOROFORM (V)	28.4	220	
5. 1,1-DICHLOROETHENE (V)	25.2		
6. METHYLENE CHLORIDE (V)	19.2	7,800	11,209
7. 1,1,1-TRICHLOROETHANE(V)	18.9	618	,=\>
8. 1,1-DICHLOROETHANE (V)	17.9		
9. 1,2-DICHLOROETHANE (V)	14.2	440	6,327
10. PHENOL (A)	13.6	7,713	33,952
11. ACETONE (V)	12.4	250	9,524
12. TOLUENE (V)	11.6	1,100	5,182
13. bis-(2-ETHYLHEXYL)PHTHALATE (B	) 11.5	-,	5,102
14 BENZENE (V)	11.2	1,200	4,977
15. VINYL CHLORIDE (V)	8.7	-,===	~~~~
16. bis-(2-CHLOROETHYL)ETHER (B)		3,300	282, 189
17. p-CHLORO-=-CRESOL (A)		1,800	225,320
18. 2-BUTANONE (V)		190	11,404
19. STYRENE (V)		\$1	11,404
20. NITROBENZENE (B)	·	•1	9,524
21. 2,4,5-TRICHLOROPHENOL (A)			
22. bis-(2-CHLOROISOPROPYL)ETHER (1	B)		4,407
2,4-DICHLOROPHENOL (A)			3,816
			3,686

V)=VOLATILE; (A)=ACID EXTRACTABLE; (B)=BASE/NEUTRAL EXTRACTABLE

Most Frequently Detected Compounds

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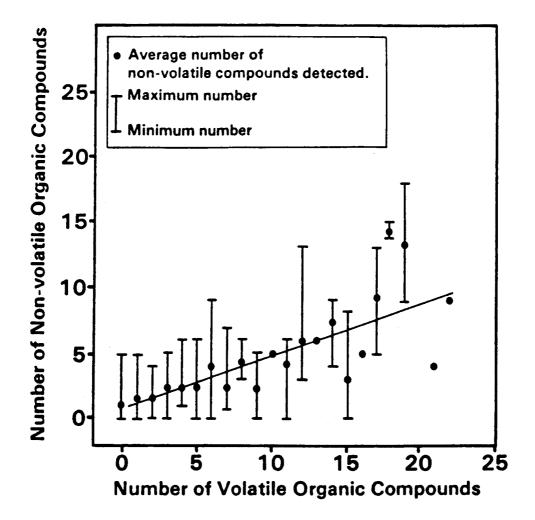


Figure 3. Observed relationship between volatile compounds and the number of non-volatile organic priority pollutants detected in ground water. Only sites where all four organic priority pollutant scans were performed are included in the data summary.

Plum and Pitchford, 1985

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#### METHOD 502.2 VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

**Revision 2.0** 

R. W. Slater, Jr. and J. S. Ho - Method 502.2, Revision 1.0 (1986)

J. S. Ho - Method 502.2, Revision 2.0 (1989)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY OFFICE OF RESEARCH AND DEVELOPMENT U.S. ENVIRONMENTAL PROTECTION AGENCY CINCINNATI, OHIO 45268

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#### METHOD 502.2

#### VOLATILE ORGANIC COMPOUNDS IN WATER BY PURGE AND TRAP CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES

#### 1. <u>SCOPE AND APPLICATION</u>

Analyte

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage (1-3). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection byproducts, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. The following compounds can be determined by this method.

-	Chemical Abstract Services
	<u>Registry Number</u>

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Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
1,1-DICHIOLOGUIGHE	10-00-4

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cis-1,2-Dichloroethene	156-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-IsopropyItoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	108-38-3
h-vliene	100-42-3

- 1.2 This method is applicable to the determination of total trihalomethanes and other volatile synthetic compounds as required by drinking water regulations of 40 Code of Federal Regulations Part 141. Method detection limits (MDLs) (4) are compound and instrument dependent and vary from approximately 0.01-3.0  $\mu$ g/L. The applicable concentration range of this method is also compound and instrument dependent and is approximately 0.02 to 200  $\mu$ g/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.
- 1.3 Two of the three isomeric xylenes may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

#### 2. <u>SUMMARY OF METHOD</u>

2.1 Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas

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through a 5 mL aqueous sample. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components onto a capillary gas chromatography (GC) column. The column is temperature programmed to separate the method analytes which are then detected with a photoionization detector (PID) and a halogen specific detector placed in series.

- 2.2 Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Additional confirmatory information can be gained by comparing the relative response from the two detectors. Each identified component is measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard. For absolute confirmation, a gas chromatography/mass spectrometry(GC/MS) determination according to method 524.1 or method 524.2 is recommended.
- 3. <u>DEFINITIONS</u>

Added to each environmental sample Andded after extraction + right before injection

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- 3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component. Usually added to each environmental sample
- 3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction\_and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.
- 3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.5 Laboratory reagent blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method anal, tes or other interferences are present in the laboratory environmert; the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

- 3.7 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.8 Laboratory fortified blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.
- 3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

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- 3.10 Stock standard solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.
- 3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
- 3.12 Calibration standard (CAL) -- a solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.13 Quality control sample (QCS) -- a sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

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#### 4. INTERFERENCES

- 4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks (Sect. 10.3) provide information about the presence of contaminants. When potential interfering peaks are noted in laboratory reagent blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted.
- 4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross contamination.
- 4.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

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4.4 When traps containing combinations of silica gel and coconut charcoal are used, residual water from previous analyses collects in the trap and can be randomly released into the analytical column. To minimize the possibility of this occurring, the trap is reconditioned after each use as described in Sect. 11.4.

#### 5. <u>SAFETY</u>

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available (5-7) for the information of the analyst.

#### METHOD 8010

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#### HALOGENATED VOLATILE ORGANICS

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit for other matrices.

#### 2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a halogen-specific detector (HSD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

#### 3.0 INTERFERENCES

#### 3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

#### 4.0 APPARATUS AND MATERIALS

#### 4.1 Gas chromatograph:

4.1.1 Gas Chromatograph: analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

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TABLE 1.	CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR HALOGENATED VOLATILE ORGANICS

	Retention time (min)		Method detection
Compound	Col. 1	Col. 2	limita (ug/L)
Benzyl chloride			
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
romoform	19.2	19.2	0.20
romomethane			
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
hloroethane	3.33	8.68	0.52
hloroform -Chlorohexane	10.7	12.1	0.05
-Chloroethyl vinyl ether	10.0		
chloromethane	18.0	5 20	0.13
hloromethylmethyl ether	1.50	5.28	0.08
hlorotoluene			
ibromochloromethane	16.5	16.6	0.09
)ibromomethane	10.5	10.0	0.09
L,2-Dichlorobenzene	34.9	23.5	0.15
, 3-Dichlorobenzene	34.0	22.4	0.32
,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane		2217	V.L4
1,1-Dichloroethane	9.30	12.6	0.07
,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
rans-1,2-Dichloroethylene	10.1	9.38	0.10
ichloromethane			
,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
,1,2,2-Tetrachloroethane	21.6		0.03
,1,1,2-Tetrachloroethane		,	
etrachloroethylene	21.7	15.0	0.03
,1,1-Trichloroethane	12.6	13.1	0.03
,1,2-Trichloroethane	16.5	18.1	0.02
richloroethylene	15.8	13.1	0.12
richlorofluoromethane	7.18		
richloropropane	A 73	F 00	<b>A</b>
inyl chloride	2.67	5.28	0.18

<sup>a</sup> Using purge-and-trap method (Method 5030).

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#### METHOD 8020

#### AROMATIC VOLATILE ORGANICS

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. Table 1 indicates compounds which may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

#### 4.0 APPARATUS AND MATERIALS

#### 4.1 <u>Gas chromatograph</u>:

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

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	Retention time (min)		Method detection limit <sup>a</sup>
Compound	Col. 1	Col. 2	(ug/L)
Benzene	3.33	2.75	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene Xylenes	5.75	4.25	0.2

## TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR AROMATIC VOLATILE ORGANICS

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<sup>a</sup> Using purge-and-trap method (Method 5030).

## TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge Non-water miscible waste	1250
Non-water miscible waste	1250

<sup>a</sup>Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

<sup>b</sup>PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet-weight basis.

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#### METHOD 8040

#### PHENOLS

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8040 is used to determine the concentration of various phenolic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

#### 2.0 SUMMARY OF METHOD

2.1 Method 8040 provides gas chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques (see Chapter Two for guidance). Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 Method 8040 also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives, with additional cleanup procedures for electron capture gas chromatography. This is to reduce detection limits of some phenols and to aid the analyst in the elimination of interferences.

#### 3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.3 Interferences coextracted from samples will vary considerably from source to source, depending upon the waste being sampled. Although general cleanup techniques are recommended as part of this method, unique samples may require additional cleanup.

#### 4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required

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Compound	Retention time (min)	Method Detection limit (ug/L)
2-sec-Butyl-4,6-dinitrophenol (DNBP)		
4-Chloro-3-methylphenol	7.50	0.36
2-Chlorophenol	1.70	0.31
Cresols (methyl phenols)		
2-Cyclohexyl-4,6-dinitrophenol		
2,4-Dichlorophenol	4.30	0.39
2,6-Dichlorophenol		
2,4-Dimethylphenol	4.03	0.32
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
2-Nitrophenol	2.00	0.45
4-Nitrophenol	24.25	2.8
Pentachlorophenol	12.42	7.4
Phenol	3.01	0.14
Tetrachlorophenols		
Trichlorophenols		
2,4,6-Trichlorophenol	6.05	0.64

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

# TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

<sup>a</sup>Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

 $b_{PQL} = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.$ 

Revision 0 Date September 1986

#### METHOD 8080

#### ORGANOCHLORINE PESTICIDES AND PCBs

#### 1.0 SCOPE AND APPLICATION

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1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

#### 2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

#### **3.0 INTERFERENCES**

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

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Revision 0 Date September 1986

	Retention	time (min)	Method
Compound	Col. 1	Col. 2	Detection limit (ug/L)
Aldrin	2.40	4.10	0.004
z-BHC	1.35	1.82	0.004
9-BHC	1.90	1.97	0.005
-BHC	2.15	2.20	0.009
-BHC (Lindane)	1.70	2.13	0.004
chlordane (technical)	e	e	0.014
,4'-DDD	7.83	9.08	0.011
,4'-DDE	5.13	7.15	0.004
4'-DDT	9.40	11.75	0.012
)ieldrin	5.45	7.23	0.002
ndosulfan I	4.50	6.20	0.014
ndosulfan II	8.00	8.28	0.004
ndosulfan sulfate	14.22	10.70	0.066
ndrin	6.55	8.10	0.006
ndrin aldehyde	11.82	9.30	0.023
eptachlor	2.00	3.35	0.003
leptachlor epoxide	3.50	5.00	0.083
lethoxychlor	18.20	26.60	0.176
oxaphene	e	e	0.24
CB-1016	e	e	nd
CB-1221	e	e	nd
CB-1232	e	e	nd
CB-1242	e	e	0.065
CB-1248	e	e	nd
CB-1254	e	e	nd
CB-1260	e	e	nd

10-58TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs<sup>a</sup>

<sup>a</sup>U.S. EPA. Method 617. Organochloride Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd - not determined

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# TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES<sup>a</sup>

Matrix	Factor <sup>b</sup>
Ground water . Low-level soil by sonication with GPC cleanup	10
High-level soil and sludges by sonication	670 10,000
Non-water miscible waste	100,000

<sup>a</sup>Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

 $^{b}PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.$ 

#### METHOD 8270A

#### SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS): CAPILLARY COLUMN TECHNIQUE

#### 1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications. The following compounds can be determined by this method:

		te Pre	paration Technique:			
Compounds	CAS No"	3510	3520	3540	3550	3580
Acenaphthene	83-32-9	X	X	X	X	X
Acenaphthene-d <sub>10</sub> (I.S.)		X	X	X	Ŷ	Ŷ
Acenaphthylene	208-96-8	X	X	X	X	X
Acetophenone	98-86-2	X	ND	ND	ND	Ŷ
2-Acetylaminofluorene	53-96-3	X	ND	ND	ND	Χ
1-Acety1-2-thiourea	591-08-2	LR	ND	ND	ND	LR
Aldrin	309-00-2	X	X	X	X	X
2-Aminoanthraquinone	117-79-3	X	ND	ND	ND	Ŷ
Aminoazobenzene	60-09-3	X	ND	ND	ND	Ŷ
4-Aminobiphenyl	92-67-1	X	ND	ND	ND	x
Anilazine	101-05-3	X	ND	ND	ND	Ŷ
Aniline	62-53-3	X	X	ND	X	Ŷ
o-Anisidine	90-04-0	X	ND	ND	ND	Ŷ
Anthracene	120-12-7	x	X	X	X	Ŷ
Aramite	140-57-8	HS(43)	ND	ND	ND	Ŷ
Aroclor - 1016	12674-11-2	X	X	X	X	Ŷ
Aroclor - 1221	11104-28-2	X	Ŷ	X	Ŷ	Ŷ
Aroclor - 1232	11141-16-5	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ
Aroclor - 1242	53469-21-9	Ŷ	Ŷ	. X	Ŷ	Ŷ
Aroclor - 1248	12672-29-6	X	Ŷ	Ŷ	Ŷ	Ŷ
Aroclor - 1254	11097-69-1	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ
Aroclor - 1260	11096-82-5	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ
Azinphos-methyl	86-50-0	HS(62)	ÑD	ÑD	ÑD	Ŷ
Barban	101-27-9	LR	ND	ND	ND	ĹR
Benzidine	92-87-5	CP	CP	CP	CP	CP
Benzoic acid	65-85-0	X	X	ND	X	X
Benz(a)anthracene	56-55-3	Ŷ	Ŷ	X	Ŷ	Ŷ
Benzo(b)fluoranthene	205-99-2	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ
		x	X	X	x	X
Benzo(k)fluoranthene	207-08-9	x	X	X	X	X
Benzo(g,h,i)perylene	191-24-2	X	X	X	X	X
Benzo(a)pyrene	50-32-8					X
p-Benzoquinone	106-51-4	0E	ND	ND	ND	X
Benzyl alcohol	100-51-6	X	X	ND	X	X

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	Appropriate Preparation Techniques					
Compounds	CAS Noª	3510	3520	3540	3550	3580
α-BHC	319-84-6	X	X	X	X	X
B-BHC	319-85-7	X	X	X	X	X
δ-BHC	319-86-8	X	X	X	X	X
$\gamma$ -BHC (Lindane)	58-89-9	X	X	X	X	X
Bis(2-chloroethoxy)methane	111-91-1	X	X	X	X	X X X X X X X X X X X X X X X X X X X
Bis(2-chloroethyl) ether	111-44-4	X	X X	X	X	X
Bis(2-chloroisopropyl) ether	108-60-1	X	X	X	X	X
Bis(2-ethylhexyl) phthalate	117-81-7	X	X	X	X	X
4-Bromophenyl phenyl ether	101-55-3	X	X	X	X	X
Bromoxynil	1689-84-5	X	ND	ND	ND	X
Butyl benzyl phthalate	85-68-7	X	X	X	X	X
Captafol	2425-06-1	HS(55)	ND	ND	ND	X
Captan	133-06-2	HS(40)	ND	ND	ND	X
Carbaryl	63-25-2	X Í	ND	ND	ND	X
Carbofuran	1563-66-2	X	ND	ND	ND	X X
Carbophenothion	786-19-6	X	ND	ND	ND	X
Chlordane	57-74-9	X	X	X	X	X
Chlorfenvinphos	470-90-6	X	ND	ND	ND	X
4-Chloroaniline	106-47-8	X X X X X X	ND	ND	ND	X X X X X
Chlorobenzilate	510-15-6	X	ND	ND	ND	X
5-Chloro-2-methylaniline	95-79-4	X	ND	ND	ND	X
4-Chloro-3-methylphenol	59-50-7	X	X	X	X	X
3-(Chloromethyl)pyridine						
hydrochloride	6959-48-4	X	ND	ND	ND	X
1-Chloronaphthalene	90-13-1	X	X	X	X	X
2-Chloronaphthalene	91-58-7	X	Χ.	X	X	X
2-Chlorophenol	95-57-8	X	X X	X	X	X
4-Chlorophenyl phenyl ether	7005-72-3	X	X	X	X	X
Chrysene	218-01-9	X	X	X	X	X
Chrysene-d <sub>12</sub> (I.S.)		X	X	X	X	X
Coumaphos	56-72-4	X	ND			X
p-Cresidine	120-71-8	X	ND	ND	-	X
Crotoxyphos	7700-17-6	X	ND			
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	X	ND			
4,4'-DDD	72-54-8	X	X	X	X	X
4,4'-DDE	72-55- <b>9</b>	X	X	X	X	X
4,4'-DDT	50-29-3	X	X	X	X	, Å
Demeton-0	298-03-3	HS(68)	ND			
Demeton-s	126-75-0	X	ND			
Diallate (cis_or trans)	2303-16-4	X	ND			
2,4-Diaminotoluene	95-80-7	DC,0E(42	2) ND			
Dibenz(a,j)acridine	224-42-0	X	ND			Y A
Dibenz(a,h)anthracene	53-70-3	X	Ŷ	X		X X
Dibenzofuran	132-64-9	X	X		-	
Dibenzo(a,e)pyrene	192-65-4	ND	ND	) NE X		Ϋ́ χ
Di-n-butyl phthalate	84-74-2	X	X	•	*	~

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		Appropriate Preparation Technique				
Compounds	CAS Noª	3510	3520	3540	3550	3580
Dichlone	117-80-6	OE	ND	ND	ND	X
1,2-Dichlorobenzene	95-50-1	X	X	X	X	
1,3-Dichlorobenzene	541-73-1	X	X	X	Ŷ	Ŷ
1,4-Dichlorobenzene	106-46-7	X	X	X	Ŷ	Ŷ
1,4-Dichlorobenzene-d <sub>4</sub> (I.S)		X	X	Ŷ	x	X X X X X X
3,3'-Dichlorobenzidine	91-94-1	X	X	x	Ŷ	Ŷ
2,4-Dichlorophenol	120-83-2	X	X	Ŷ	Â	Ŷ
2,6-Dichlorophenol	87-65-0	X X X	ND	ND	ND	Ŷ
Dichlorovos	62-73-7	Ŷ	ND	ND	ND	Ŷ
Dicrotophos	141-66-2	Ŷ	ND	ND	ND	Ŷ
Dieldrin	60-57-1	Ŷ	X	X	X	Ŷ
Diethyl phthalate	84-66-2	x	Ŷ	Ŷ	Ŷ	X X
Diethylstilbestrol	56-53-1	AW, 05(67)		ÑD	ÑD	Ŷ
Diethyl sulfate	64-67-5	LR	ND	ND	ND	ĹR
Dimethoate	60-51-5	HE,HS(31)		ND	ND	X
3,3'-Dimethoxybenzidine	119-90-4	Χ	ND	ND	ND	LR
Dimethylaminoazobenzene	60-11-7	Ŷ	ND	ND	ND	X
7,12-Dimethylbenz(a)-	57-97-6	CP(45)	ND	ND	ND	ĈP
anthracene	J7-37-0	01(43)	NU		ND	UP
3,3'-Dimethylbenzidine	119-93-7	X	ND	ND	ND	X
α,α-Dimethylphenethylamine	122-09-8	ÑD	ND	ND	ND	Ŷ
2,4-Dimethylphenol	105-67-9	X	X	X		
Dimethyl phthalate	131-11-3	Ŷ	Ŷ	Ŷ	X X	X
1,2-Dinitrobenzene	528-29-0	x	ND	ŇD	ŇD	X X
1,3-Dinitrobenzene	99-65-0	Ŷ	ND	ND	ND	÷
1,4-Dinitrobenzene			ND	ND	ND	X X
4,6-Dinitro-2-methylphenol	100-25-4 534-52-1	HE(14)	X	X	X	X
		X	Ŷ	Ŷ	Ŷ	Ŷ
2,4-Dinitrophenol	51-28-5	X			÷	Ŷ
2,4-Dinitrotoluene	121-14-2	X	X	X	X	X
2,6-Dinitrotoluene	605-20-2	X CD_115(20)	X	X	X	X
Dinocap	39300-45-3	CP,HS(28)		ND	ND	ÇP
Dinoseb	88-85-7	x	ND	ND	ND	X
Diphenylamine	122-39-4	X	X	X	X	X
5,5-Diphenylhydantoin	57-41-0	X	ND	ND	ND	X
1,2-Diphenylhydrazine	122-66-7	X	X	X	X	X
Di-n-octyl phthalate	117-84-0	X	X	X	X	X
Disulfoton	298-04-4	X	ND	ND	ND	X
Endosulfan I	959-98-8	X	X	X	X	X
Endosulfan II	33213-65-9	X	X	X	X	X
Endosulfan sulfate	1031-07-8	X	X	X	X	X
Endrin	72-20-8	X	X	X	X	X
Endrin aldehyde	7421-93-4	X	X	X	X	X
Endrin ketone	53494-70-5	X	X	ND	X	X
EPN	2104-64-5	X	ND	ND	ND	X
Ethion	563-12-2	X	ND	ND	ND	X
Ethyl carbamate	51-79-6	DC(28)	ND	ND	ND	X

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	Appropriate Preparation Techniqu					
Compounds	CAS No <sup>®</sup>	3510	3520	3540	3550	3580
Ethyl methanesulfonate	62-50-0	X	ND	ND	ND	X
Famphur	52-85-7	X	ND	ND	ND	X
Fensulfothion	115-90-2	X	ND	ND	ND	X
Fenthion	55-38-9	X	ND	ND	ND	X
Fluchloralin	33245-39-5	X	ND	ND	ND	X
Fluoranthene	206 <b>-44-0</b>	X	X	X	X	X
Fluorene	86-73-7	X	X	X	X	X
2-Fluorobiphenyl (surr.)	321-60-8	X	X	X	X	Ŷ
2-Fluorophenol (surr.)	367-12-4	X	X	X	X	Ŷ
Heptachlor	76-44-8	X	X	X	X	Ŷ
Heptachlor epoxide	1024-57-3	X	X	X	X	X
Hexachlorobenzene	118-74-1	X	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X	X	X	X	X
Hexachloroethane	67-72-1	X	X	X	X	X
Hexachlorophene	70-30-4	AW, CP(62	) ND	ND	ND	ĈŁ
Hexachloropropene	1888-71-7	X	ND	ND	ND	X
Hexamethyl phosphoramide	680-31-9	X	ND	ND	ND	X
Hydroquinone	123-31-9	ND	ND	ND	ND	X
Indeno(1,2,3-cd)pyrene	193-39-5	X	X	X	X	X
Isodrin	465-73-6	X	ND	ND	ND	X
Isophorone	78-59-1	X	X	X	X	X
Isosafrole	120-58-1	DC(46)	ND	ND	ND	X
Kepone	143-50-0	X	ND	ND	ND	X
Leptophos	21609-90-5	X	ND	ND	ND	X
Malathion	121-75-5	HS(5)	ND	ND	ND	X
Maleic anhydride	108-31-6	HE	ND	ND	ND	X
Mestranol	72-33-3	X	ND	ND	ND	X
Methapyrilene	91-80-5	X	ND	ND	ND	X
Methoxychlor	72-43-5	X	ND	ND	ND	X
3-Methylcholanthrene	56-49-5	X	ND	ND	ND	X
4,4'-Methylenebis(2-chloraniline	) 101-14-4	OE,0S(0)	) ND	ND	ND	L
Methyl methanesulfonate	66-27-3	X	ND			X
2-Methylnaphthalene	91-57-6	X	X	ND		X
Methyl parathion	298-00-0	X	ND			X
2-Methylphenol	95-48-7	X	ND			X
3-Methylphenol	108-39-4	X	ND			X X X X X
4-Methylphenol	106-44-5	X	ND			X
Mevinphos	7786-34-7	X	ND			
Mexacarbate	315-18-4	HE,HS(68	3) ND		_	X
Mirex	2385-85-5	X I	ND			X
Monocrotophos	6923-22-4	HE	ND			X
Naled	300-76-5	X	ND			X
Naphthalene	91-20-3	X	X	X	X	X
Naphthalene- $d_{s}$ (I.S.)		X	X	X	X	X
1,4-Naphthoquinone	130-15-4	X	ND			
				) NC	) ND	. v

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Appropriate Preparation Tec				on Tec	<u>hniques</u>	
Compounds	CAS No <sup>®</sup>	3510	3520	3540	3550	3580
2-Naphthylamine	91-59-8	X	ND	ND	ND	X
Nicotine	54-11-5	DE(67)	ND	ND	ND	X
5-Nitroacenaphthene	602-87-9	XÍ	ND	ND	ND	X
2-Nitroaniline	88-74-4	X	X	ND	X	X
<b>3-Nitroaniline</b>	99-09-2	X	X	ND	X	X
4-Nitroaniline	100-01-6	X	X	ND	X	Ŷ
5-Nitro-o-anisidine	99-59-2	X	ND	ND	ND	Ŷ
Nitrobenzene	98-95-3	X	X	X	X	Ŷ
Nitrobenzene-d <sub>s</sub> (surr.)		X	X	Ŷ	Ŷ	X X X X
4-Nitrobiphenyl	92-93-3	X	ŇD	ND	ÑD	Ŷ
Nitrofen	1836-75-5	Ŷ	ND	ND	ND	Â.
2-Nitrophenol	88-75-5	X X	X	X	X	Ŷ
4-Nitrophenol	100-02-7	Ŷ	Ŷ	Ŷ	Ŷ	Ŷ
5-Nitro-o-toluidine	99-55-8	Ŷ	ÑD	ÑD	ÑD	Ŷ
Nitroquinoline-1-oxide	56-57-5	Ŷ	ND	ND	ND	Ŷ
N-Nitrosodibutylamine	924-16-3	Ŷ	ND	ND	ND	× ×
N-Nitrosodiethylamine	55-18-5	Ŷ	ND	ND		, Č
N-Nitrosodimethylamine	62-75-9	Ŷ	X		ND	X X X X X X X X X X
		Ŷ		X	X	, X
N-Nitrosomethylethylamine	10595-95-6	X	ND	ND	ND	X
N-Nitrosodiphenylamine	86-30-6	X	X	X	X	X
N-Nitrosodi-n-propylamine	621-64-7	X	X	X	X	X
N-Nitrosomorpholine	59-89-2	ND	ND	ND	ND	X
N-Nitrosopiperidine	100-75-4	X	ND	ND	ND	X
N-Nitrosopyrrolidine	930-55-2	X	ND	ND	ND	X
Octamethyl pyrophosphoramide	152-16-9	LR	ND	ND	ND	LR
4,4'-Oxydianiline	101-80-4	X	ND	ND	ND	X
Parathion	56-38-2	X	ND	ND	ND	X
Pentachlorobenzene	608-93-5	X	ND	ND	ND	X
Pentachloronitrobenzene	82-68-8	X	ND	ND	ND	X
Pentachlorophenol	87-86-5	X	X	X	X	X
Perylene-d <sub>12</sub> (I.S.)		X	X	X	X	X
Phenacetin	62-44-2	X	ND	ND	ND	X
Phenanthrene	85-01-8	X	X	X	X	X
Phenanthrene-d <sub>10</sub> (I.S.)		X	X	X	X	X
Phenobarbital	50-06-6	X	ND	ND	ND	X
Phenol	108-95-2	DC(28)	X	X	X	X
Phenol-d <sub>s</sub> (surr.)		DC (28)	X	X	X	Ŷ
1,4-Phenylenediamine	106-50-3	X	ÑD	ÑD	ÑD	X X X X X X X X
Phorate	298-02-2	Ŷ	ND	ND	ND	Ŷ
Phosalone	2310-17-0	HS(65)	ND	ND	ND	Ŷ
Phosmet	732-11-6	HS(15)	ND	ND	ND	Ŷ
			ND	ND	ND	Ŷ
Phosphamidon Phthalia aphydmide	13171-21-6	HE(63)		ND		СР
Phthalic anhydride	85-44-9	CP,HE(1)	ND		ND	
2-Picoline	109-06-8	ND	ND	ND	ND	ND
Piperonyl sulfoxide	120-62-7	X	ND	ND	ND	X
Pronamide	23950-58-5	X	ND	ND	ND	X
<b>Pro</b> pylthiouracil	51-52-5	LR	ND	ND	ND	LR

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	Appropriate Preparation Techniq					hnique
Compounds	CAS No <sup>®</sup>	3510	3520	3540	3550	3580
Pyrene	129-00-0	X	X	x	x	X
Pyridine	110-86-1	ND	ND	ND	ND	ND
Resorcinol	108-46-3	DC,0E(10)	) ND	ND	ND	X
Safrole	94-59-7	X	ND	ND	ND	X
Strychnine	60-41-3	AW, OS(55)	) ND	ND	ND	X
Sulfallate	95-06-7	X	ND	ND	ND	X X
Terbufos	13071-79-9	X	ND	ND	ND	X
Terphenyl-d <sub>14</sub> (surr.)		X	X	ND	X	X
1,2,4,5-Tetrachlorobenzene	95-94-3	X	ND	ND	ND	X
2,3,4,6-Tetrachlorophenol	58-90-2	X	ND	ND	ND	X
Tetrachlorvinphos	961-11-5	X	ND	ND	ND	X
Tetraethyl pyrophosphate	107-49-3	X	ND	ND	ND	X
Thionazine	297-97-2	X	ND	ND	ND	X
Thiophenol (Benzenethiol)	108-98-5	X	ND	ND	ND	X
Toluene diisocyanate	584-84-9	HE(6)	ND	ND	ND	X
o-Toluidine	95-53-4	X	ND	ND	ND	X
Toxaphene	8001-35-2	X	X	X	X	X
2,4,6-Tribromophenol (surr.)		X	X	X	X	X
1,2,4-Trichlorobenzene	120-82-1	X	X X	X	X	X
2,4,5-Trichlorophenol	95- <b>95-4</b>	X	X	ND	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X	X
Trifluralin	1582-09-8	X	ND	ND	ND	X
2,4,5-Trimethylaniline	137-17-7	X	ND	ND	ND	X
Trimethyl phosphate	512-56-1	HE(60)	ND	ND	ND	X
1,3,5-Trinitrobenzene	99-35-4	X	ND	ND		X
Tris(2,3-dibromopropyl) phosphate		X	ND			LR
Tri-p-tolyl phosphate	78-32-0	X	ND	ND		X
0,0,0-Triethyl phosphorothioate	126-68-1	X	ND	ND	ND	X

Chemical Abstract Se. ce Registry Number. a

AW = Adsorption to walls or glassware during extraction and storage.

- CP = Nonreproducible chromatographic performance.
- DC = Unfavorable distribution coefficient (number in parenthesis is percent recovery).
- HE = Hydrolysis during extraction accelerated by acidic or basic conditions (number in parenthesis is percent recovery).
- HS = Hydrolysis during storage (number in parenthesis is percent stability).
- LR = Low response.
- ND = Not determined.
- OE = Oxidation during extraction accelerated by basic conditions (number in parenthesis is percent recovery).
- OS = Oxidation during storage (number in parenthesis is percent stability).
- X = Greater than 70 percent recovery by this technique.

Percent Stability = Average Recovery (Day 7) x 100/Average Recovery (Day 0).

1.2 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fusedsilica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step,  $\alpha$ -BHC,  $\tau$ -BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 1 mg/Kg (wet weight) for soil/sediment samples, 1-200 mg/Kg for wastes (dependent on matrix and method of preparation), and 10  $\mu$ g/L for ground water samples (see Table 2). EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

#### **3.0 INTERFERENCES**

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation

and/or cleanup of the samples and take corrective action to eliminate the problem.

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3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

#### 4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 1  $\mu$ m film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1  $\mu$ L of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

- 4.2 Syringe 10  $\mu$ L.
- 4.3 Volumetric flasks, Class A 10 mL to 1000 mL.
- 4.4 Balance Analytical, 0.0001 g.
- 4.5 Bottles glass with Teflon-lined screw caps or crimp tops.

Section 11

# Organic Geochemistry of Ground Water

Lecture by: Patrick Longmire Los Alamos National Laboratory

# SECTION CONTENTS

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# ORGANIC GEOCHEMISTRY OF GROUND WATER

## I. INTRODUCTION

II. ORGANIC CARBON IN SURFACE AND GROUND WATER: CLASSIFICATION, AMOUNT AND ORIGIN

A. Classification of Organic Carbon

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## TOC Determinations in Ground Water

by Michael J. Barcelona<sup>a</sup>

#### ABSTRACT

Determinations of total organic carbon (TOC) can provide valuable diagnostic evidence of the extent of ground-water contamination by organic compounds. The usefulness of conventional TOC results in monitoring efforts is limited by the bias introduced during the purging of inorganic carbon prior to analysis. A modified TOC procedure has been evaluated to permit the quantitation of the volatile organic carbon (VOC) fraction in water samples. The methodology consists of trapping the VOC in a manner analogous to commercial purge and trap instruments which are used for specific organic compound separations. The method has been found to be sensitive, accurate and reasonably precise for TOC determinations of standard solutions as well as on ground-water samples. Volatile organic carbon levels can range from 9-50% of the TOC in both uncontaminated and contaminated ground waters. The reporting of the volatile and nonvolatile fractions of the TOC will enhance both monitoring and research efforts, since it permits more complete characterization of the organic carbon content of ground-water samples.

#### INTRODUCTION

Monitoring total organic carbon (TOC) in ground-water samples is useful because contamination by synthetic organic compounds may be indicated when TOC concentrations are detected above background levels. This surrogate parameter provides a rapid, inexpensive indication of the extent of organic contamination and has been used extensively in studies of contaminant plume migration (Robertson and others, 1974; Spiker and Rubin, 1975; Leenheer and others, 1976; Kimmel and Braids, 1980). In this respect, TOC determinations permit the screening of samples prior to specific organic compound identification and quantitation.

TOC measurements are considered superior to laborious manual determinations of chemical (COD) or biological (BOD) oxygen demand as the latter methodologies may be significantly biased by the presence of reducing agents, refractory compounds or toxic materials. For these and other reasons, TOC determinations are frequently required by regulatory agencies for compliance monitoring (for example, RCRA, NPDES or CERCLA programs). The usefulness of TOC data has been limited though, because it is an operationally defined parameter which may be representative of the total dissolved organic carbon content of a water sample.

The nonvolatile organic carbon levels of uncontaminated ground water are generally observed to be quite low, 0.1-4 mg/l (Leenheer and others, 1974; Junk and others, 1980). Inorganic carbon, comprised of aqueous carbon dioxide, bicarbonate and carbonate ions, may exceed 100-200 mg/l, depending on the pH, temperature and partial pressure of  $CO_2$ . The routine TOC procedure consists of three steps. Firstly, acidification and purging of the water sample are performed to remove inorganic carbon species as CO<sub>2</sub>. CO<sub>2</sub> purging is followed by an oxidation procedure to convert organic carbon to CO<sub>2</sub>. The principal procedures in use are wet-chemical oxidation (Menzel and Vaccaro, 1964; Sharp, 1973; Goulden and Anthony, 1978) and ultraviolet photooxidation (Collins and Williams, 1977; Mueller and

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Bandaranayake, 1983), as well as high-temperature oxidation. The relative oxidation efficiencies of these procedures may vary relative to the mixture of organic compounds making up the TOC (Gershey and others, 1979). Thirdly, the quantitation of the  $CO_2$  produced in the oxidation step is then usually performed by infrared absorption spectrometry.

Regardless of the oxidation or quantitation steps employed in various instrumental methods, a common source of bias in TOC measurements results from purging volatile forms of organic carbon along with inorganic carbon. Variations in CO<sub>2</sub> purging methodologies may explain, in part, the poor interlaboratory comparisons of TOC measurement performance which has resulted in suggestions that TOC be dropped entirely from recommended methods for landfill leachate analysis (De Walle and others, 1981). Several authors have recognized the fact that such TOC data must be reported as a lower limit, since only the nonvolatile fraction of the organic carbon is available after purging (Baedeker and Back, 1979; Kimmel and Braids, 1980).

There are instruments commercially available which determine both the volatile (VOC, purged with CO2 on acidification) and nonvolatile fractions of total dissolved organic carbon (NVOC). Several of these instrument designs are quite sensitive. These instruments convert the CO<sub>2</sub> produced by oxidation of organic materials to methane which is then detected by a flame ionization detector. However, many laboratories have earlier instrument designs which are limited to the determination of NVOC. VOC concentrations have not been reported, since standard methodologies do not distinguish between the two fractions of TOC (USEPA, 1979). Therefore, the available data on the organic carbon content of ground water are biased by the omission of the VOC fraction.

Knowledge of the volatile organic carbon fraction of TOC in ground-water samples is important for several reasons. Interconversion of TOC between the volatile and nonvolatile fractions due to chemical reaction or microbial activity limits the capability to quantitatively assess net organic compound migration if only NVOC is reported. Moreover, volatile organic solvents are among the most frequently observed substances in untreated ground-water supplies for potable uses (Dyksen and Hess, 1982). These compounds are mobile in the subsurface since they are water-soluble, and they frequently appear as early indicators of contaminant release and transport. Observed levels of volatile compounds in ground-water supplies have been reported to be two to three orders of magnitude higher than those in surface supplies (CEQ, 1981).

Therefore, a study was undertaken of the determination of TOC (VOC and NVOC) in ground-water samples. Emphasis was focused on the development and application of a precise, accurate methodology which was verifiable for volatile and nonvolatile organic compounds previously identified in ground water. It was therefore necessary to identify standard compounds which show comparable analytical performance in both carbon fractions.

#### METHODS AND MATERIALS

The 12 compounds chosen for this study, in addition to the usual TOC standard, potassium hydrogen phthalate (KHP), are shown in Table 1. They range from volatile halocarbon and aromatic solvents frequently observed in ground-water samples to low molecular weight, carboxylic acids which have been identified in landfill leachate (Colenutt, 1979; Chian, 1977). Acetone and trichlorophenol were included as partially volatile standards for both the VOC and NVOC fractions.

The modified TOC procedure was developed on an Oceanography International Model 524 Total Organic Carbon Analyzer with standard direct injection module (DIM), purging and glass ampoule sealing units. Five ml water samples were first acidified and purged with oxygen for five minutes at 80 ml/min in a flow system incorporating a 25 cm  $\times$  2.5 mm i.d. stainless steel trap filled with Tenax-GC® support (60-80 mesh) which adsorbed the volatile organics and allowed H<sub>2</sub>O and inorganic  $CO_2$  to vent. The volatile compounds were desorbed from the trap in an oxygen stream (140 ml/min) into the combustion tube (950°C) of the DIM module for conversion to CO<sub>2</sub>. The purging step and subsequent reversal of gas flow through the trap as it was heated (180°C) for five minutes (to desorb the volatiles) is analogous to

Table 1. Model Compounds Used in This Study

Chloroform	Acetaldehyde
Trichloroethylene	Dimethylformamide
Benzene	Acetic acid
Dichloromethane	Propanoic acid
Toluene	Pentanoic acid
Trichlorophenol	Potassium hydrogen phthalate
Acetone	

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the routine purge and trap separation of volatile organics in the priority pollutant analytical protocols (Bellar and Lichtenberg, 1974; EPA, 1982). From the combustion tube, the gases passed through a series of columns to remove water (anhydrous magnesium perchlorate) and hydrochloric acid (finely divided tin particles) prior to entering the infrared detector. After purging the TOC samples of the volatile fraction and inorganic CO<sub>2</sub>, the ampoules were sealed and processed for NVOC by the usual persulfate wet oxidation procedure. Standard solutions (0.05-10 mg-C/l) of the model compounds were made by careful dilution of 50-1,000 mg-C/l stock solutions gravimetrically prepared in 10<sup>-3</sup> N bicarbonate solution immediately prior to use. All standards and most samples were processed in triplicate where volume permitted. All TOC determinations on model compound solutions were calculated relative to calibration curves determined for KHP.

#### **RESULTS AND DISCUSSION TOC Method Performance**

The primary objectives of the work were to develop and apply a TOC methodology which would reproducibly recover the volatile organic carbon fraction of water samples. In the concentration range of 0.1 to 10.0 mg-Cl, acetone and trichlorophenol were found to be the most suitable combined VOC and NVOC standards. Both of these compounds exhibited better than 90% recovery throughout the TOC procedure and an average 30% higher sensitivity than did KHP

standards. Details of the relative performance of the method for acetone are shown in Table 2. The volatile fraction of aqueous acetone standards averaged 9% of the TOC. No significant differences in VOC were noted in parallel standard runs made with a 10<sup>-3</sup> M NaHCO<sub>3</sub> background solution. Therefore, no observable carryover of inorganic CO<sub>2</sub> occurred through the trapping, desorption and combustion steps. Trichlorophenol results were comparable to those for acetone. The slight losses of volatile organic carbon in the desorption and combustion steps were more than compensated for by the more complete wet oxidation of both trichlorophenol and acetone relative to KHP. Trichlorophenol standard solutions were found to be less stable than those for acetone and for this reason acetone was chosen as a more suitable volatile standard compound.

A comparison of the TOC results for the model compounds is presented in Table 3. The percent volatile carbon for each compound was determined by the difference between purged and unpurged standard solutions as described above, for acetone and trichlorophenol. In general, the volatile fraction observed for each volatile organic solvent standard was quite similar to that predicted from purging efficiencies reported by previous workers (Bellar and Lichtenberg, 1974; Kuo and others, 1977).

The sensitivity of the modified method for volatile compounds was found to be very dependent on the ease of persulfate oxidation. Compounds which were less volatile under the test

Standard o	concentration	Percent	High temperature combustion	– – – – Percent – – – Trapping/ desorption	Overall procedure
(mg-C/l)	(µg-C/5 ml)	volatile <sup>*</sup>	efficiency*	efficiency**	efficiency***
1.0	5	8.2	98	88	133
2.0	10	8.6	94	88	149
5.0	25	9.3	91	84	120
10.0	50	9.9	93	78	118
Mean		9.0	94	85	130 ± 11% (relative standard deviation
(N)		(12)	(12)	(24)	(12)

	Table 2. Average Performance	e Data for	Acetone in	the TOC	Procedure
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Determined by difference between purged and unpurged standards after wet combustion relative to KHP.

Carbon recovered by vapor injections X 100.

Volatile carbon

Carbon recovered by purging, trapping and desorption  $\times$  100; corrected for combustion efficiency.

Volatile carbon

Instrument response for acetone (VOC + NVOC) relative to KHP.

Compound	Volatile fraction (%)	Sensitivity* (integrator counts/µg-C)	Recovery** (% bias)	Limit of quantitation <sup>*</sup>
Chloroform	84	143 ± 69	21	0.52
Trichlorocthylene	59	$115 \pm 54$	9.8	0.65
Benzene	53	$113 \pm 16$	-19	0.66
Dichloromethane	48	51 ± 28	-17	1.46
Foluene	46	91 ± 55	-13	0.82
Frichlorophenol	8.8	<b>208 ± 8</b> 0	9.1	0.36
Acetone	9.0	196 ± 38	10	0.38
Acetaldehyde	<0.1	178 ± 33	16	0.42
Dimethylformamide	<0.1	202 ± 32	21	0.37
Acetic acid	<0.1	199 ± 29	9.5	0.38
Propanoic acid	<0.1	165 ± 28	10	0.45
Pentanoic acid	<0.1	$155 \pm 21$	-9.0	0.48
КНР	<0.1	$150 \pm 17$		0.50
All compounds		$151 \pm 32$	4,0	0.57

\* Average sensitivity for TOC values between 1 and 10 mg-C/l. Mean value and the relative standard deviation in percent are tabulated.

\*\* Recoveries calculated as percent bias from the mean value relative to KHP at the 1.0 mg-C/l level.

<sup>•</sup> Defined as the equivalent carbon content of 10<sup>-3</sup> M NaHCO<sub>3</sub> solution blanks plus 10 times the standard deviation of the blank values.

conditions and resistant to persulfate oxidation showed marked reductions in sensitivity relative to KHP or acetone. Nonetheless, the sensitivity for all model compounds with the exception of dichloromethane and toluene was within two relative standard deviations of the value for KHP. The average recoveries varied ±20% from the KHP standard. The limits of quantitation (ACS, 1980) of the modified TOC procedure for the model compounds (excepting dichloromethane) were quite comparable to that of KHP, acetone or trichlorophenol. The average quantitation limit of 0.57 mg-C/l may be accepted as the lowest TOC concentration that can be reliably determined by infrared detection methods. Since most shallow ground-water samples have exhibited NVOC values alone greater than 0.5 mg-C/l, this is not a serious drawback for screening purposes.

The preceding performance data on the modified TOC procedure establish that, within experimental error, volatile organic carbon represented by a range of model compounds can be reliably determined on a routine basis. Overall, precision and accuracy for replicate carbon standards at 1.0-10 mg-C/l over an 18-month period averaged less than  $\pm 20\%$  relative standard deviation and  $\pm 20\%$  bias, respectively. Sample analysis times for the modified TOC procedure were approximately 20 minutes, excluding setup and overnight wet chemical oxidation. The need to individually process each sample for VOC results in longer sample analysis times, but the value of complete TOC data seems to be well worth it. This is particularly true when TOC is used as a surrogate parameter for contaminant plume definition (Leenheer and others, 1976), a contamination screening tool (Hughes and others, 1974), or as a basis for evaluating the reactivity of the organic carbon in ground-water samples—for example, sorption interactions (Humenick and Mattox, 1978).

#### **TOC Determinations on Ground-Water Samples**

The analysis and reporting of both VOC and NVOC have potential application for the screening of volatile organic carbon contaminant plumes, particularly when "background" VOC levels are quite low. The modified TOC procedure described above was applied to selected ground-water samples. Ground-water samples were collected in 40-ml Teflon-sealed vials directly from the pump outputs. The intent in this part of the study was to determine both the amount of volatile organic carbon present in shallow ground-water samples in the absence of organic contamination, as well as in a situation where large amounts of organic matter have been introduced anthropogenically.

Replicate TOC determinations were made on 11 samples of ground water from a residential area in northern Illinois. The wells were privatelyowned, steel-cased wells, finished between 60-70 feet (18.3 m) in sand and gravel outwash deposits, described by Berg and others (1981). The

Sample	VOC	NVOC	TOC	% Vol.
1	0.23	3.20	3.43	6.6
2	0.21	2.24	2.45	8.4
3	0.39	3.57	3.96	9.8
4	0.33	2.34	2.67	12.3
5	0.31	3.25	3.56	8.6
6	0.18	2.60	2.78	6.6
7	0.10	2.60	2.70	3.7
8	0.25	2.10	2.35	10.5
9	0.31	2.16	2.47	12.6
10	0.35	2.72	3.07	11.4
11	0.31	2.68	2.99	10.4
Limit of quantitation*	0.10	0.24	0.34	
Mean TOC			2.95	
Average percent VOC				9.2

Table 4. TOC Determinations in Shallow Ground Water (mg-C/l)

• Limit of quantitation defined as blank value in  $\mu$ g-C + 10  $\sigma$  (relative standard deviation) relative to the response for KHP.

analytical results from these samples are compiled in Table 4. The levels of TOC in these samples averaged 2.95 mg-C/l of which 0.27 mg-C/l or 9.2% was present as VOC. Precision of the modified TOC determination on these samples was better than ±5% (relative standard deviation) from triplicate analytical runs. The improved precision for natural samples relative to acetone (Table 2) was probably the result of less handling prior to analysis. Parallel determinations of conductivity, pH, TDS, nitrate and Kjeldahl nitrogen were performed on these samples, and the results showed essentially no correlation with the TOC data. Although the volatile organic carbon contents of these TOC results was low, each was above the limit of quantitation established for the procedure. Therefore, a significant percentage of VOC may be expected in uncontaminated ground-water samples.

Complete TOC determinations can provide valuable diagnostic evidence of contaminated subsurface situations. Two examples of the application of the modified TOC procedure include the investigation of the effects of organic drilling fluids and natural organic substances (petroleum) on ground-water organic content.

In the course of establishing a ground-water research field site near Havana, Illinois, in Mason County, an array of large-diameter PVC observation wells was installed in shallow sand and gravel deposits (Naymik and Sievers, 1983). Several of these wells were rotary drilled using an organic drilling fluid (Revert <sup>®</sup>), while the bulk of the wells were constructed by either hollow-stem auger

or driven-sand point techniques. Those wells drilled with organic drilling fluids were chlorinated and developed when they were completed in March 1982. Figure 1 shows the results of TOC determinations on ground-water samples from the site for one year after construction. Augured or driven wells screened through two water-yielding strata showed an average background TOC level of 4.38 mg-C/l (N = 6) with a relative standard deviation (r.s.d.) of 11%. The VOC made up an average of 15 ± 40% r.s.d. of the total organic carbon. The wells drilled with the organic fluid, however, showed average TOC levels two to three times the background concentrations (• SR1 and  $\odot$  SR2) during a three to six month period after construction. VOC made up nearly 95% of the TOC in samples collected prior to November 1982. Thereafter, the TOC content of the rotary-drilled well samples increased to over five times the background, and the VOC fraction gradually decreased to within background levels of 0.4-1.0 mg/l. Although exhaustive pumping of wells SR1 and SR2 in April 1983 yielded samples that were only twice the background levels, the effect of the

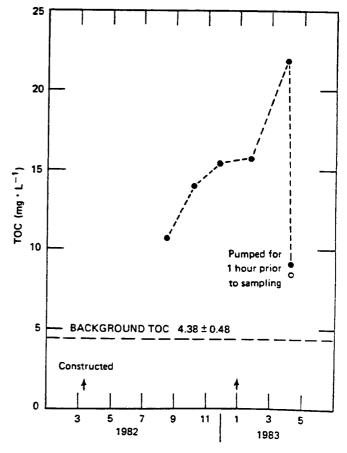


Fig. 1. Drilling mud effects on TOC levels in ground water (• SR1,  $\odot$  SR2 wells drilled with Revert  $\odot$ ).

introduction of foreign organic matter during the drilling operation was clearly persistent. Major cations, anions and alkalinity showed little or no correlation with the variations in TOC or VOC concentrations. Total iron, however, showed significant increases which may be linked to organic carbon content.

The TOC results after well construction demonstrate the impact of organic drilling muds on ground-water quality. High levels of VOC during this period may have been the result of the initial breakdown of the drilling mud near the well bore by microorganisms. If this indeed occurred, then the TOC increases over the later study period may be due to the release of nonvolatile, soluble organic materials or other biotransformation products. The large increases in TOC over background levels could have important effects on the separation and identification of specific organic compounds, given the shift in organic carbon from predominately volatile to nonvolatile forms.

The second example of the diagnostic application of TOC determinations in contaminated shallow ground-water systems involved the investigation of a complaint of an abrupt change in taste and odor of a private well supply near Sullivan, Illinois, in rural Moultrie County. The 36 foot (11 m) steel-cased well was finished in glacial till, and provided the potable and livestock water for a farmstead. Initial measurements of TOC showed that 50% of the total organic carbon  $(1.4 \pm 0.2)$ mg-C/l) was volatile. Samples taken several months later were analyzed, and TOC levels were significantly higher than the previous results  $(3.23 \pm 0.1)$ mg-C/l). Greater than 95% of the observed increase was due to volatiles (excluding methane which was present at 11 ml/l). It was known that investigation of shallow petroleum deposits in the area using seismic prospecting methods had been conducted about six months before the water quality change was noticed. Dynamiting during the prospecting activity may have permitted the migration of petroleum-related constituents into formations intercepted by the potable-water well.

#### CONCLUSIONS

The routine wet digestion IR detection procedure for TOC determinations in ground-water samples has been modified to include the volatile organic fraction. The method was validated for model organic compounds and applied to selected ground-water samples. The performance of the method for a suite of volatile and involatile compounds was found to be good and on the average quite comparable to that observed for the usual TOC standard, potassium hydrogen phthalate.

The value of TOC determinations as a screening tool for contaminated ground-water situations is markedly improved by the quantitation of VOC, as well as NVOC. The VOC fraction can make up from 9-50% of the total organic carbon in ground-water samples. The usefulness and reliability of future monitoring efforts can be significantly enhanced by the determination of volatile organic carbon.

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\* \* \* \* \*

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### ORGANIC GEOCHEMISTRY OF GROUND WATER

#### INTRODUCTION

Organic geochemistry has historically been the study of the origin of petroleum, coal, and oil shale. Organic geochemistry of natural waters, including ground water, is different from this definition and is the application of organic chemistry to study earth processes involving the hydrologic cycle. Lecture material is derived from Thurman's "Organic Geochemistry of Natural Water."

The purpose of this lecture is to provide an overview of organic geochemistry and to illustrate its importance to ground water systems. This lecture will be concerned mainly with natural organic matter, e.g., humic materials.

Humic substances are important because they are precursors to trihalomethanes (THM's), they can complex with toxic metals, and they influence the fate of "man-made" organic compounds such as aromatic hydrocarbons and pesticides.

#### CLASSIFICATION OF ORGANIC CARBON

#### ACRONYMS OF COMMONLY USED TERMS FOR ORGANIC MATTER IN WATER

ACRONYM	MEANINGS	
DOC SOC POC	Dissolved Organic Carbon Suspended Organic Carbon Particulate Organic Carbon	
TOC VOC DOM POM TOM COM	Total Organic Carbon Volatile Organic Carbon Dissolved Organic Matter Particulate Organic Matter Total Organic Matter Colloidal Organic Matter-imp. transport of	Radioactive + metal
		Constituents

DOC is less than 0.45 micron and only contains carbon.

SOC is greater than 0.45 micron (silver filter) and only contains carbon.

POC is greater than 0.45 micron (glass-fiber filter) and only contains carbon.

TOC is the summation of DOC and SOC or DOC and POC.

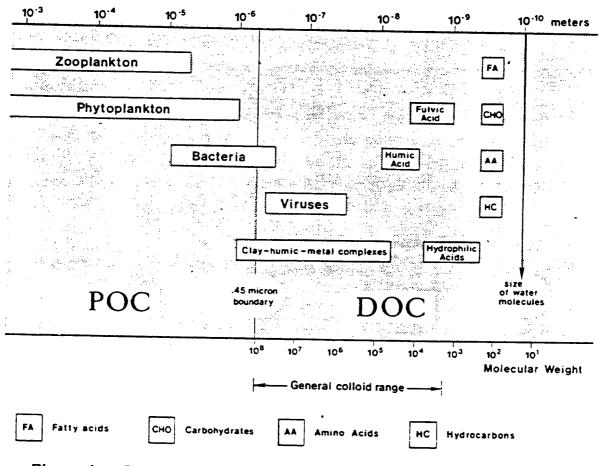
VOC is the amount of volatile organic compounds in water that are measured by purging them from the sample and trapping them on an adsorbent.

DOM is less than 0.45 micron and contains carbon, oxygen and hydrogen.

POM is greater than 0.45 micron and contains carbon, oxygen and hydrogen.

TOM is the summation of DOM and POM.

COM mainly contains DOC and is associated with clay-humic metal complexes.

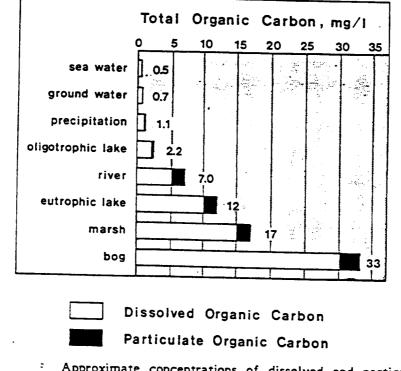


Organic Carbon Continuum

Continuum of particulate and dissolved organic carbon in Figure 1. natural waters (Thurmon, 1985).

This figure shows the continuum of organic carbon in natural waters. Filtration removes macroscopic particulate organic carbon (POC), such as zooplankton, algae, bacteria, and detrital organic matter from soils and plants. The majority of dissolved organic carbon (DOC) present in water are polymeric organic acids, called humic substances.

### AMOUNT OF ORGANIC CARBON IN SURFACE AND GROUND WATER





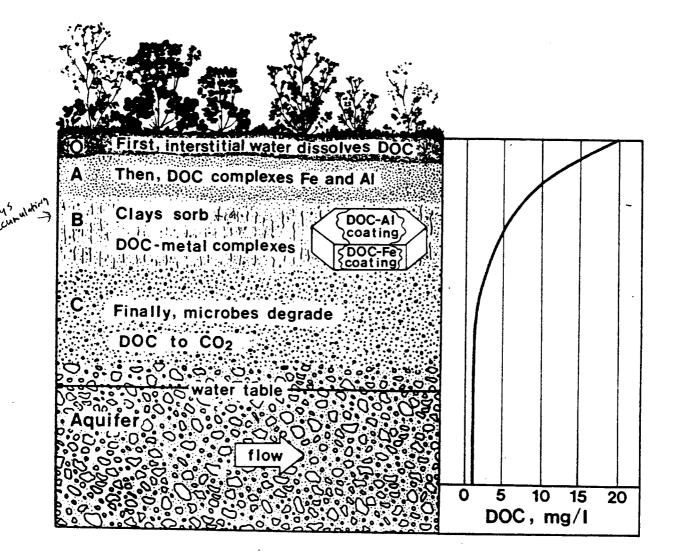
This figure shows the average concentrations of DOC and POC in surface and ground waters. DOC varies with the type of water from approximately 0.5 mgC/L for ground water and sea water to over 30 mgC/L for colored waters from swamps. TOC mainly contains DOC with lesser amounts of POC.

### DOC IN GROUND WATER

- Range of DOC: 0.2 to 15 mg C/L
- Median concentrations: 0.7 mg C/L
- Coal deposits: 5 to 10 mg C/L
- Oil shale: up to 40,000 mg C/L
- Oil field brines: 1,000 mg C/L
- Hydrocarbons: 100s mg C/L

# WHY IS THE CONCENTRATION OF ORGANIC CARBON IN GROUND WATER SO SMALL?

- Long residence time Carbon oxidizes to CO<sub>2</sub> (g) Contributes to alkalinity Forms methane
- Adsorption onto aquifer material
- Aquifer materials contain trace amounts of organic matter that is water soluble



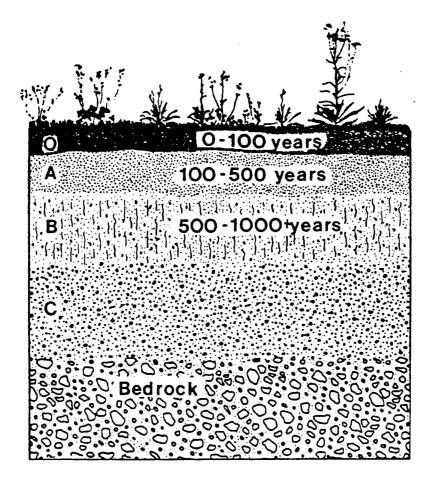
Podzolization and decrease of organic carbon in interstitial water of soils (*Thurman*, 1985).

Interstitial soil waters have a range of DOC from 2 to 30 mg C/L. This figure shows the podzolization process. The organic matter is dissolved humic and fulvic acid originating from the decay processes of plants and soil.

See P. 9-34 A Jan - Uranium-Carbonak Complexes

## COLLOIDAL ORGANIC MATTER

- Aggregates of humic acids 2 to 50 nanometers (10<sup>-9</sup>m) in diameter
- Commonly associated with clay minerals or oxides of aluminum and iron
- Constitutes approximately 10% of DOC
- Molecular weight is from 2000 100,000



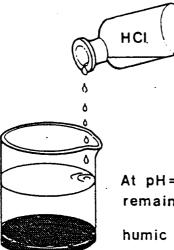
Age of organic carbon in various soil horizons, compiled from the data of O'Brien and others (1981).

Age of organic carbon in various soil horizons is illustrated in this figure. Humic and fulvic acids from soil are older than DOC in water. Oxidation of these acids is inhibited in deeper portions of the soil column because of reduced biological activity.

### HUMIC AND FULVIC ACIDS HUMIC SUBSTANCES

- The majority of DOC present in surface and ground water
- Polyelectrolytes of carboxylic, hydroxyl, and phenolic functional groups
- Comprise 50% to 70% of DOC

Huffman-Lab-in Golden, CO-specialize in analyzing humic + fulvic



At pH=1 fulvic acid remains in solution

humic acid is precipitated

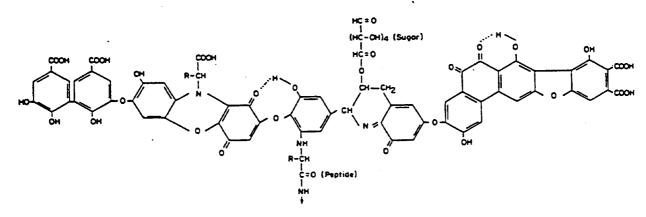
Separation of humic and fulvic acids by acid precipitation(Thurman, 1985).

Humic Acid -- The dark colored organic material which can be assoc. w/ netals extracted from soil by various reagents and which is not as reactive insoluble in dilute acid.

Fulvic Acid -- The colored material which remains in solution after -> more active removal or humic acid by acidification.

### HUMIC ACID

- The dark-colored organic matter which can be extracted from soil by various reagents and which is insoluble in dilute acid
- Associated with clay minerals and metal oxides
- Fewer carboxylic acid functional groups enhances precipitation
- Molecular weight is greater than 2,000



Hypothetical structure of humic acid. (From J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay (Eds.), *Micronutrients in Agriculture*, American Society of Agronomy, Madison, Wisconsin, 1972.)

Humic acids are very complex organic polymers that contain different functional groups. Some of these functional groups include carboxylic acids (R-COOH), phenols (R-OH), and alcoholic (R-OH) groups where R denotes the carbon atom or organic molecule attached to the particular functional group.

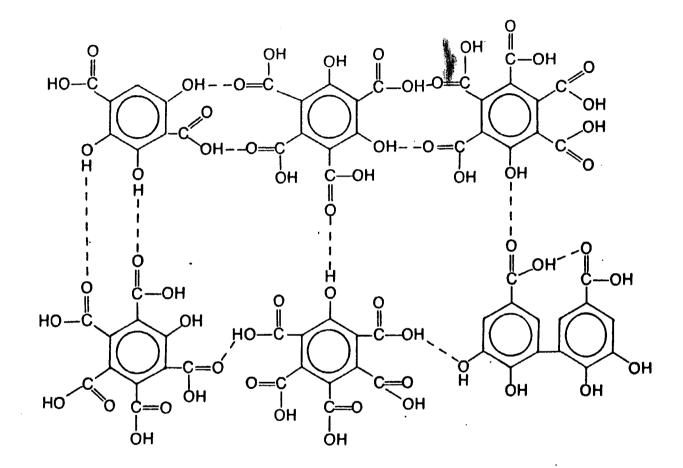
### FULVIC ACID

• The colored material which remains in solution after removal of humic acid by acidification

and more reactive

- Fulvic acid is more water soluble because it contains more carboxylic and hydroxyl funtional groups
  - -- molecular weight ranges from 800 to 2,000

#### STRUCTURE OF FULVIC ACID (Schnitzer, 1972)



Fulvic acids are more soluble than humic acids because of the greater amounts of carboxylic acid functional groups (R-COOH) and, therefore, fulvic acids are geochemically more reactive than humic acids.

#### GENERAL PROPERTIES OF HUMIC AND FULVIC ACIDS

Property	Remarks	Effect of Soil
Color	The typical dark color of many soils is caused by organic matter	May facilitate warming
Water retention	Organic matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking. May significantly improve the moisture-retaining properties of sandy soils
Combination with clay minerals	Cements soil particles into structural units called aggregates	Permits exchange of gases Stablizes structure Increases permeability
Chelation	Forms stable complexes with Cu <sup>2+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup> , and other polyvalent cations	May enhance the availability of micronutrients to higher plants
Solubility in water	Insolubility of organic matter is because of its association with clay. Also, salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly soluble in water	Little organic matter is lost by leaching
Buffer action	Organic matter exhibits buffering in slightly acid, neutral, and alkaline ranges	Helps to maintain a uniform reaction in the soil
Cation exchange	Total acidities of isolated fractions of humus range from 300 to 1400 meq/100 g	May increase the cation exchange capacity (CEC) of the soil. From 20 to 70% of the CEC of many soils (e.g Mollisols) is caused by organic matter
Mineralization	Decomposition of organic matter yields CO <sub>2</sub> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>-</sup> , and SO <sub>4</sub> <sup>2-</sup>	A source of nutrient elements for plant growth
Combines with organic molecules	Affects bioactivity, persistence and biodegradability of pesticides	Modifies application rate of pesticides for effective control

Source: Stevenson, 1982

### RESULTS OF BATCH TESTS (All concentrations in mg/L except as noted)

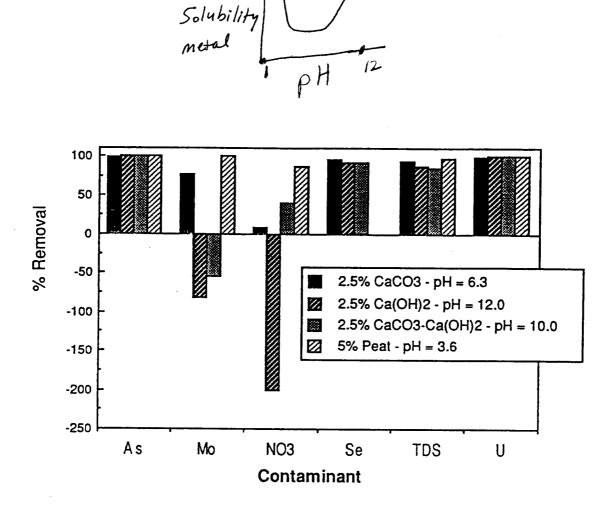
<u></u>	ŝ.	A aid Tallings	
	Acid Tailings	Acid Tailings plus Peat	
Species/parame	eter Conce	ntration	
Al	550	1.9	
As	22.4	0.54	
Ca	271	40.2	
CI	4.6	0.02	
Fe	2070	1.75	
К	0.31	4.6	
Mg	48.7	5.2	
Mn	4.63	0.67	
Мо	2.1	0.02 uravi	um mill tailing
Na	10.3	3.82	peat mo barrier
Ni	7.33	0.05	
Pb	0.64	0.03 fer	poraRy
SO <sub>4</sub>	6790	<b>13</b> 4 9 <sup>e</sup>	nporary to chemi <i>lia</i> anien
U	6.21	<sup>له</sup> 0.0036	amer
TDS	13300	196   pent c	ipitotion
pH	2.2	3.18 abs	t sorption

1. Batch test (72 hours) contains tailings plus 10% by weight fibric peat. Batch test consists of 250 g tailings to 600 ml deionzed water.

Seventy-two hour batch tests were performed on acid-leach tailings containing very high concentrations of heavy metals, including iron, lead, molybdenum, and nickel. Fibric peat was added to the tailings to investigate the adsorption capacity of solid organic matter. The addition of peat resulted in concentration decreases of several metals, although the pH increased only slightly.

better at Complexing Cations as anion S

11-27



PERCENT REMOVAL (POSITIVE VALUE) AND ELUTION (NEGATIVE VALUE) FOR As, Mo, NO<sub>3</sub>, Se, TDS, and U USING SPHAGNUM PEAT, CaCO<sub>3</sub>, AND Ca(OH)<sub>2</sub>.

Batch experiments, mineralogical studies, and geochemical modeling were conducted to evaluate the effectiveness of sphagnum peat, calcium carbonate, and hydrated lime in removing dissolved concentrations of As, Mo, NO<sub>3</sub>, and U present in uranium-tailings pore water at Gunnison, Colorado. Amounts of As, Mo, U removal by sphagnum peat, calcium carbonate, and hydrated lime at 5.0, 2.5, and 2.5 wt%, respectively, were typically above 97%. This resulted in contaminant decreases up to four orders of magnitude. Nitrate removal ranged between 55 and 80%. Highest contaminant removal was achieved by sphagnum peat along at pH 3.18. Addition of 2.5 wt% calcium carbonate to the sphagnum peat-tailings system resulted in formation of solube uranyl carbonate complexes, which decreased the amount of U(VI) fixed onto sphagnum peat by a factor of 2. Addition of 2.5 wt% hydrated lime to the acidic tailings increased Mo concentrations by a factor of 2 under moderately alkaline conditions (pH 12). During neutralization of tailings-pore water, precipitation of ferric oxyhydroxides may provide additional removal of As, Mo, and U(VI) from solution through adsorption and coprecipitation processes.

	•							
	Ĺ	10z	At 2 pH	4-6			•	
			UO <sub>2</sub>	— ( 0 отрlex	WAR H	umic Ac	ð	
ELEMENT FROM DIF AND MAL(	<b>FEREN</b>	t Aqu	FION OI ATIC E	F AQU NVIR(	ATIC H Onmen	IUMIC	SUBSTA	NCES J
SAMPLE	- C	Η	0	N	Р	S	ASH	
GROUND	WATER	(MEAI	N OF 5	SAMP	LES)			
FULVIC Humic								wt.
SEAWATEI PAYNE, 19		ERMEI	R AND I	HARVI	EY, 197	74; STU	JERMER	AND
FULVIC HUMIC	50.0 	6.8	36.4	6.4		0.46	3.4	
RIVER WA	TER (M	EAN O	F 15 SA	MPLI	ES)			
FULVIC	51.9	5.0	40.3	1.1	0.2	0.6	1.5	

5

5.0

HUMIC

50.5

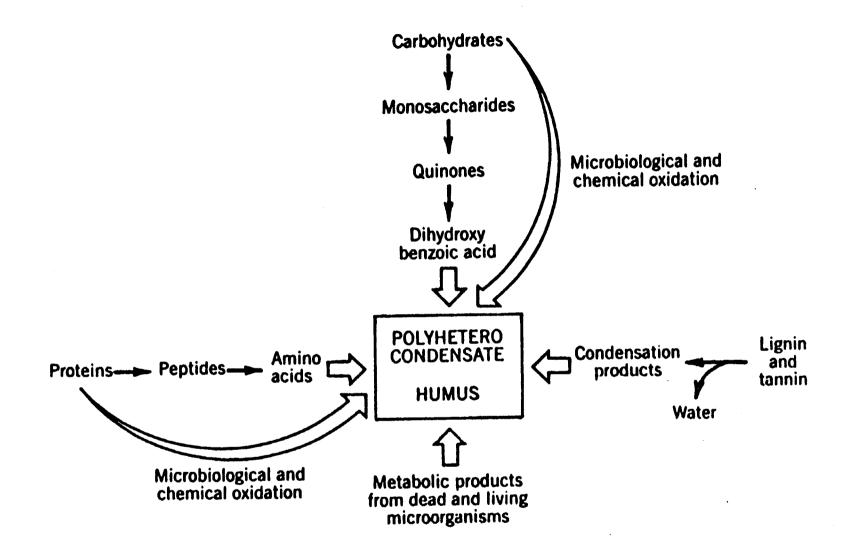
4.7

39.6

This table shows the elemental analysis for typical aquatic humic substances (humic and fulvic acids) from ground water, sea water, and river water.

2.0

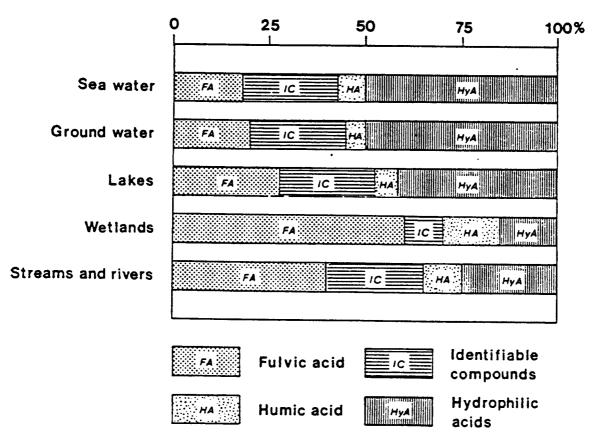
There are number of simple, important ways of characterizing humic substances based on elemental analysis of C, H, O, N, P, S, halogen atoms, ash, and elemental ratios, H/C and C/N. Carbon is the major element in aquatic humic and fulvic acids; it varies from 45 to 55 percent, with an average of 52% by weight.



This schematic diagram shows the generation and origin of humic substances (humic and fulvic acids). Phenolic polymers are formed by intramolecular condensation of ligins and tannins (a complex organic molecule derived from bark and fruit of many plants) derived from plants. These reactants then combine with the metabolites of living and deceased microorganisms to yield an amorphous polyhetero condensate product called humic substances. Other sources of humic substances include microorganisms and petroleum residues.

11-30

R+-.-



% of DOC

Distribution of humic substances in natural waters(Thurman, 1985)

This figure shows the distribution of humic substances in natural waters, where fulvic acid is approximately 20%; humic acid approximately 5-8%; identifiable compounds approximately 25%; and hydrophilic acids "water liking" approximately 50%.

#### FUNCTIONAL GROUPS OF DOC

The atom or group of atoms that defines the structure of a particular family of organic compounds and determines their properties is called the functional group.

- Acidic functional groups -- donates a proton in water
- Neutral functional groups -- neither donates nor accepts a proton in water
- Basic functional groups -- accepts a proton in water

## IMPORTANT FUNCTIONAL GROUPS OF DISSOLVED ORGANIC CARBON

Functional group	Structure	Where found
Carboxylic acid Enolic hydrogen Phenolic OH Quinone	Acidic Groups R-CO₂H R-CH=CH-OH Ar-OH Ar=O	90% of all dissolved organic carbon Aquatic humus Aquatic humus, phenols Aquatic humus, quinones
Alcoholic OH Ether Ketone Aldehyde Ester, lactone	Neutral Groups $R-CH_2OH$ $R-CH_2-O-CH_2-R$ R-C=O(-R) R-C=O(-H) R-C=O(-OR)	Aquatic humus, sugars Aquatic humus Aquatic humus, vola- tiles, keto-acids sugars Aquatic humus, tannins, hydroxy acids
m		

These functional groups contain oxygen and form hydrogen bonds with water, and the solubility of DOC increases where the OH (hydroxyl) group imparts greatest solubility.

Amine Amide Basic Groups R-CH<sub>2</sub>-NH<sub>2</sub>

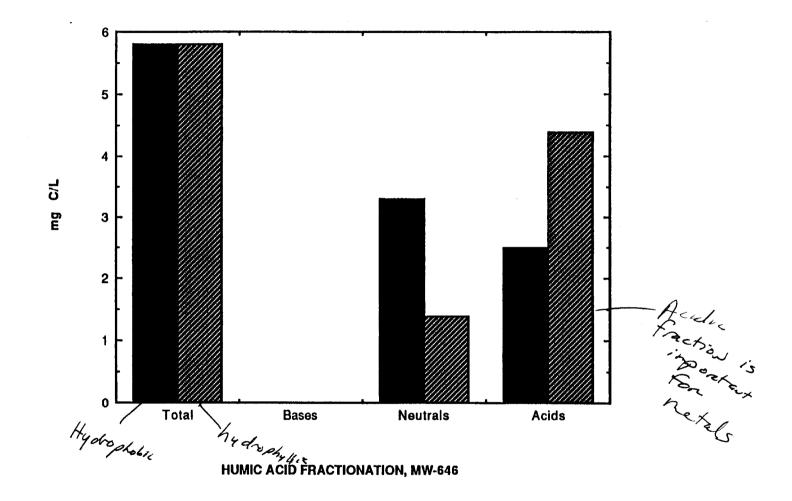
R-C=O(-NH-R)

Amino acids Peptides

The basic functional groups form hydrogen bonds with water, which increases the solubility of organic matter. These groups accept protons and can be sorbed by sediment, especially onto silica surfaces.

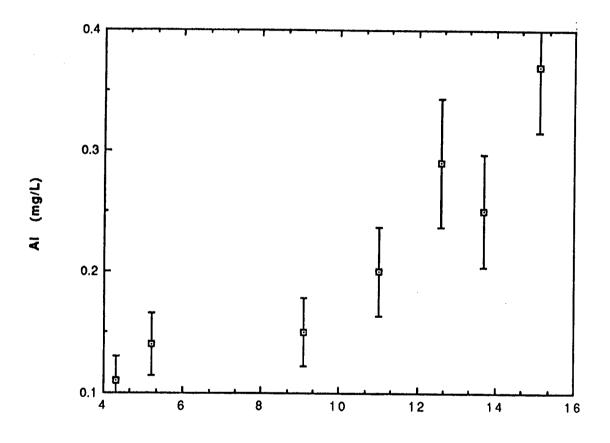
Where **R** is an aliphatic backbone, and **Ar** is an aromatic ring.

SOURCE: Thurman, 1985



Results of fractionation of DOC of Browns Park Formation, Maybell, Colorado (reported as mg/L). Dr. E. W. D. Huffman, analyst.

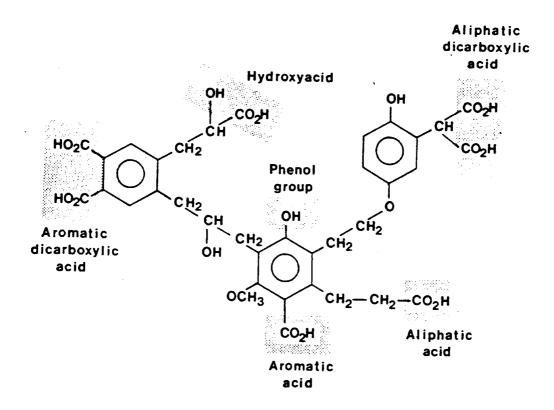
11-34

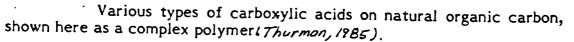


DOC (mg C/L)

Dissolved Al versus DOC, Maybell, Colorado. Monitor wells selected for this plot include 644, 646, 648, 663, 668, 690, and 691.

11-35



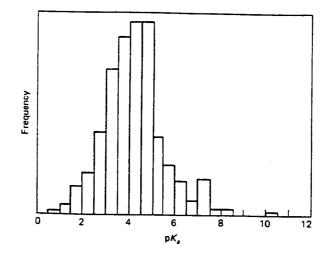


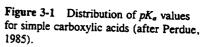
This figure shows some of the various carboxylic acid functional groups found in humic substances. They include aromatic acids, aliphatic acids, and different aromatic and aliphatic dicarboxylic acids. Carboxylic acid group is an important functional group because it contributes to aqueous solubility and acidity of humic substances.

### **TABLE 3-1**DISSOCIATION CONSTANTSFOR SOME ORGANIC ACIDS

1

		pK.
Acetic	СН₃СООН	4.9
Lactic	СН3—СН—СООН   ОН	3.1
Oxalic	соон   Соон	1.2, 4.2
Benzoic	СООН	4.2
Salicylic	СООН	2.9
o-Phthalic	Соон	2.9, 5.5





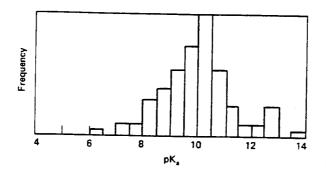


Figure 3-2 Distribution of  $pK_a$  values for phenolic groups (after Perdue, 1985).

11-37

### **EXAMPLE OF pKa CALCULATION**

THE MOST IMPORTANT FUNCTIONAL GROUP IN NATURAL DOC IS THE CARBOXYLIC ACID GROUP.

 $RCOOH = H^+ + RCOO^-$ 

 $Ka = \underline{aH+aRCOO} = \log_{10}K = -4.8$ aRCOOH

 $pKa = -log_{10}Ka;$   $pH = -log_{10}aH+$ 

#### VARIOUS pKa<sup>S</sup> OF ORGANIC ACIDS

ORGANIC ACID	ANIC ACID Pka	
Phenol	Weak	9.9
Acetic Acid	Strong	4.9
Benzoic Acid	Strong	4.2
Carboxylic Acid	Strong	4.8

1

Source: Thurman, 1985

Between pH6-8 organic acids exist as ions and make up 90% of organic carbon in water. An example of the dissociation of an acidic organic functional group such as carboxylic acid is shown below, and the acid dissociation constant, ka, is a measure of dissociation.

 $R - COOH = R - COO^{-} + H^{+}$ 

 $Ka = \frac{(R - COO^{-}) (H^{+})}{(R - COO^{+})}$ Log Ka = -4.8, pH = 4.8

The negative log of Ka is the pka of an acid. Different pka's are listed above. Because water generally has a pH of 7 (neutral), organic acids with a pka below pH7 are ionic, and those above are nonionic. Thus, phenols are not ionized. Natural organic matter ranges in acidity from a pka of 1.2 to 13.

### **CLASS EXERCISE**

DISSOCIATION CONSTANTS FOR SOME ORGANIC ACIDS ARE GIVEN BELOW. CALCULATE pH ASSOCIATED WITH pKa.

ORGANIC ACID	рКа	pH
ACETIC	4.9	4.9
LACTIC	3.1	3,1
OXALIC	1.2, 4.2	1.2, 4.2
BENZOIC	4.2	4.2
SALICYCLIC	2.9	2,9
o-PHTHALIC	2.9, 5.5	29, 5.5

### AT pH 7, WHAT IONIC FORM DO THESE ORGANIC ACIDS OCCUR AS?

#### IONIC ORGANIC ACIDS

- The solubility of the organic acid is much greater in the dissociated form than in the associated form.
- The increased solubility is a major control on solubilizing DOC in water
- Organic acids contribute hydrogen ions to weathering processes in the aquatic environment
- The ionic groups are sites for metal complexation

At pH of 7 as in most g.w.1 the organic acids will disassociated If DOC is It WOC is scenter than ImplL , then organic usids man affect Solubility of metals, radioactive

### **CLASS EXERCISE**

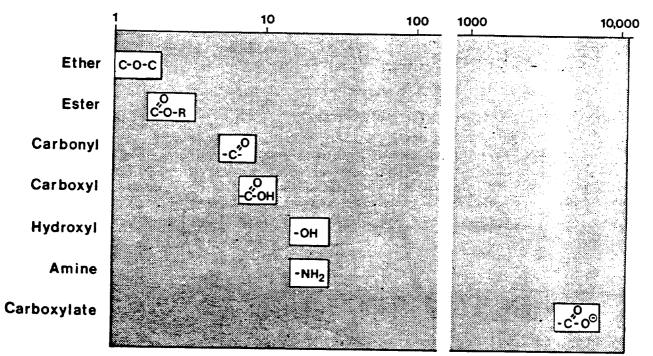
SUPPOSE A RIVER WATER CONTAINS NATURALLY OCCURRING ORGANIC ACIDS (DOC) AS FOLLOWS

SPECIES	MG/L	MEQ/L
СООН	270	

 $\frac{\text{PHENOLIC}}{\text{NOTE: MW COOH} = 45, \text{PHENOLIC} = 94}$ 

HOW MANY MILLEQUIVALENTS (MEQ) PER LITER OF ORGANIC ANIONS WOULD BE PRESENT? [MEQ/L = MG/L X (VALENCE/MW)]

IF THE ANIONS WERE BALANCED BY Ca<sup>2+</sup>, HOW MANY MG/L CALCIUM WOULD THIS REPRESENT? (AW Ca<sup>2+</sup> = 40.08)



#### Relative Aqueous Solubility

Relative aqueous solubility of different functional groups (Thurman, 1985).

This figure shows the relative aqueous solubility of different functional groups present in humic substances. For example, the hydroxyl group (-OH) gives more aqueous solubility to an organic compound than the carboxyl group (-COOH). Solubility probably controls the types of functional groups on the natural organic matter in water, where the more water-soluble organic compounds (those containing many carboxylic or hydroxyl functional group) are dissolved.

#### CASE HISTORY

The weathering of a late Tertiary volcanic ash: importance of organic solutes. By R.C. Antweiler and J.I. Drever.

#### INTRODUCTION

This study is based on the work of Antweiler and Drever (1983) which concerns the geochemical interactions of humic substances and the weathering of a late Tertiary volcanic ash near Jackson, Wyoming (Figure 1). Lysimeters were installed in the volcanic ash and pore fluid samples were obtained (Figure 2). Sodium, potassium, calcium, magnesium, silica, chloride, nitrate, sulfate, aluminum, iron, phosphate, oxalate, formate, acetate, and DOC were analyzed from the lysimeter samples.

#### RESULTS

The pH values of the samples are variable and generally range between 4.3 and 6.5 with an average of 5.2. The low pH values are due to the presence of organic acids (Figure 3), indicated by the high values of DOC. The DOC values ranged between 20 and 260 mg C/L. Based on charge balance calculations, Antweiler and Drever (1983) estimated that organic anions contributed at least 50% of the negative charge in solution. The pH shows a strong negative correlation with DOC (Figure 6). This suggests that the organic acids control pH.

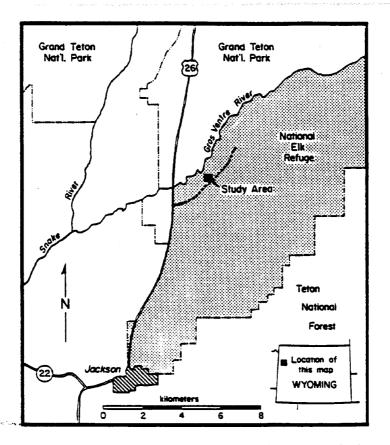
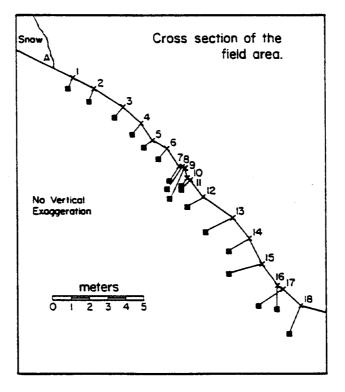
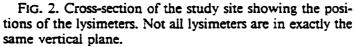


FIG. 1. Location of the study area. Stippled area is the National Elk Refuge.





11-45

Samples were separated into acid, base, and neutral fractions for DOC analyses (Table 1). The hydrophilic fraction consists of small organic molecules and some humic and fulvic acids with high molar solubility, whereas the hydrophobic fraction consists entirely of humic substances.

Concentrations of dissolved silica, calcium, magnesium, potassium, sodium, aluminum and iron follow the same pattern as the concentration of DOC (Figures 4, 5, and 8). Aluminum concentrations range up to 5 mg/l. This concentration of aluminum is several orders of magnitude higher than the concentration predicted by the solubility of amorphous (Al(OH)<sub>3</sub> at pH 4.5) in the absence of complexing ligands. Antweiler and Drever (1983) attribute this to complexation by dissolved organic matter, namely humic and fulvic acids. These acids comprise 80-90% of the total DOC in the ash water.

Table 1. Results of fractionation of DOC (reported as % of total DOC)

	DCC (mg/l)	Total	Hydro Base	phobic Neutral	Acid	Total	Hydro Base	Ophilic Neutral	Acid	Hole (day)
	152	27	0	3	24	72	3	5	64	6 (5)
	18	25	1	10	14	74	11	8	8	9(8)
oring -	<b>9</b> 196	41	1.	2	38	60	6	0	54	11 (16)
	<b>≯</b> <sup>89</sup>	50	1	10	39	51	5	3	43	11 (101)

SOURCE: Antweiler and Drever (1983)

Lot 70

Org. EDOC --=== Hydrophilic Hydrophobic increased of time

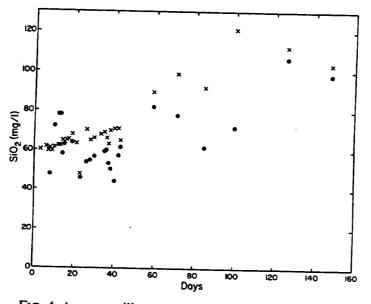


FIG. 4. Aqueous silica concentration as a function of time for hole 5 ( $\times$ ) and hole 11 ( $\bullet$ ).

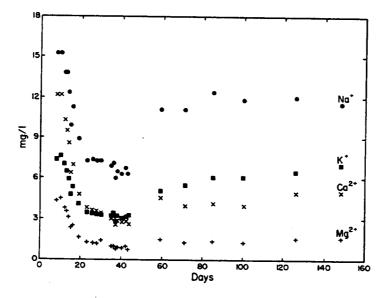
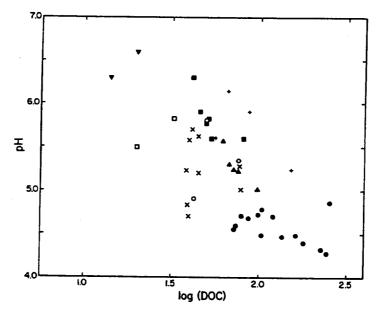
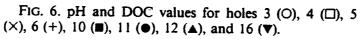


FIG. 5. Calcium ( $\times$ ), magnesium (+), sodium ( $\bigcirc$ ), and potassium ( $\square$ ) concentrations as a function of time for hole 11.





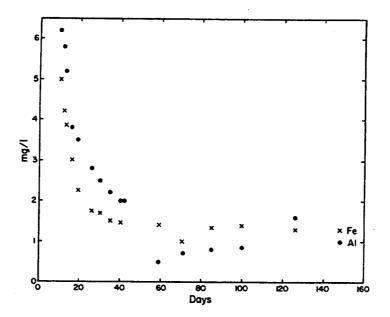


FIG. 8. Dissolved aluminum ( $\bullet$ ) and iron ( $\times$ ) concentrations as a function of time for hole 11.

#### SUMMARY

Organic material provides the major control on the chemistry of near-surface waters in the volcanic ash by complexation of aluminum and iron and by lowering the pH. Biological activity is probably important for the mass transfer of the aqueous species (highest solute concentrations occur in the spring).

#### REFERENCE

Antweiler, R.C. and Drever, I.I., 1983. The weathering of a late Tertiary volcanic ash: importance of organic solutes: Geochemica et Cosmochimica Acta, Vol. 47, pp. 623-629.

REFERENCES FOR ORGANIC GEOCHEMISTRY OF GROUND WATER

Stevenson, F.J., 1982. <u>Humus Chemistry: Genesis, Composition, Reactions</u>. John Wiley and Sons, New York, 443 pages.

Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martinus Nijhoff/W. Junk Publishers, Dordrecht (Netherlands), 497 pages.

### SOLUTION TO CLASS EXERCISE

for organic acids form from bacteria fermenting organic matter

### DISSOCIATION CONSTANTS FOR SOME ORGANIC ACIDS ARE GIVEN BELOW. CALCULATE pH ASSOCIATED WITH pKa.

ORGANIC ACID	<u>pKa</u>	рН
ACETIC	4.9	4.9
LACTIC	3.1	3.1
OXALIC	1.2, 4.2	1.2, 4.2
BENZOIC	4.2	4.2
SALICYCLIC	2.9	2.9
o-PHTHALIC	2.9, 5.5	2.9, 5.5

#### AT pH 7, WHAT IONIC FORM DO THESE ORGANIC ACIDS OCCUR AS?

**ANSWER: ANIONIC** 

## SUMMARY

- Total organic carbon consists of dissolved organic carbon (<0.45 micron) and particulate organic carbon (>0.45 micron)
- The majority of DOC present in ground water are polymeric organic acids called humic substances (40–60%)
- Humic acids are insoluble in dilute acid
- Fulvic acids are soluble in dilute acid
- Humic substances contain several functional groups including carboxylic acid, phenolic OH, alcoholic OH, Ketone, and ether
- Decomposition of organic matter yields CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup>
- Organic solutes are geochemically important for complexation reactions of many transition metals (Fe and A1) and contribute to the weathering of rocks and minerals

## SOLUTION TO CLASS EXERCISE

SUPPOSE A RIVER WATER CONTAINS NATURALLY OCCURRING ORGANIC ACIDS (DOC) AS FOLLOWS

SPECIES	MG/L	MEQ/L		
СООН	270	6		
PHENOLIC	188	2		
NOTE: MW COOH = 45, PHENOLIC = 94				

HOW MANY MILLEQUIVALENTS PER LITER OF ORGANIC ANIONS WOULD BE PRESENT? [MEQ/L = MG/L X (VALENCE/MW)]

EIGHT MEQ OF ORGANIC ACIDS ARE PRESENT.

IF THE ANIONS WERE BALANCED BY Ca<sup>2+</sup>, HOW MANY MG/L CALCIUM WOULD THIS REPRESENT? (AW Ca<sup>2+</sup> = 40.08)

MG/L Ca<sup>2+</sup> =  $\underline{MEQ/L X \text{ ATOMIC WEIGHT}}$ VALENCE MG/L Ca<sup>2+</sup> =  $\underline{8 X 40.08}$ 2 MG/L Ca<sup>2+</sup> = 160 Section 12

C

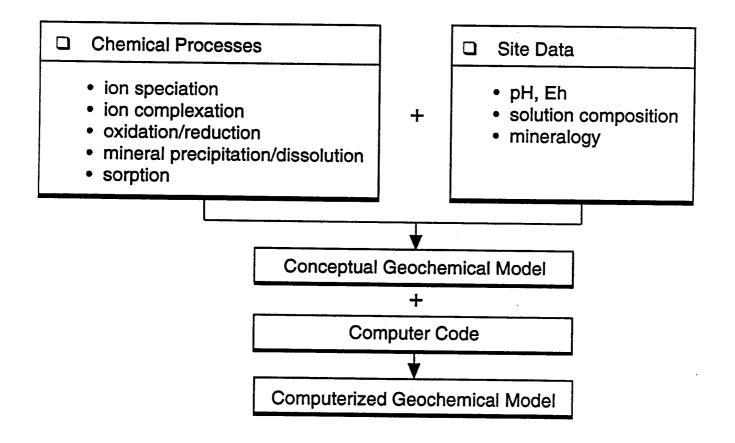
# Geochemical Reaction Modeling

Lecture by: William Deutsch Woodward-Clyde Consultants

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## **Geochemical Reaction Modeling**



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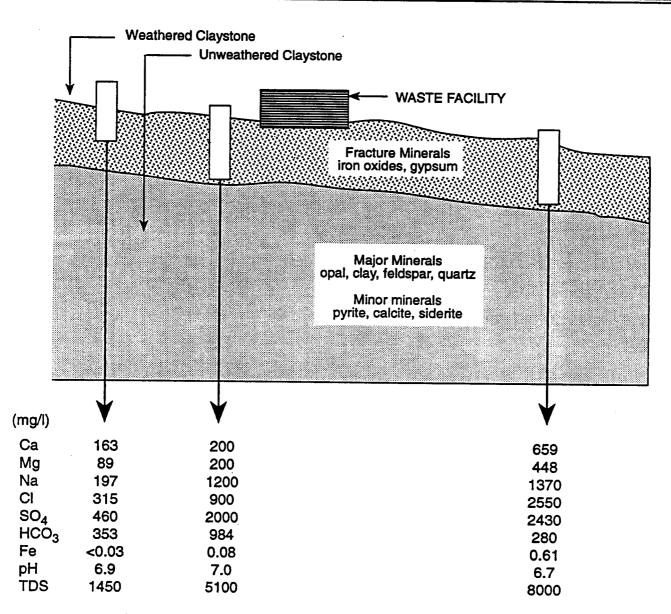
### **Geochemical Reaction Modeling**

### **Topics**

- Data requirements
- Conceptual model development
- Computer modeling codes
  - Mass balance approach
  - Equilibrium approach
- Limitations of modeling

Marine claystone Calif. coast

## Site Geochemistry



#### Reactive Solid Phases

Unweathered Zone: pyrite, calcite, siderite, clays

Weathered Zone: gypsum, ferric hydroxide, clays

### Data Requirements Water Chemistry

**Physical Parameters** 

Temperature pH Control speciation Eh Control speciation Alkalinity - Inorganic carbon- field titration Specific Conductivity Total Dissolved Solids Total Suspended Solids Color - tannic acids-brown- car add to alkalinity- forests

Major Cations and Anions

Ca, Mg, Na, K HCO3, CO3, Cl, SO4, NO3

Other Metals and Nonmetals Filtered - Dissolved always measure because other metals sorb to them Fe, Mn, Al, As, Se, Mo NH<sub>4</sub>, Ba, B, Ag, CN, H<sub>2</sub>S, F, PO<sub>4</sub> etc.

## Data Requirements Water Chemistry (continued)

Stable Isotopes	<i>distinguish</i>	d.ff.	water	tupes, t	mixing
D/H, <sup>18</sup> O/ <sup>16</sup> O, <sup>13</sup> C/ <sup>12</sup> C					

#### **Radioactive Isotopes**

<sup>14</sup> C, <sup>36</sup> Cl, <sup>3</sup> H	< measures age of water <50 years if there is tritium-3H
Gases	50,000 "C 4000 36 C1 100,000 + years

Ch4, CO2, O2 € can back calculate CO2 using alkalivity

#### **Organics**

Volatiles, Semi-Volatiles, Humic and Fulvic Acids, Herbicides, Pesticides

## Data Requirements Soil/Rock Mineralogy and Chemistry

- Elemental analysis can be useful but total is not that inp.
   but total is not that inp.
   really want to know reactive minerals
- Mineralogy of major minerals and clays
- pH
- Total clay fraction
- Cation exchange capacity
- Exchangeable cations

Manual by Black, Methods Manual by Black, Methods That discusses book That big snew book Soil/Rock Data (continued) Same thing due to carbowate niveral said Neutralizing due to carbowate Carbonate mineral content Acid neutralizing capacity Reactive Fe and Mn oxides and hydroxides - affect movement of Reactive Fe and Mn oxides and hydroxides - affect movement of Critrate-bicarbounte-dithionite-CBD method better method Ammonium Oxylate in the Dark- ADD Method Organic matter content Kd = For Koc (need for to calculate Retardation) Pyrite content

- Gypsum content
- Petrographic analysis
  - Mineral identification
  - Mineral distribution fractures?
  - Proportion of matrix material vs. interstitial grains

## Data Requirements Thermodynamic Data

These have already These have already been conculted and been computer code are in computer

Equilibrium Constants and Enthalpies for all Important Reactions

- Speciation  $H_2CO_3 = HCO_3^- + H^+$
- Complexation  $Ca^{2+} + HCO_3^{-} = CaHCO_3^{+}$
- Solubility  $Ca^{2+} + CO_3^{2-} = CaCO_3$  (calcite)
- Adsorption NaX +  $NH_4^+ = NH_4X + Na^+$
- Redox  $Fe^{2+} = Fe^{3+} + e^{-}$
- Gas exchange  $CO_2$  (gas) +  $H_2O = H_2CO_3$

## Data Requirements Hydrology

- Hydrostratigraphy
- Flow speed and direction
- Mode of flow matrix vs. fracture
- · Dispersivities -physical process changes concentration along Flow path
- Degree of interaquifer connection can change concentration along flow path

Book- Willard Lindsay- Chemical Equilibria in Soils. discusses 2 dozen elements Very helpful - can direct you to consider in cluding additional elements in your sampling program - by telling You potential complexes that may be important

### **Conceptual Model Development**

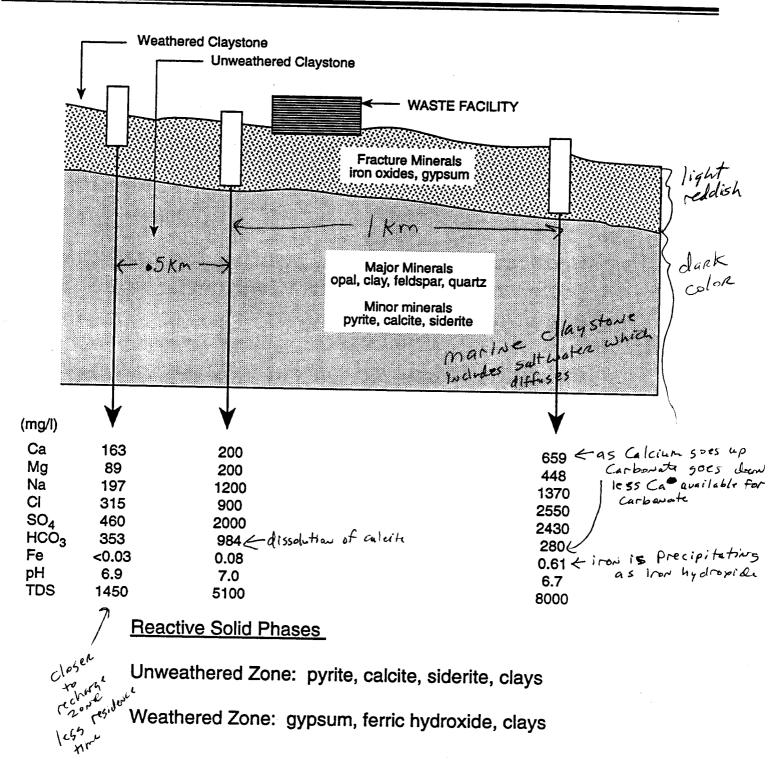
A conceptual chemical model is a mental picture of how a water/rock system interacts to produce the observed water composition and rock mineralogy and chemistry.

Basis of the Conceptual Model:

- Available site data
- Speciation/solubility calculations Sati Index,
- Experimental data on reaction rates and products
- Field experience soils and groundwater literature

Weathering of Pyrite: hydronia Weathering of Pyrite Fessoz V V Pyrite Fessoz FeO2 + O2 = Fe(OH)3t SO2<sup>2+</sup> + H t) Produces Calcium + sulfate evolutually H<sup>+</sup> + Ca(O3 = Ca<sup>2+</sup> + HCO3<sup>-</sup> ) will form 54psam (with water)

## Site Geochemistry



## **Development of Multiple Hypotheses**

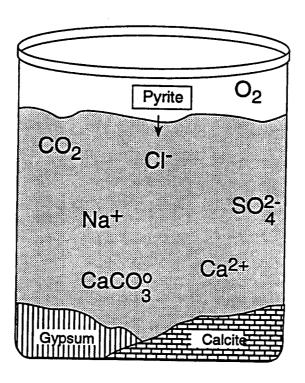
More than one set of chemical reactions may account for the observed changes in chemistry along the flow path. For example:

- Reducing conditions may be caused by the presence of methane, pyrite, hydrogen sulfide gas, or organic matter
- Changes in dissolved carbonate concentration in groundwater will be affected by whether or not the system is open or closed to CO, gas

## **Computer Modeling Codes**

### **Basic Approaches**

- Mass balance
- Equilibrium thermodynamic



12-13

## Mass Balance Approach

BALANCE Code: USGS

Calculates the mass transfer (amount of material entering or leaving the water phase) necessary to account for the observed changes in composition between two solutions.

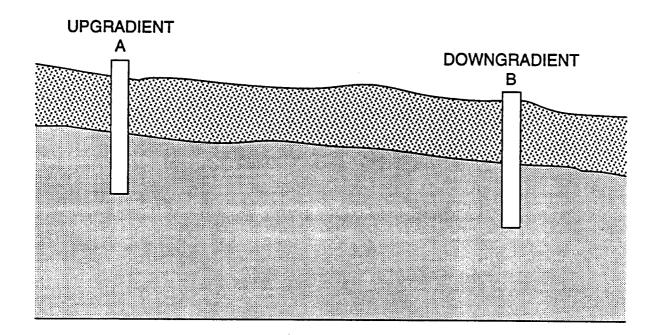
## **BALANCE** Methodology

"BALANCE" derives balanced reactions of the form:

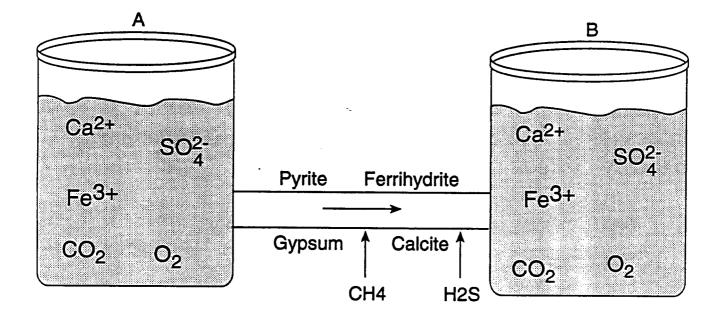
Initial solution (A) + reactant phases =

Final solution (B) + product phases

A chemical reaction model is defined by the selected phases and the calculated amount of each phase necessary to satisfy this equation.



## **Balance Modeling Schematic**



 $\Delta Fe = \alpha_{\text{pyrite}} + \alpha_{\text{ferrihydrite}}$ 

 $\Delta Ca = \alpha_{calcite} + \alpha_{gypsum}$ 

etc.

### **Balance Example Number 1**

Incongruent dissolution of dolomite accompanying dissolution of gypsum in a system closed to  $CO_2$  gas.

	Total Concentration (mmol/kg)		
<u>Element</u>	Water A	Water B	
Calcium	1.118	3.230	
Magnesium	0.950	2.668	
Sulfur	0.0	4.000	
Carbon	4.464	4.294	

Selected Reactive Phases

Calcite:  $CaCO_3$ Dolomite:  $CaMg (CO_3)_2$ Gypsum:  $CaSO_4 \cdot 2H_2O$  $CO_2$  gas

### Mass Balance Equations

1. Change in dissolved mass of calcium =  $\Delta$  Ca

3.230 - 1.118 = 2.112 mmol/kg =

 $1^* \alpha_{\text{calcite}} + 1^* \alpha_{\text{dolomite}} + 1^* \alpha_{\text{gypsum}}$ 

2. Change in dissolved mass of magnesium =  $\Delta$  Mg

2.668 - 0.950 = 1.718 mmol/kg =

 $1^* \alpha_{\text{dolomite}}$ 

3. Change in dissolved mass of sulfur =  $\Delta S$ 

4.000 - 0.0 = 4.000 mmol/kg =

 $1^*\alpha_{gypsum}$ 

4. Change in dissolved mass of carbon =  $\Delta C$ 

4.294 - 4.464 = -0.170 mmol/kg =

 $1^*\alpha_{calcite} + 2^*\alpha_{dolomite} + 1^*\alpha_{CO2}$ 

## Amount of Reactive Phases Transferred In or Out of Solution

 $\alpha_{calcite} = -3.606 \text{ mmol/kg}$ 

 $\alpha_{dolomite} = 1.718$ 

 $\alpha_{gypsum} = 4.000$ 

 $\alpha_{\rm CO2\,gas} = 0$ 

**Balanced Reaction** 

Initial Solution + 1.718 mmol dolomite +

4 mmol gypsum =

Final Solution + 3.606 mmol calcite

## **General Capabilities of the Balance Code**

- Mass balance on elements
- Mixing end-member waters
- Oxidation-reduction reactions
- Simple isotope balance

## Sources of Error in Mass Balance Modeling

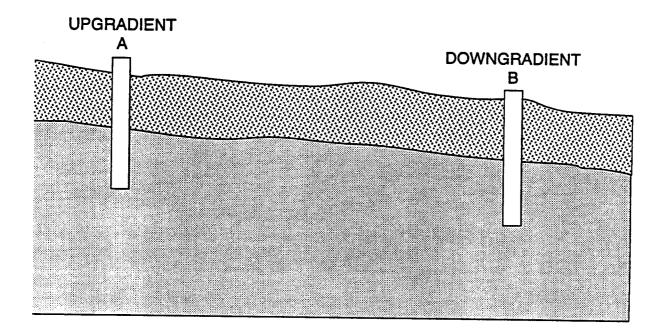
- Incorrect flow path chosen
- An important process has been neglected. For example, mixing of waters
- Non-steady state conditions exist for the time interval modeled
- Selected phases may not be reactive or in equilibrium with the groundwater

## Equilbrium Thermodynamic Modeling

- Most commonly used chemical reaction modeling method
- The majority of the computer codes have been written for this application
- By using mass balance and mass action relationships these codes:
  - determine the state of the solution with regard to ion speciation/complexation and
  - the likelihood that minerals will dissolve or precipitate from the solution Saturation Index
- These modeling codes can be used to:
  - characterize existing geochemical conditions and
  - make predictions on the effect of changing conditions on solution and mineral chemistry

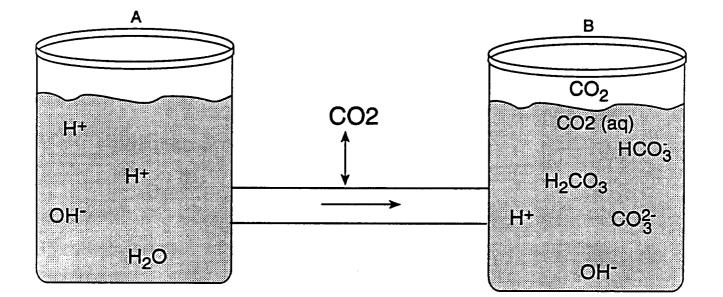
## **Equilibrium Modeling**

#### Solution A + reactants = Predicted solution B + products



Model validated by comparing results with solution composition at point B.

### CO<sub>2</sub> Gas Equilibrium with Water



can compare the end result calculated by computer code with real results observed IN the field

### **Basic Equations**

Mass Balance

$$T_{CO_3} = m_{H_2CO_3} + m_{HCO_2} + m_{CO_3}^2$$

where,

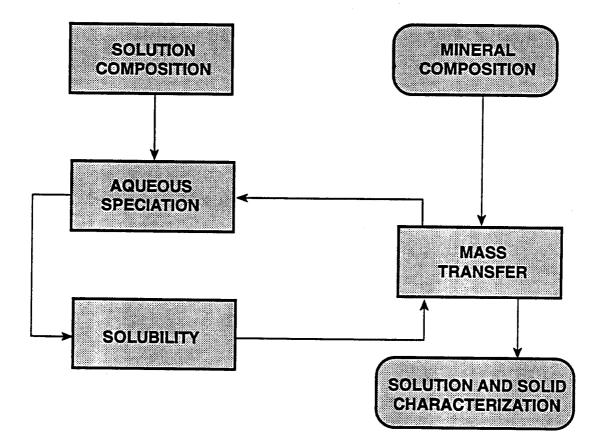
 $T_{CO_3^2}$  = measured concentration  $m_{CO_3^2}$  = concentration of uncomplexed CO  $_3^2$   $m_{HCO_3^2}$  = concentration of bicarbonate etc.

Mass Action

 $CO_{2} + H_{2}O = H_{2}CO_{3} K_{1} = 10^{-1.5}$   $H_{2}CO_{3} = HCO_{3} + H^{+} K_{2} = 10^{-6.4}$   $HCO_{3} = CO_{3}^{2-} + H^{+} K_{3} = 10^{-10.3}$ 

Simultaneous solution of the set of equations to determine equilibrium solution composition.

## **Equilibrium Model Components**



Only Inorganic Models

## **Equilibrium Modeling Code Capabilities**

- 1

		EPA provides free - bulletin board		
		$\int$	us G-S V	
CAPABILITIES	WATEQ	MINTEQ	PHREEQE	
Ion Speciation	•	•	•	
Temperature Correction	•	•	•	
Redox Equilibrium		•	•	
Gas Phase Equilibrium		•	•	
Determines Saturation Indices	•	•	•	
Database	•	••	•	
Mass Transfer		•	•	
Ion Exchange			•	
Adsorption/Desorption		•		
Titration		•	•	
Mixing			•	
Reaction Path	· · · ·			
		1	L OH	

PH, REPOX Equil

4 day class NGWA Classteach codes Pat Longmine + Bill Deutch

# **Limitations of Geochemical Modeling**

- 1. Field and Lab Data
  - A. Water chemistry and physical parameters
  - B. Soil chemistry and mineralogy
- II. Thermodynamic Data Aqueous Species, Gases and Solids
  - A. Accuracy and completeness of the data base
  - B. Modification methods e.g., temperature extrapolations, calculation of activity coefficients.

# **Modeling Limitations (continued)**

If contami is moving very fast thro aquifer equilibing not occur

## III. Equilibrium vs. Kinetic Control on Chemistry

- IV. Chemical Theories Upon Which the Code is Based Work for 10-20,00 mg/L - Fresh water, do not work for brives
  - A. Ion association vs. ion interaction theory Here are codes for brive (PhREQU

## V. Capability of Code to Model all Important Processes

- A. Ion complexation
- B. Dissolution/precipitation
- C. Redox changes
- D. Gas phase equilibria
- E. Adsorption/desorption
- F. Solid solution
- G. etc.

# Modeling Summary

- Modeling can help define the data collection requirements for specific sites
- Site chemistry data can be understood with the help of chemical reaction modeling
- Mass balance modeling can be used to determine the validity of conceptual chemical models
- Equilibrium thermodynamic modeling can be used to predict the impact of future conditions on water and rock chemistry

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## A REVIEW OF GEOCHEMICAL COMPUTER MODELS FOR EQUILIBRIUM CALCULATIONS WITH APPLICATIONS IN NATURAL AQUEOUS SYSTEMS

by

Kevin Ault

Student Research Assistant

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October 1982

International Ground Water Modeling Center Holcomb Research Institute Butler University 4600 Sunset Avenue Indianapolis, Indiana 46208

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### ABSTRACT

To facilitate the use of geochemical models in the analysis of ground water quality problems the current stateof-the-art in the modeling of equilibrium calculations is reviewed. An introduction to the chemical and physical characteristics of the modeling process includes a description of the equilibrium constant approach, which is basic to all discussed models. Corrections for interionic forces and temperature are generally accounted for. Most models also includes redox-reactions.

There are two numerical methods used to solve the equations of equilibrium reactions in the reviewed models: successive approximation and the Newton-Raphson method. Each of these approaches have led to the development of a "family" of models. Other prominent differences between the models are the number of species included, the equation used to calculate the activity coefficients, options include redox reactions, output facilities, error checking capabilities, numerical efficiency and accuracy, programming language and the data base of equilibrium constants used in each model. The chemical characteristics and computer code information of selected models are summarized in tables for quick compari-

The use of geochemical computer models has some limitations related to such aspects as the accuracy of the chemical input data, the assumption that the solution is at equilibrium, and the lack of a database of equilibrium constants for certain environmentally important chemicals as organic ligands and trace metals.

#### FOREWORD

The International Ground Water Modeling Center (IGWMC) was established in 1978 to serve as an information and training center for modeling ground water related problems. From its start the Center has been emphasizing development and efficient use of mathematical models in the management of ground water resources.

In addition to prediction and optimization type models for ground water flow, solute and heat transport and deformation in porous media, the Center is interested in ground water related issues as data handling and hydrochemistry.

In recent years the quality of ground water has become a frequently discussed topic. Its local and regional deterioration have caused numerous environmental problems. To assist related field and laboratory studies, hydraulic and chemical models are suitable analytical tools.

In this report the results of an inventory of chemical equilibrium models are presented to serve as a base for the Center's information activities in hydrochemical modeling.

This project has been carried out in cooperation with Dr. J. Kirsch of Butler University's Chemistry Department.

Paul K.M. van der Heijde Principal Investigator IGWMC

### ACKNOWLEDGEMENTS

The problems presented in this paper require an interdisciplinary approach. Many people have influenced this paper and a few deserve special thanks. Joe Kirsch and Paul van der Heijde helped to develop the interdisciplinary approach of this paper from their respective viewpoints, chemistry and ground water modeling. Both are excellent educators. Dotty Mack, Barb Howes and Jean Cauger searched far and wide for pieces of scientific information relevant to this paper. Vicki Townsend deserves special mention for wading through many drafts of this paper.

#### 1. INTRODUCTION

As there continues to be concern with both the quantity and quality of water resources, there is a need for understanding of the basic natural processes affecting them and developing methods for prediction of the effect of changes on these resources. The chemical and physical behavior of aqueous (with water as the solvent) solutions is characterized adequately enough to allow us to build models of natural systems. Such chemical models involve numerous calculations and large amounts of data and therefore lend themselves to calculation on modern digital computers. This paper presents a brief explanation of the chemistry involved, an inventory of the current state of the art in geochemical computer models and discuss their limitations.

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The creation of such models requires an interdisciplinary approach, drawing on such fields as physical and geochemistry, environmental engineering, numerical analysis and computer programming. The computer models presented have two main thrusts, calculation of species distribution and testing of solubility hypotheses. All models discussed have their own individual emphasis, and their individual characteristics will be discussed. Exemplary uses of these models include: examining the availability of free and reactive ions; determining the potential bioavailability of nutrients or toxic substances (Nordstrom <u>et al</u>. 1979); predicting the chemical changes caused by seawater encroachment in a fresh water aquifer; predicting the solubility of minerals in a given solution (Plummer <u>et al</u>. 1975); examining the effects of the agricultural practices such as irrigation and fertilization on groundwater quality (Truesdall and Jones 1973); and examining the effects of the addition of pollutants, such as organic ligands, to a given system (Ball et al. 1979).

The species distribution problem can be solved in two different ways, the Gibbs free energy approach and the equilibrium constant approach. There are excellent reviews of the differences between the two approaches and other general aspects of chemical computer modeling (Perrin 1977, Legget 1977, Nordstrom <u>et al</u>. 1979, Mercer <u>et al</u>. 1981) and here it will suffice to say that geochemical models reviewed in this report have used the equilibrium constant approach. There are more reliable and available data for the equilibrium constant approach (Nordstrom <u>et al</u>. 1979).

As will be shown later, for every chemical equation a unique equilibrium constant exists. The equilibrium constant is a function of the temperature and the nature of the reaction.

All chemical reactions are also subject to the restraint of mass balance. Roughly mass balance is "chemical bookkeeping" where computed sum of all free and complexed species must equal the given concentrations. Numerically stated, the system of chemical equations given is a set of nonlinear equations. The standard method of solving the problem by equilibrium constant approach is linearized matrix inversion (Nordstrom <u>et al</u>. 1979). A more detailed treatment of the numerical methods involved are given by the individual models and publications by Zeleznik and Gordon (1968), by Van Zeggeren and Storey (1970) and by Mercer <u>et al</u>. (1981).

Before describing the individual models, a more detailed treatment of the interionic forces, temperature correction, and reduction and oxidation processes is needed.

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### 2. CHEMICAL EQUILIBRIUM

### 2.1 General

For a reaction at equilibrium (ignoring charges for simplicity):

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$$z\vec{z} \neq x\vec{X} + y\vec{Y} \tag{1}$$

where

x, y, z are stoichmetric coefficients and X, Y,  $\dot{Z}$  are species reacting

. . **.** . **. . .** 

there exists a constant, K, such that:

$$K = \frac{[X]^{X} [Y]^{Y}}{[Z]^{Z}}$$
(2)

where

[i] = molar concentration, moles of solute per  $\pounds$  of solution, of the ith ion at equilibrium (where i = X, Y or  $\Xi$ ).

. .

Equilibrium constants are determined by measurement of equilibrium concentrations and calculated using equation 2. For example, the K value for the reaction

$$HF \neq H^{+} + F^{-}$$

at 25° C and in aqueous solution is  $3.53 \times 10^{-4}$ . For the reaction

at 25°C and in aqueous solution the K value is  $4.30 \times 10^{-7}$ .

### 2.2 Corrections for Interionic Forces

Because it ignores interionic forces, Equation 2 only holds true at low concentrations. Correcting for interionic forces, Equation 2 becomes

$$K = \frac{(a_{\chi})^{\chi} (a_{\gamma})^{y}}{(a_{\chi})^{z}}$$
(3)

(4)

where  $a_i = the$  activity of the ith ion (where i = X, Y, Z)

Activity of the ith ion can be defined as

where

 $\gamma_i$  = activity coefficient of the ith ion

 $m_i = molality$ , or mole concentration, of the ith ion. Molality can be defined as moles of solute per kg of solvent.

The activity coefficient ( $\gamma$ ) approaches unity (1) at low concentrations.

Individual activity coefficients can be calculated from the extended Debye-Hückel equation (Robinson and Stokes 1959, Lewis and Randall 1961)

$$\log \gamma_{i} = \frac{-A z_{i}^{2} \sqrt{I}}{1 + Ba \sqrt{I}} + bI$$
 (5)

where

A and B = Debye-Hückel parameters dependent on dielectric constant, the absolute temperature and the density of solvent (i.e., water)  $z_i = charge of ith ion$ 

a = "the distance of closest approach", i.e., hydrated ion size b = empirical parameter I = ionic strength

By convention, ionic strength can be calculated from the equation

$$I = \frac{1}{2} \sum_{i} m_{i} z_{i}^{2}$$
(6)

The extended Debye-Hückel equation is generally accurate for ionic strengths less than .1 molal. For greater ionic strengths (less than .5 molal), the Davies equation is more accurate (Stumm and Werner 1970). Equation 7 is the version of the Davies equation used by Plummer <u>et al</u>. (1976).

$$\log \gamma_{i} = \frac{-A z_{i}^{2} \sqrt{I}}{1 + \sqrt{I}} - 0.3I$$
(7)

As a reference, the ionic strength of sea water has been calculated at approximately .67 molal (Nordstrom <u>et al</u>. 1979).

### 2.3 <u>Corrections for Temperature</u>

The equilibrium constant, K, is dependent on the temperature and nature of the reaction. Temperature correction of K values can be made by the Van't Hoff's equation.

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(8)

where

∆H°	=	standard change in enthalpy of the reaction
R	Ξ	ideal gas constant
Т	=	absolute temperature (°K)
۵S°	=	standard change in entropy of the reaction

Since ln K versus  $\frac{1}{T}$  is linear, it can be shown

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
(9)

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where

$\nabla H_0 =$	average change in enthalpy over $T_1$ to $T_2$
K <sub>2</sub> =	equilibrium constant at $T_2$
K <sub>1</sub> =	equilibrium constant at $T_1$

If the K value at 298°K (25°C) and  $\Delta H^{\circ}$  are known, the K at any given temperature can be easily calculated.

## 2.4 Consideration of Reduction and Oxidation Processes

Reduction and oxidation reactions are reactions which involve the transfer of electrons. The processes of reduction and oxidation always occur together known as a redox reaction. The following example was taken from Freeze and Cherry (1979, p. 119). It involves the oxidation of Fe++ to Fe+++ by free oxygen (e- represents an electron).

Reduction half reaction	${}^{1}_{2}0_{2} + 2\text{H}^{+} + 2\text{e}^{-} = \text{H}_{2}0$
Oxidation half reaction	$2Fe^{++} = 2Fe^{+++} + 2e^{-}$
Redox reaction	$\frac{1}{2}O_2 + 2Fe^{++} + 2H^+ = 2Fe^{+++} + H_2O$

Although these reactions always occur as redox reactions, not as half reactions, it is useful to define a relative electron activity. This quantity, pE, is defined as

$$pE = -\log \left[e^{-1}\right] \tag{10}$$

and corresponds to the definition of pH

$$pH = -\log [H^+]$$
 (11)

which assumes that the hydrogen ion activity  $(\gamma H^{+})$  equals one.

For the reduction half-reaction

$$\frac{1}{2}O_2 + 2H^+ + 2e^- + H_2O$$
 (12)

we can define an equilibrium constant (given that the activity coefficients are unity, the concentration of  $H_20$  in  $H_20$  is 1, and the concentration of  $0_2$  is directly in proportion to the partial pressure of oxygen,  $P_{0_2}$ )

$$K = \frac{1}{P_{o_2}!_2 [H^+]^2 [e^-]^2} = 10^{41.55}$$
(13)

Taking the square root of and rearranging equation 13 gives

$$1 = 10^{20.78} P_{0_2}^{\frac{1}{4}} [H^+] [e^-]$$
 (14)

Taking the negative log of equation 14 and solving for pE results in

$$pE = 20.78 + \frac{1}{2} \log P_{0_2} - pH$$
(15)

Equation 15 gives us a relative state of redox potential for a solution using two important parameters,  $P_{o_n}$  and pH.

In several of the models, the redox term Eh is also used, commonly referred to as the redox potential. Eh can be defined as the energy gained in the transfer 1 mole of electrons from an oxidant to  $H_2$ . The h in Eh indicates that the potential is measured against a standard hydrogen electrode and E signifies electromotive force (Freeze and Cherry 1979). Eh can be related to pE by

$$pE = \frac{nF}{2.3RT} Eh$$
(16)

where

n = Moles of electrons in the half reaction

F = Faraday's constant (9.65 x 10<sup>4</sup> coulombs per mole of electrons)

It should be noted that Eh was a convention used mainly before 1970 (Freeze and Cherry 1979) and is quantitatively related only to the behavior of iron species (Barnes and Clarke 1969).

### 2.5 Interface of Computers and Chemistry in Natural Systems

All solutions, however complex, will obey LeChâtelier's principle: "If a system at equilibrium is altered, the system will shift so as to minimize the effect of the change." Examples of alterations that can occur are a change of concentration of the reactants in solution, a change in temperature, or addition or subtraction of reactants from the solution.

To compute the new equilibrium when a large number of equations is involved, is complex. Such a problem is typically suited for computer solving. Computers are designed to handle the numerous tedious computations involved in finding the most stable composition of a defined solution. Each reaction can be represented by a non-linear equation and numerical methods can be used to find most stable composition of the overall system.

Computers are also useful for storage and retrieval of numerous constants used in the chemical reactions, the Van't Hoff equation and the various ionic strength correction equations. The user can be freed from finding constants and concentrate on the required input.

Computers become virtually essential when natural systems with hundreds of constitutents are solved.

### 3. REVIEW OF CURRENT GEOCHEMICAL COMPUTER MODELS

### 3.1 <u>Successive Approximation Based Models</u>

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Current geochemical models can be divided into two families according to the numerical method used to solve the equations of equilibrium reactions.

The first family of geochemical models evolved from the aqueous model for seawater developed by Garrells and Thompson (1962) and uses successive approximation as its numerical method. The geochemical computer model SOLMNEQ was developed by Kharaka and Barnes in 1973 based on this approach. SOLMNEQ requires the input of temperature (°C), pH, Eh and concentrations of 27 major species (see Table 1) in ppm, mg/2, or meg/2 concentration units. Optional input includes the density of the solution and variations of the measured Eh.

The data base for SOLMNEQ consists of K values over a range of temperatures from 0-350°C in increments of 25°C. The data base was generated from reported data, computer programs (using standard entropies, enthalpies, free energies and heat capacities) and extrapolation of K values known at single temperature. SOLMNEQ computes activity coefficients using the extended Debye-Hückel equation (equation 5). The b term is computed as a function of temperature as reported by Helgeson (1969). The distribution of species Fe+++, Cu++, Hg++ and Mn+++ may be computed using equations involving electron transfer. SOLMNEQ also uses the Gibbs free energy difference equation to show states of supersaturation, saturation or undersaturation relative to the solid phase.

SOLMNEQ has been extensively updated since 1973. Updated equilibrium constants and correction for pressure effects on equilibrium constants are included. Subsurface pH can be calculated from surface pH of a given sample. The data base has expanded to include several more organic and inorganic complexes (Kharaka 1982). A published update is forthcoming.

Another early computer model developed from Garrells and Thompson (1962) is WATEQ by Truesdell and Jones (1973). WATEQ requires the input

of temperature, pH, Eh and the concentration of 17 major species (see Table 1) in units of ppm, mq/2, meq/2 or mole/2. Optional input includes density, variations on the Eh measurement, ppm of dissolved oxygen and concentration of certain trace elements (Li, Sr and Ba).

The program corrects for temperature using the Van't Hoff equation. The data base for WATEQ comes from an extensive literature search. Activity coefficients are computed from the extended Debye-Hückel equation with the MacInness assumption for terms a and b (MacInness 1939, Truesdell and Jones 1974). Eh is converted into pE within this program and is used to calculate equilibrium in redox reactions. WATEQ computes degree of saturation by comparing the activity product with the equilibrium constant (see Trusedell and Jones 1974).

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From the original WATEQ program, several "second generation" programs have been developed. WATEQ2 was developed by Ball et al. in 1979. The existing data base was updated using several analytic chemistry computer Ten elements, numerous complexes and some sparingly soluble programs. salts were added to the data base. Additional input includes conductivity, total dissolved solids, dissolved organic carbon and salinity. Organic ligands fulvate and humate are optional and require user inputted equilibrium constants. Activity coefficients can be calculated using either the extended Debye-Hückel equation or the Davies equation (Equations 5 and 7). The option of using pE from dissolved oxygen for redox reactions was dropped and only 12 specific redox reactions were considered. An option to create a data base for program EQPRPLOT (Ball 1979) has been added. EQPRPLOT constructs ratio and scatter plots of dissolved constituents, activity products or activity products/equilibrium constant ratios. Progated standard deviations are computed for a subset of the activity products. Also added to the output is specific conductance.

Many of the changes from WATEQ to WATEQ2 involve the code itself and its error checking ability. Standard deviations have already been mentioned; additional error checking includes a complete rejection of the input if the charge balance is off by more than 30%. WATEQ2 also includes improved documentation and faster, more reliable numerical methods for

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checking mass balance. The structure of the program is taken from WATEQF, which is discussed later in this report. WATEQ2 was further updated by Ball <u>et al</u>. (1980).

WATEQ3 (Ball <u>et al</u>. 1981) adds 7 species of uranium and further documentation to WATEQ2. There are no other notable differences between WATEQ2 and WATEQ3.

WATEQF is a FORTRAN version of WATEQ developed in Pl/I in 1976 by Plummer <u>et al</u>. WATEQF has added 100 aqueous species including 14 species of manganese to the WATEQ data base. The data base can be directly augmented during the input phase by the user. The program also uses either the extended Debye-Hückel equation or the Davies equation to compute the individual activity coefficients. In addition to calculating pE from dissolved oxygen and Eh (as in WATEQ), pE can be set by the dissolved oxygen relation of Sato (1960) and by the SO<sub>4</sub> /S ratio. The output has been modified to allow for several print options, thus limiting the volume of output. WATEQF also includes improved numerical methods for checking mass balance resulting in faster execution times.

WATEQF was updated by Lueck (1978) to include 21 species of uranium and improved documentation and data entry.

WATSPEC (Wigley 1977) is a shorter version of WATEQF, designed for distribution of species problems in routine hydrological analyses.

MIX2 (Plummer <u>et al</u>. 1975) is a different variation of the WATEQ family. MIX2 uses WATEQ data base and develops its model from reaction progress in closed system. Plummer <u>et al</u>. suggest three general classes of problems: 1) mixing of two solutions in fixed volume, 2) titration of one solution into another, 3) addition or subtraction of a net stoichiometric reaction to or from the defined aqueous system. Input includes volume specifications, temperature, specific reactions to be followed, pH, density of solution and concentrations of 6 species (see Table 1) and total carbon in concentration units of meq/ $\ell$ , mg/ $\ell$ , ppm or mole/kg.

## Table 1. Required Chemical Analyses

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MODEL NAME	ANALYSES REQUIRED
SOLMNEQ	$Ca^{++}$ , $Mg^{++}$ , $Na^{+}$ , $K^{+}$ , $C1^{-}$ , $S0_{4}^{}$ , $HC0_{3}^{-}$ , $Si0_{2}^{-}$ , Ag <sup>+</sup> , A1 <sup>+++</sup> , Ba <sup>++</sup> , Cu <sup>++</sup> , Fe <sup>+++</sup> , Fe <sup>+++</sup> , Hg <sup>++</sup> , Li <sup>+</sup> , Mn <sup>+</sup> , Pb <sup>++</sup> , Sr, Zn <sup>++</sup> , As(OH) <sub>4</sub> , PO <sub>4</sub> <sup></sup> , F <sup>-</sup> , H <sub>3</sub> BO <sub>3</sub> , NH <sub>3</sub> , CO <sub>3</sub> <sup></sup> , and NO <sub>3</sub> <sup></sup>
WATEQ	$Ca^{++}$ , $Mg^{++}$ , $Na^{+}$ , $K^{+}$ , $C1^{-}$ , $S0_{4}^{}$ , $HC0_{3}^{-}$ , $Fe^{++}$ , $Fe^{+++}$ , $H_2S$ , $C0_{3}^{}$ , $Si0_2$ , $NH_{4}^{+}$ , $B^{+++}$ , $P0_{4}^{}$ , $A1^{++}$ , $F^{-}$ and $N0_{3}^{}$
MIX2	$Ca^{++}$ , $Mg^{++}$ , $Na^{+}$ , $K^{+}$ , $Cl^{-}$ and $SO_4^{}$

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The input also includes an option to balance the charge of the defined solution using K+ or Cl- (the defined solution must be electrically balanced for the program to work). Activity coefficients are computed from the extended Debye-Hückel equation with given values for parameter b. Output includes volume changes, pH changes and thermodynamic data.

EQ3/6 (Worley 1979) is actually a combination of two geochemical programs. EQ3 is a equilibrium constant/distribution of species program of the type already discussed in this paper. The data base was taken mainly from the work of Hegleson and others (1974, 1978) and covers in 25°C increments and two possible pressures. Input is flexible in this program including such values as pH, several redox parameters, and concentrations of specific ions, either "free" or "total" concentrations. Individual activity coefficients are computed from the extended Debye-Hückel EQ6, the second geochemical program, is a reaction-path model. equation. This is a member of a relatively small family of computer models based on the PATHI (also known as PATHCAL, Hegleson 1970) computer model. A more extensive review of these models and their approach can be found in Mercer <u>et al. (1981).</u>

EQ6 takes the aqueous system defined by EQ3 and checks first for homogenous equilibrium. If there are any supersaturated constituents, they are "precipitated" from the aqueous phase up to their solubility limits. The resulting solids may be retained or discarded from the system. Titration or irreversible reactions are then modeled for either closed to solids or a flow-thru model. The whole system (including 0 and H present in solvent) is subject to mass and charge balance. All these steps will change such parameters as pH, Eh and distribution of species.

Most members of WATEQ family have been developed by the United States Geological Survey, and the geochemical model PHREEQE (Parkhurst <u>et al</u>. 1980) represents the most recent addition to that family. The authors suggest three general uses of PHREEQE: additions of reactants to a solution, mixing of two waters, and titrating one solution with another.

The database for PHREEQE is completely external to the actual program. However, a preliminary database is suggested. Input includes analytical concentrations of defined elements, pE, pH, temperature (in °C) and density.

Individual activity coefficients are calculated by either the Debye-Hückel (without bI term - see equation 5), extended Debye-Hückel, or the Davies equation. If specified, PHREEQE can calculate two parameters as reactions progress: 1) pH as defined by electroneutrality and mass balance 2) pE as determined by species whose valence might change in the defined system. Output also includes concentration of each element, distribution of species, mass transfer of specific mineral in and out of solution and the saturation state of specific minerals. As suggested above, PHREEQE has limited capacity to model reaction paths, similar to EQ 3/6.

#### 3.2 Newton-Raphson Based Models

The second approach to solving the problem of speciation in complex solutions has been developed by Morel and Morgan (1972), resulting in the computer model REDEQL. Based on this initial work, McDuff and Morel (1973) developed REDEQL2. Both models use the Newton-Raphson numerical method to solve the set of nonlinear equations generated by the equilibrium reactions. Since the last update of the REDEQL2 program in 1976, a new generation of programs using the Newton-Raphson method has been developed. These programs differ considerably from REDEQL2.

REDEQL.EPAK is one of these second-generation computer models and it was developed by Ingle <u>et al</u>. (1980). The data base for REDEQL.EPAK comes from a literature survey. The database can also be directly augmented by the user. Input includes concentration of specified ligands and metals, print options, estimated ionic strength, estimated pH, redox reactions considered, partial pressure of  $CO_2$  and  $N_2$ , and pE. Individual activity coefficients are calculated using the Davies equation. For temperature corrections, the Van't Hoff equation is used. There are twenty-four redox reactions that can take place which must be referenced by the user during the input. pH can be calculated by the program. The user can specify whether the solution is electroneutral or not. The program includes an adsorption routine using a surface complexation adsorption model. Only the ligand surfaces are considered. A prototype of this model is described by McDuff and Morgan (1976).

Output includes saturation data, speciation and various user specified options.

Another program based on the work of Morel and Morgan (1972) is the chemical computer model GEOCHEM (Mattigod and Sposito 1979). This model is especially suited to the speciation of trace, or "heavy" metals. The database for GEOCHEM was generated by a literature search and estimation of values for unknown species, based on properties of the unknown species such as electronegativity, radius, charge and coordination number. The individual activity coefficients are calculated from the Davies equation. The program also includes a cation exchange routine for clay materials based on a thermodynamic model.

MINEQL2 (Westhall <u>et al</u>. 1976) is a direct descendant of the original REDEQL models. It includes a "Swiss" adsorption model and an external, user-augmented data base. Several versions of MINEQL2 exist, but no information on any of them was available to include in this report.

#### 3.3 Summary of Computer Model Characteristics

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Chemical characteristics and computer code information of the discussed models are summarized in Tables 2 and 3.

Table 2 lists the computer coding characteristics of the models. A comparison of utilized computer languages, program length and availability of user's manual and documentation is given. References including program listing are cited.

Table 3 compares the number of elements, species, organic chemicals and redox reactions used in each model.

Nanc	SOLINEQ <sup>1</sup>	WATEQ3	WATEQF <sup>3</sup>	WATSPEC <sup>4</sup>	<u>.H1X2</u>	l'HREEQK	EQ 3/6	REDEQL. EPAK	GEOCHEN <sup>4</sup>	111NEQ1.24
tanguage	PL-1	PL-1	FORTHAN	FORTRAN	FORTRAN	FORTRAN-N	FORTRAN	FORTRAN	FORTRAN	FORTRAN
Computer	18H 370	Noneyvel 1 <sup>2</sup> 60/68/80	IUH 370	ILL 1903 IDH 370	1 <b>d</b> h 370	Amiabl 470V/7	CUC 6600 CDC 7700	LINH 370	IWI 360	CUC CYBER 74
Humber of Statements		3,000	<b>1,8</b> 57	423	1,150	2,434	30,000	4,000	3,630	1,500
Documentation & User's Hanual Available?	RØ	yes	yes	H/A	yes ;	yes	included in program	yes	N/A	· N/A
ls Code Avallable?	yes	yes -	yes	W/A	yes	yes	only from NESC	yes .	N/A	W/A
Gode Listing in Reference	Kharaba et <u>al</u> . 1973	Ball <u>et al</u> . 1981	Plümmer et <u>al</u> . 1976	Vigley 1977	Plummer et <u>al</u> . 1975	Parkhurst <u>et</u> <u>al</u> . 1980	N/A	•	N/A	N/A

HODEL CODE INFORMATION - TABLE 2

<sup>1</sup>Host recent version (Kharaka 1982). <sup>2</sup>WATEQ3 has been extensively suited to the Honeywell computer (Ball memo 1981). WATEQ2 is available in versions suitable for both the Honeywell 60/68/80 and the IRH 370 (Ball <u>et al</u>. 1979). <sup>3</sup>Plummer <u>et al</u>. (1976) version. <sup>4</sup>From Nordstrom <u>et al</u>. (1979). <sup>6</sup>Code available through COMNET computer system. Instructions given in Ingle <u>et al</u>. (1980). <sup>6</sup>Estimated.

N/A Indicates no information obtained.

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Name	SOLANEQ	WATEQ3	WATEQF <sup>2</sup>	WATSPEC <sup>3</sup>	<u>H1X2</u>	PIREQE	EQ 3/64	REDEQL.EPAK	<u>CEOCHEH3</u>	HINEUTS3
Elements	24	30	19	16	7 <sup>8</sup>	★	18	42 <sup>8</sup>	44	38
Aqueous Species	181	227	105	69	18 <sup>6</sup>	*	140	' 150 <sup>8</sup>	2000	•
<b>Oigenics</b>	10 -	12	0	Q	0	*	0	348	889	*
Redox Reactions	12	12	8	6	0	*	14	24	20	•
Hinerals	158	309	101	40	61		130	• N/A	185	•
Temperature Range	0-350	6-100	0-100	0-100	N/A	0-100 <sup>6</sup> .	6-300	D-100 <sup>4</sup>	25	25
Pressure Range bars	1-1000	<b>1</b> ·	1	1	N/A	1	1 or 500	1	1	1

HODEL DESCRIPTION - TABLE 3

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1 1982 version (Kharaka 1982).

2 1976 version (Plummer et al. 1976).

3 From Nordstrom et al. (1979).

From Nordstrom et al. (1979) data for EQ3 only. Data for EQ6 not included.

<sup>6</sup> Entimated.

N/A No Information obtained.

\* Variable dependent on data base used.

### 4. LIMITATIONS OF GEOCHEMICAL COMPUTER MODELS

E.A. Jenne (1979) contends that support for pure research in environmental science has weakened in recent years, hence ". . . increasing emphasis has been given to the 'black-box' type of modeling solutions to environmental problems." Therefore, it is important to know the limitations of such models. They provide a means for understanding rather than a method for precise solution of particular, real-world problem. Many of the weakenesses of the discussed geochemical models involve critical problems which must be further researched before they become useful in applications involving pollution chemistry.

First of all, no computer program output is any better than the data it is given. Most geochemical models rely on chemical data which are easily measured by analytical chemistry techniques, however, a few commonly-encountered chemicals are difficult to measure. Another source of inaccuracy lies in the field analysis of samples. Transport to the lab causes changes in partial pressure of gases and temperature as well as the possibility of contamination. Therefore these changes affect such vital parameters as pH and redox potential, and force field analyses.

Secondly, a computer equilibrium model assumes that the described solution is at equilibrium. This is not always true, especially in regard to systems which involve biological activity (Ingle <u>et al</u>. 1978). Microorganisms act as catalysts in many reactions, especially redox reactions, and their action is hard to quantify. A corollary to the problem of equilibrium is that many models ignore chemical kinetics, the rate at which reactions occur. If a reaction is slow in proceeding to equilibrium, the model is not accurate. However in ground water systems movement and transport of water and solutes are generally very slow and assuming equilibrium might be appropriate depending on the involved chemical species (Freeze and Cherry 1979)

Thirdly, equilibrium constants and other data for environmentally important chemicals such as organic (both natural and synthetic) ligands and trace metals do not exist. Jenne (1979) points this out as one of the most important problems facing researchers and modelers in quantifying and characterizing natural aqueous systems.

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Finally, the aqueous models are constructed with certain assumptions. For example, such equations as the Davies, the extended Debye-Hückel and the Van't Hoff equations are derived assuming medium or low ionic strength, low temperature and low pressure. Deviations from these conditions are a source of error. Related to this problem, the models contain numerical methods which can generate errors. Most programs reviewed here contain warning messages when such problems occur.

### CONCLUSION

The models reviewed in this report require the input of a chemical analysis and relative redox potential. Most of the models are flexible in their input, allowing for different degrees of analysis and direct augmentation of the data base. The output includes chemical speciation and, in most cases, saturation data. Output options vary widely among the discussed models. The practical consideration of actual running time is related to the complexity of the program, the efficiency of the computer and the complexity of the problem being solved. A comparision of the output of many of these models can be found in Nordstrom et al. (1979).

The reviewed models are potentially useful tools for the hydrologist, the geochemist or the environmental engineer. Each model represents a synthesis of relevant work in several fields, and are generally enough to model ". . . an aqueous system, whether it be a lake water or the fluid in the human digestive system . . . given the requisite input data as well as adequate reference data" (Jenne 1979). Some potential uses were given in the introduction of this paper.

However, there is a need for further pure and applied research, especially in characterizing such natural system components as organic ligands and trace metals. As research progresses in these and related fields, geochemical computer models will become more useful and accurate tools in environmental problem assessment.

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# A COMPUTER PROGRAM FOR CALCULATING MASS TRANSFER FOR GEOCHEMICAL REACTIONS IN GROUND WATER

By David L. Parkhurst, L. Niel Plummer, and Donald C. Thorstenson

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BALANCE -

1982

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES J. WATT, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

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Requests, at cost, for the card decks listed in Attachment A should be directed to:

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For tape copies, a blank tape should accompany your request.

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BALANCE - A COMPUTER PROGRAM FOR CALCULATING MASS TRANSFER FOR GEOCHEMICAL REACTIONS IN GROUND WATER

David L. Parkhurst, L. Niel Plummer, and Donald C. Thorstenson

### ABSTRACT

BALANCE is a Fortran computer program designed to define and quantify chemical reactions between ground water and minerals. Using (1) the chemical compositions of water samples from two points along a flow path and (2) a set of mineral phases hypothesized to be the reactive constituents in the system, the program calculates the mass transfer (amounts of the phases entering or leaving the aqueous phase) necessary to account for the observed changes in composition between the two water samples. Additional constraints can be included in the problem formulation to account for mixing of two end-member waters, redox reactions, and, in a simplified form, isotopic composition. The computer code and a description of the input necessary to run the program are presented. Three examples typical of groundwater systems are described.

### DESCRIPTION OF THE PROGRAM

BALANCE is a Fortran computer program designed to help define and quantify chemical reactions between ground water and minerals. Data required to run the program are: (1) the chemical compositions of two water samples, generally assumed to represent points along a flow path, and (2) the chemical compositions of a set of minerals, organic substances, or gases, which we will call phases, selected as the reactants or products in the system. Implicit in this treatment is the assumption that only these selected phases participate in the chemical reactions that determine the composition of the final water.

The program calculates the mass transfer (amounts of phases entering or leaving the aqueous phase) necessary to account for the observed changes in composition between the two solutions. The purpose of BALANCE is to derive balanced reactions of the form:

Initial Solution + Reactant Phases + Final Solution + Product Phases (1)

A "reaction model" is defined by the selected phases and the calculated amount of each phase necessary to satisfy equation 1. In general, many reaction models can account for an observed change in water chemistry. BALANCE alone cannot determine if any one, unique set of phases governs the reactions in the ground-water system.

BALANCE models are not constrained by any thermodynamic criteria and may imply reactions that are thermodynamically impossible. Methods for identifying reaction models that do not satisfy thermodynamic or other criteria are presented in Plummer and others (1982). In the the ideal case, all but one reaction model can be eliminated, leaving one unique chemical model consistent with the available data.

The program BALANCE is designed specifically for mineral-water interactions, but essentially BALANCE solves any set of linear equations formulated by the user. The report includes discussions of several processes which can be formulated as linear equations: (1) mass balance on elements, (2) mixing end-member waters, (3) oxidationreduction reactions, and (4) simple isotope balance. Following these discussions, the input necessary to run the program and three examples in a carbonate system are presented.

### Elements

In order to use BALANCE, the chemical composition of two waters must be known. Only the total concentrations of each element are required for models in which redox reactions are not considered. BALANCE accepts two kinds of concentration data as input: (1) the total concentration of each element in the initial and final solutions, or (2) the <u>difference</u> in total concentration for each element between the final and initial solutions (final - initial). If <u>data are unavailable</u> for some element, reasonable assumptions may describe the <u>change in concentration for that element</u>. For example, if the total concentration of iron is not known but can be assumed to be very low, then it may be reasonable to assume that iron is essentially conserved in any reaction and that the difference in iron concentration between the initial and final solution is zero. The problem of missing analytical data is discussed more thoroughly in Plummer and others (1982).

### Phases

The phases to be used in the calculations are selected by the user on the basis of the geology, hydrology, or mineralogy of the system. These "plausible" phases generally are mineral solids but may also include gases, ion exchangers, or (in the special case of mixing) other aqueous solutions. For the purposes of this program, a phase represents a set of chemical elements that enter or leave the initial solution in fixed ratios. The objective in selecting phases is to provide a source or sink for each element in the initial and final solutions. The result is a set of linearly independent equations which can be solved simultaneously to yield values that describe the amount of each phase participating in the reaction.

In general, the number of phases must equal the number of elements in order to solve the set of equations. Although the calculated mass transfer for one or more phases might be zero, indicating that the phase(s) did not participate in the reaction, the phase(s) must still be included in the input to BALANCE in order to perform the calculations.

### Element Mass Balance Equations

The equations for mass balance on elements are:

 $\sum_{p=1}^{P} \alpha_{p} b_{p,k} = m_{T,k}(final) = m_{T,k}(initial) = \Delta m_{T,k}$ 

### for each element k = 1 to J.

(2)

where the notation is defined as follows: P is the number of total reactant and product phases in the net reaction,  $\alpha_p$  is the calculated mass transfer of the p<sup>th</sup> phase, b<sub>p,k</sub> denotes the stoichiometric co-efficient of the k<sup>th</sup> element in the p<sup>th</sup> phase,  $m_{T,k}$  is the total molality of the k<sup>th</sup> element in solution, and J is the number of elements included in the calculation. In problems with only element mass balance equations (no redox or mixing), P = J.

#### Mixing

This program also allows for the following type of problem: Two end-member waters mix in unknown proportions and, in addition, phases dissolve and precipitate to produce a final water. In this problem, the two initial solutions are treated exactly like other phases and  $\alpha_1$  is the fraction of initial solution 1 and  $\alpha_2$  is the fraction of initial solution 2 which combine, along with mineral reactions, to produce the final solution. In addition to the element mass balance equations, an additional equation is automatically included to ensure the sum of the two fractions is equal to 1.

$$a_1 + a_2 = 1.0$$

(3)

(4)

For a mixing problem, the number of phases (other than solutions) that must be included is equal to the number of elements minus one, P = J - 1.

### Redox

When studying systems involving oxidation and reduction, it is necessary to conserve electrons in chemical reactions. Each mole of electrons released in oxidizing certain species must be consumed by reducing other species. We use the electron counting convention from the program PHREEQE (Parkhurst and others, 1980) to ensure conservation of electrons. (See also Plummer and others, 1982.) The convention defines a redox state for a solution as:

$$RS = \sum_{i=1}^{I} m_i v_i$$

where RS is the redox state of the solution,  $m_1$  is the molality of the i<sup>th</sup> aqueous species,  $v_1$  is the "operational valence" of the i<sup>th</sup> species, and I is the total number of species.

<u>A redox species is defined as a species of any element which can</u> occur in more than one oxidation state in natural aqueous environments. The rules for determining the operational valence of aqueous species are: (1) use the formal elemental valence for aqueous redox species, (2) use zero for non-redox species, (3) use the sum of the operational valences of species which associate to form redox complexes, (4) assign zero to the valences of H and O in aqueous species, (5) use zero for H<sup>+</sup> and OH<sup>-</sup>, (6) use -2.0 for  $H_{2(aq)}^{0}$  and +4.0 for  $O_{2(aq)}^{0}$ . The operational value of a phase is defined in the same way as for a dissolved complex. Table 1 lists examples of the operational valence of selected species and minerals.

Using these definitions, a linear equation ensuring the conservation of electrons can be formulated. The redox state is included in

inerals 1	, and up for selected aqueous	species
, <b>*</b> i .	Mineral	up
0.0	CaCO3	4.0 ·
0.0		8.0
0.0		8.1
0.0	NaCl	0.0
2.0	CaSO4	6.0
3.0	FeOOH	3.0
0.0	Fe <sub>2</sub> 0 <sub>3</sub>	6.0
6.0	FeCO3	6.0
-2.0	FeS	0.0
-2.0	FeS2	0.0
4.0	-	6.0
-4.0	"CH20"	0.0
4.0	KAISI308	0.0
4.0	A1 (OE) 3	0.0
0.0	KOH .	0.0
5.0	E <sub>2</sub> S gas	2.0
-3.0	CH4 gas	4.0
3.0		4.0
8.0	_	2.0
0.0		4.0
-2.0	-	0.0
4.0		3.0
0.0		0.0
	v1 0.0 0.0 0.0 2.0 3.0 0.0 6.0 -2.0 4.0 -2.0 4.0 4.0 4.0 4.0 5.0 -3.0 3.0 8.0 0.0 5.0 -3.0 4.0	inerals $\frac{1}{2}$ Mineral Vi Mineral 0.0 CaCO <sub>3</sub> 0.0 CaMg(CO <sub>3</sub> ) <sub>2</sub> 0.0 5 percent Fe-Dolomite <sup>2</sup> / 0.0 NaCl 2.0 CaSO <sub>4</sub> 3.0 FeOOH 0.0 Fe <sub>2</sub> O <sub>3</sub> 6.0 FeCO <sub>3</sub> -2.0 FeS -2.0 FeS -2.0 FeS <sub>2</sub> 4.0 CaSO <sub>4</sub> · 2H <sub>2</sub> O -4.0 "CH <sub>2</sub> O" 4.0 KAISi <sub>3</sub> O <sub>8</sub> 4.0 Al (OH) <sub>3</sub> 0.0 KOH 5.0 H <sub>2</sub> S gas -3.0 CH <sub>4</sub> gas 3.0 CO <sub>2</sub> gas 8.0 H <sub>2</sub> gas 0.0 O <sub>2</sub> gas -2.0 N <sub>2</sub> gas 4.0 NH <sub>3</sub> gas

Table 1.-Definition of  $v_1$  and  $u_p$  for selected aqueous species and minerals $\frac{1}{2}$ 

.

 $\frac{1}{1}$  The list is obviously incomplete but should serve as an example for other species and minerals that may be considered.

2/ Ca<sub>1.05</sub>Mg<sub>0.90</sub>Fe<sub>0.05</sub>(CO<sub>3</sub>)<sub>2</sub>.

BALANCE input as an "element". In this report we have chosen the letters "RS" to designate this pseudo-element.

$$\sum_{p=1}^{P} u_p \alpha_p = RS_{(\text{final})} - RS_{(\text{initial})} = \Delta RS$$
(5)

where  $u_p$  is the operational valence of the  $p^{th}$  phase and RS denotes the redox state of the solution. If we consider RS to be another element, then the same equalities hold for the number of phases and the number of elements. For non-mixing problems, P = J (including RS) and for mixing P = J - 1.

#### Results

The results of running the program BALANCE are a set of numbers indicating the moles of each phase which react with the initial solution to produce the final solution (positive for dissolution, negative for precipitation). In the mixing case, the numbers for solution 1 ( $\alpha_1$ ) and solution 2 ( $\alpha_2$ ) are the mixing fractions for the two solutions.

### Error Messages

Two error messages may be printed by the program. If the number of phases does not match the number of elements, the number of phases counted by the program is printed, followed by the number of elements counted, with the message, "NUMBER OF PHASES DOES NOT MATCH NUMBER OF EQUATIONS". If the linear equations are found to be linearly dependent, then "THE PHASE RULE HAS BEEN VIOLATED" is printed. If the selected phases do not include a source or sink for each element or if they include minerals whose compositions can be derived by linear combinations of other minerals in the set, this error message will be printed. For example, if CaCO<sub>3</sub>, MgCO<sub>3</sub>, and CaMg(CO<sub>3</sub>)<sub>2</sub> are chosen as phases, an error will result because:

$$CaCO_3 + MgCO_3 + CaMg(CO_3)_2$$
.

(6)

In BALANCE, a division by zero often occurs before this message is printed which may result in an abnormal termination of the program. Although the reason may not be immediately obvious to the user, the cause of the latter error message nearly always lies in the choice of the mineral phases.

#### PROGRAM INPUT

The program BALANCE requires three types of input to run: (1) A title, (2) a set of elements and their total concentrations or changes in concentrations, and (3) a set of minerals defined in terms of their elemental stoichiometry (and operational valence for redox problems). In the description that follows the Fortran format for each card is given in parentheses. The input is as follows:

TYPE 1: TITLE (20A4) The title is any name or description of 80 characters or less (one card).

TYPE 2: Solution data. Only one of the following type 2 forms of input may be used for a single simulation.

2.a. ENAME, EDELTA (A2,F8.3)

- ENAME The standard element abbreviation (e.g. K, NA, or CL). The abbreviation must be left justified and if redox is considered, RS must be one of the elements.
  - EDELTA The difference in total concentration of the element between the final and the initial solution (final - initial). The units used may be molal, mmolal, or umolal. No distinction is made between molarity and molality. The same units must be used for all elements.
- 2.b. ENAME, SFINAL, SINIT (A2,F8.3,F10.3)

ENAME - Same as above.

- SFINAL The total concentration of the element in the final solution in mole, mmole or umole units, provided the same unit is used for all elements.
- SINIT The total concentration of the element in the initial solution.
- 2.c. ENAME, SFINAL, SINIT1, SINIT2 (A2,F8.3,F10.3,F10.3)

ENAME - Same as above.

SFINAL - Same as above.

- SINITI The total concentration of the element in one of the two end-member solutions which mix to form SFINAL.
- SINIT2 The total concentration of the element in the other end-member solution assumed to mix in forming SFINAL.
- BALANCE calculates the fractions of the two initial solutions, with or without additional reaction, which combine to form the final solution.

Any number of elements for which there are data may be included (one element per card) but a mineral source or sink must be included for each element. All elements for a single simulation must use a single type (2.a., 2.b., or 2.c.) of input.

Note: The final card of type 2 input must be blank.

TYPE 3: Phase data. PNAME, (PELT(J), PCOEF(J), J=1,7) (A8,2X,7(A2,F8.3))

PNAME - An eight character name for the phase.

- PELT The standard abbreviation for a constituent element of the phase (must be left justified and identical to ENAME used in type 2 input). Seven sets of PELT and PCOEF (see below) can be read on this card but only those necessary to define the mineral need to be entered. RS must be included if redox is being considered. Omission of an element or RS implies zero.
- PCOEF Read as a pair with PELT, this is the stoichiometric coefficient for the element in the phase. For RS, PCOEF is the operational valence of the phase. (See table 1 for examples.)

A number of phases equal to the number of elements must be entered for types 2.a and 2.b. For mixing cases, the number of phases must be one less than the number of elements. Elements in the phases which are not included in the list of elements will be ignored in the calculations. Note: The final card in type 3 input must be blank.

Sequential mass balance calculations may be run by repeating the input sequence starting with the title.

### EXAMPLES

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Three examples are presented below to demonstrate how to code problems for BALANCE and to show some of the varieties of reactions and data that can be considered.

### Example 1

The observed analytical data for initial and final waters for example 1 are given in table 2:

Table 2.-Analytical data for example 1  $\frac{a}{a}$ 

Element	Total concentrat Final Water	tion (mmol/kg H <sub>2</sub> O) Initial water
Calcium	3.230	1.118
Magnesium	2.668	0.950
Sulfur	4.000	0.0
Carbon	4.294	4.464

Note that accompanying the increases in total dissolved calcium, magnesium, and sulfur (sulfate in this case), total inorganic carbon decreases in the final water. The four elements for which analytical data are given allow four phases to be included in testing reaction models. The four phases chosen for this example are calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), and CO<sub>2</sub> gas.

The mass balance equations (equation 2) for this choice of phases are given as follows:

 $\Delta m_{T,Ca} = 3.230 - 1.118 = l\alpha_{calcite} + l\alpha_{dolomite} + l\alpha_{gypsum}$ (7)  $\Delta m_{T,Mg} = 2.668 - 0.950 = l\alpha_{dolomite}$ (8)  $\Delta m_{T,S} = 4.000 - 0.0 = l\alpha_{gypsum}$ (9)  $\Delta m_{T,C} = 4.294 - 4.464 = l\alpha_{calcite} + 2\alpha_{dolomite} + l\alpha_{CO_2}$ (10)

<u>a</u>/ Although the analytical data of table 2 are realistic, they were generated from thermodynamic data using the equilibrium model PHREEQE (Parkhurst and others, 1980). Both solutions are constructed to be in equilibrium with dolomite and calcite, but undersaturated with gypsum. Table 3 lists the input data set for BALANCE. Card 1 is the title card. Cards 2-5 define the element concentrations in the final and initial water using type 2.b input (as defined earlier). Card 6 is a blank card denoting the end of type 2 input. Cards 7-10 define the selected phases for the reaction model, type 3 input, and card 11 is blank denoting the end of type 3 input. BALANCE will accept successive reaction model data sets but only one data set is given in table 3.

Table 4 gives the results computed by BALANCE including the linear matrix of coefficients used to solve the reaction model and the computed mass transfers of the selected phases (DELTA PHASES). Note that the coefficients of the array are the same as the coefficients in the mass balance equations in equations 7-10. The units of DELTA PHASES in table 4 are mmol/kg H<sub>2</sub>O ( $\equiv$  mmol/L). Negative values indicate precipitation between the initial and final water and positive values indicate dissolution.

The results of table 4 show that if calcite, dolomite, gypsum, and  $O_2$  are the minerals reacting in the ground-water between the initial and final solution, then the reaction is incongruent dissolution of dolomite (dolomite dissolution with calcite precipitation) accompanying the dissolution of gypsum in a system closed to  $O_2$  gas.

### Example 2

This example assumes that an observed final water composition has resulted from the mixing of two end-member (initial) solutions with subsequent reactions. The final observed water and the two initial solutions are summarized in table 5. As with example 1, the water chemistry was constructed using PHREEQE (Parkhurst and others, 1980).

The end-member waters are (1) a calcium bicarbonate water in equililibrium with calcite at a  $P_{OO}$  of  $10^{-2}$  atm, and (2) seawater. The final water has been constructed<sup>2</sup> to be in equilibrium with calcite and dolomite. In this example, we are interested in computing the fractions of solutions 1 and 2 in the mixture and the amounts of subsequent mineral-water reactions. The phases chosen for these calculations are calcite, dolomite, gypsum,  $OO_2$  gas, NaCl, and  $Ca^{2+}-Na^{+}$  ion exchange. Note that because this is a mixing problem, the number of phases (6) is one less than the number of elements (7). The ion exchange reaction is written

$$Na_2X + Ca^{2+} + 2Na^{+} + CaX$$
(11)

CARD	•						(	COLUMN					
		1 0 +'++		20++++	++++-	30 +++'+		4 0 +++ +++	5	-	6 0 + • + + + + + + +	70 +++'++++++	8 0 ++'
1	EXAMPLE	<b>#</b> 1 :	NON-F	EDOX	REA	CTION	(түрі	2.B I	NP(IT)				
2	CA 3.23		1.11										
1	MG 2.66		0.95										
	S 4.00												
7			0.0										
5	C 4.29	4	4.46	94									
6			• •										
7	CALCITE		1.0	C	1.0								
8	DOLOMITE	CV	1.0	MG	1.0	С	2.0						
9	CO2 GAS	С	1.0										
10	GYPSUM	CA	1.0	S	1.0	•						-	
11										·		-	
•	+++++++	+'++	+++++	++++	+++++	+++++	+++++	++'+++	++++++	++++++++	• • • • • • • • • •		++'
		10		20		30		4 0	5	0 (	5 0	70	8 0

Table 3.--Card images of input data set for example 1

### Table 4.-Printout listing results for example 1

;

### EXAMPLE #1: NON-REDOX REACTION (TYPE 2.B)

#### DELTA CALCITE DOLOMITE CO2 GAS GYPSUM 2.112 CA 1.000 1.000 0.0 1.000 1.718 MG 0.0 1.000 0.0 0.0 4.000 S 0.0 0.0 0.0 1.000 -0.170 C 1.000 2.000 1.000 0.0

### DELTA PHASES

CALCITE	-3.6060			
DOLOMITE	1.7180			
CO2 GAS	0.0000			
GYPSUM	4.0000			

Element	Final water	End-member wat Solution 1	ers (mmol/kg H <sub>2</sub> O) Solution 2
Calcium	11.567	1.651	10.661
Magnesium	9.156	0.0	55.083
Sodium	145.626	0.0	485.418
Potassium	3.174	0.0	10.579
Chloride	170.025	0.0	566.751
Sulfur	8.778	0.0	29.259
Carbon	3.029	3.635	2.138

Table 6 lists the card deck to solve example 2. Card 1 is the title card. Cards 2-8 define the total concentrations of the elements in the final water and in the end-member solutions 1 and 2. Card 9 is blank. Cards 10-15 define the stoichiometry of the mineral reac-

Table 7 gives the results computed by BALANCE which indicates that the final water contains 70 percent calcium bicarbonate water (solution 1) and 30 percent seawater (solution 2). In addition to mixing, the water has dissolved 14.58 mmol of calcite and precipitated 7.37 mmol of dolomite per kg H<sub>2</sub>O. None of the other phases considered in this example have contributed significantly to the evolution of the final water.

tions included in the model and card 16 is blank.

### Example 3

This example uses observed chemical data from the Floridan aquifer and is similar to the modeling considered by Plummer and others (1982). The analytical data for the initial and final waters, including data on the sulfur isotopes, are summarized in table 8.

In calculating the mass transfer in the evolution of the initial water to the final water, three types of linear equations are solved simultaneously: (1) chemical mass balance, (2) conservation of electrons, and (3) a linear sulfur isotope balance equation. These equations are developed below for a reaction model that assumes the following set of seven phases: calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), organic matter (CH<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), ferric hydroxide (FeOOH), and pyrite (FeS<sub>2</sub>). It is important to note that these choices of phases are arbitrary. Other sets of phases will also lead to valid reaction models. That is, all the mass balance and redox criteria included in BALANCE can be satisfied by other sets of phases.

Table 5.-Analytical data for example 2

Table 6.-Card images of input data set for example 2

CARD #

.

### COLUMN

		,0 '++		0 '++		3 ++'	0 ++1	+++++	4 ++'	0 *+++	++++	5 + •	0 ++++	6 ++++	; 0 '++	7 0 +++++++	80 ++++
1	EXAMPLE (	2:	MIXING	WI	TH NO	N-A	EDO	DX RE	ACI	rions	3 (TY	PE	2.0	INPE	IT)		
2	CA11.5666	4 1	.651		10.66												•
3	MG9.15602	3		5	5.083	283											
4	NA145.625	5		4	85.41	83											
5	K 3.17366	9		1	0.578	90									-		•
6	CL170.025	4		5	66.75	133											
7	S 0.77778	3		2	9.259	20											
8 9	C 3.02943	3	.635	2	.1374	85											
10	CALCITE	CA	1.0	С	1.0												
11	DOLONITE		1.0	-	1.0		С	2.0									
12	CO2 GAS	Ċ	1.0				-										
13	ION EXCH		-1.0	NA	2.0												
14	GYPSUM	CA	1.0	S	1.0												
15 16	NACL	NA	1.0	CL	1.0												
	+++++++++	•++•	++++++	•+++		•+•	+++	+++++	•••	++++	++++	<b>+ •</b> •	•+++•	*****	•++	******	*****
	1	0		0		3			4			5 (			Ö	70	80

.

.

### Table 7.-Printout listing results for example 2

### EXAMPLE 12: MIXING WITH NON-REDOX REACTIONS (TYPE 2.C INPUT)

FINAL	INIT]	INIT2	CALCITE	DOLOMITE	CO2 GAS	ION EXCH	GYPSUM	NACL
11.567 CA 9.156 MG 145.626 NA 3.174 K 170.025 CL 8.778 S 3.029 C 1.000 MIX	1.651 0.0 0.0 0.0 0.0 0.0 3.635 1.000	10.661 55.083 485.418 10.579 566.751 29.259 2.137 1.000	1.000 0.0 0.0 0.0 0.0 0.0 1.000 0.0	1.000 1.000 0.0 0.0 0.0 0.0 2.000 0.0	0.0 0.0 0.0 0.0 0.0 0.0 1.000 0.0	-1.000 0.0 2.000 0.0 0.0 0.0 0.0 0.0	1.000 0.0 0.0 0.0 0.0 1.000 0.0 0.0	0.0 0.0 1.000 0.0 1.000 0.0 0.0

DELTA PHASES

INIT1	0.7000
INIT2	0.3000
CALCITE	14.5816
DOLOMITE	-7.3689
CO2 GAS	0.0000
ION EXCH	0.0000
GYPSUM	0.0000
NACL	0.0001

Element	Final water	Initial water	$\Delta$ concentration (Final - initial)
Calcium	1.647	0.848	0.799
Magnesium	1.193	0.230	0.963
Carbon	2.845	2.055	0.790
Total Sulf	ur 1.649	0.025	1.624
Sulfate	1.614	0.025	
Sulfide	0.035	0.0	
Iron	~0.0	~0.0	~0.0
6 <sup>34</sup> S(S04)	24.9	14.0	-
δ <sup>34</sup> S(H <sub>2</sub> S)	-32.9	-	-

### 1. Chemical mass balance

Using the values of  $\Delta m_{T,k}$  (in mmol/kg H<sub>2</sub>O) from table 8, the mass balance equations (equation 3) for Ca, Hg, C, S, and Fe are:

$\Delta m_{T,Ca} = 0.799 = \alpha_{calc}$	ite + adolomite + agypsum (12)
Am <sub>T,Mg</sub> = 0.963 = adolo	nite (13)
$\Delta m_{T,C} = 0.790 = \alpha_{calc}$	ite + $2\alpha$ dolomite + $\alpha$ CH <sub>2</sub> 0 + $\alpha$ CO <sub>2</sub> (14)
Δm <sub>T,S</sub> = 1.624 = α <sub>gyps</sub>	um + 2apyrite (15)
$\Delta m_{T,Fe} = 0.0 = \alpha_{Fe00}$	E + apyrite (16)

### 2. Conservation of electrons

Because our problem involves changes in oxidation state, one equation of the form of equation 5, must be included. In this system, carbon, sulfur, and iron are the only redox elements we have included.

<sup>&</sup>lt;u>a</u><sup>/</sup> All concentrations of elements are given in mmol/kg H<sub>2</sub>O and are taken from Back and Hanshaw (1970). Isotope values are in per mil (°/oo) by Rightmire and others (1974) and Rye and others (1981).

Using equation 4, RS for the initial solution is given by RS = 4(2.055) + 6(0.025) + 0 = 8.370. In the final solution, RS = 4(2.845) + 6(1.614) -2(0.035) = 20.994, where each redox state of sulfur is considered. ARS is then equal to 20.994 - 8.370 = 12.624 and equation 5 is as follows:

$$\Delta RS = 12.624 = 4a_{calcite} + 8a_{dolomite} + 6a_{gypsum} +$$

$$Da_{CH_{2}0} + 4a_{CO_{2}} + 3a_{FeOOE} + 0a_{pyrite}$$
(17)

Note that the pyrite and organic matter terms drop out of the electron conservation equation because their operational valence is zero (table 1). The coefficient for the dolomite term, 8, is the product of the operational valence of carbon in dolomite, 4, and the stoichiometric coefficient of carbon in dolomite, 2.

### 3. Linear isotope equation

Linear isotope balance equations may be included with the mass balance and electron balance equations provided the reaction is either congruent (that is, mineral dissolution only), or, if incongruent, the fractionation between solution and solid can be neglected. Along our flow path, the measured fractionation is approximately  $55^{\circ}/00$  in the reduction of sulfate to sulfide. Because of this large difference in isotopic composition of sulfate and sulfide, we will ignore the small fractionation between dissolved total sulfide and pyrite of perhaps 1 to  $2^{\circ}/00$ . The general form for the linear sulfur isotope balance equation is

 $\sum_{p=1}^{P} \alpha_p b_{s,p} \delta^{34} S_p = \Delta^{34} S$ (18)

where,

 $\Delta^{34}S = (\mathbf{m}_{T,S}\delta^{34}S_{T})_{final} - (\mathbf{m}_{T,S}\delta^{34}S_{T})_{initial}$ (19)

and the subscript T denotes total sulfur (sulfide plus sulfate). In this example, the isotope equation is as follows:

$$\Delta^{34}S = a_{gvp}\delta^{34}S_{gvp} + 2a_{pvrite}\delta^{34}S_{pvrite}$$
(20)

The isotopic composition of dissolved sulfur,  $\delta^{34}S_T$ , in the final water is given by

$$\delta^{34}S_{T} = \frac{m_{T,SO_{2}^{2}} \delta^{34}S_{SO_{2}^{2}} + m_{T,H_{2}S}\delta^{34}S_{H_{2}S}}{S_{T}}.$$
 (21)

Using the isotopic composition and total concentrations of sulfate and sulfide in the final water (table 8), the calculated  $\delta^{34}S_T$  is 23.673°/00. Because dissolved sulfides are not present in the initial water,  $\delta^{34}S_T$  for this water is that of sulfate alone (14°/00). Using these values of  $\delta^{34}S_T$  and the total concentrations of sulfur in the final and initial waters (1.649 and 0.025, respectively),  $\Delta^{34}S$ from equation 19 is 38.687. Using a  $\delta^{34}S$  value of +22°/00 for dissolving gypsum (Rightmire and others, 1974) and -32.9°/00 for precipitating pyrite (table 8), the linear sulfur isotope equation (equation 20) is

 $22.0a_{gyp} = 65.8a_{pyrite} = 38.687$ 

Equations 12 to 17 and 22 are linear and may be solved simultaneously, using BALANCE, to yield values for the seven unknowns,  $\alpha_p$ .

Table 9 lists the card deck to solve the problem. Card 1 is the title card. Cards 2-8 define the delta values (final - initial) for the elements, redox state, RS, and sulfur isotope, DS. Card 9 is blank. Cards 10-16 define the stoichiometry, redox state, and sulfur isotopic data for the phases. Card 17 is blank.

Table 10 gives the results computed by BALANCE, indicating  $a_{calcite} = -1.842$ ,  $a_{dolomite} = 0.963$ ,  $a_{gypsum} = 1.678$ ,  $a_{CH_20} = 0.171$ ,  $a_{CO_2} = 0.535$ ,  $a_{FeOOH} = 0.027$ , and  $a_{pyrite} = -0.027$ . This

particular choice of phases gives the net reaction between initial and final water as follows:

Initial water + 1.678 gypsum + 0.963 dolomite +

0.171 CH20 + 0.535 CO2 + 0.027 FeOOH +

Final water + 1.842 calcite + 0.027 pyrite. (23)

(22)

Table 9.-Card images of input data set for example 3

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CARD	•			co	LUMN		
		1 0 +	20 ++'+++++++	3 0 ++'++++++++	4 0 5 0 +'++++++++	6070 ++ ' + + + + + + + + + + + + + + + + +	80 +++
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	EXAMPLE ( CA 0.79 MG 0.96 S 1.62 C 0.79 FE 0.0 RS 12.62 DS 38.68 DOLOMITE CALCITE CALCITE CO2 GAS GYPSUM "CH2O" GOETHITE PYRITE	99 53 24 90	MG 1.000 MG 0.000 RS 4.000 S 1.000 RS 0.000 RS 3.000	C 2.000 C 1.000 RS 6.000	AR ISOTOPE BALANCE RS 8.000 RS 4.000 DS 22.000 DS -65.800	(TYPE 2.A INPUT)	
	********* 1	'+++++++ 0		+ * + + + + + + + + + + + + + + + + + +	*++++++++*****************************	6 0 7 0	++* 8 0

. .

12-85

DELTA		DOLOMITE	CALCITE	CO2 GAS	GYPSUM	"CH2O"	COETHITE	e pyrite
0.799 0.963 1.624 0.790 0.0 12.624	CA NG S C FE RS	1.000 1.000 0.0 2.000 0.0	1.000 0.0 1.000 0.0	0.0 0.0 1.000 0.0	1.000 0.0 1.000 0.0 0.0	0.0 0.0 0.0 1.000 0.0	0.0 0.0 0.0 0.0 1.000	0.0 0.0 2.000 0.0 1.000
38.687	DS	8.000 0.0	4.000 0.0	4.000 0.0	6.000 22.000	0.0 0.0	3.000 0.0	0.0 . -65.800

### Table 10.-Printout listing results for example 3

1

DELTA PHASES

DOLOMITE	0.9630
CALCITE	-1.8419
CO2 GAS	0.5348
GYPSUM	1.6779
"C1120"	0.1711
GOETHITE	0.0269
PYRITE	-0.0269

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### HOW TO RUN BALANCE ON THE USGS AMDAHL COMPUTER

In order to run BALANCE on the USGS Amdahl 470V/7 computer the first card of the job must be a legitimate JOB card as defined in the Computer Center Division's user's manual.

//AAlyyyxx JOB (....),'user name',CLASS=x

The following Job Control Language (JCL) statements will execute the program BALANCE:

// EXEC FORTRUN, PROG=BALANCE, ULIB='BFJONES.PGMLIB'

Insert input data deck here

11

Attachment A contains a listing of the Fortran source code for BALANCE. This code is stored in a catalogued partitioned data set named BFJONES.CARDS. The member name is BALANCE. Chapter two of the USGS Computer User's manual gives the JCL necessary to obtain listings and card decks for a partitioned data set.

The cards for the test problems in this report are stored in a card image file named PARK.BALANCE.TEST. This is a catalogued sequential data set and can be listed or punched using the JCL from the user's manual. By using the following JCL statements it is possible to run the test cases directly from the disk, without making a deck of the test cases. The cards for the run stream are:

// EXEC FORTRUN,PROG=BALANCE,ULIB='BFJONES.PGMLIB'
//SYSIN DD DSN=PARK.BALANCE.TEST,DISP=SHR
//

All jobs should end with // in the first two columns of the last card.

### REFERENCES

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- Rye, R. O., Back, William, Hanshaw, B. B., Rightmire, C. T., and Pearson, F. J., Jr., 1981, The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas: Geochimica et Cosmochimica Acta, v. 45, p. 1941-1950.

Attachment A: Program listing of BALANCE

### PROGRAM BALANCE

THIS PROGRAM CALCULATES THE MASS TRANSFER OF AN INPUT SET OF PHASES, NECESSARY TO PRODUCE AN OBSERVED FINAL SOLUTION OR OBSERVED CHANGES IN CONCENTRATION.

### INPUT:

- 1 TITLE (20A4)
- 2 SOLUTION INPUT (A2, F8.3, 2F10.3)

ONE CARD FOR EACH ELEMENT CONSIDERED. ONLY ONE OF THE FOLLOWING THREE TYPES OF INPUT MAY BE USED FOR A SINGLE SIMULATION.

- 2.A. ELEMENT NAME, DELTA ELEMENT CONCENTRATION.
- 2.B. ELEMENT NAME, FINAL SOLUTION CONCENTRATION, INITIAL SOLUTION CONCENTRATION.
- 2.C. ELEMENT NAME, FINAL SOLUTION CONCENTRATION, INITIAL SOLUTION CONCENTRATION, ADDITIONAL AQUEOUS PHASE CONCENTRATION.
- 3 BLANK CARD ENDS SOLUTION INPUT.
- 4 PHASE INPUT
  - CARD 4.A. IS REQUIRED FOR EACH PHASE. CARD 4.B. IS USED FOR ANY PHASE WHICH CONTAINS MORE THAN 7 ELEMENTS. MFLAG
  - MUST BE EQUAL TO 1 TO USE CARD 4.B. FOR A PARTICULAR PHASE. 4.A. PHASE NAME, MFLAG, COMPOSITION (ELEMENT NAME, COEFFICIENT
  - IN PHASE). (A8,1X,11,7(A2,F8.3))
  - 4.B. COMPOSITION (ELEMENT NAME, COEFFICIENT IN PHASE). (8(A ,F . USE CARD 4.B. ONLY IF PHASE CONTAINS MORE THAN 7 ELEMENTS AND MFLAG=1 IN PREVIOUS CARD.
- 5 BLANK CARD ENDS SOLUTION INPUT.

THE NUMBER OF ELEMENT CARDS MUST EQUAL THE NUMBER OF PHASES UNLESS TYPE 2.C INPUT IS USED. IN THAT CASE THE NUMBER OF PHASES FLUS ONE (THE OTHER AQUEOUS PHASE) MUST EQUAL THE NUMBER OF ELEMENTS.

INPUT FOR MORE SIMULATIONS MAY FOLLOW. SIMPLY REPEAT THE INPUT PROCESS.

D.PARKHURST, N.PLUMMER, AND D.THORSTENSON REVISED MARCH, 1982

#### \*\*\*\*\*

REAL \* 8 TNAME, PELT(20,15), BLANK 1010 REAL \* 8 ENAME (20), HEAD, DELTAL, DINITI, DINITZ, DMIX, FINAL 1020 REAL \* 8 DELANK 1030 REAL \* 8 PNAME (20) 1040 DIMENSION EDELTA(20), PCOEF(20,15), TITLE(20) .1050 DIMENSION A(20,20), DELTA(20), SINIT(20), SFINAL(20), SMIX(20) 1060 DATA BLANK/' '/, DBLANK/' '/, DELTA1/'DELTA'/, DINIT1/'INIT1' 1070 1/,DINIT2/'INIT2'/,DMIX/'MIX'/,FINAL/'FINAL'/ 1080

C C

С

	20		
		CONTINUE	1090
		• •	1100
l		INPUT TITLE	1110
(	Ç		
		READ(5,15,END=1000) (TITLE(I),I=1,20)	1120
	15	FORMAT (20A4)	1130
		PRINT 25, (TITLE(I), I=1,20)	1140
	25	FORMAT(1H1,///1X,20A4///)	1150
(	2		1160
	2	BECTN INDEE WITH IT ENDERE BOD WARE DATE	1170
Ċ		BEGIN INPUT WITH ELEMENTS FOR MASS BALANCE EQUATIONS	1180
		I=0	1190
		ISOLN=0	1200
		IMIX=0	1210
	20	CONTINUE	1220
	20		1230
			1240
		READ (5,10, END=1000) ENAME(1), SFINAL(1), SINIT(1), SMIX(1)	1250
	TO		1260
		IF (SINIT(I).GT.0.0) ISOLN=1	1200
		IF(SMIX(I).GT.0) IMIX=1	
		EDELTA(I)=SFINAL(I)-SINIT(I)	1280
$\sim 1$	•	IF (ENAME (I) .NE. BLANK) GO TO 20	1290
		NELTS=I-1	1300
		NEQ=NELTS+IMIX	1310
C			1320
С			1330
C C		ZERO ARRAYS PELT AND A	1340
С			1350
		DO 35 J=1,20	1360
		DO 35 I=1,15	1370
		PELT(J,I)=BLANK	1380
	35	CONTINUE	1390
		DO 200 I=1,20	1400
		$200 \ 1^{-1}, 20$	1410
			1420
		A(I,J) = 0.0	1430
~	200 1	CONTINUE	1440
C			1450
С		ARRANGE ARRAY FOR MIXING IF IMIX=1	1460
С			1400
		HEAD=DELTA1	
		LF (IMIX.EQ.0) GO TO 220	1480
		IF (ISOLN.GT.O) GO TO 230	1490
	]	PRINT 250	1500
		CORMAT(1X,70('*')/1X,'A MIXING SOLUTION WAS ENTERED BUT NO',	1510
	1	' INITIAL SOLUTION WAS ENTERED. ')	1520
		TOP	1530
С	-	·····	1540
-	230	INTINUE	1550
		NAME(1)=DINITI	1560
		NAME(2)=DINIT2	1570
	-		1580

:

1

HEAD=FINAL 1590 ENAME (NEO) = DMIX 1600 EDELTA(NEO) =1.0 1610 A(NEQ, 1) = 1.01620 A(NEQ, 2) = 1.01630 DO 240 I=1,NELTS 1640 A(I,1) = SINIT(I)1650 A(I,2) = SMIX(I)1660 EDELTA(I) = SFINAL(I) 1670 PELT(I,1) = ENAME(I)1680 PELT(I,2) = ENAME(I)1690 240 CONTINUE 1700 С 1710 С INPUT PHASE DATA 1720 С 1730 220 CONTINUE 1740 I=2\*IMIX 1750 40 CONTINUE 1760 I=I+1 1770 READ 50, PNAME(I), (PELT(I,J), PCOEF(I,J), J=1,7) 1780 50 FORMAT(A8, 2X, 7(A2, F8.3)) 1790 IF (PNAME(I).NE. DBLANK) GO TO 40 1800 NMINS=I-1 1810 IF (NMINS-IMIX. EQ. NELTS) GO TO 60 1820 PRINT 70, NMINS, NELTS 1830 70 FORMAT(1X,100('\*')//1X, 'NUMBER OF PHASES DOES NOT MATCH NUMBER OF 1840 1EQUATIONS',214) 1850 STOP 1860 С 1870 С PUT COEFFICIENTS INTO ARRAY A 1880 Ĉ 1890 60 CONTINUE 1900 J1=2\*IMIX+1 1910 DO 80 I=1,NED 1920 TNAME=ENAME(I) 1930 DO 90 J=J1,NMINS 1940 DO 160 K=1,15 1950 IF (PELT (J, K) .NE. TNAME) GO TO 160 1960 A(I,J) = PCOEF(J,K)1970 160 CONTINUE 1980 90 CONTINUE 1990 A(I,NEQ+1)=EDELTA(I) 2000 80 CONTINUE 2010 С 2020 Ĉ PRINT OUT ARRAY WHICH IS TO BE SOLVED 2030 č 2640 PRINT 100, HEAD, (PNAME(I), I=1, NMINS) 2050 100 FORMAT(4X, A5, 10X, 11A10) 2060 PRINT 110 2070 110 FORMAT(1X) 2080

:

		DO 150 I=1,NED	
		PRINT 120, A(I, NED+1), ENAME(I), (A(I,J), J=1, NMINS)	2090
	120	) FORMAT(1X,F8.3,2X,A5,11F10.3)	2100
	150	CONTINUE	2110
С			2120
ē		SOLVE SET OF LINEAR EQUATIONS	2130
č		Salve sei ur liinear equations	2140
•		CALL SLNQ(NEQ, A, DELTA)	2150
С		CHEL SLAV (REC, A, DELTA)	2160
č		PRINT SOLUTION	2170
č			2180
•		PRINT 130	2190
	120	FORMAT(//,25X, 'DELTA PHASES',/)	2200
	100	PORTAL (//, 20%, 'DELTA PHASES', /)	2210
	140	PRINT 140, (PNAME(I), DELTA(I), I=1, NMINS) FORMAT(21X, AB, F12.4)	2220
	140	GO TO 30	2230
1	000	CONTINUE	2240
-	000	STOP	2250
		END .	2260
			2270
		SUBROUTINE SLNQ(N, A, X)	2280
С		DIMENSION A(20,20), X(20), IOPT(10)	2290
č			2300
c		SOLUTION OF N LINEAR EQUATIONS IN N UNKNOWNS BY GAUSSIAN	2310
č		ELIMINATION OR DETERMINANT EVALUTAION.	2320
c		A CONTAINS THE MATRIX OF THE COEFFICIENTS AND N INDICATES THE	2330
ž		ORDER OF THE MATRIX. IF J EDUALS ZERO, D CONTAINS THE VALUE OF THE	2340
<b>C</b>		DETERMINANT. IF J DOES NOT EQUAL ZERO, X CONTAINS THE N VALUES OF	2350
ć		THE UNKNOWNS.	2360
C			2370
		IOPT(9)=0	2380
		J=1 D=0.0	2390
			2400
		NP1=N+1	2410
			2420
		IF (IOPT (9) .NE.1) GO TO 120	·2430
		DO 110 II=1,N	2440
-		PRINT 210, (A(II,JJ),JJ=1,NP1)	2450
		CONTINUE	2460
-	20	CONTINUE	2470
		IF (N. EQ.1) GO TO 300	2480
		DO 130 I=1,NM1	2490
		M=I	2500
		K=I+ <u>1</u>	2510
		B=A(I,I)	2520
		DO 30 L=K,N	2530
		IF(ABS(B)-ABS(A(L,I))) 20,30,30	2540
		MEL	2550
		B=A(L,I)	2560
		CONTINUE	2570
		IF (B) 40,170,40	2580
			2000

:

40	) CC=A(M, I)	2590
	IF (I-M) 50,70,50	2600
- 50	) <b>D=-</b> D	2610
	DO 60 L=I,NP1	2620
	B=A(I,L)	2630
	A(I,L) = A(M,L) / CC	2630
60	A(M,L) = B	
	GO TO 90	2650
70	DO 80 L=I,NP1	2660
		2670
	A(I,L) = A(I,L) / CC	2680
90	D=D*CC	2690
	DO 100 M=K,N	2700
	B=A(M,I)	2710
	DO 100 L=I,NP1	2720
100	A(M,L) = A(M,L) - B + A(I,L)	2730
130	CONTINUE	2740
	$D=D^*A(N,N)$	2750
	IF (J) 140,200,140	2760
140	X(N) = A(N, NP1) / A(N, N)	2770
	K=NM1	
150	M=R+1	2780
100	B=0.0	2790
		2800
100	DO 160 L=M,N	2810
100	B=B+A(K,L)*X(L)	2820
	X(K) = A(K, NP1) - B	2830
	K=K-1	2840
	IF (K) 170,200,150	2850
170	IF (J) 180,190,180	2860
180	PRINT 230	2870
	STOP	2880
190	D=0.0	2890
	IF (IOPT (9) .LT.1) GO TO 320	
	PRINT 330	2900
330	FORMAT(1X, 'DELTA VALUES')	2910
200	FURTHILLA, DELIA VALUES)	2920
240	PRINT 340, (X(I), I=1, N)	2930
340	FORMAT(5X,1P10D12.3)	2940
	PRINT 220	<b>29</b> 50
	CONTINUE	2960
	RETURN	2970
300	CONTINUE	2980
	IF(A(1,1).EQ.0D0) GO TO 180	2990
	X(1) = A(1,2)/A(1,1)	3000
	CO TO 190	3010
		3020
		3030
, כוכ	FORMAT(/(5X,1P10D12.3))	3040
		3050
220	FORMAT (1X)	3060
230	FORMAT (1H1, 'THE PHASE RULE HAS BEEN VIOLATED')	3070
	END	3080

...

С С С С Section 13

# Evaluation of Laboratory Analytical Data

Lecture by: Richard Meyerhein New Mexico Scientific Laboratory Division

## SECTION CONTENTS

Reliability of Chemical Analyses of Water Samples -	
The Experience of the UMTRA Project, by G. Rice, J.	•
Brinkman and D. Muller, Ground Water Monitoring Review,	
Summer 1988, pp. 71-75	

Additional References:

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COMPUTER NOTES

TRILINEAR DIAGRAM REVISITED: APPLICATION, LIMITATION, AND AN ELECTRONIC SPREADSHEET PROGRAM

### by Songlin Cheng<sup>a</sup>

Abstract. The trilinear diagram has been used extensively in hydrochemical studies. The concept of hydrochemical facies based on the trilinear diagram can effectively characterize the chemical composition of water in a qualitative manner. However, its application is rather limited for quantitative and precise study, because it is difficult, if not impossible, to distinguish various mechanisms that may cause similar change in water chemistry by this diagram alone. This limitation is illustrated with various hypothetical water-rock interactions and mixing trends plotted on the trilinear diagram.

### Introduction

The trilinear diagram (Hill, 1940; Piper, 1944) has been used extensively in hydrochemical studies. It effectively delineates the change of water types as the water migrates from one region of an aquifer to the other. In case of mixing between waters, the data distribution on the diagram may reveal the end members of the intermediate mixtures. Simple mixing between two end members should result in a straight line in all three fields of the trilinear diagram, provided all ions remain in the solution. However, the assumption that all ions remain in the solution may not be valid in most ground-water systems. For example, dissolution and precipitation of minerals are rather common in ground-

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water systems. Any post-mixing reaction may cause deviation from a straight mixing line. Besides, a straight line may be caused by reaction, rather than mixing. Therefore, identifying a mixing situation from straight alignment on a trilinear diagram is not an accurate approach. In this paper, the data distribution on the trilinear diagram as a result of water-rock interactions and mixing will be illustrated.

The speed and accuracy of computer plotting can relieve the tedium and remove the chance of error of hand plotting. Morris *et al.* (1983) published a BASIC program for plotting data on the trilinear diagram. This program also checks for the possibility of mixing. They applied the tangent function to convert a tertiary system to X-Y coordinates. In this paper, a sine and cosine function set for coordinate conversion are presented. This approach has the advantage of assigning 100 units to the side length of triangles of the trilinear diagram and easily scaling the diagram on the X-Y coordinate system.

As it is becoming increasingly common to maintain chemical databases on electronic spreadsheets, it is desirable to be able to use the same database for various applications and manipulations. Based on these considerations and available programs on our computer the LOTUS 1-2-3 (TM) is ideal for trilinear application, as it has the spreadsheet, plotting routines, and capability for programming. The macros on a floppy diskette and users' instructions are available from the author upon request.

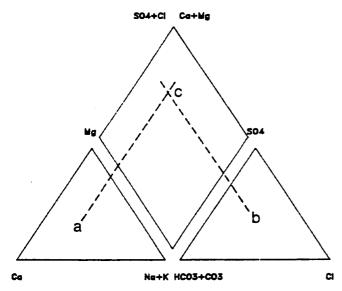


Fig. 1. The trilinear diagram. The cation and anion ratios of each sample are plotted in the cation (lower left) and anion (lower right) triangles (points a and b, respectively). The data point in the center diamond field is the intersection of the lines extended from the ion ratios and parallel to the sides of the triangles.

### The Geometry of Trilinear Diagram

Hill and Piper's trilinear diagram (Figure 1) consists of a cation triangle on the lower left, an anion triangle on the lower right, and a diamond field in the center. The equivalent percentage of cations and anions are plotted first on the correspondent triangles (points a and b, respectively). Lines parallel to the sides of the triangles are drawn through these percentage points and extended into the diamond field. The intersection (point c) represents the sample in the diamond field.

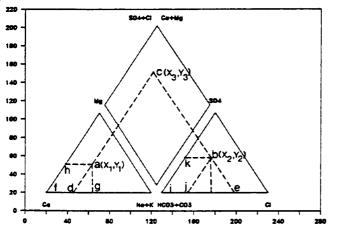


Fig. 2. The tertiary plot of trilinear diagram can be converted to X-Y plot by trigonometric function (see text for detail). 13-10

Referring to Figure 2, if the triangles of the trilinear diagram are drawn as equilateral, the mathematics of computation will be simple. If a, the trib, and c on Figure 2 are sample points linear diagram, then the triangle cde is 'ateral. The tertiary system can be converted \*\*.V.Odimensional X-Y coordination. The d. cation and anion triangles, and in the cfield are then located by correspondent pairs. If the lower left apex of the cation t f, is located on (20,20), the X-axis runs parallel to the base of the triangle, and the Y-axis is perpendicular to the X-axis; then, ion ratios and (Xi,Yi)'s on the new X-Y coordination system have the following mathematical relationship (assuming side length equals 100 units and spacing between triangles is 10 units):

### Cation triangle:

- $X1 = 20 + fg = 20 + fd + dg = 20 + fd + ad \times \sin 30^{\circ}$ = 20 + fd + fh × sin 30° = 20 + (Na + K%) + (Mg%) × sin 30°
- $Y1 = 20 + ag = 20 + ad \times \cos 30^{\circ} = 20 + fh \times \cos 30^{\circ} = 20 + (Mg\%) \times \cos 30^{\circ}$

### Anion triangle:

- $X2 = 20 + (side length) + (spacing) + ij + bj \times sin 30^{\circ}$ 
  - =  $20 + (side length) + (spacing) + ij + ik \times sin 30^{\circ}$
  - $= 20 + 100 + 10 + (Cl\%) + (SO_4\%) \times \sin 30^\circ$
- $Y2 = 20 + bj \times cos30^{\circ}$ 
  - $= 20 + ki \times cos30^{\circ}$
  - $= 20 + (SO_4\%) \times \cos 30^\circ$

Diamond field:

- cd = de (equilateral triangle)
  - = [(side length) fd] + (spacing) + ie
  - = [100 (Na + K%)] + 10
    - $+ [100 (HCO_3 + CO_3\%)]$

$$= [100 - (Na + K\%)] + 10 + [SO_4\% + Cl\%]$$

- $X3 = 20 + fd + cd \times \sin 30^{\circ}$ 
  - $= 20 + (Na + K\%) + cd \times sin 30^{\circ}$
- $Y3 = 20 + cd \times cos30^{\circ}$

The apex, f, can be any convenient location on the X-Y coordinate system. The trilinear diagram macro locates this apex on (20,20), and therefore, 20 units is included in each of the above equations for calculating (Xi,Yi). The spacing between triangles can be other than the 10 units selected here.

### **Application of Trilinear Diagram**

Many graphic methods are commonly used for representing hydrochemical data, such as the Schoeller diagram, Stiff diagram, and Hill and Piper's trilinear diagram. The trilinear diagram has the advantage of representing multiple parameters

	A	В	с	D	E	F	G	н	I	J	ĸ	L	м
2: 3:	SAMPLE #		TEMP( <sup>0</sup> C)	рН	ALKAL.	S102	Ca	Mg	Na	ĸ	C1	S04	NO 3
	END MEMBER A+GYP1	A	22.50	7.40 7.46	2.82	0.55	2.54	0.34	1.16	0.04	0.23	0.66	0.1
7: 8:	A+GYP2 A+GYP3	_	22.50 22.50	7.42	2.85	0.55	3.10 3.57 4.04	0.34 0.34 0.34	1.16 1.16 1.16	0.04 0.04 0.04	0.23 0.23 0.23	1.16 1.66 2.16	0.1 0.1 0.1
0:	END MEMBER END MEMBER	-	22.50	7.36	2.79	0.55	4.51 2.54	0.34	1.16	0.04	0.23	2.66	0.1
2:	MIXI MIX2		22.50 22.50	7.39	2.81	0.55	2.94	0.34 0.34	1.16 1.16 1.16	0.04 0.04 0.04	0.23 0.23 0.23	0.66 1.06 1.46	0.1
:	MIX3 MIX4 MIX5		22.50 22.50 22.50	7.38 7.37 7.37	2.80	0.55	3.53	0.34	1.16	0.04	0.23	1.66	0.1
	END MEMBER	B	22.50	7.36	2.80 2.79	0.55 0.55	4.12 4.51	0.34 0.34	1.16	0.04 0.04	0.23 0.23	2.26 2.66	0.1 0.1

Table 1. Chemical Compositions of Water Generated from Computer Simulation with the Program PHREEQE [See text section "Application of Trilinear Diagram: I. Gypsum Dissolution" for detail. Ion concentrations are in meq/l. This table also includes the column designation (alphabetic) and row number (numeric) of the worksheet.]

of a quantity of data on the same graph without losing clarity of data points; therefore, it is the most frequently used graphic method for hydrochemical study.

Because the locations of the data points in the trilinear diagram reflect the chemical characteristics of the water, the concept of hydrochemical facies is frequently used to describe the chemical property of water. This concept has been discussed in many hydrogeology textbooks. The concept of hydrochemical facies is very useful to illustrate the change in chemical characteristics as water migrates down the hydraulic gradient. The trend observed on the trilinear diagram would give an indication of the type of reactions that are responsible for the change in a qualitative way. For example, dissolution of gypsum (CaSO<sub>4</sub>  $\cdot$  2H<sub>2</sub>O) may change a Ca-HCO<sub>3</sub> type water to a Ca-SO<sub>4</sub> water. However, it is dangerous to define the mechanism responsible for the change of water type solely by the trend observed on the trilinear diagram. Alternative mechanisms should be considered and tested by other means.

In addition to the concept of hydrochemical facies, a straight line on the trilinear diagram may indicate a mixing system. Recently, Morris *et al.* (1983) published a program in BASIC which plots a trilinear diagram and tests for the possibility of mixing. The two end-members mixing line bears the assumption that all the ions remain in the solution after mixing. Therefore, a mixing line conclusion hinges on the validity of this assumption. Precipitation, dissolution of minerals, and ion exchange reaction are very common in natural water, and they may cause deviation from a straight line. Therefore, it is risky to base a mixing conclusion on a straight line on the trilinear diagram. Besides, pure mineral dissolution can also result in a straight line on the trilinear diagram, i.e. a straight line on the trilinear diagram may not definitely indicate mixing. Therefore, this approach should be used with great care when searching for mixing in a ground-water system.

In order to illustrate the above generalized statements, we used the computer program PHREEQE (Parkhurst, Thorstenson, and Plummer, 1980) to generate a series of water compositions along mixing and/or reaction trends. Two mixing/ reaction paths will be examined in the next two sections.

#### I. Gypsum Dissolution

Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is a common mineral in most ground-water systems and dissolution of gypsum may cause calcite to precipitate. For example, Back et al. (1983) found that dolomite dissolution and concurrent precipitation of calcite in the Mississippian Pahasapa Limestone aquifer is driven by gypsum dissolution. Table 1 lists the results of computer simulation with PHREEQE. One mmole/liter of gypsum is added to end member A in four equal steps to generate end member B. Calcite equilibrium is maintained at each step. Intermediate waters are designated A+GYP1, A+GYP2, and A+GYP3. Table 1 also lists intermediate mixtures (MIX1 through MIX5) between end members A and B. Both products of gypsum dissolution  $(\Box)$  and mixtures (+) between

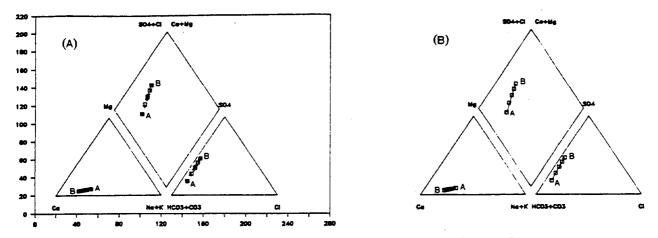


Fig. 3. (A): Trilinear diagram of water A with progressive gypsum dissolution to B (symbol  $\Box$ ). Intermediate mixtures between A and B are also plotted (symbol +).

(B): Same as Figure 3(A). Mixing trend is shown as a line by redefining the plotting format. The X-Y coordination was eliminated by specifying different colors for grid and by not loading the pen during plotting. However, this trick cannot be used if a dot matrix printer is used rather than a pen plotter.

end members A and B as listed in Table 1 are plotted on Figure 3. Figure 3(A) is the trilinear diagram generated from LOTUS 1-2-3 macros. Figure 3(B) is generated by redefining the plotting format of Figure 3(A). The mixing trend between end members A and B is plotted as a line on Figure 3(B). It is clear from this figure that a straight line on the trilinear diagram does not prove "mixing." The mixing line is indistinguishable from the gypsum-dissolution-calcite equilibrium trend.

#### II. Ca-Na Ion Exchange Reaction

Ca-Na ion exchange reaction is a common and important reaction in many aquifers. In the central San Juan Basin, New Mexico, dissolution of calcite driven by Ca-Na ion exchange explain the high Na, low Ca, high alkalinity, and high pH of the water (Phillips et al., 1987). Similar reaction has been observed in Maryland (Chapelle and Knobel, 1983).

Table 2 lists a computer-simulated chemical

PLE # MEMBER A XCH1 XCH2 XCH3 XCH4 MEMBER B MEMBER A		22.50 22.50 22.50 22.50 22.50 22.50 22.50 22.50 22.50	pH 7.40 8.32 8.72 9.12 9.46 9.76	ALKAL. 2.82 3.33 3.54 3.98 4.87 6.47	S102 0.55 0.55 0.55 0.55 0.55	Ca 2.54 0.37 0.15 0.07 0.03	Mg 0.34 0.34 0.34 0.34	Na 1.16 3.84 4.27 4.80 5.72	K 0.04 0.04 0.04 0.04	C1 0.23 0.23 0.23 0.23	SO4 0.66 0.66 0.66	NO3
XCH1 XCH2 XCH3 XCH4 MEMBER B		22.50 22.50 22.50 22.50 22.50 22.50 22.50	7.40 8.32 8.72 9.12 9.46	2.82 3.33 3.54 3.98 4.87	0.55 0.55 0.55 0.55	2.54 0.37 0.15 0.07	0.34 0.34 0.34 0.34	3.84 4.27 4.80	0.04 0.04 0.04	0.23 0.23	0.66	0.1
XCH1 XCH2 XCH3 XCH4 MEMBER B		22.50 22.50 22.50 22.50 22.50 22.50	8.32 8.72 9.12 9.46	3.33 3.54 3.98 4.87	0.55 0.55 0.55	0.37 0.15 0.07	0.34 0.34 0.34	3.84 4.27 4.80	0.04 0.04 0.04	0.23 0.23	0.66	0.1
XCH1 XCH2 XCH3 XCH4 MEMBER B		22.50 22.50 22.50 22.50 22.50 22.50	8.32 8.72 9.12 9.46	3.33 3.54 3.98 4.87	0.55 0.55 0.55	0.37 0.15 0.07	0.34 0.34 0.34	3.84 4.27 4.80	0.04 0.04 0.04	0.23 0.23	0.66	0.1
XCH1 XCH2 XCH3 XCH4 MEMBER B		22.50 22.50 22.50 22.50 22.50 22.50	8.32 8.72 9.12 9.46	3.33 3.54 3.98 4.87	0.55 0.55 0.55	0.37 0.15 0.07	0.34 0.34 0.34	3.84 4.27 4.80	0.04 0.04 0.04	0.23 0.23	0.66	0.1
XCH2 XCH3 XCH4 MEMBER B		22.50 22.50 22.50 22.50 22.50	8.72 9.12 9.46	3.54 3.98 4.87	0.55	0.15 0.07	0.34	4.27 4.80	0.04	0.23	0.66	0.1
XCH3 XCH4 MEMBER B		22.50 22.50 22.50	9.12 9.46	3.98 4.87	0.55	0.07	0.34	4.80	0.04			
XCH4 MEMBER B		22.50 22.50	9.46	4.87						0.23	A //	
MEMBER B		22.50			0.55	0.03	0 2/	6 7 7			0.66	0.1
			9.76	6.47			0.34	* * * *	0.04	0.23	0.66	0.1
MEMBER A					0.55	0.02	0.34	7.33	0.04	0.23	0.66	0.1
MEMBER A												
		22.50	7.40	2.82	0.55	2.54	0.34	1.16	0.04	0.23	0.66	0.1
1+CALCE	Q	22.50	7.71	3.06	0.55	1.55	0.34	2.39	0.04	0.23	0.66	0.1
2+CALCE	Q	22.50	8.17	3.27	0.55	0.52	0.34	3.63	0.04	0.23	0.66	0.1
3+CALCE	Q	22.50	8.69	3.52	0.55	0.16	0.34	4.24	0.04	0.23	0.66	0.1
4+CALCE	•	22.50	9.15	4.04	0.55	0.06	0.34	4.86	0.04	0.23	0.66	0.1
5+CALCE	Q	22.50	9.55	5.24	0.55	0.03	0.34	6.10	0.04	0.23	0.66	0.1
MEMBER B		22.50	9.76	6.47	0.55	0.02	0.34	7.33	0.04	0.23	0.66	0.1
MEMBER A												0.1
1							+ ·					0.1
2												0.1
3												0.1
4			-									0.1
5												0.1
		22.50	9.76	6.47	0.55	0.02	0.34	7.33	0.04	0.23	0.66	0.11
1 2 3 4 5			22.50 22.50 22.50 22.50 22.50 22.50	22.50 8.60 22.50 9.16 22.50 9.31 22.50 9.43 22.50 9.62	22.50 8.60 3.55 22.50 9.16 4.28 22.50 9.31 4.64 22.50 9.43 5.01 22.50 9.62 5.74	22.50         8.60         3.55         0.55           22.50         9.16         4.28         0.55           22.50         9.31         4.64         0.55           22.50         9.43         5.01         0.55           22.50         9.62         5.74         0.55           22.50         9.62         5.74         0.55           22.50         9.76         6.47         0.55	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22.50         8.60         3.55         0.55         2.04         0.34           22.50         9.16         4.28         0.55         1.54         0.34           22.50         9.16         4.28         0.55         1.54         0.34           22.50         9.31         4.64         0.55         1.28         0.34           22.50         9.43         5.01         0.55         1.03         0.34           22.50         9.62         5.74         0.55         0.53         0.34           22.50         9.76         6.47         0.55         0.02         0.34	22.50       8.60       3.55       0.55       2.04       0.34       2.39         22.50       9.16       4.28       0.55       1.54       0.34       3.63         22.50       9.31       4.64       0.55       1.28       0.34       4.24         22.50       9.43       5.01       0.55       1.03       0.34       4.86         22.50       9.62       5.74       0.55       0.53       0.34       6.10         MEMBER B       22.50       9.76       6.47       0.55       0.02       0.34       7.33	22.50         8.60         3.55         0.55         2.04         0.34         2.39         0.04           22.50         9.16         4.28         0.55         1.54         0.34         3.63         0.04           22.50         9.16         4.28         0.55         1.54         0.34         3.63         0.04           22.50         9.31         4.64         0.55         1.28         0.34         4.24         0.04           22.50         9.43         5.01         0.55         1.03         0.34         4.86         0.04           22.50         9.62         5.74         0.55         0.53         0.34         6.10         0.04           22.50         9.76         6.47         0.55         0.02         0.34         7.33         0.04	22.50       8.60       3.55       0.55       2.04       0.34       2.39       0.04       0.23         22.50       9.16       4.28       0.55       1.54       0.34       3.63       0.04       0.23         22.50       9.31       4.64       0.55       1.28       0.34       4.24       0.04       0.23         22.50       9.43       5.01       0.55       1.03       0.34       4.86       0.04       0.23         22.50       9.62       5.74       0.55       0.53       0.34       6.10       0.04       0.23         MEMBER B       22.50       9.76       6.47       0.55       0.02       0.34       7.33       0.04       0.23	22.50       8.60       3.55       0.55       2.04       0.34       2.39       0.04       0.23       0.66         22.50       9.16       4.28       0.55       1.54       0.34       3.63       0.04       0.23       0.66         22.50       9.31       4.64       0.55       1.28       0.34       4.24       0.04       0.23       0.66         22.50       9.43       5.01       0.55       1.03       0.34       4.86       0.04       0.23       0.66         22.50       9.62       5.74       0.55       0.53       0.34       6.10       0.04       0.23       0.66         22.50       9.62       5.74       0.55       0.53       0.34       6.10       0.04       0.23       0.66         MEMBER B       22.50       9.76       6.47       0.55       0.02       0.34       7.33       0.04       0.23       0.66

Table 2. Chemical Compositions of Water Generated from Computer Simulation with the Program PHREEQE [See text section "Application of Trilinear Diagram: II. Ca-Na Ion Exchange Reaction" for detail. Ion concentrations are in meq/l. This table also includes column designation (alphabetic) and row number (numeric) of the worksheet.]

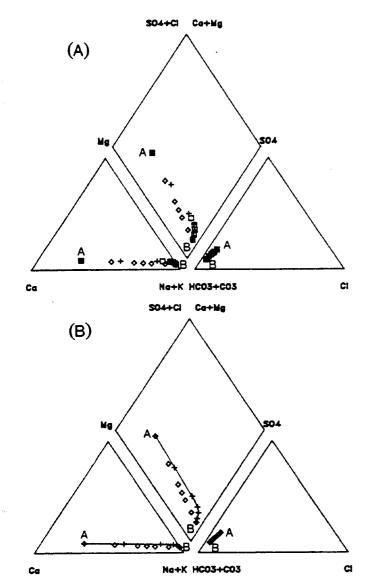


Fig. 4. (A): Trilinear diagram of water A with progressive Ca-Na ion exchange reaction (symbol □). Various mixtures between A and B are represented by symbol ◊. Post-mixing equilibration with calcite (symbol +) would deviate the mixing trend from the original straight line and become indistinguishable from the Ca-Na ion exchange reaction. Calcite equilibrium is maintained during the Ca-Na ion exchange reaction.

(B): Same as Figure 4(A). The Ca-Na ion exchange trend is represented as a line by redefining the graph format.

composition of water. End member B is generated by progressive Ca-Na ion exchange while maintaining calcite-equilibrium (rows 5 through 10, Table 2). Also listed in Table 2 are chemical composition of mixtures between end members A and B. Calcite-equilibrium is maintained for the waters on rows 13 through 17.

Figure 4 is a trilinear diagram of the three groups of water listed in Table 2. Although simple mixing (symbol  $\diamond$ ) is distinguishable from a Ca-Na ion exchange trend (symbol  $\Box$ ), post-mixing equilibration with calcite deviates from a simple mixing line (symbol +). Therefore, mixing may also take place in a series of waters plotted on a curved line on the trilinear diagram.

In this example, the similarity in chemical composition between a Ca-Na ion exchange trend (first group, Table 2) and post-mixing calciteequilibration trend (second group, Table 2) does not mean that it is impossible to identify the correct mechanism. Other parameters, such as stable isotopes of hydrogen, oxygen, carbon, and sulfur, should help solve the puzzle.

#### Summary and Conclusions

Hill and Piper's trilinear diagram is a valuable graphic tool for representing hydrochemical data. It effectively illustrates the chemical characteristics of a ground-water system from recharge to the deeper portion of the aquifer. The tedious plotting task can be greatly reduced if one takes advantage of the speed and accuracy of a computer. A set of simple equations is presented to transfer the tertiary system of the trilinear diagram to X-Y coordination and electronic spreadsheet macros for plotting a trilinear diagram.

The concept of hydrochemical facies is useful in characterization of the chemical nature of water. However, it can be misleading to define hydrogeochemical reactions based on changes in hydrochemical facies.

Although mixing may be a common phenomenon, post-mixing reactions may obscure the mixing trend on a trilinear diagram. Reactions such as dissolution, precipitation, ion exchange reaction, and even CO<sub>2</sub> outgassing, are common in natural waters. The assumption that all ions remain in solution after mixing for a linear mixing line on a trilinear diagram cannot be adopted unconditionally. On the other hand, simple mineral dissolution may result in a straight line on a trilinear diagram, and therefore, a straight line on the diagram does not necessarily indicate mixing. In reality, due to the heterogeneity of most ground-water systems, the chemical composition of the end member may not be well defined. Analytical errors may introduce additional uncertainty. All of these would make it difficult to recognize a mixing line on a trilinear diagram.

Based on the above considerations, the trilinear diagram is a useful tool to characterize the chemical composition of a ground-water system, that is, hydrochemical study. However, for detailed hydrogeochemical investigations, such as water-rock interaction, quantitative hydrogeochemical study, one should include efforts such as consideration of the isotopic composition, mineralogy, and reaction path simulation for screening hypotheses. The real mechanism(s) that is (are) operating in a groundwater system may elude the researcher if these hydrogeochemical approaches are ignored.

#### Acknowledgments

The author wishes to thank Dr. Austin Long and the Laboratory of Isotope Geochemistry, Department of Geosciences, University of Arizona, for supporting this study.

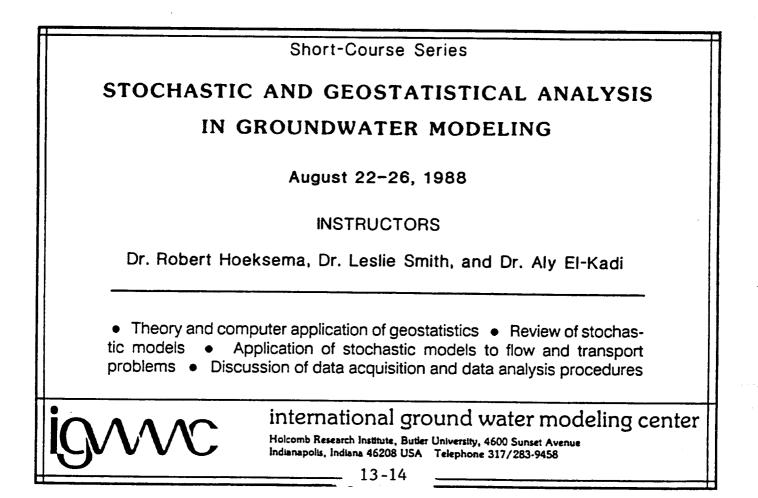
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# Reliability of Chemical Analyses of Water Samples — The Experience of the UMTRA Project

by George Rice, James Brinkman, and Dianna Muller

#### Abstract

Ground water quality investigations require reliable chemical analyses of water samples. Unfortunately, laboratory analytical results are often unreliable. The Uranium Mill Tailings Remedial Action (UMTRA) Project's solution to this problem was to establish a two-phase quality assurance program for the analysis of water samples. In the first phase, eight laboratories analyzed three solutions of known composition. The analytical accuracy of each laboratory was reliability of the selected laboratories.

The following conclusions are based on two years of experience with the UMTRA Project's Quality Assurance Program:

- The reliability of laboratory analyses should not be taken for granted.
- Analytical reliability may be independent of the prices charged by laboratories.
- Quality assurance programs benefit both the customer and the laboratory.

#### Introduction

The purpose of the Department of Energy's Uranium Mill Tailings Remedial Action (UMTRA) Project is to reduce or eliminate the hazards posed by inactive uranium mill tailings. One hazard is the contamination of ground water by heavy metals, radionuclides and milling reagents leached from the tailings.

Major project objectives are to determine the extent of existing ground water contamination, and to predict the effects of remedial actions on future ground water quality. Meeting these objectives requires reliable chemical analyses of water samples. When the project began, the reliability of laboratory analyses was taken for granted. Laboratories were awarded contracts on the basis of laboratory visits by project quality assurance personnel. During these visits, the laboratory's internal quality control program and the qualifications of key laboratory personnel were checked. The contracted laboratories also participated in state or EPA sponsored water-quality performance evaluation programs. However, it soon became apparent that this was not sufficient. Laboratories often submitted sample analyses having cation-anion balances greater than 50 percent. When solutions of known composition were sent to the laboratories, the reported results were often wrong by a factor of more than 10.

These unreliable results caused the UMTRA Project to establish a two-phase quality assurance program for the analysis of water samples. At the same time, it was recognized that reliable analyses of improperly taken samples were also of little value. Therefore, a stringent set of protocols designed to assure proper sampling and field testing of water samples was implemented.

In the first phase of the program, eight laboratories participated in prequalification. Each laboratory analyzed three solutions of known composition. The accuracy of each laboratory analysis was scored and three laboratories were selected to receive contracts.

The second phase consists of monitoring the reliability of analyses submitted by the selected laboratories. This phase will continue as long as the project requires analysis of water samples.

#### Phase One: Prequalification

The purpose of the prequalification was to find at least three laboratories that could provide the project with reliable analyses. This phase consisted of several steps.

First, initial accuracy criteria were established (Table 1). These criteria were based on project requirements and what it was hoped most laboratories could achieve. The

criteria were reviewed by personnel at the Pacific Northwest Laboratory, the Nuclear Regulatory Commission, and Bendix Field Engineering Corp. Some reviewers stated that the criteria should be speciesspecific, although they could not specify which species should be subjected to more or less stringent criteria. Therefore, it was decided that if the criteria were to be revised, the revision would occur after evaluating the performance of laboratories participating in the prequalification.

In the second step, laboratories were invited to participate in the prequalification through an advertisement in the *Commerce Business Daily*. Thirteen laboratories chose to participate.

Thirteen sets of solutions of known composition were then prepared by Bendix. Each set consisted of three samples, each of which contained varying concentrations of all of the constituents listed in Table 1. The sets sent to each laboratory were identical. Bendix provided the project with the known concentrations of constituents in each solution, as well as the uncertainties associated with the preparation of each solution. The known values and uncertainties were used to calculate an acceptable range for each constituent.

The lower limit of the acceptable range is:

<u>C(1-U)</u>	
(1 + E)	(1)
where:	

C = known concentration

- U = uncertainty associated with preparation of known solution (percent/100)
- E = acceptable error, from accuracy criteria, Table 1 (percent/100)

The upper limit of the acceptable range is:

C(1+U)(1+E) (2)

where the variables are as defined.

Eight of the 13 laboratories submitted analytical results. Their results were evaluated according to the initial accuracy criteria. This evaluation made it clear that some of the criteria were too stringent and needed to be revised. The revised criteria reflected the analytical abilities of the laboratories while preserving the accuracy required to meet project objectives. The constituents were divided into three groups (Table 1).

- Group 1 contains the toxic trace constituents that are commonly associated with uranium mill tailings. The criteria for Group 1 constituents were not revised.
- Group 2 contains most of the trace constituents not included in Group 1.
- Group 3 contains the major ions and the trace constituents that may control leachate chemistry.

The revised criteria were used to score the eight responding laboratories. When analytical results were not within the acceptable range, or results were not reported, an unacceptable result was recorded. The laboratories scored 77, 74, 72, 70, 69, 46, 31, and 16

TABLE 1         Accuracy Criteria						
Group	Concentration of Constituent in Known Concentration (mg/L)	Acceptable Error, in Percent				
I*	<0.01 >0.01 to <0.1 >0.1 to <1.0 >1.0	100 50 25 10				
II	<pre>&gt;1.0 &lt;0.01 &gt;0.01 to &lt;0.1 &gt;0.1 to &lt;1.0 &gt;1.0</pre>	200 100 50 20				
III	<0.01 >0.01 to <0.1 >0.1 to <1.0 >1.0	200 100 50 10				

\*The initial accuracy criteria for all constituents were identical to the Group I criteria.

Group I: Sb, As, Ba, Co, Cr, Pb, Hg, Mo, Se, U, Pb-210, Po-210, Ra-226, Ra-228, Th-230. Group II: B, CN,  $H_2S$ ,  $NH_4$ ,  $NO_2$ ,  $PO_4$ , Co, Cu, Ni, Ag, Sr, Sn, V, Zn, TOC. Group III: Cl,  $SO_4$ ,  $NO_3$ , Na, K, Mg, Ca, F, Al, Fe, Mn, SiO<sub>2</sub>, TDS.

percent acceptable results. A summary of the prequalification results is given in Table 2.

Sixty-seven percent of all analyses were within the acceptable range. Sixty percent of the reported values were higher than the known concentration. The laboratories performed best when analyzing for TDS, zinc, tin, and radionuclides. More than 50 percent of analyses for most of the common ions and toxic metals were acceptable. Iron and aluminium were among the constituents for which the laboratories performed most poorly. Both of these metals exert a strong influence on leachate chemistry.

It should be noted that the prequalification analyses were probably more accurate than most analyses performed by the laboratories. This is because they knew they were being tested and the known solutions were made with very pure materials that minimized analytical interferences. The results of the prequalification clearly showed the need for independent checks of analytical reliability after laboratories were selected to receive contracts.

The five laboratories with the top scores were visited by project personnel. After considering quality control procedures, equipment, space, and personnel qualifications, three laboratories were selected to receive contracts. Although the cost of analyses was not considered in the selection process, there were large differences among the three laboratories. For an analysis of all the constituents listed in Table 2, Laboratory A charged \$447, Laboratory B \$235, and Laboratory C charged \$575.

Analyte	Known Concentration (mg/L)	Acceptable Range (mg/L)	Range of Reported Values (mg/L)	Percent Reported Values Acceptable
Ca	$636. \pm 1.1\%$	572 - 707	285 - 865	29
K	$5.72 \pm 1.1\%$	5.14 - 6.36	5.24 - 7.64	71
Mg	$55.9 \pm 1.1\%$	50.3 - 62.2	50.0 - 99.8	57
Na	$33.0 \pm 1.1\%$	29.7 - 36.7	24.2 - 41.4	71
Cl	$206. \pm 1.0\%$	185 - 229	200 - 245	86
F	$0.987 \pm 2.0\%$	0.645 - 1.51	0.80 - 1.57	86
SiO <sub>2</sub>	$6.85 \pm 2.8\%$	6.05 - 7.75	2.16 - 7.0	43
SO₄	$1520 \pm 2.0\%$	1350 - 1710	1450 - 1740	86
TDS	$3200 \pm 2.5\%$	2840 - 3610	2970 - 3600	100
Al	$0.126 \pm 1.2\%$	0.083 - 0.191	<0.05 - 3.75	0
Fe	$0.126 \pm 1.2\%$	0.083 - 0.191	0.149 - 0.42	43
Mn	$0.126 \pm 1.2\%$	0.083 - 0.191	0.025 - 0.16	86
Ag	$0.076 \pm 1.2\%$	0.050 - 0.115	0.015 - 0.12	57
As	$0.088 \pm 1.2\%$	0.058 - 0.134	0.039 - 0.106	83
Ba	$0.114 \pm 1.2\%$	0.09 - 0.144	<0.05 - 0.54	33
Cd	$0.076 \pm 1.2\%$	0.050 - 0.115	0.020 - 0.090	86
Cr	$0.076 \pm 1.2\%$	0.050 - 0.115	<0.05 - 0.27	71
Hg	$0.076 \pm 1.2\%$	0.050 - 0.115	0.026 - 0.074	75
Mo	$0.033 \pm 1.2\%$	0.022 - 0.050	0.011 - 0.14	43
Sb	$0.01 \pm 1.2\%$	0.007 - 0.015	0.009 - 0.032	83
Se	$0.076 \pm 1.2\%$	0.050 - 0.115	0.055 - 0.102	100
*Pb-210	$4.8 \pm 7.0\%$	2.23 - 10.3	1.9 - 7.2	75
*Po-210	$17.1 \pm 3.0\%$	8.22 - 35.2	1.1 - 25.0	88
*Ra-226	$10.0 \pm 1.4\%$	4.93 - 20.3	5.7 - 14.9	100
*Ra-228	$14.8 \pm 7.0\%$	6.88 <b>-</b> 31.7	5.86 - 86.2	62
*Th-230	$13.5 \pm 2.3\%$	6.59 - 27.6	8.0 - 20.0	100
J	$0.076 \pm 1.2\%$	0.050 - 0.115	0.007 - 0.49	75
Co	$0.101 \pm 1.2\%$	0.067 - 0.153	0.088 - 0.36	71
Cu	$0.101 \pm 1.2\%$	0.067 - 0.153	0.015 - 0.20	71
Ni	$0.101 \pm 1.2\%$	0.067 - 0.153	0.09 - 0.28	71
Sn	$0.050 \pm 1.2\%$	0.025 - 0.101	0.044 - 0.075	100
Sr	$0.176 \pm 2.9\%$	0.115 - 0.272	0.178 - 0.6	57
Zn	$0.101 \pm 1.2\%$	0.067 - 0.153	0.084 - 0.15	100
В	$0.088 \pm 1.2\%$	0.043 - 0.178	<0.01 - 4.0	50
S	$22.9 \pm 2.5\%$	17.9 - 29.3	1.1 - 45	57
ALK	$16.1 \pm 0.7\%$	14.5 - 17.8	14.3 - 21.6	43
CN	$0.59 \pm 4.2\%$	0.38 - 0.92	0.13 - 0.91	83
TOC	$1.46 \pm 1.0\%$	1.16 - 1.84	1.5 - 4.0	33

 TABLE 2

 Summary of Prequalification Results<sup>1</sup>

\*units = pCi/L

<sup>1</sup>Each laboratory analyzed three solutions with total dissolved solid concentrations of 430 mg/L, 3200 mg/L, and 6400 mg/L. This table summarizes the results of the 3200 mg/L solution.

### Phase Two: Post-Laboratory Selection Monitoring

• Complete analytical results would be submitted to the project within five weeks of receiving each sample set.

The purpose of this phase is to monitor the reliability of analyses reported by the three laboratories selected in the prequalification. The laboratories agreed to the following conditions. • The acceptability of analytical results would be judged by the project according to pre-established cationanion balance and accuracy criteria. There would be no payment for unacceptable results.

#### **Cation-Anion Balance Criterion**

The analysis of a sample is unacceptable if the absolute value of the cation-anion balance is greater than 5 percent. The cation-anion balance is calculated as follows.

$$Balance = \frac{meq Cations - meg Anions}{meq Cations + meg Anions} (100) (3)$$

The balance is calculated using every constituent that contributes more than 0.1 percent to the sample's total dissolved solids content. If redox sensitive constituents are used in the balance, the balance is calculated for both oxidizing and reducing conditions and the laboratory is given the benefit of the doubt. Alkalinity, a major contributor to the balance, is measured in the field by project personnel. The alkalinity value is not given to the laboratory. The laboratory is required to re-analyze those samples that do not satisy the balance criterion. The laboratory is not paid for analyzing these samples until re-analysis results in a balance of less than 5 percent.

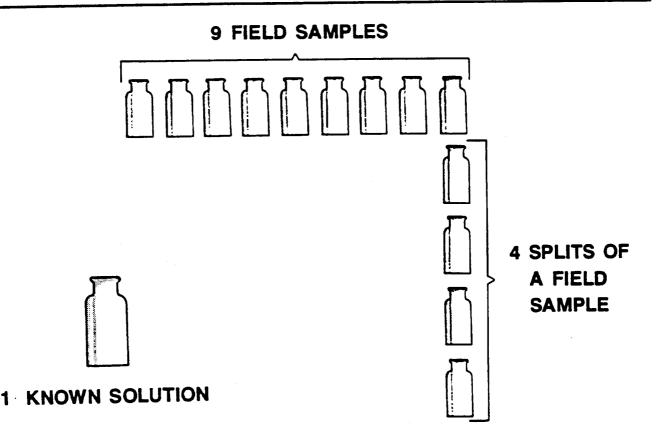
#### **Accuracy Criteria**

Each sample set is divided into lots consisting of no more than nine field samples and at least one solution of known composition (Figure 1). Known solutions are disguised as field samples. The value reported for a constituent in a known solution is compared to the acceptable range of values for that constituent. The acceptable range is calculated from Equations 1 and 2. When the analysis of a constituent in a known solution does not fall within the acceptable range, the laboratory is required to reanalyze the entire lot for that constituent. The laboratory is not paid for that constituent until re-analysis produces acceptable results.

In addition to monitoring cation-anion balances and accuracy, analytical precision is monitored by including at least four replicates of a field sample in each sample set sent to the laboratory. The replicates are disguised as individual samples. The coefficient of variation is calculated for each constituent in the set of replicates and compared to the precision criteria shown in Table 3. The precision criteria are based on the degree of accuracy required for each constituent. When replicate analyses exceed the coefficients of variation, the laboratory is notified. This information helps the laboratory identify and correct analytical problems. Payment is not withheld.

The evaluation of laboratory performance indicates that initial analytical results are often unreliable (Table 4). Decisions based on these analyses could lead to costly mistakes. Re-analysis usually results in data that are significantly more reliable. Both the project and the laboratories benefit from the monitoring program. The project gets more reliable data, and the laboratories are able to improve the quality of their work. In general, the reliability of analyses has improved over time.

Two of the laboratories are no longer used by the project. Although analytical results from Laboratory A improved with time, the laboratory was unable to improve enough to satisfy the project's requirements. Laboratory C was unable to meet the required five-week turn-around time. This leaves the project in the undesirable position of having to rely on a single laboratory. Should significant problems develop with Laboratory B, the project could be without a prequalified laboratory.



### TABLE 3 Precision Criteria

Acceptable Percent Error for Constituent	Maximum Coefficient of Variation
200	1.38
100	0.84
50	0.45
20	0.18
10	0.09

However, thus far, Laboratory B has shown it can serve all the project's analytical needs in a timely and reliable manner.

#### Conclusions

Based on the experience of the UMTRA Project, the following conclusions are made:

- The reliability of laboratory analyses cannot be taken for granted. Reliability is not necessarily guaranteed by laboratory in-house quality control programs or by a laboratory's participation in state or EPA waterquality performance evaluation programs.
- Quality assurance programs benefit both the client and the laboratory. The client gets more reliable results, and the laboratory is able to identify and correct analytical problems.
- The reliability of analyses and the quality of service provided may be independent of the prices charged by a laboratory.

#### Acknowledgment

This study was completed as part of the Department of Energy's Uranium Mill Tailings Remedial Action Project, headquartered in Albuquerque, New Mexico, and was supported under DOE Contract No. DE-AC04-82AL14086 to Jacobs Engineering Group Inc., the Technical Assistance Contractor (TAC). The TAC consists of Jacobs Engineering Group Inc., Roy F. Weston Inc., and Sergent, Hauskins & Beckwith Geotechnical Engineers Inc.

#### **Biographical Sketches**

George F. Rice, geohydrologist, joined Sergent, Hauskins & Beckwith Geotechnical Engineers Inc. (4700 Lincoln Rd., N.E., Albuquerque, NM 87109) in 1983, and is working on the UMTRA Project. His duties include characterization of low-level nuclear waste sites, design of monitor well and vadose zone monitoring networks, application of ground water transport codes, and prediction of the effects of remedial actions on ground water.

Dianna L. Muller, civil engineer, joined the UMTRA Project in 1985 as a member of the Hydrological Services Group. She works for Roy F. Weston Inc. (5301 Central Ave., N.E., Suite 1000, Albuquerque, NM 87108). Her

# TABLE 4Laboratory Performance,Post-Selection Monitoring

Accuracy C	riteria		
Laboratory	A	В	С
Number of Known			
Constituents Analyzed	354	1543	274
% Acceptable Analyses			
Initial analysis	83	82	68
lst re-analysis	90	96	80
2nd re-analysis		99.5	
Balance Crit	erion		<u></u>
Number of Samples Analyzed	145	495	73
% Acceptable Analyses			
Initial analysis	90	83	45
lst re-analysis	92	91	65
2nd re-analysis		96	_

duties include primary responsibility for laboratory water quality data analyses meeting UMTRA quality assurance specifications and support to the staff geohydrologists.

James E. Brinkman, senior geohydrogeologist, joined R.oy F. Weston Inc. (5301 Central Ave., N.E., Suite 1000, Albuquerque, NM 87108) in February 1987, as senior geohydrologist. His duties include project management for hydrogeologic field investigations at mill tailings and hazardous and mixed waste sites, design of ground water monitoring networks, design of contaminant control and removal measures, and predictive analysis of future impacts utilizing computer modeling techniques.

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# EVALUATION OF LABORATORY ANALYTICAL DATA

by Richard Meyerhein N.M. Scientific Laboratory Division

Considering the cost of collecting samples and their analyses it would be sensible to expend some time and effort in selecting an analytical laboratory. Most laboratories now expect their clients to demand accurate analyses, and the labs expend considerable effort to maintain a Quality Assurance/Quality Control (QA/QC) program. Most labs have available documents demonstrating their QA/QC and are willing to send them to and/or discuss them with clients. Labs doing analyses for the government are required to take part in external proficiency programs for certification. Even considering the above, it is a good idea for each client to determine for himself the precision and accuracy of their laboratory. This can best be done with "blind" check samples and duplicates, and by splitting samples with other laboratories.

Whenever a lab result doesn't make "sense", advise the laboratory and work with them to find the error if one has occurred. Laboratories are not infallible, and most of them will willing admit to that fact. Most will work with clients to correct errors, and to assure that the client gets the "best" result. Often however, inaccurate results come about because of an improper request or improperly collected sample and not because of laboratory error.

#### SAMPLE COLLECTION AND SUBMISSION

Proper sample collection and submission are very important for meaningful results. The analytical request form should be completely filled out with as much information about what might be in the sample added in the remarks. The sample itself should be clearly labeled to decrease the chance of misidentification. If there is a chance that there might be legal action as a result of the sample then the sample should be sealed with an evidentiary seal and a chain of custody be established. The best results will be achieved when there is good communication between the submitter and the analytical laboratory.

Whenever a sample is collected, considerable attention should be given to what type of sample (soil, water, etc.), what volume, what it should be collected in, and how it should be preserved during shipment to the laboratory.

#### **Evaluation of Laboratory Analytical Data**

Generally bottles for organic analyses should be obtained directly from the laboratory. Since most organic analyses involve very small concentrations of somewhat volatile compounds, care should be taken to avoid any possibility of contamination of the sample bottles both before and after the sample is collected. Make sure that the sample collected is representative of the result desired. Samples with two phases (oil on water) are impossible for a laboratory to quantify and give a meaningful result. When having water analyzed, even a trace of free product (gasoline) could cause extreme errors in the analytical result. Samples exposed to the air or poured from one container to another will loose volatiles. Samples that come into contact with plastic, rubber, paper or wax seals will almost certainly loose most of their organics into the seal. Make sure that only the Teflon<sup>R</sup> side of the seal comes into contact with the sample.

12-2

Since most organics are food to one type of bacteria or another, it is important to consider sample preservation. This should be discussed with the laboratory and be consistent with the methodology which might be required (EPA, etc.). Generally organic samples should be preserved at  $4^{\circ}$ C (wet ice - do not freeze) and kept out of sunlight. Trihalomethane analyses for the Safe Drinking Water Act require that a reducing substance be added to the sample when it is collected to reduce any free chlorine. Free chlorine will react with organics to form Trihalomethanes.

Often field blanks will confirm that there was no contamination of the sample or bottles. For volatile samples field blanks are a good idea and are required by many analytical methods. Obtain field blanks from the laboratory, because it is very difficult to obtain "pure" water.

There are a number of factors which should be considered when sampling for organics. Below are listed some problems which can affect the accuracy and useability of the results:

#### SAMPLING PROBLEMS

NO SAMPLING PLAN

Once the purpose of sampling has been established the appropriate sampling strategy can be chosen. Considering the cost of analyses, make sure that there aren't too many or too few samples collected, and that you are prepared when you need to collect a sample.

#### CONTAMINATED SAMPLE CONTAINERS OR EQUIPMENT

There should be considerable concern about the contamination of sample containers and sampling equipment as well as quality control to show that the sample was not contaminated.

#### IMPROPER SAMPLE CONTAINERS

Organic samples must be collected in glass and not come into contact with plastics, rubber, or other organics.

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#### IMPROPER SAMPLE COLLECTION

There are many possible errors in the collection of organics. Sample collection should be completely understood and defined in the sampling plan. It is especially easy to obtain inconsistent results with volatile organics.

#### **CROSS CONTAMINATION**

Volatile organics can leave one sample and contaminate nearby samples. Keep highly contaminated samples in a separate container.

#### INSUFFICIENT DOCUMENTATION

Complete field notes can make a considerable difference in being able to interpret results. The observations recorded should include:

- . Collectors names
- . Well identification

. Static water level depth and measurement technique

. Presence of immiscible layers, detection method and thickness

. Well yield, high or low

- . Evacuation procedure/equipment
- . Purge volume, pumping rate and time pumped
- . Appearance of ground water
- . Sample collection procedure/equipment
- . Equipment cleaning procedure
- . Date and time of collection
- . Sample treatment and containers
- . Parameters requested for analysis
- . Field analysis procedures and results
- . Sample packing, distribution, and transportation
- . Other field observations including climatic conditions and problems encountered

#### INCORRECT PRESERVATION/TRANSPORTATION

Most organics are not stable for long periods of time. All organic samples should be kept on ice at 4°C until they are analyzed. Any chlorine residual in the sample should be reduced with ascorbic acid, sodium thiosulfate or sodium sulfite to stop the formation of trihalomethanes and other compounds.

#### INCORRECT ANALYTICAL REQUEST

Without a good understanding of the analytical procedures used by the laboratory it is possible that the analytical results won't provide the desired information. Some labs do only "target" compound analyses and don't report unknown compounds that were detected.

#### EVALUATION OF LABORATORY RESULTS

The laboratory user should assure himself the the laboratory is providing quality results. The user should be aware of the laboratories quality control program and

know the precision and accuracy of their analyses. The user may wish to assure himself of the labs reliability by submitting a "blind" spiked sample. Because of the complexity of the analyses often organic results are not as precise as other analyses, and interfering substances can cause the lower detection limit to be considerably higher than the method states.

13-4

#### VISUALIZATION OF RESULTS

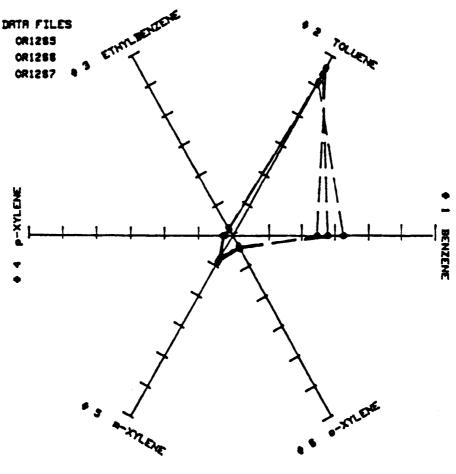
When comparing results from several wells at the same site one can often have too much data to easily spot trends. The graphic representation of data often makes it much easier to understand and interpret the multitude of data that one often obtains. John D. Hem in his paper "Study and Interpretation of the Chemical Characteristics of Natural Water" provides some excellent information on the interpretation of water analyses. While it is beyond the scope of this talk to cover his paper, I have included a portion (pp. 162-188) of his paper on the "Organization and Study Of Water Analysis Data. He shows several different ways of graphically presenting data to make it easier to understand.

Unfortunately little has been done to aid in the interpretation of organics in ground water. Generally one can say that man made organics should not be in ground water, but it is often difficult to determine when, where, how and by whom organics got into the ground water. Often the specific organic compounds detected in ground water will give a clue to the source or cause of the contamination. However, it is important that one knows something about organic nomenclature, the use of organics, and their solubility in water. In the case of contamination from hydrocarbon fuels it is not always possible to say absolutely which fuel actually caused the contamination because of the "weathering" of the sample. Gasoline allowed to "weather" by evaporation or dissolution of the "lighter" components might appear to be stoddard solvent or kerosene. By looking at only the dissolved contamination, diesel fuel might appear to be gasoline. Often there is more than one fuel involved with a spill or leak. In the case of gasoline, probably the most common threat to ground water, it is often difficult to determine which of several possible sources is responsible and to prove the age of the spill. By graphing relative concentrations of the organic constituents in a ground water contamination case, it it possible to get a better picture of what has happened to the organics. Using the principles of solubility, adsorption, etc. it is often possible to predict movement of individual organics in

ground water, and by graphing the analytical data in the "right" manner it is possible to verify predictions and/or explain results. One method of graphing data is to use a multivariate plot. I have used the multivariate plot to graph the changing concentrations of aromatic hydrocarbons from gasoline contamination of ground water. As expected the more soluble and mobile benzene clearly moves with the front of the plume. Below is a plot showing the subtle changes in relative concentrations of aromatics for three wells which were close together.

13-5

# MULTIVARIANT PLOT OF WATER SOLUBLE AROMATICS FROM GASOLINE CONTAMINATED GROUND WATER



PERCENT OF TOTAL (8-68%)

By looking at the benzene/toluene ratios it is possible to predict which well is closer to the source. It is hoped that someday plots such as the one above will help to determine the ground water geochemistry and aid the investigator in the interpretation of the analytical results. Multivariate plots need not be limited to six parameters or to the investigation of gasoline in ground water. They could be used with any combination of compounds (inorganic and organic).

Carrying this line of reasoning a step further, it is possible to plot data in more than two or three dimensions using a computer. The computer can relate to data plotted in many dimensions and there are non-linear mapping programs which can take data plotted in many dimensions and simplify it (without loosing too much information) into two or three dimensions so that it can be more easily visualized. One such algorithm is described by Stephen L.Morgan et al. (see paper). While the examples which he gives do not relate directly to interpretation of ground water contamination, it is not hard to see the possibilities for using this method. I have been plotting BTX data from hydrocarbon fuel contamination cases and attempting to determine the relationship between the age, type of fuel, distance from the source, etc. using multivariate plots and non-linear mapping. While it is apparent that there are relationships I have not yet determined what they are. However, on a very local scale (one site) plotting the data with these methods does illustrate the ground water geochemistry discussed in this course and is often helpful in interpretation of the analytical data.

#### REFERENCES

Hem, John D., 1985, Study and Interpretation of the Chemical Characteristics of Natural Water, U.S. Geological Survey Water-Supply Paper 2254

13-7

Morgan, Stephen L, Walla, Michael L., and Rogers, James C., 1987, Measuring and Displaying Chromatographic Similarity Using Cluster Analysis, Chromatography, Cahners Publishing Co., Barrington, Il.

Also see the references for "Introduction to Organic Chemistry"

# CHOOSING AN ORGANIC ANALYTICAL LABORATORY

13-8

CHECK OUT THE LABORATORY - VISIT - REVIEW DATA

- 1. QA/QC PROGRAM WITH RECORDS;
- 2. PROFICIENCY RESULTS;
- 3. PRECISION/ACCURACY STATEMENTS;
- 4. TURN AROUND TIMES;
- 5. CHECK REFERENCES;
- 6. REQUEST RAW DATA AT TIMES; \_\_ med. range concentration
- 7. SEND BLIND DUPLICATES; -> Send Inwillevel samples less error possible
- 8. SEND IN BLIND CHECK SAMPLES; > \$450 companies (Not Labs) that specialize in making

standards. For

9. SPLIT SAMPLES WITH OTHER LABS.

#### ORGANIC ANALYSES ARE RELATIVELY NEW AND COMPLEX -REQUIREING CONSIDERABLE TIME, EXPENSIVE EQUIPMENT AND TRAINED PERSONNEL.

TE Lab makes mistake, tell them, discuss it.

@ Tell lab that you are going to send them duplicates, blind samples, etc. They will take more care if they know.

# INTERPRETATION OF LABORATORY RESULTS

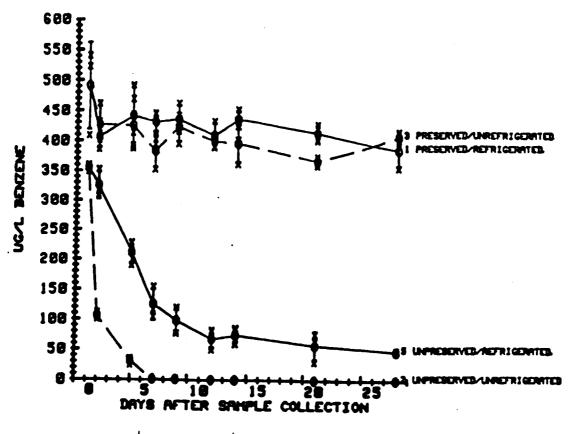
- 1. DO THE RESULTS MAKE SENSE?
- 2. WAS THE "RIGHT" ANLYSIS REQUESTED? RUN?
- 3. WAS THE SAMPLE COLLECTED PROPERLY?
- 4. COULD THE SAMPLE HAVE BEEN CONTAMINATED?
- 5. WAS THE LABORATORY ANALYSIS "CORRECT"?
- 6. COULD COMPOUNDS HAVE BEEN "LOST"? ----
- 7. WAS THERE ENOUGH FIELD INFORMATION?

dint on threads of jan cans prevent Scal

Lab contaminants- Lab will be aware of them methylence chloride acetone freon phthalates-(lab on fre(d) dichloro prethone

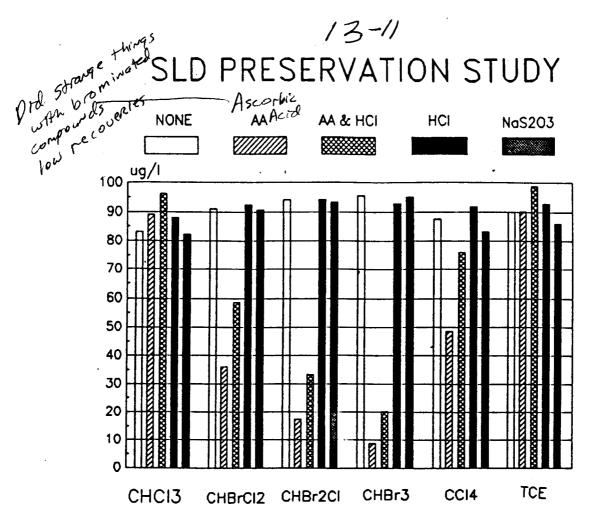
) Talk to Lab - is it a possible Lab contam. Should also (but not always) show up in Lab Blanks

# BIODEGRADATION STUDY



Water samples

The New Mexico Scientific Laboratory Division studied the stability of Benzene and other aromatics under different preservation conditions. The above graph shows an example the results obtained. Some of the samples were preserved with mercuric chloride (curves 1 & 3) at 20 ppm HgCl<sub>2</sub>. Of these, one set was refrigerated at 4°C and the other was stored at room temperature. Another set of samples (curve 5) was not preserved but was kept at 4°C, while the last set (curve 7) was not preserved and stored at room temperature. The samples were all analyzed in triplicate on nine different dates over a one month period. As can easily be seen an unpreserved, unrefrigerated sample can drop from several hundred to zero ppb benzene in five days. Even refrigerated samples can show substantial losses in short time periods. Hydrochloric Acid is also a good preservative if the pH is brought down to 2. In many UST situations, because of the high biological activity, the alkalinity can be very high and buffer the Ph. The high carbonate levels will also cause the loss of CO<sub>2</sub> when the sample is acidified.



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SCIENTIFIC LABORATORY DIVISION ASCORDIC ACID STUDY

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	NO PRES.	AA (AVG)	AALHCL(avg)	NCL	Na\$203
CHLOROFORM	78.0	91.0	96.7	85.5	88.8
CHLOROFORM	86.7	85.4	90.5	85.7	76.6
CHLOROFORM	84.6	90.8	101.3	92.6	81.2
CHLOROFORM (AVG)	83.1	89.0	96.1	87.9	82.2
CHLOROFORM (COV)	5.5%	3.6%	5.6%	4.6%	7.5%
BRONOD I CHLOROMET HANE	88.2	54.2	66.2	91.8	94.6
BRCHOD I CHLOROME THANE	93.0	18.8	59.7	89.0	87.4
BRONOD I CHLOROMET HANE	91.7	35.7	49.8	96.6	89.6
BRONDD I CHLORONE THANE (AVG)	91.0	36.2	58.6	92.5	90.5
BRONOD I CHLOROMETHANE (COV)	2.7%	48.9%	14.1%	4.2%	4.1%
DIBRONOCHLOROMETHANE	90.9	30.7	41.5	95.2	96.9
DISCHOCHLOROHETHAKE	96.5	6.6	35.9	89.6	89.8
DIBRONOCHLOROMETHANE	94.7	14.9	22.1	97.8	92.7
DIBROHOCHLOROHETHANE (AVG)	94.0	17.4	33.2	94.2	93.1
DIBRONOCILOROMETHANE(COV)	3.0X	70.6%	30.2%	4.4%	3.8%
BRONOFORM	92.0	17.5	27.8	95.5	95.9
BRCHOFORN	96.0	2.3	23.0	89.5	92.0
BROHOFORM	96.4	6.5	10.2	93.2	96.8
BROHOFORH(AVG)	95.5	8.8	20.3	92.7	94.9
BRONOFORN(COV)	3.3%	89.9%	44.7%	3.3X	2.7%
CARBON TETRACHLORIDE	82.8	56.7	81.3	91.1	90.1
CARBON TETRACHLORIDE	91.4	37.2	73.3	88.7	79.2
CARSON TETRACHLORIDE	88.2	51.8	73.7	95.2	80.3
CARBON TETRACHLORIDE (AVG)	87.5	48.5	76.1	91.7	83.2
CARBON TETRACHLORIDE(COV)	5.0%	20.9%	6.0%	3.6X	7.2%
TRICHLOROETHENE	86.6	91.5	97.9	92.2	92.6
TRICHLOROETHENE	92.9	86.7	94.1	89.8	82.1
TRICHLOROETHENE	90.6	92.5	104.1	96.7	83.1
TRICHLOROETHENE (AVG)	90.0	90.2	98.7	92.9	85.9
TRICHLOROETHENE (COV)	3.5%	3.4%	5.1%	3.8%	6.7%

# LEVELS OF QUALITY CONTROL

I	LEV	EL		L/	BREVIE		
	E P A - D Q O	HAZWRAP	TYPE OF TESTING	Qt plan Q A P	Proficience Evaluatio P E	9 0 0 1 T	EXAMPLES OF DATA USE
	I	•	QUALITATIVE OR SEMIQUANTITATIVE; FIELD TESTING; INDICATOR PARAMETERS	NO	NO	OPTIONAL	DELINEATION OF CONTAMINATED ZONES; GROSS DETERMINATION OF ANALYTES; HEALTH & SAFETY SCREENING; SITE CHARACTERIZATION; MONITORING DURING IMPLEMENTATION
	Ħ	8	QUANTITATIVE OR SEMIQUANTITATIVE; ON SITE FIELD TESTING; COMPOUND SPECIFIC	YES	OPTIONAL	OPTIONAL	ALL OF THE ABOVE PLUS: EVALUATION OF ALTERNATIVES; ENGINEERING DESIGN
	81	с	QUANTITATIVE; CLP OR SW-846 METHODS REQUIRED FOR NPL	YES	YES	YES	ALL OF THE ABOVE PLUS: RISK ASSESSMENT AND TECHNICALLY DEFENSIBLE DATA ; SITES NEAR POPULATED AREAS
	N	D	QUANTITATIVE; CONTRACT LAB ONLY	YES	YES	YES	ALL OF THE ABOVE PLUS: LEGALLY DEFENSIBLE DATA; QC DOCUMENTATION
	v	E	QUANTITATIVE FOR NON STANDARD SAMPLE MATRIXES; METHODS MUST BE PRE-APPROVED	YES	OPTIONAL	OPTIONAL	QUALITATIVE TO QUANTITATIVE ANALYSES METHOD SPECIFIC

NON-FOUTINE awalyses Not EPA method for compound

	Maximum score	Weight of rank
Precision	20	20
Accuracy	20	20
Quality assurance plan inspection	36	40
Blind check samples (4 points)		
Method detection limits (1)		
Method blanks (3)		
Equipment calibration (4)		
Matrix spike samples (4)		
Check samples (4)		
Replicate samples (4)		•
Internal audits (4)	•	
EPA-CLP <sup>b</sup> laboratory (2)		
Chain of custody use (2)		•
Corrective action program (4)		
Ability to customize reports	10	10
Instructions to be included on reports:		
EPA methods listed (2.5 points)		
Confidence limits indicated (2.5)		
Dates of analyses listed (2.5)		
Chain-of-custody forms returned (2.5)		-
Turnaround time of results vs. "promised" time	10	10
Price of analyses	10	_10
Total		100

REF: Einerson and Pei,

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Environmental Science and Technology, Vol.22, No.10, 1988

	Sample concentrations* (ppm)								
	As	Cd	Crno	Cu	Pb*	Hg			
True value Lab	1	0.05	0.05	5	5	0.5			
A	1200	0.04	0.11 0.06	5.1	4.8 4.9	0.485			
В	< 0.01 (0.005)	0.03	<0.05 (0.025) <0.05 (0.025)	4.78	< 0.05 (0.025) 0.55	0.05			
С	0.959	0.053	0.048 0.047	4.59	4.5 4.34	0.395			
D	0.861	0.052	0.062 0.060	4.85	4.94 4.95	0.495			
E	0.052	0.050	0.0 <b>60</b> 0.070	4.8	3.9 4.5	0.5			
F	< 0.05 (0.025)	0.05	0.074 0.084	4.77	4.84 5.09	0.409			
G	0.86	0.057	0.05 0.05	5.2	5.0 5.0	0.5			
н	0.87	0.05	0.0 <del>0</del> 0.06	5.0	5.2 4.9	0. <b>56</b>			
ł	0.90	0.051	0.05 0.05	4.98	4.9 3.5	1.23			
J	0.86	0.067	0.051 0.051	4.9	4.6 4.6	0.49			

"When values are reported to be less than detectable, half of that value (in parentheses) is used for calculations and ranking purposes.

\*Duplicate sample results are beneath the first sample results. For calculation of accuracy error, the average of the duplicates is used.

REF: Einerson and Pei,

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Environmental Science and Technology, Vol.22, No.10, 1988

13-15

Lab	Precision (root meen equere)	Accuracy (average accuracy % error)	Quality assurance (score totals)	Customizing reports (score totals)	Turneround time (days lete)	Price (8)
A	50.0	19,999.7	19	7.5	0	1711.50
8	5.2	63	19	6	0	960.00
C	1.9	23.1	14	5	5	2481.00
D	2	7.5	18	8.5	13	1307.00
E	11.8	24.2	20.5	7.5	17	1016.00
F	10.3	29.8	12	6.5	10	598.00
G	0	5.3	23.5	10	11	1134.00
н	3	7.7	24.5	10	11	750.00
t	14.0	29.1	18	0	12	748.00
J	0	10.3	15	2.5	13	453.00

#### TABLE 4

Overall ranking of laboratories in all categories\*

Lab	Precision	Accuracy	QA	Reports	Time	Price	Average weighted rank*	Overall rank
<b>A</b>	10	9	4.5	4.5	1.5	9	110.8	8
B	6	10	4.5	7	1.5	5	98.3	Ğ
C	3	8	9	8	3	10	116.7	9.5
D	4	3.5	6.5	3	8.5	8	90	3
E	8	6	3	4.5	10	6	95.8	5
F	7	7	10	6	4	2	116.7	9.5
G	1.5	2	2	1.5	5.5	7	45	2
H	5	1	1	1.5	5.5	4	· 43.3	1
1	9	3.5	6.5	10	7	3	107.5	7
J	1.5	5	8	9	8.5	1	92.5	4
Weight of acore	20	20	30	10	10	10		

"The average weighted rank is derived from  $(r_1 \times w_2)$  where  $r_1$  is the ranks for each category and  $w_1$  is the weights of the categories.

**REF: Einerson and Pei,** 

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TABLE 5
Analyses of results: known check sample vs. blind check sample
Analyses of results, known check sample vs. blind check sample

	True value (ppm)	Κηοι	VII.	Blind		
Parameter		Values (ppm)	% error	Values (ppm)	% error	
As	1	1.1/1.1	10	1200	119,000	
Cd	0.05	0.05/0.06	10	0.04	20	
Cr	0.05	0.05	0	0.11	120	
Cu	5	5.1	2	NR <sup>e</sup>	_	
РЪ	5	4.9/4.9	2	4.8	4	
Hg	0.5	0.31/0.33	36	0.53/0.44	4	
*NR = not requ NOTE: Duplica	uested. te results were pro	vided voluntarily	by the laborator	<b>x</b>		

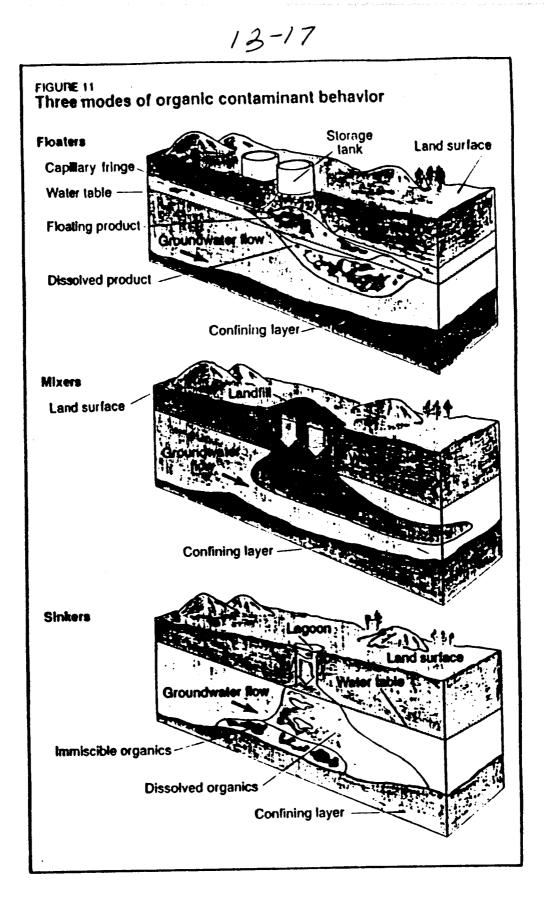
REF: Einerson and Pei,

Environmental Science and Technology, Vol.22, No.10, 1988

13-16

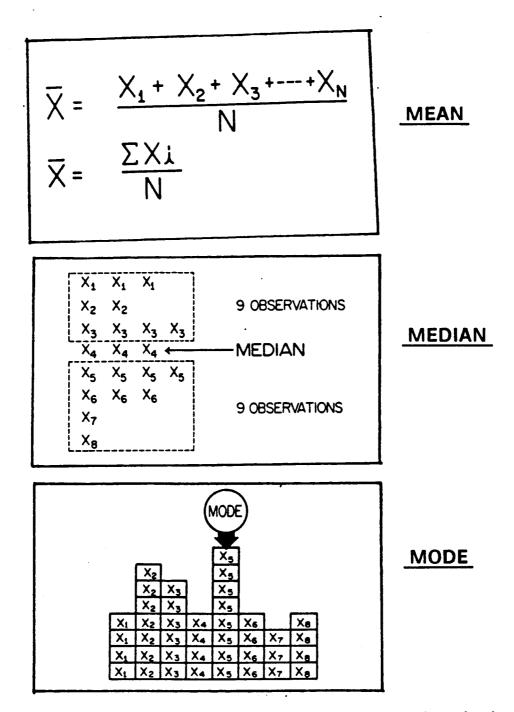
# SAMPLING PROBLEMS

NO SAMPLING PLAN CONTAMINATED SAMPLE CONTAINERS OR EQUIPMENT IMPROPER SAMPLE CONTAINERS IMPROPER SAMPLE COLLECTION CROSS CONTAMINATION INSUFFICIENT DOCUMENTATION INCORRECT PRESERVATION/TRANSPORTATION INCORRECT ANALYTICAL REQUEST

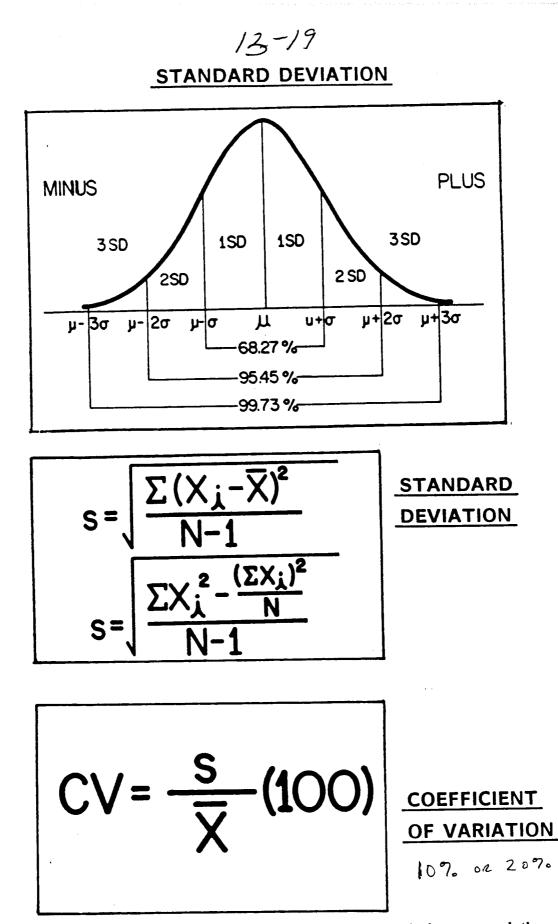


12-18

# **VARIABILITY: STATISTICS**

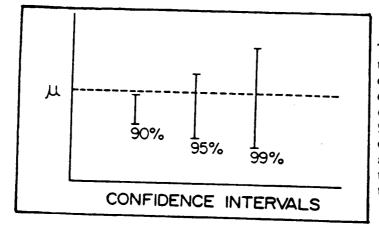


Most series of observations tend to cluster about some particular value in a distribution. This characteristic of measurement data is termed the <u>central tendency</u>. The most common measures of the central tendency are the arithmetic mean (average), the mode and the median.

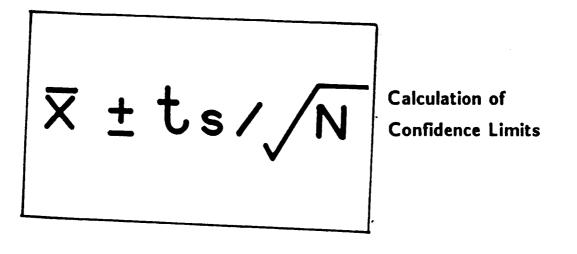


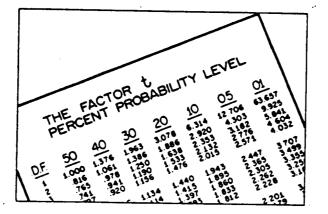
The coefficient of variation (CV) is a relative standard deviation or a relative measure of dispersion.

# 13-20 CONFIDENCE LIMITS



The confidence interval is the % probability that the confidence limits will encompass the results obtained. That is if the 95% confidence limits are calculated, the chances are about 95 in 100 that the limits will encompass the universe mean, u.

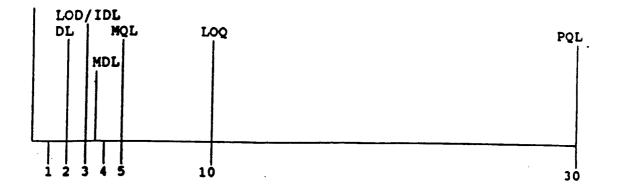




The t (Student's t) factors are correction factors used to calculate confidence limits at various probability levels.

Suppose you wish to find the 80% confidence limits for a series of four observations. For four observations there are three (N-1) degrees of freedom. Locate the three row in a DF column in a t-table. Scan the numbers in the three DF row. The t factor in the 20% probability level column (100-80=20) is 1.638.

# **DEFINITION OF DETECTION LIMIT TERMS**



#### MULTIPLIER OF STANDARD DEVIATION OF REPLICATES

Note: The values along the horizontal "Standard Deviation (SD)" axis are approximate values and are meant to show the relative, not absolute, relationship between the terms.

- DL Detection Limit Distinctly detectable but close to a blank. Two times the SD. (Methods for Chemical Analysis of Water and Wastes)
- LOD Limit of Detection statistically different from a blank. Three times the SD. (ACS)
- MDL Method Detection Limit 99% confidence that concentration is greater than zero. The SD times the Student t-value at the desired confidence level. For 7 replicates the value is 3.14. (40 CFR for EPA Water Programs)
- 1DL Instrument Detection Limit Smallest signal above background noise an instrument can detect. Three time the SD. (CLP)
- MQL Method Quantitation Limit Minimum concentration that can be detected and reported. Five times the SD. (SW-846)
- LOQ Limit of Quantitation Level above which quantitative results may be obtained with a specified degree of confidence. Ten times the SD. (ACS)
- POL Practical Quantitation Limit Lowest level that can be reliably determined within specified limits of precision and accuracy during routine lab operations. Ten times the MDL OR Value where 80% of labs are within 20% of true value. (RCRA & SDWA)
- CRDL Contract Required Detection Limit Reporting limit specified for labs under contract to EPA for Superfund Activities (CLP)

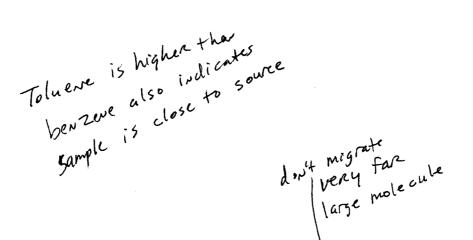
13-21

12-22

The following analytical results were obtained from a recently completed monitor well. About three well bore volumes were bailed before the sample was collected. Give as much information as possible about what may have caused the water contamination.

# ANALYTICAL REPORT QUIZ #1

COMPOUND DETECTED	[ug/l]
BENZENE	780
TOLUENE	920
ETHYLBENZENE	63
XYLENES (TOTAL)	1100
C3 SUBSTITUTED BENZENES	PRESENT
1,2-DICHLOROETHANE	130

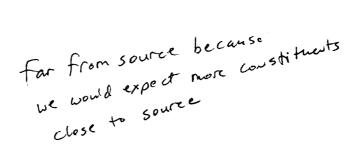


The above compounds, often referred to as BTX (for benzene, toluene, and xylene) would indicate ground water contaminated with gasoline. The BTX compounds are not normally associated with diesel fuel or hydrocarbon fractions higher boiling than gasoline. The relatively high concentrations present plus the presence of  $C_3$  substituted benzenes indicate that this water is close to the source of the contamination. The presence of the 1,2-dichloroethane indicates that the gasoline was leaded since 1,2-dichloroethane is added to leaded gasoline to volatilize lead from the combustion chamber.

The following analytical results were obtained from a domestic drinking water well. The line (kitchen faucet) was flushed for 15 minutes before the sample was collected. Give as much information as possible about what may have caused the water contamination.

## ANALYTICAL REPORT QUIZ #3

COMPOUND DETECTED[ug/l]t-BUTYLMETHYLETHER (MTBE)560 7 most<br/>mobileBENZENE120 7 constituing<br/>gas



Both t-butylmethylether (an octane enhancer) and benzene could be found at the edge of a ground water plume associated with gasoline contamination. The MTBE has only been used in gasoline since about 1984, and mainly in the eastern part of the country. MTBE and benzene are the most soluble and mobile components of gasoline along with 1,2-dichloroethane (added to leaded gasoline as a lead scavenger). Being the most mobile, MTBE and benzene (and 1,2-dichloroethane) are often found at the edge of contaminated plumes without the other compounds associated with gasoline (toluene, ethylbenzene, and xylenes). MTBE is so soluble in water that it can not only "travel" very fast, but it can also increase the concentrations of other organics dissolved in the water through a cosolvency effect.

13-24

The following analytical results were obtained from the rest room of a gas station to check for compliance with the Safe Drinking Water Act. The line (coid water) was flushed for 15 minutes before the sample was collected. Give as much information as possible about what may have caused the water contamination. What would be the implications from the levels of the compounds detected?

## ANALYTICAL REPORT QUIZ #4

COMPOUND DETECTED	[ug/l]
CHLOROFORM	80
BROMODICHLOROMETHANE	40
DIBROMOCHLOROMETHANE	12
BROMOFORM	4
p-DICHLOROBENZENE	1

Chloroform, bromodichloromethane, dibromochloromethane, and bromoform are the usual trihalomethanes formed when water, with some organic matter in it, is chlorinated. Usually the concentrations decrease from chloroform to bromoform, although sometimes the reverse is true. The Safe Drinking Water Act (SWDA) limit for trihalomethanes is a total of 100 ug/l (ppb). The "Total THM" value of 136 ppb is above the acceptable value and would require the water supply to reduce the THM level or stop using the water.

The p-dichlorobenzene is not a compound usually found in drinking water, but it is frequently used as a deoderizer in public rest rooms and could easily contaminate a sample collected in such a rest room.

13-25

The following analytical results were obtained from a recently completed monitor well. About three well bore volumes were bailed before the sample was collected. Give as much information as possible about what may have caused the water contamination.

# ANALYTICAL REPORT QUIZ #5

COMPOUND DETECTED	[ug/l]
DIBUTYLPHTHALATE	12
DI-2-ETHYLHEXYLPHTHALATE	6
DICHLOROMETHANE	4

Phthlates are a class of compounds used frequently in plastics. These compounds, at low concentrations, are often found as contaminates in samples. They may come from the sample collection device, the sample container, or laboratory glassware.

Dichloromethane is probably the most commonly used laboratory solvent and can easily contaminate samples for VOC analyses. Laboratories are aware of this problem and usually check for it.

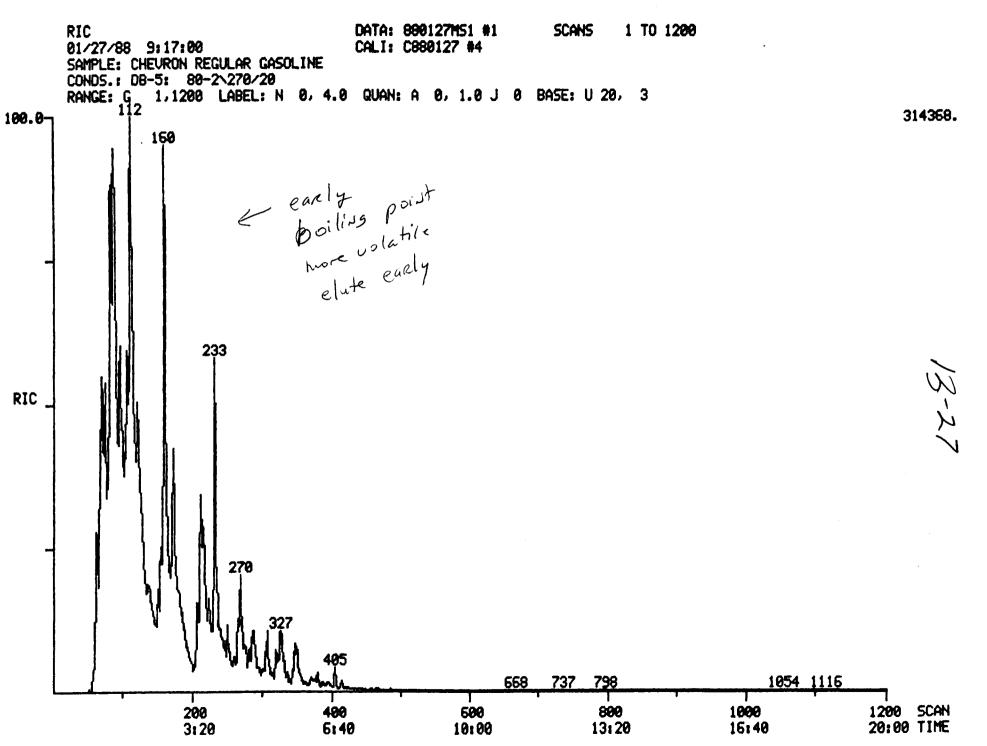
13-26

The following analytical results were obtained from a recently completed monitor well. About three well bore volumes were bailed before the sample was collected. Give as much information as possible about what may have caused the water contamination.

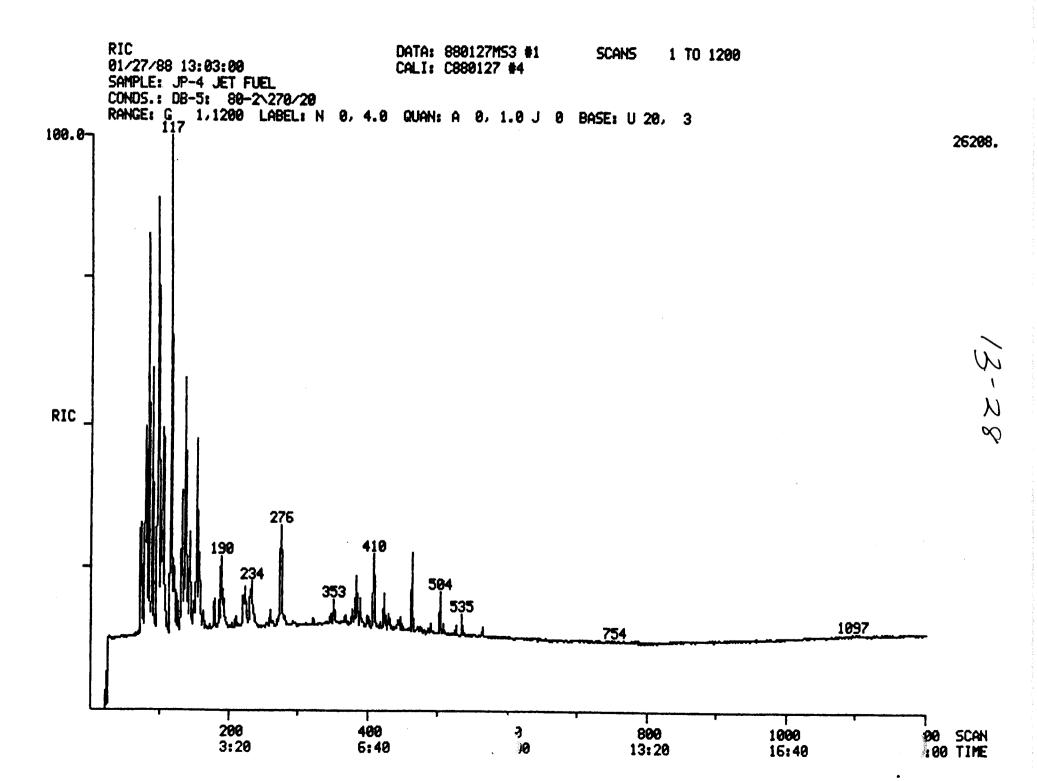
# ANALYTICAL REPORT QUIZ #6

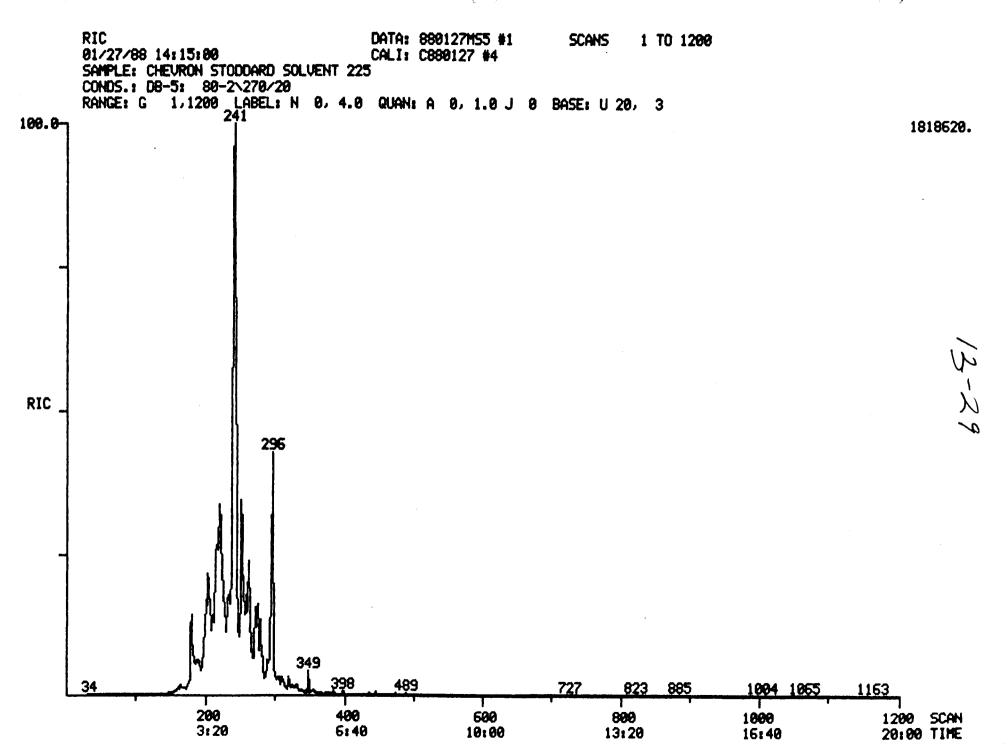
COMPOUND DETECTED	[ug/l]
BUTANONE	80
TETRAHYDROFURAN	120

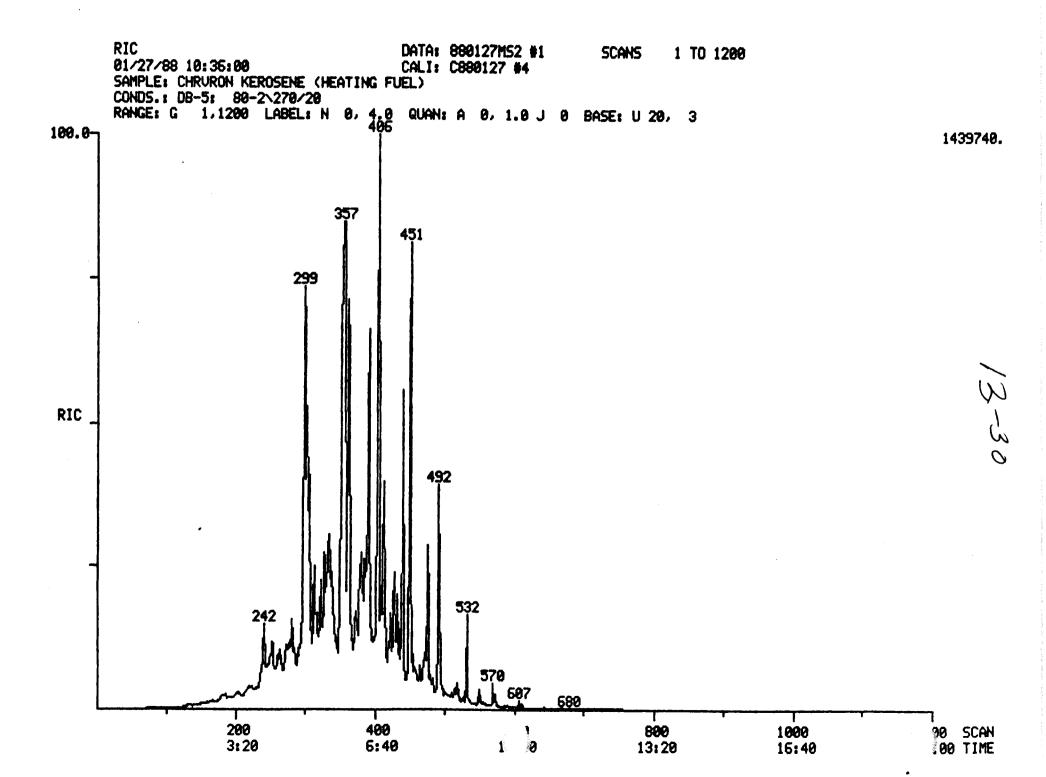
Butanone and tetrahydrofuran are both solvents used in gluing PVC pipe together. These compounds can "bleed" out of the glued pipe joints for months.

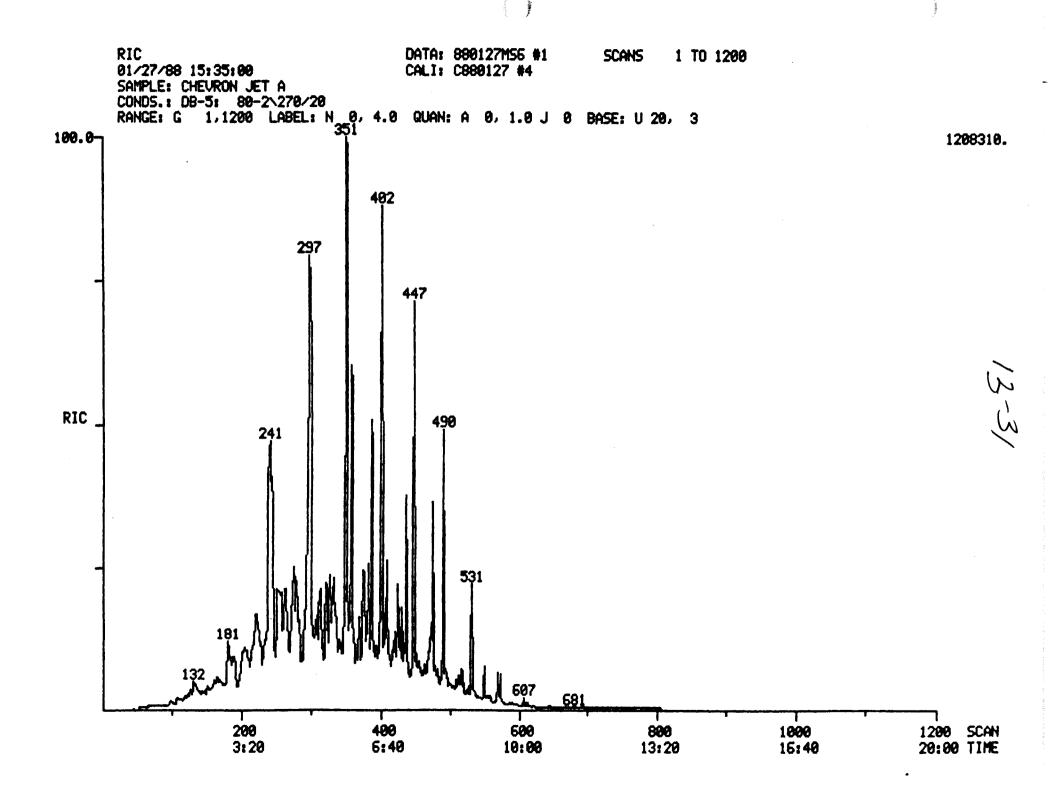


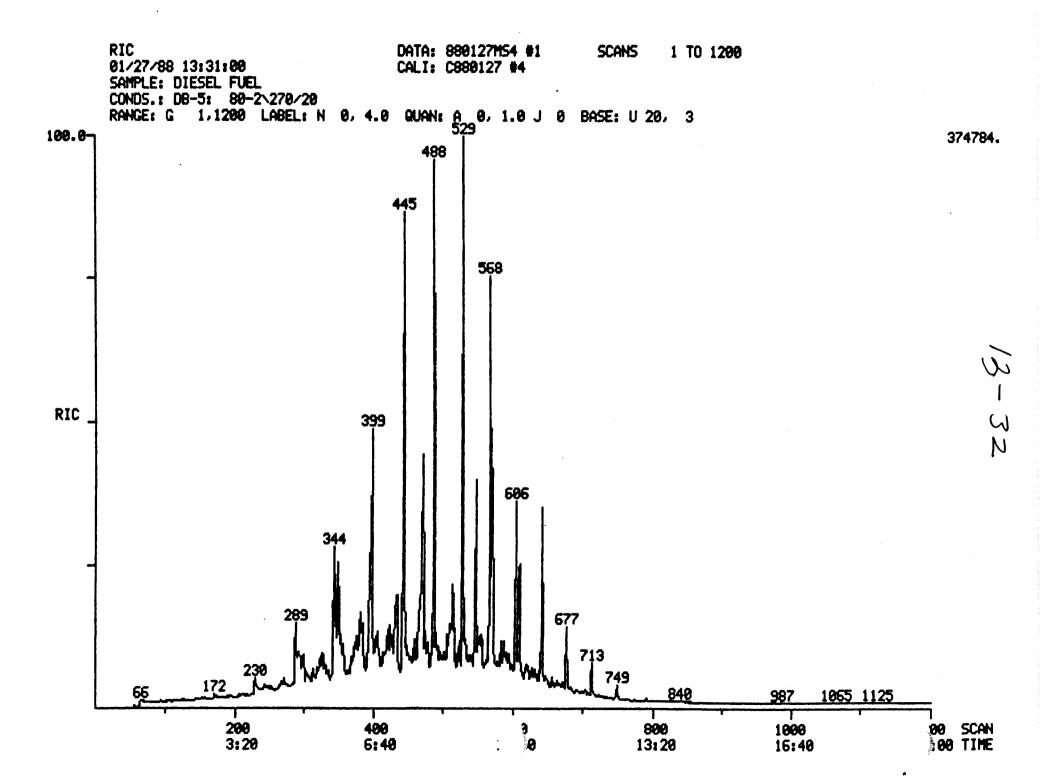
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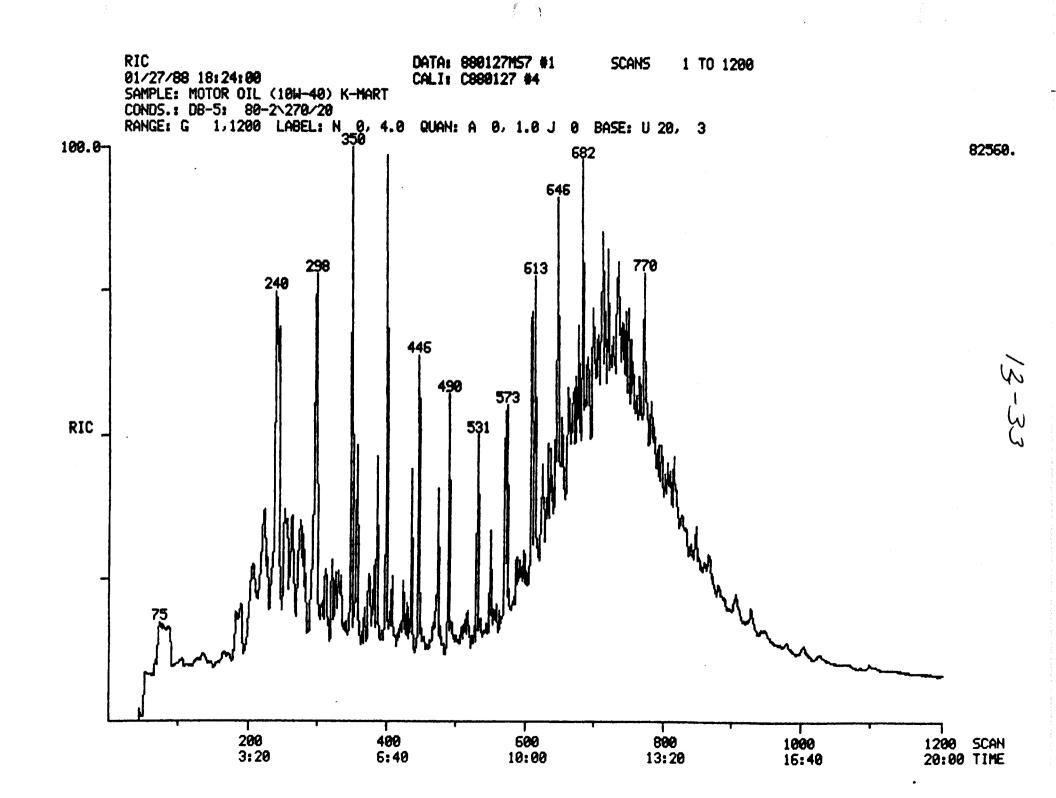


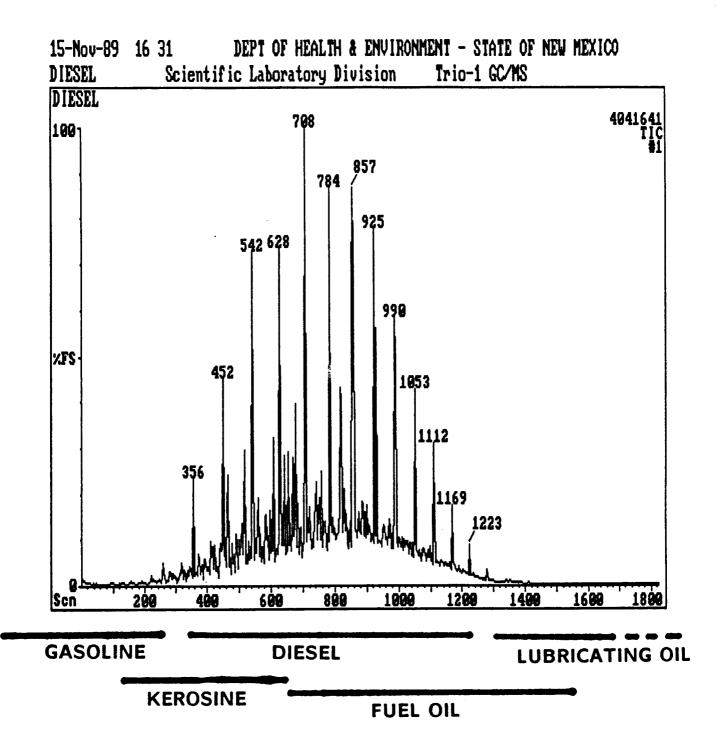


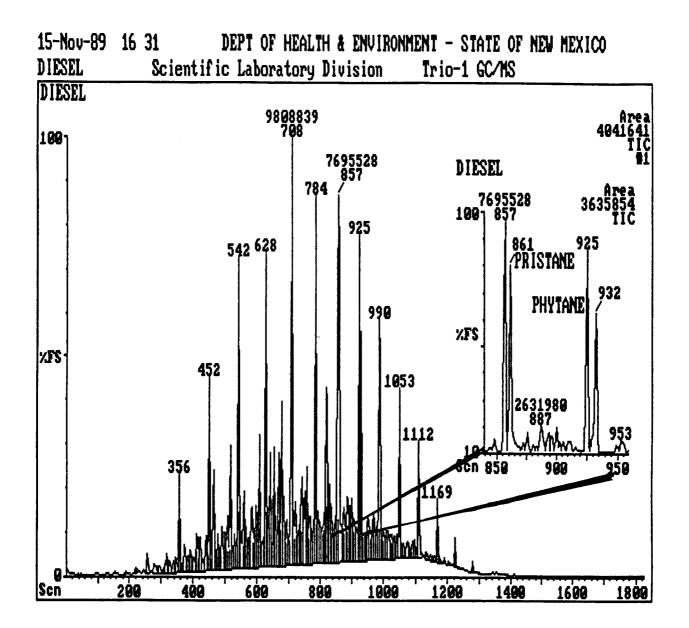


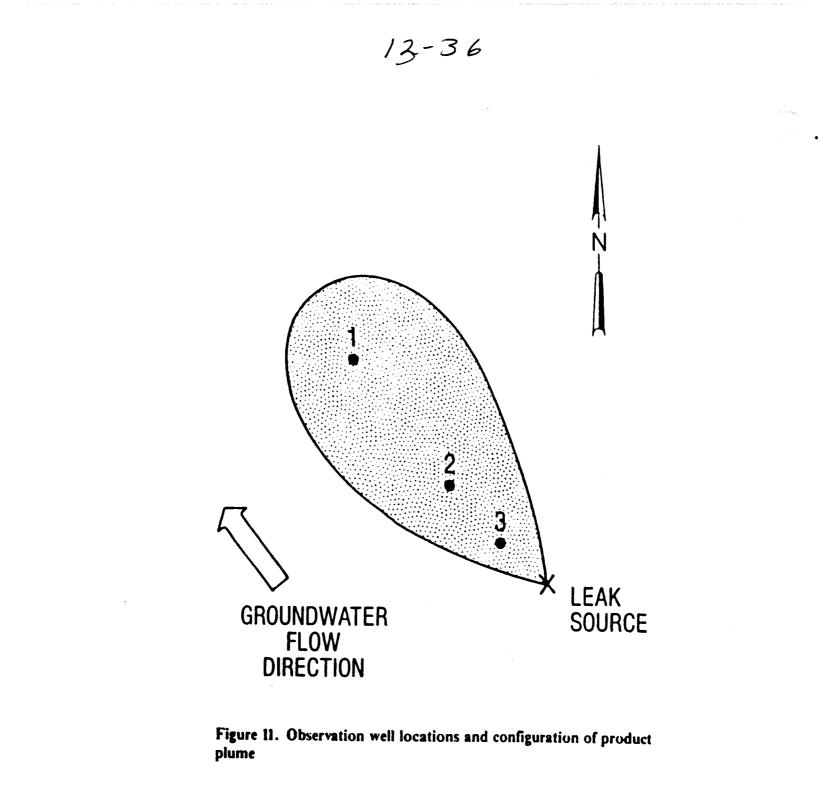












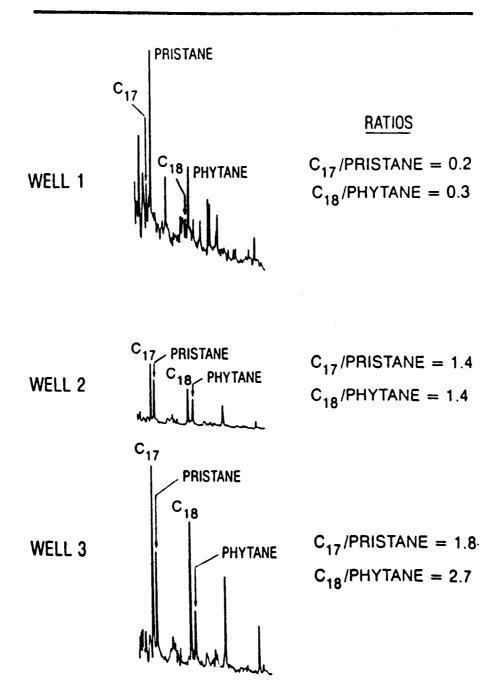
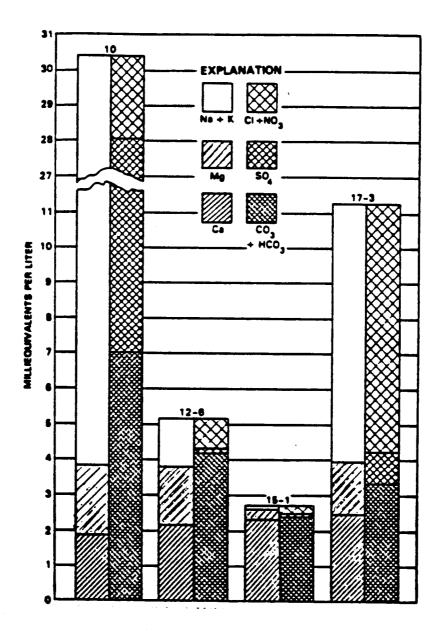


Figure 11. Observation well locations and configuration of product plume

Figure 12. Comparison of peak height ratios for three observation wells

13-38

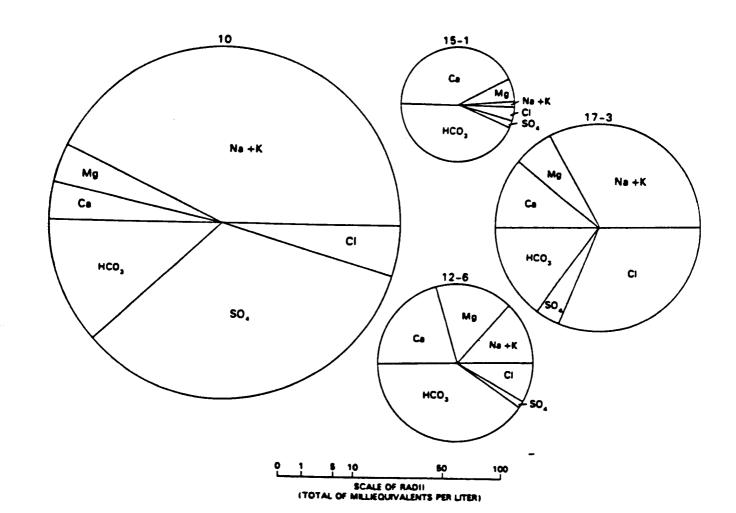
### COLLIN'S BAR GRAPH PROCEDURE



### (Hem, 1985)

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Each analysis is represented by a vertical bar graph whose total height is proportional to the concentration of determined anions or cations, in milliequivalentes per liter. The bar is divided by a vertical line, with the left half representing cations and the right half anions. The segments are then divided by horizontal lines to show the concentrations of the major ions.



### PIE DIAGRAMS

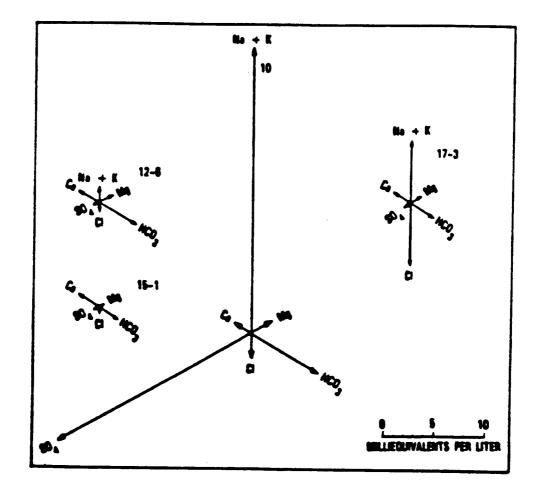
## (Hem, 1985)

The "pie" diagram can be drawn with a scale for the radii which makes the area of the circle represent the total ionic concentration and the subdivisions of the area represent proportions of the different ions.

13-39

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### **RADIATING VECTORS**

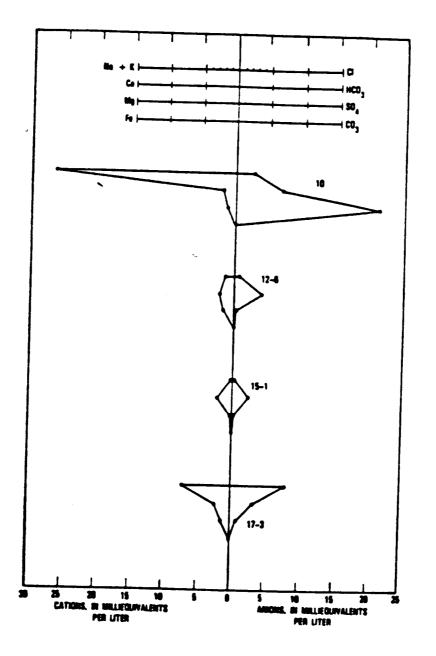


### (Hem, 1985)

The system of plotting analyses by radiating vectors was proposed by Maucha (1949) of Hungary. The distance each of the six vectors extends from the center represents the concentration of one or more ions in milliequivalents per liter. This plotting systemhas not been used widely but may have some potential as a means of showing analytical results in a small space, for example, as a symbol on a map.

## **GRAPHICAL REPRESENTATION OF DATA**

### STIFF DIAGRAMS

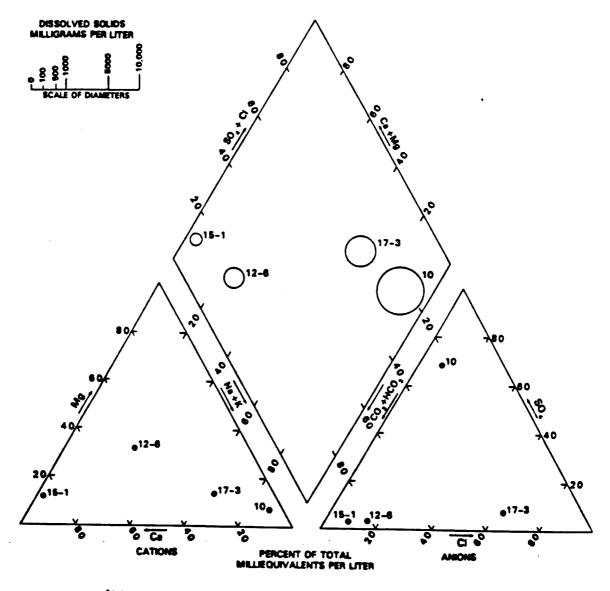


## (Hem, 1985)

A system suggested by Stiff(1951) gives a distinctive pattern, and has been used in many papers, especially those dealing with oilfield waters. The Stiff plotting technique uses four parallel horizontal axes extending to each side of a verticle axis. Concentrations of four cations can be plotted, one on each axis to the left of zero, and likewise four anion concentrations can be plotted, one on each axis to the right of zero.

13-42

## TRILINEAR DIAGRAMS



(Hem, 1985)

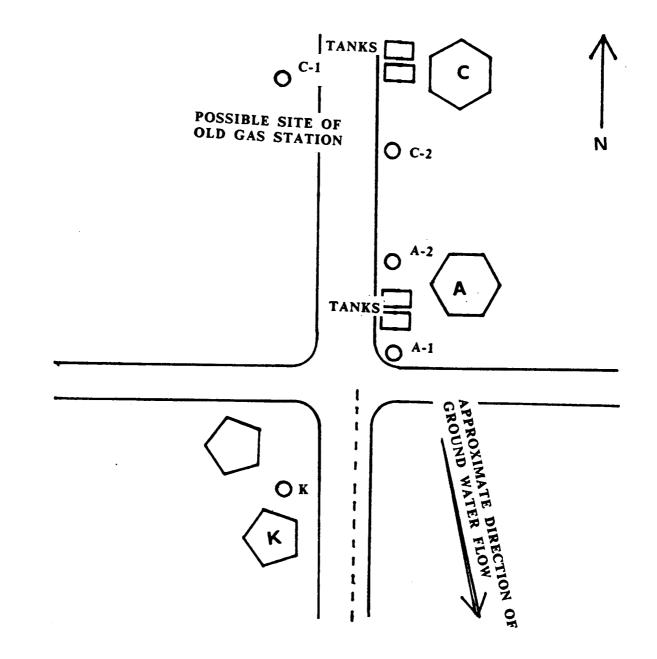
With this type of Trilinear plot the cation composition for a water sample is plotted on the left triangle and the anions are plotted on the right triangle as percent of total. The points are then extended into the central diamond field by projecting them along lines parallel to the upper edges of the diamond. The intersection of these projections represent the composition of the water with respect to the combination of ions shown. The analysis of any mixture of waters <u>A</u> and <u>B</u> will be on a straight line <u>AB</u> in the plotting field if the ions do not react chemically as a result of the mixing. Trilinear diagrams have been used to study contamination of changed, to show similarities and/or differences between waters, and effects of industries such as logging and mining on water composition.

1

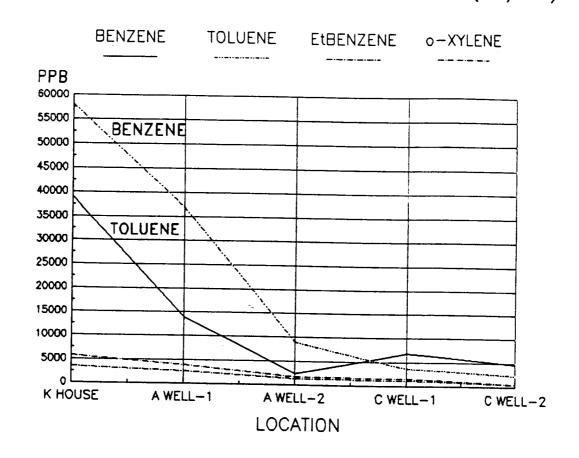
## GASOLINE CONTAMINATION SITE: CASE STUDY (OCT. 1987)

SAMPLE		CONCENTRATION OF ORGANICS DETECTED IN UG/L (PPB)						
LOCATION	BENZENE		EtBENZENE				EDC	MTBE
K HOUSE	39000	58000	3500	5800	9900	3400	240	72000
A WELL-1	14000	37000	2600	4000	7100	2400	33	ND <50
A WELL-2	2300	9000	1300	1700	3500	1300	ND <50	ND <50
C WELL-1	6900	3700	1200	1600	3300	1100	22	ND <50
C WELL-2	4700	2400	480	540	860	360	21	ND <50

LOCATIONS A AND C ARE BOTH GAS STATIONS WHILE K IS A PRIVATE RESIDENCE. THE STUDY WAS STARTED WHEN K HAD TO MOVE FROM HIS HOME BECAUSE OF GAS FUMES. THE DIRECTION OF GROUND WATER FLOW IS BELIEVED TO BE GENERALLY FROM C TO K.



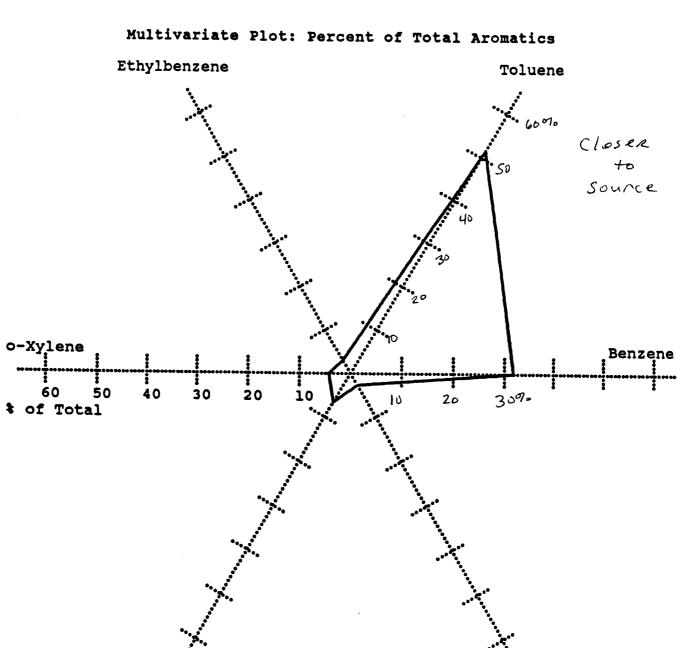
## GASOLINE CONTAMINATION: CASE STUDY (10/87)



By plotting the concentrations of Benzene, Toluene, Ethylbenzene, and o-Xylene it appears that the contamination is comming from "K House" and migrating to "A" and "C" wells. Without looking closely at the ratios of the various aromatic compounds it is difficult to conclude much about the well except that it is "badly" or only slightly contaminated. By plotting the percentages of the aromatics on a multivatiat plot one can get a feel for how the percentages have changed from a sample close to the source of contamination. This can give considerable information about the distance/direction to the source, loss of components into the vadose zone and/or biodegradation, the composition of the source (gasoline Vs. natural gas/oil), and possibly the age of the spill.

13-45

Accesion #: 8702043 Date Collected: 12/03/87 at 955 by Mag Location Data: 00N00E00000 City: Albuquerque Submitter: 77 Comment: MW-7 Roberts Oil



m-Xylene

Component	<b>t</b> of Total	PPB
Benzene	31.9	8402
Toluene	51.6	13591
Ethylbenzene	3.0	790
o-Xylene	4.2	1106
m-Xylene	6.6	1738
p-Xylene	2.7	711

Total: 26340 PPB

p-Xylene

13-46

Accesion #: 8701674 Date Collected: 10/21/87 at 1210 by Lea 00N00E00000 Location Data: City: Bernalillo Submitter: 79 Comment: Franks Conoco Well#2

Multivariate Plot: Percent of Total Aromatics

Furthere from source, the Aromatics higher the Toluene 70 of Ethylbenzene benzence o-Xylene Benzene 60 50 40 30 20 10 \$ of Total p-Xylene

m-Xylene

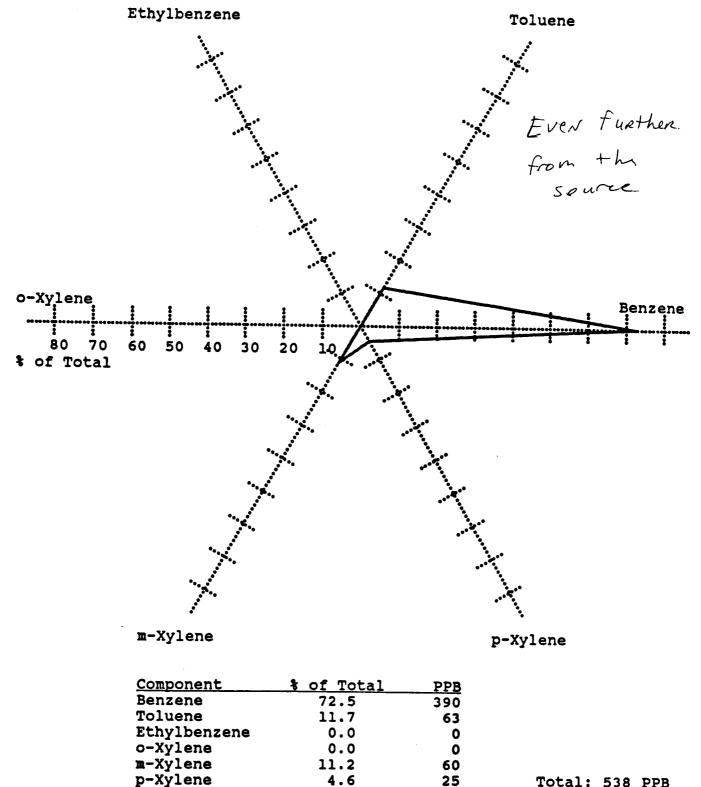
Component	<pre>% of Total</pre>	PPB
Benzene	50.2	4699
Toluene	25.6	2396
Ethylbenzene	5.3	496
o-Xylene	6.0	562
m-Xylene	9.1	852
p-Xvlene	3.7	346

13-47

Accesion #: 8701721 Date Collected: 10/29/87 at 1520 by Swa Location Data: 00N00E00000 City: Bernalillo Submitter: 79 Comment: Franks #1

1

## Multivariate Plot: Percent of Total Aromatics



13-48

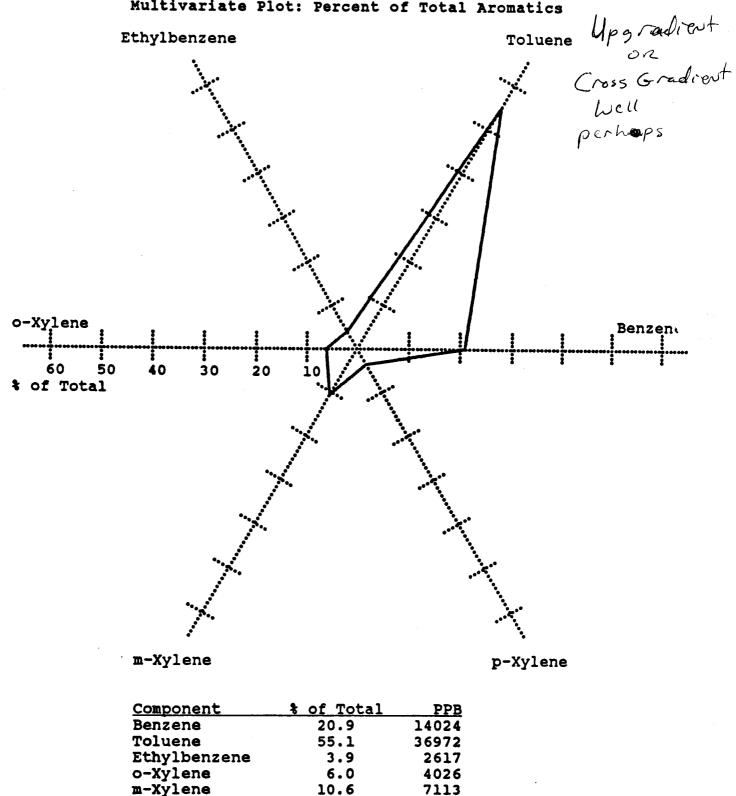
Accesion #: Date Collected: Location Data: City: Submitter: Comment:

p-Xylene

8701675 10/21/87 at 1430 by Lea 00N00E00000 Bernalillo 79 Allsups well#1

Maybe benzeve is Volatizing (shallow aquifer) or perhaps this is upgradienst from source

Multivariate Plot: Percent of Total Aromatics



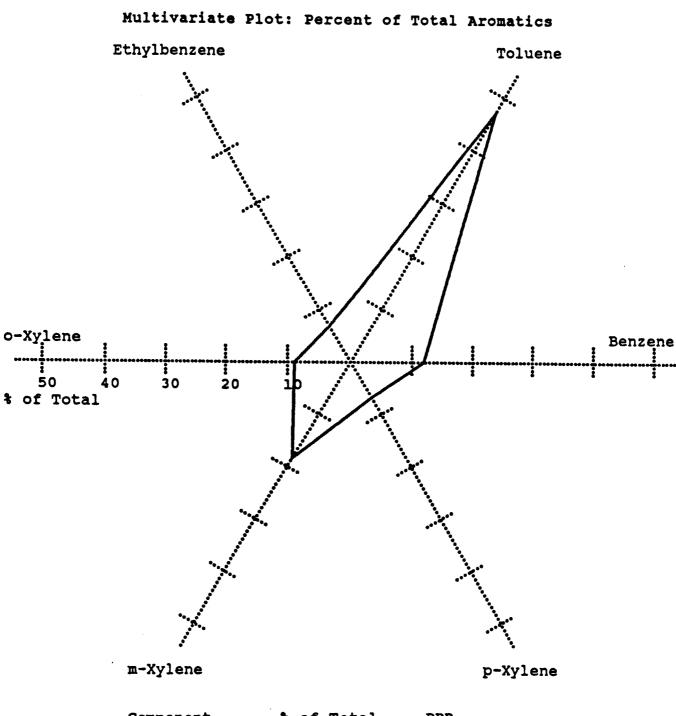
3.6

2416

Total: 67100 PPB

13-49

Accesion #: 8701678 Date Collected: 10/21/87 at 1545 by Lea Location Data: 00N00E00000 City: Bernalillo Submitter: 79 Comment: Allsups well #2

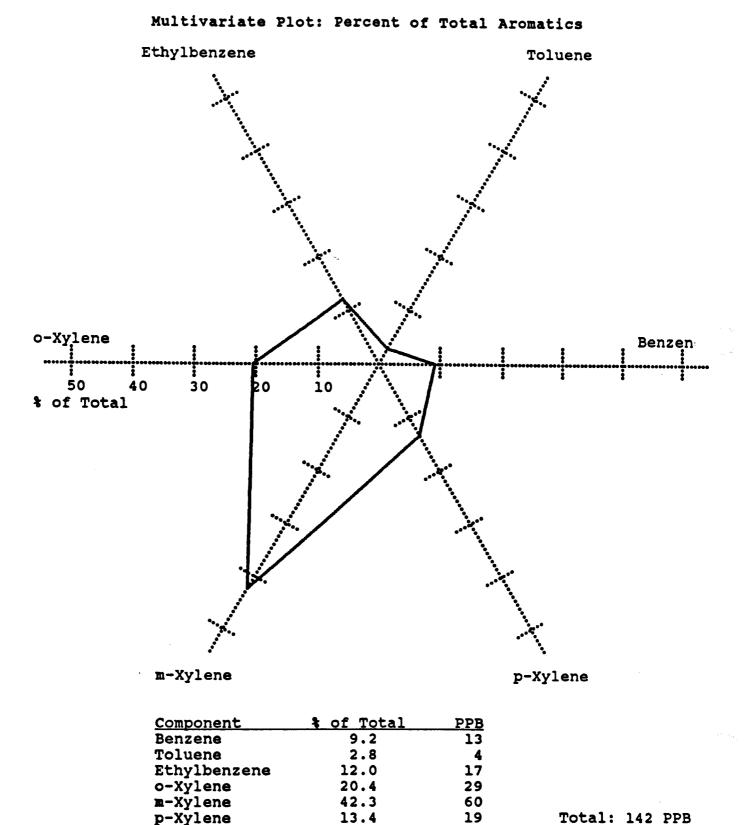


Component	<b>3</b> of Total	PPB
Benzene	12.0	2292
Toluene	47.1	8996
Ethylbenzene	6.8	1299
o-Xylene	8.9	1700
m-Xylene	18.3	3495
p-Xylene	6.8	1299

Total: 19100 PPB

13-50

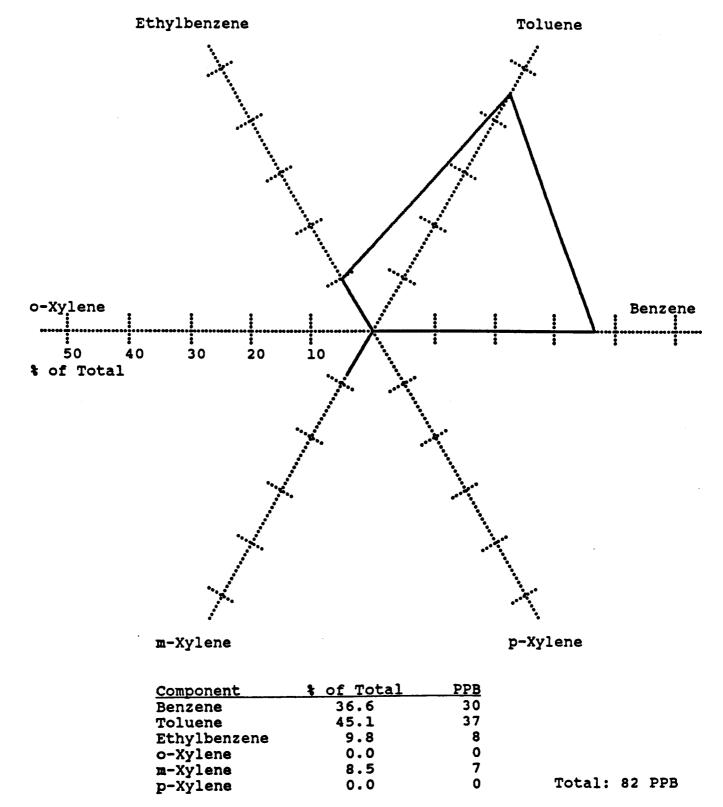
Accesion #:	8700641	
Date Collected:	04/22/87 at 1315 by Mag	
Location Data:	29N13W15	
City:	Farmington	
Submitter:	79	
Comment:	storm sewer pipe	



13-51

Accession #: 8700739 Date Collected: 05/01/87 at 1155 by Boy Location Data: City: Loco Hills Submitter: 260 Comment: Disposal Pond #2

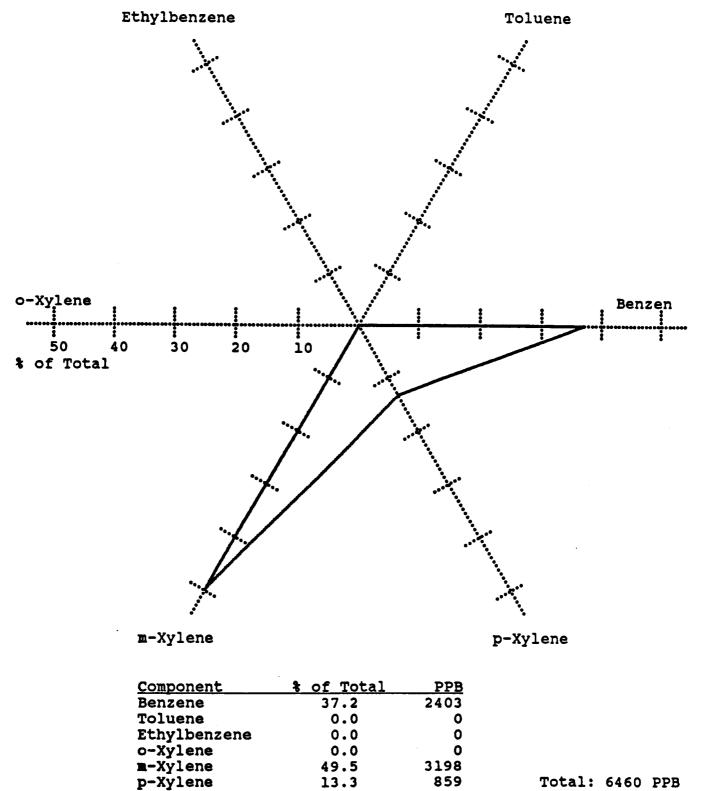




13-52

Accesion #: 8700349 Date Collected: 03/18/87 at 1405 by Boy Location Data: 29N12W28 City: Farmington Submitter: 260 Comment: MW#3 Amoco well site GCU #153E

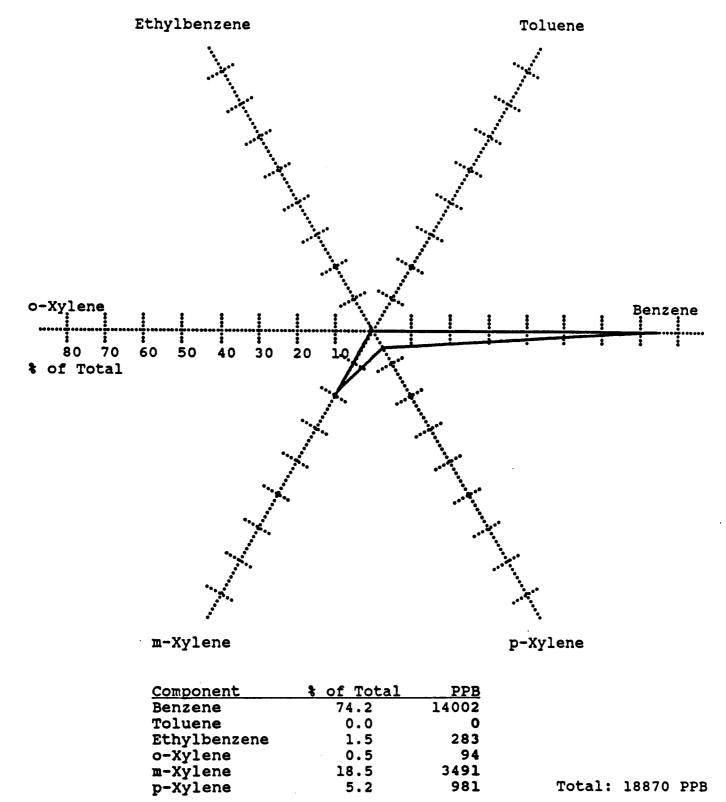
Multivariate Plot: Percent of Total Aromatics

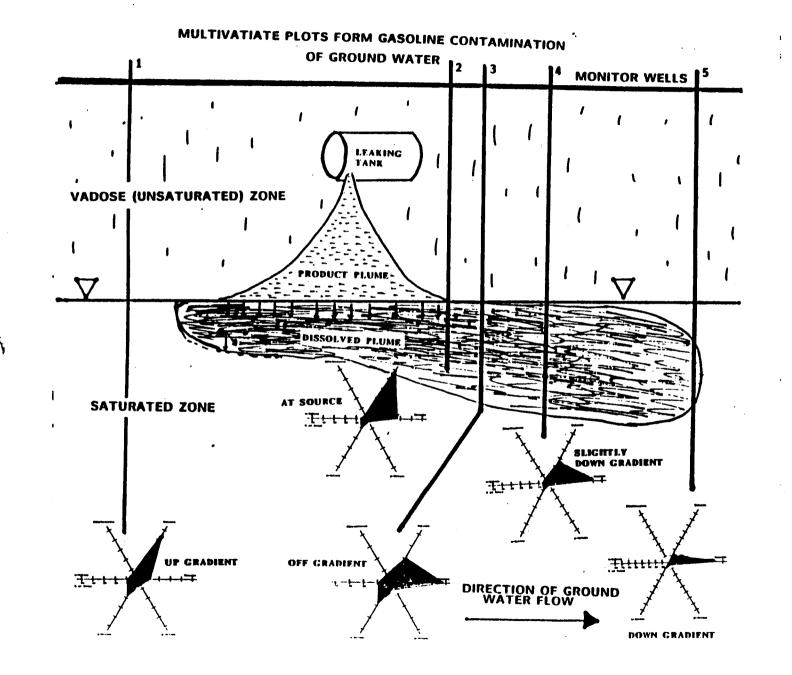


13-53

Comment:	MW#2 Amoco well site GCU#153E
Submitter:	260
City:	Farmington
Location Data:	29N12W28
Date Collected:	03/18/87 at 1430 by Boy
Accesion #:	8700352

Multivariate Plot: Percent of Total Aromatics





Section 14

# **Inorganic Problem Session**

Lecture by: William Deutsch/Woodward-Clyde Consultants and Patrick Longmire/Los Alamos National Laboratories

# SECTION CONTENTS

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Answe	rs		

#### CLASS EXERCISE NUMBER 1

### MOBILITY OF METALS IN GROUNDWATER AT A FORMER PAINT PRODUCING PLANT

#### BACKGROUND INFORMATION

At a former paint manufacturing facility on the East Coast, the inorganic contaminants barium, zinc, cadmium and lead were detected in the unsaturated and saturated zones. As part of the Feasibility Study, the application of groundwater sweeping to remove these contaminants was evaluated. Groundwater sweeping for aquifer cleanup consists of the installation of extraction wells in the zone of contamination to remove the contaminants as a dissolved phase in the groundwater. Contaminants that are present in the solid phase will dissolve into clean groundwater as it flows into the zone of contamination during pumping. Given sufficient time, the contaminants will be flushed from the system. The amount of time will depend on: 1) the mass of contaminant in the aquifer material, 2) the rate at which groundwater can be pumped from the aquifer, and 3) the solubility of the solid phases containing the contaminants. Because of the low solubility of some barium minerals, it is decided to focus on the removal rate of barium in the evaluation of groundwater sweeping for the Feasibility Study.

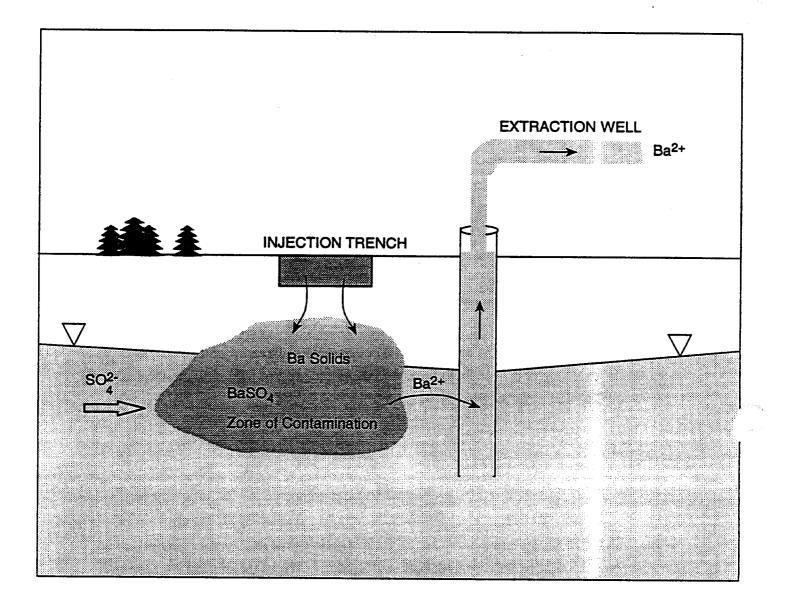
#### **EXERCISE**

Figure 1-1 is a representation of the groundwater sweeping technique for removing barium from the soil and aquifer. It consists of 1) an injection trench to flush the soil, 2) various solid phases of barium with the most important being barite (BaSO4) because of its low solubility and 3) an extraction well to remove the dissolved barium. Figure 1-2 shows the mineral equilibrium constraint on the amount of barite that can dissolve in water. The figure provides the expected dissolved concentrations of barium in the effluent water given various sulfate concentrations.

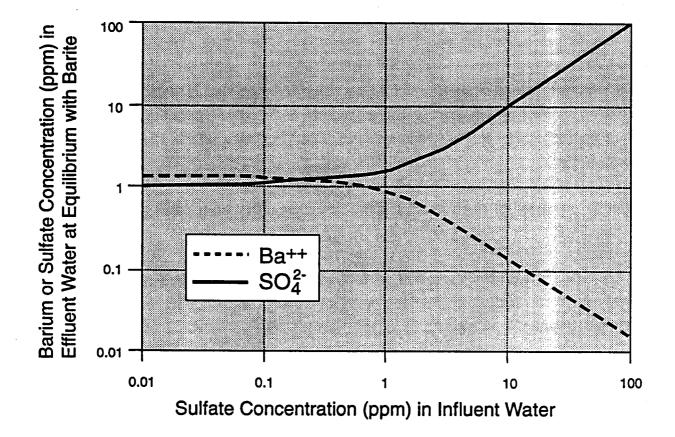
If the sulfate concentration in the influent water is 0.01 ppm, what will be the barium concentration in the extraction well assuming equilibrium with barite?

If the sulfate concentration in the influent water is 1 ppm, what will be the barium concentration in the extraction well assuming equilibrium with barite?

If the sulfate concentration in the influent water is 10 ppm, what will be the



## FIGURE 1-1. Contaminant Removal by Soil Flushing and Groundwater Sweeping





barium concentration in the extraction well assuming equilibrium with barite?

Why is the barium concentration approximately the same for sulfate concentrations of 0.01 and 1 ppm, but so much lower for a sulfate concentration of 10 ppm?

Assume that the extraction wells can pump at a rate of 1.5 gpm from wells placed on a twenty meter grid and that the initial concentration of barium in the solid phase in the zone of contamination is 3,000 ppm. The contaminated thickness of the aquifer is 10 meters and the bulk density is 2 g/cc.

What is the mass of barium that must be removed by each extraction well?

If the influent sulfate concentration is 1 ppm and barite solubility limits the dissolved concentration of barium, how much barium will be removed by the extraction well per day?

How long will it take to remove all of the barium?

How long will it take to remove all of the barium if the influent sulfate concentration is 10 ppm?  $g_{000}g_{ears}$ 

Is groundwater sweeping a reasonable remedial technology for barium given these conditions?  $\sim 0$ 

Can you think of some ways of increasing the efficiency of groundwater sweeping for this situation?

more extraction wells

## CLASS EXERCISE NUMBER 2

## CALCITE PRECIPITATION DUE TO CO2 DEGASSING OR TEMPERATURE INCREASE BACKGROUND INFORMATION

This is two related problems in one. A common occurrence in groundwater treatment systems is mineral precipitation that may block pipes or treatment units thereby lowering the efficiency of the system. In the first case, we will look at the precipitation of calcite when groundwater in equilibrium with a  $pCO_2$  pressure higher than atmospheric is pumped to the surface. In the second case, we will look at the effect of heating groundwater on calcite solubility.

Case 1. Treating Contaminated Groundwater in Equilibrium with Calcite by Air Stripping.

As part of a Feasibility Study for a landfill, you must evaluate treatment technologies for removing volatile organic compounds from groundwater. You have identified air stripping as one of the viable technologies. Figure 2-1 shows a schematic of how the system would work. The contaminated groundwater is pumped from the ground and injected at the top of the tower. The groundwater cascades down through the packing material and encounters fresh air that is blown up the tower. The volatile organics partition into the air and are removed from the water.

Being an experienced professional, you realize that there might be secondary processes that could effect the operation of this unit. You obtain a good chemical analysis of the groundwater that includes all major cations and anions plus a pH value measured in the field. Using a geochemical modeling code, you calculate the saturation index of calcite and the equilibrium  $CO_2$  gas pressure for the groundwater. Low and behold, you find that the groundwater is in equilibrium with calcite and the calculated p $CO_2$  gas pressure is 0.1 atmospheres (log p $CO_2 = -1$ ). Immediately you know that you have a potential problem because atmospheric p $CO_2$  is 0.0003 atmospheres (log p $CO_2 = -3.5$ ).

Your client wants to know why this is such a big deal when you are supposedly treating a volatile organics problem. Explain it in 25 words or less.

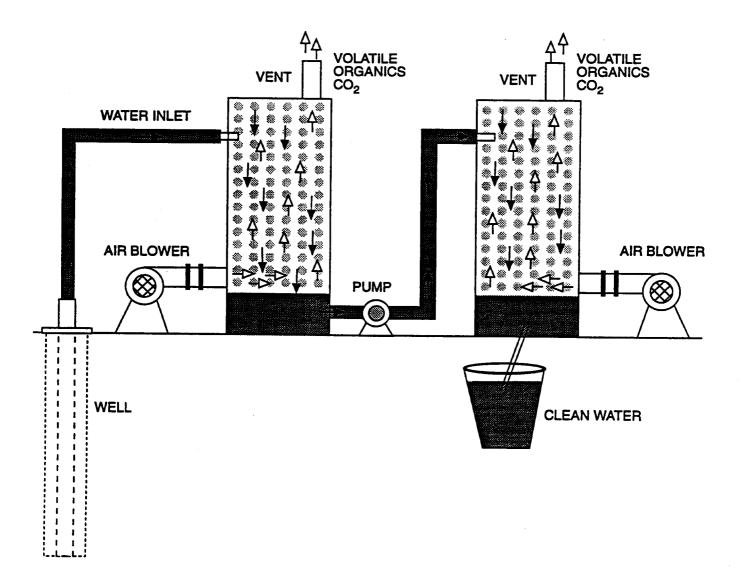


FIGURE 2-1. Packed Tower Air Strippers

Now that you have explained why this is a potential problem, your client wants to know how big a problem it could be. You could do the problem with your geochemical modeling code, but for simplicity you will use Figure 2-2.

How much calcite (in milligrams per liter) will precipitate when the groundwater is equilibrated with the atmosphere in the air stripping tower? (molecular weight of calcite = 100 grams/mole)

If the system is designed to pump 100 gpm, how much calcite (in milligrams) will precipitate per month?

about 44 grams per cubic inches per month. (calcite has a density of 1361000 Cubic inches (month

Can you suggest some ways of dealing with the calcite precipitation problem in this treatment unit? udd acid

High POOZ Complexing Agent- Polyphosphoto

Case 2. Heating Groundwater in Equilibrium with Calcite.

Typical groundwater has a temperature of around 10C. When this groundwater is pumped to the surface it may be exposed to higher land surface temperatures (20 to 30C) depending on the season and it may be heated for some process use. Equilibrium constants for mineral solubility are temperature dependent. Most minerals are more soluble at higher temperatures, however calcite is less soluble. This can have important implications if the groundwater pumped from the ground was at equilibrium with calcite at an aquifer temperature lower than that to which the water is exposed after pumping.

Your client would like to pump groundwater in equilibrium with calcite at a temperature of 10C to a processing plant and heat it to 80C. Your job is to evaluate the degree of calcite precipitation that might occur as a result of this temperature change. Once again, you obtain a complete chemical

14-7

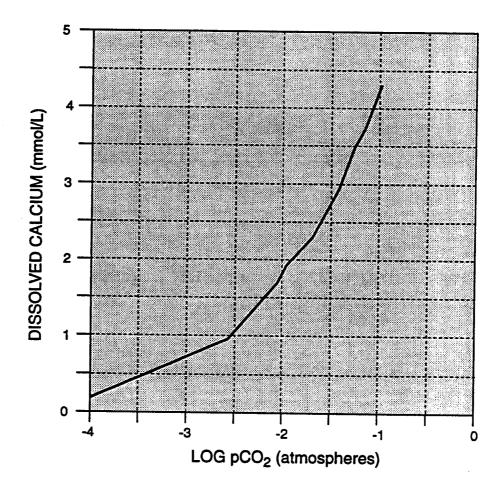


FIGURE 2-2. Concentration of Dissolved Calcium in Water in Equilibrium with Calcite as a Function of PCO<sub>2</sub>

analysis of the water for major cations and anions plus a field pH value. You run your geochemical modeling code and find that the water is in equilibrium with calcite at this temperature  $(K_{calcite,10C} = 10^{-8.4})$ . Using the Van't Hoff equation (see any introductory chemistry or geochemistry textbook), you then calculate the equilibrium constant for calcite at 80C and find that  $K_{calcite,80C} = 10^{-9.2}$ . The calcite reaction for this equilibrium constant is:

$$CaCO_3 = Ca^{2+} + CO_3^{2-}$$

Without doing the detailed calculations, what is the general effect of this change in equilibrium constant for this reaction on the dissolved concentrations of calcium and carbonate in equilibrium with calcite?

(Remember, at equilibrium the equilibrium constant equals the ion activity product for the reaction.)

Next, you simulate heating the groundwater to 80C with your geochemical reaction model. The result is that over 70% of the dissolved calcium and carbonate precipitate as calcite. Can you think of some clever way of either eliminating calcite precipitation or dealing with the precipitated calcite?

iower pH udd complexing agent add softening agent - best option

#### CLASS EXERCISE NUMBER 3

#### ACID MINE DRAINAGE IMPACTS ON GROUNDWATER QUALITY

#### BACKGROUND INFORMATION

Acidic water is commonly associated with mining activities because acid may be used in ore processing or it may be produced as an unwanted byproduct when sulfide minerals are exposed to atmospheric oxygen. Whatever the case, the low pH water typically has high concentrations (> 1 mg/L) of heavy metal contaminants and sulfate (> 1,000 mg/L). The low pH water and metals may not be particularly mobile in the subsurface if the soil and aquifer material contain carbonate minerals which will neutralize the water. This exercise requires an evaluation of the mobility of the low pH plume at a site as well as a review of the various geochemical reactions that might affect the concentration and mobility of sulfate in an aquifer.

#### **EXERCISE**

Table 3-1 provides water quality data at a mine site that has been impacted by acid leachate. Compare the natural groundwater values to contaminated water with a low pH and high sulfate and metals concentrations. Note that at low pH values many of the metals (Cu, Fe, Mn, Pb and Zn) are not limited to low concentrations by solubility-limiting solid phases as they normally are at more neutral pH values.

Under normal conditions, the sulfate concentration in groundwater is limited to about 2,500 mg/L because of the formation of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). What are some possible explanations for the sulfate concentration of almost 60,000 mg/L in the contaminated groundwater?

Normally bicarbonate (HCO<sub>3</sub>·) and carbonate (CO<sub>3</sub><sup>2</sup>·) are major anions in groundwater. What parameter is used to denote these compounds in Table 3-1? Why is the value so low in the contaminated groundwater?

14-11

PARAMETER	NATURAL GROUNDWATER (typical values)	ACID LEACHATE CONTAMINATED GROUNDWATER
pH	7.5	3.1
TDS	500	84,600
Alkalinity as CaCO <sub>3</sub>	150	< 5
SO <sub>4</sub>	150	59,600
Na	30	17
Ca	80	563
Mg	30	7,960
As	< 0.01	0.7
Cd	< 0.01	0.34
Cu	0.01	52
Fe	<1	1,270
Mn	0.5	319
Pb	< 0.005	5
Zn	0.02	187

#### TABLE 3-1. Water Quality (mg/L)

Figure 3-1 is a schematic of a cross section through the contaminated aquifer. It shows the source of acidic leachate on the left, groundwater and mineralogical conditions in the low pH zone of the aquifer, the acid neutralization front with important geochemical reactions, and a summary of chemical data at the bottom of the figure. Take a minute to study the figure and become acquainted with this geochemical system, then answer the following questions:

What reaction(s) in the aquifer limit the rate at which the acid neutralization front moves relative to the groundwater flow rate?

What chemical reactions add to the acidity (amount of H<sup>+</sup>) in the low pH plume?

What are the sources of calcium  $(Ca^{2+})$  in the aquifer that can combine with sulfate to form gypsum?

If gypsum is the solubility-limiting solid phase for sulfate upgradient of the acid neutralizing front, how can you explain the large changes in sulfate concentration (50,000 to 2,500 mg/L) in this zone of the aquifer?

Figure 3-2 shows the results of a computer model used to simulate neutralization of the acid leachate solution. The simulation consisted of adding incremental doses of  $CaCO_3$  to the solution and calculating the resulting pH value as each increment of the neutralizing agent ( $CaCO_3$ ) was added. Considering the reactions shown on Figure 3-1, to what can you attribute the steep rise in the curve at a pH value of about 4.8?

How could you use the information on Figure 3-2 to evaluate the rate of movement of the acid neutralizing front produced by this acid leachate in an aquifer?

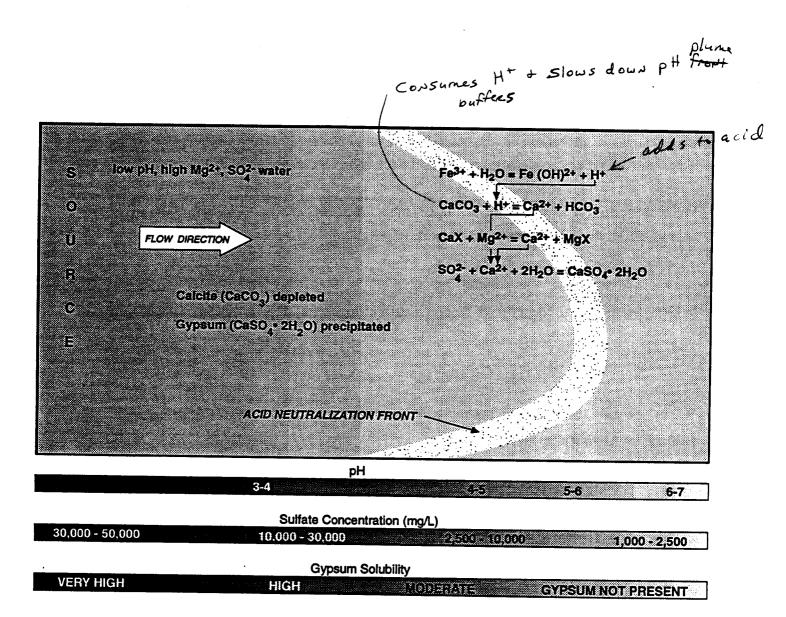
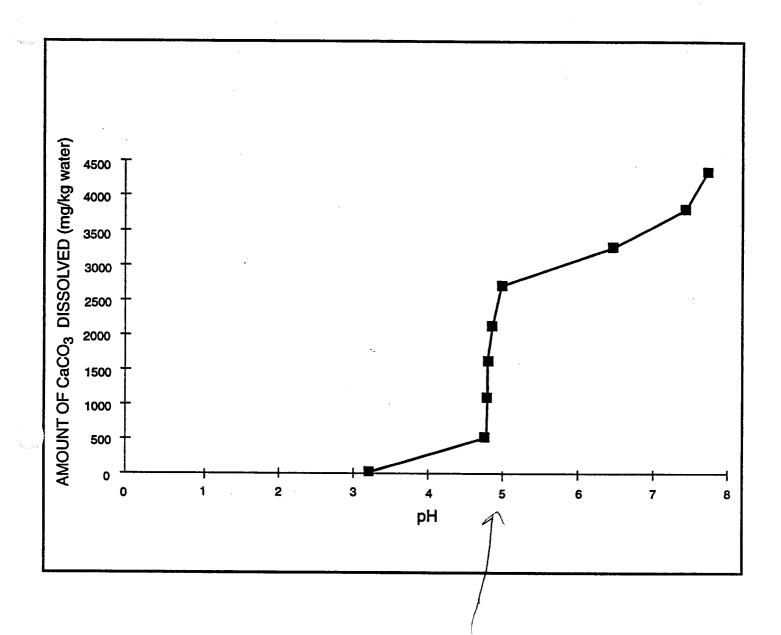


FIGURE 3-1 Neutralization of Acidic Leachate Conceptual Geochemical Model and Distribution of Indicator Parameters



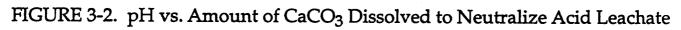


Figure 3-3 shows the results of another computer simulation in which the solubility of gypsum was calculated and compared to the dissolved magnesium concentration of contaminated groundwater from the acidic plume. The value K'' is not a true thermodynamic equilibrium constant. It represents the product of the total dissolved calcium and sulfate concentrations, i.e.

$$K'' = T_{Ca} + T_{SO4}$$

where,

 $T_{Ca}$  = total dissolved calcium concentration

 $T_{SO4}$  = total dissolved sulfate concentration

Could Figure 3-3 explain the variability of sulfate concentration shown in Figure 3-1?

If sulfate is a contaminant of concern at this site and its cleanup level in groundwater is 500 mg/L, what geochemical process will extend the cleanup time for this aquifer compared to simply removing the initial dissolved sulfate concentration?

Does Figure 3-3, give you any ideas of ways that you could enhance the removal of sulfate from this system?

The initial cation/anion charge balance calculation for the acid leachate water given in Table 3-1 gave a value of about 40%. This meant that either the chemical analysis was poor or that an important cation was not being analyzed. On re-testing, it was found that aluminum was present in the leachate at very high concentrations of about 5,000 mg/L. How might the presence of aluminum affect the conclusions you came to regarding the acidity of the water (Figure 3-2) and gypsum solubility (Figure 3-3)? (Note that aluminum hydrolyzes

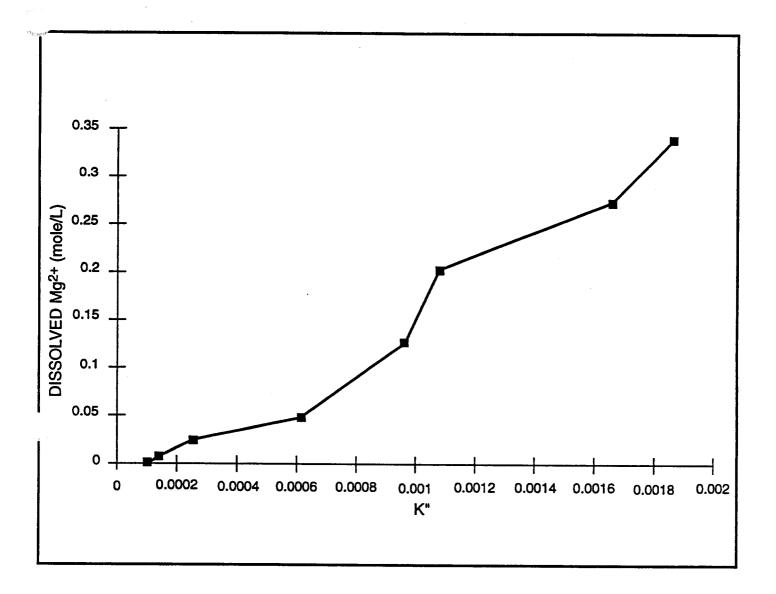


FIGURE 3-3. Dissolved Mg<sup>2+</sup> vs. Gypsum Solubility

according to the reaction  $Al^{3+} + H_2O = Al(OH)^+ + H^+$ , and aluminum forms strong dissolved complexes with sulfate.)

#### INORGANIC CLASS EXERCISE NUMBER 4

#### REDOX AND SORPTION CHEMISTRY OF ARSENIC AND FERRIC HYDROXIDE AT A FORMER CHEMICAL WASTE SITE

#### BACKGROUND INFORMATION

Arsenic (As) contamination of ground water has occurred at a former chemical waste site on the West Coast. Organic contaminants including benzene, the xylene isomers, and trichloroethene have also contaminated ground water at the site. Native ground water conditions were oxidizing characterized by a near neutral pH. Sulfuric acid and sodium hydroxide, however, were discharged at the site, and pH values of ground water vary from 3.2 to 10.0. Contaminant distributions of arsenic, iron and other metals are controlled by redox, precipitation/dissolution, and sorption/desorption reactions with Fe(OH)3, a natural and anthropogenic solid found at the site. Dispersion of organic contaminants has produced reducing conditions within the saturated zone. Several soil, sediment, and ground water samples were collected, and batch sorption experiments and characterization studies were conducted to evaluate contaminant mobility. Because of the high sorptive capacity of Fe(OH)3 for As, it was decided that quantifying geochemical processes are important for evaluating contaminant distributions and designing effective sediment and ground water remedial actions at the site.

#### EXERCISE

Results of batch sorption studies, ground-water quality analyses, and  $Fe(OH)_3$  precipitation/dissolution investigations are provided below. Figure 1 shows results of batch sorption studies with  $Fe(OH)_3$  and As. The solubility of  $Fe(OH)_3$  at different pH values and at constant Eh (0.240 V) is provided in Figure 2. Figure 3 shows concentrations of As versus Fe for several ground water samples collected at the site. Figure 4 is a solubility curve of  $Fe(OH)_3$  as a function of varying Eh. Specific questions are asked regarding these figures and tables.

After you have addressed these questions, HOW WOULD YOU CLEAN UP THIS SITE?

14-19

### **CLASS EXERCISE**

Evaluate water quality results collected at the site in terms of redox chemistry for iron (oxidizing or reducing).

ل د فترون

DOC>1, reducing

#### WATER QUALITY ANALYSIS I

. . . . .

- -

SPECIES/PARAMETER	VALUE (mg/L)
Fe	10
SO4	500
ALKALINITY	De lucito
(mg CaCO <sub>3</sub> /L)	250 reducing
Mn	2
As	2.5
DOC	3 - higher Doc
Eh (V)	-0.200
pH	7.5

#### WATER QUALITY ANALYSIS II

SPECIES/PARAMETER	VALUE (mg/L)	
Fe	350	
so <sub>4</sub>	15000	
ALKALINITY		
(mg CaCO <sub>3</sub> /L)	0	oxidizing
Mn	5	
As	50	
DOC	0 - low Doc	
Eh (V)	+0.800	
pH	3.2	

### **CLASS EXERCISE**

1

Evaluate water quality results collected at the site in terms of redox chemistry for iron (oxidizing or reducing).

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#### WATER QUALITY ANALYSIS III

----

SPECIES/PARAMETER	VALUE (mg/L)	
Fe	0.1 low	
SO4	300 oxidia	zin
ALKALINITY		
(mg CaCO <sub>3</sub> /L)	110	
Mn	0.05	
As	0.002 m vd . low	
DOC	0.2	
Eh (V)	+0.250	
pH	6.5	

#### WATER QUALITY ANALYSIS IV

SPECIES/PARAMETER	VALUE (mg/L)	
<sub>,</sub> Fe	10	
so <sub>4</sub>	300	
ALKALINITY		1 reducing
(mg CaCO <sub>3</sub> /L)	110	DOC 71, reducing
Mn	1.5	V
DOC	10	
As	0.75	
Eh (V)	-0.220	
pH	10.0	

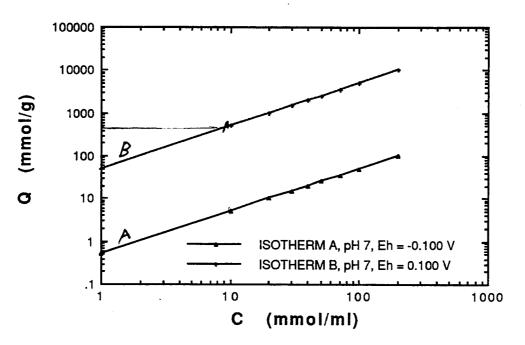


FIGURE 1, SORPTION ISOTHERM FOR ARSENIC AND Fe(OH)3. NOTE THAT Kd = Q/C (ml/g).

FROM FIGURE 1, CALCULATE Kd VALUES FOR ARSENIC FROM THE TWO ISOTHERMS. Q=Xm

NOTE: Kd = Q/C (ml/g).

**ISOTHERM A** 

X=KC **ISOTHERM B** 

GIVEN THAT Rd = 1 + pKd, where n **Rd = RETARDATION FACTOR,**  $p = DENSITY (g/cm^3),$ n = POROSITY, ANDKd = DISTRIBUTION COEFFICIENT (ml/g)

CALCULATE Rd FOR THE FOLLOWING:

SPECIES	Kd(ml/g)	p/n	Rd
As	50	8	401
As	0.5	8	5

What water-rock interactions would account for the different Rd values for arsenic?

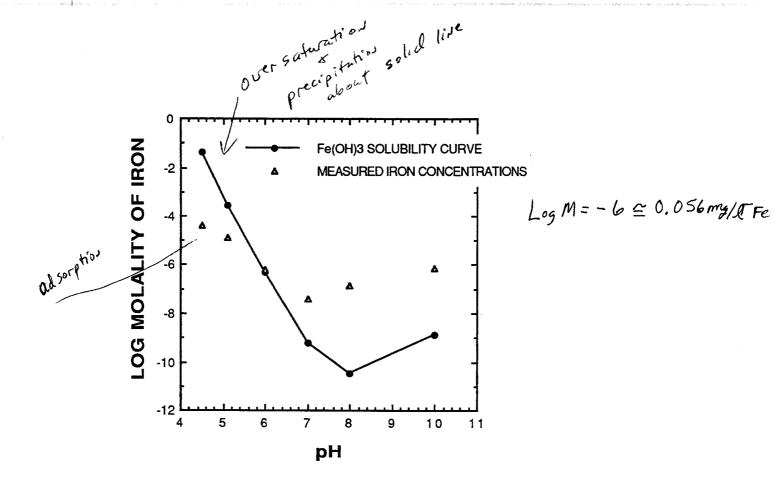
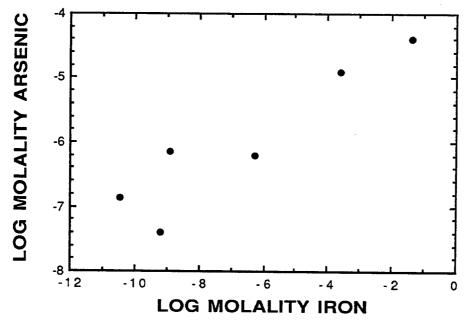


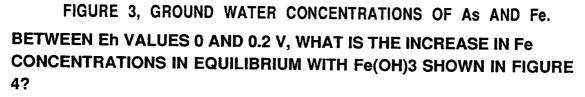
FIGURE 2, SOLUBILITY OF Fe(OH)3 AT Eh = 0.240 V.

IN FIGURE 2, WHICH DATA POINTS ARE UNDERSATURATED, SATURATED, AND OVERSATURATED WITH RESPECT TO Fe(OH)3? LABEL POINTS ON GRAPH.

IN WHAT REGIONS OF FIGURE 2 DO ADSORPTION AND PRECIPITATION PROCESSES DOMINATE?

WHAT GEOCHEMICAL PARAMETERS WOULD PRODUCE APPARENT OVERSATURATION FOR SEVERAL DATA POINTS AT pH 7 AND HIGHER? HINT: LOOK AT FIGURE 4. FROM FIGURE 3, INTERPRET THE DISTRIBUTION OF ARSENIC AND IRON FOR GROUND WATER SAMPLES COLLECTED AT THE SITE. WHY IS THERE A POSITIVE CORRELATION BETWEEN ARSENIC AND IRON?





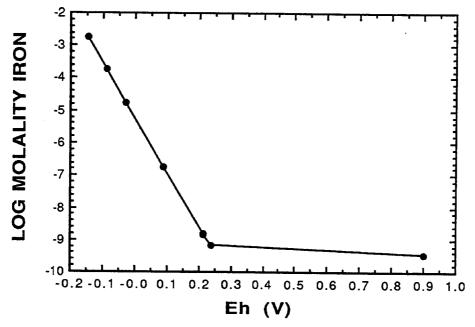


FIGURE 4, Fe(OH)3 SOLUBILITY AT pH 7

#### ANSWERS TO CLASS EXERCISE NUMBER 1

#### MOBILITY OF METALS IN GROUNDWATER AT A FORMER PAINT PRODUCING PLANT

If the sulfate concentration in the influent water is 0.01 ppm, what will be the barium concentration in the extraction well assuming equilibrium with barite? At equilibrium with barite, the equilibrium dissolved barium concentration will be about 1 ppm (Figure 1-2).

If the sulfate concentration in the influent water is 1 ppm, what will be the barium concentration in the extraction well assuming equilibrium with barite? At equilibrium with barite, the equilibrium dissolved barium concentration will be about 1 ppm. This is the same concentration of barium as in the first question even though the influent sulfate concentration has increased by 100x. The reason for this is that, as barite dissolves in the water, it releases both barium and sulfate. As long as the sulfate concentration does not exceed about 1ppm, the equilibrium barium concentration will also be about 1 ppm (Figure 1-2).

If the sulfate concentration in the influent water is 10 ppm, what will be the barium concentration in the extraction well assuming equilibrium with barite? The presence of dissolved sulfate in water greater than 1ppm will limit the amount of barium that can be present in solution in equilibrium with barite. As shown by Figure 1-2, at a sulfate concentration of 10 ppm the amount of barium in solution will be limited to about 0.1 ppm.

# Why is the barium concentration approximately the same for sulfate concentrations of 0.01 and 1 ppm, but so much lower for a sulfate concentration of 10 ppm?

In the sulfate concentration range from 0.01 to 1 ppm barite is relatively soluble and its solubility will fix the dissolved concentrations of both sulfate and barium (at values of about 1 ppm, Figure 1-2). At higher sulfate concentrations than 1 ppm, the dissolved sulfate concentration is not limited by the solubility of barite, however, if barite is the only source of barium in solution, then the dissolved concentration of barium will be limited by barite solubility at the influent sulfate concentration.

Assume that the extraction wells can pump at a rate of 1.5 gpm from wells placed on a twenty meter grid and that the initial concentration of barium in the solid phase in the zone of contamination is 3,000 ppm. The contaminated thickness of the aquifer is 10 meters and the bulk density is 2 g/cc.

#### What is the mass of barium that must be removed by each extraction well?

Volume of Material x Density of Material x Barium Concentration = Mass of Barium

 $[20m \times 20m \times 10m] \times [2 \text{ g/cc} \times 10^6 \text{ cc/m}^3] \times [3,000 \text{ mg Ba/kg soil } \times 10^{-3} \text{ kg/g}]$  $= 2.4 \times 10^{10} \text{ mg Ba}$ 

If the influent sulfate concentration is 1 ppm and barite solubility limits the dissolved concentration of barium, how much barium will be removed by the extraction well per day?

From Figure 1-2, the dissolved barium concentration will be about 1ppm (mg/L).

Amount of barium removed per day = Well Flow Rate Per Day x Dissolved Barium Concentration =

 $[1.5 \text{ gal/min x } 60 \text{ min/hr x } 24 \text{ hr/day x } 3.785 \text{ L/gal}] \text{ x } [1 \text{ mg/L}] = 8.2 \text{ x } 10^3 \text{ mg/day}$ 

How long will it take to remove all of the barium? Length of Time = Concentration / Extraction Rate =

 $[2.4 \times 10^{10} \text{ mg Ba}] / [8.2 \times 10^3 \text{ mg/day}] = 2.9 \times 10^6 \text{ days} \approx 8,000 \text{ years}$ 

### How long will it take to remove all of the barium if the influent sulfate concentration is 10 ppm?

At this sulfate concentration the dissolved barium concentration will be about 0.1 ppm or ten times less than when the sulfate concentration is at 1 ppm. It will take ten times longer to extract all the barium by this technique.

# Is groundwater sweeping a reasonable remedial technology for barium given these conditions?

No.

# Can you think of some ways of increasing the efficiency of groundwater sweeping for this situation?

• More extraction wells

• Use a flushing solution that increases the solubility of barite by complexing with barium or sulfate.



#### ANSWERS TO CLASS EXERCISE NUMBER 2

#### CALCITE PRECIPITATION DUE TO CO2 DEGASSING OR TEMPERATURE INCREASE

Your client wants to know why this is such a big deal when you are supposedly treating a volatile organics problem. Explain it in 25 words or less. Equilibration of the groundwater with atmospheric air in the stripper will cause  $CO_2$  to degas. This will raise the pH of the water and decrease the solubility of calcite, which will precipitate and may plug up the works. (all right, so it took me more than 25 words.)

Now that you have explained why this is a potential problem, your client wants to know how big a problem it could be. You could do the problem with your geochemical modeling code, but for simplicity you will use Figure 2-2.

How much calcite (in milligrams per liter) will precipitate when the groundwater is equilibrated with the atmosphere in the air stripping tower? (formula weight of calcite = 100 grams/mole)

Solubility of calcite at log  $pCO_2 = -1$  atm is  $\approx 4.2$  mmol/L (assuming that all the calcium is derived from calcite)

Solubility of calcite at log pCO<sub>2</sub> = -3.5 atm is  $\approx 0.5$  mmol/L

A rough estimate of the amount of calcite that will precipitate is the difference in the solubility at these two gas pressures.

Difference in solubility = 4.2 mmol/L - 0.5 mmol/L = 3.7 mmol/L

The formula weight of calcite is 100 g/mole, therefore the amount that will precipitate in mg/L is:

3.7 mmol/L x 100 mg/mmol = 370 mg/L.

If the system is designed to pump 100 gpm, how much calcite (in milligrams) will precipitate per month?

370 mg/L x 100 gal/min x 3.785 L/gal x 60 min/hr x 24 hr/day x 30 day/mo  $\approx$ 

#### 6 x 10<sup>9</sup> mg/mo

Convert the last quantity to cubic inches per month. (calcite has a density of about 44 grams per cubic inch)

 $6 \times 10^9 \text{ mg/mo} \times 10^{-3} \text{ mg/g} \times 1/44 \text{ g/in}^3 \approx 136,000 \text{ cubic inches (a cube <math>\approx 50 \text{ inches per side)}$ 

## Can you suggest some ways of dealing with the calcite precipitation problem in this treatment unit?

The general treatment method is to raise the solubility of calcite in the air stripper. This is done by adding acid to the water to lower the pH. It could also be done by raising the  $CO_2$  gas pressure in the air pumped into the stripper (this may not be economical because of the amount of  $CO_2$  gas required). A final method that is used is to adding a strong complexing agent for calcium (such as polyphosphate to the water as it is pumped from the ground.

Case 2. Heating Groundwater in Equilibrium with Calcite.  $CaCO_3 = Ca^{2+} + CO_3^{2-}$ 

Without doing the detailed calculations, what is the general effect of this change in equilibrium constant for this reaction on the dissolved concentrations of calcium and carbonate in equilibrium with calcite?

(Remember, at equilibrium the equilibrium constant equals the ion activity product for the reaction.)

The ion activity product for the reaction  $CaCO_3 = Ca^{2+} + CO_3^{2-}$  is:

#### $IAP = (activity Ca^{2+}) * (activity CO_3^{2-})$

If the equilibrium constant decreases with temperature then the amount of calcium and carbonate that can be at equilibrium with the solid at the higher temperature is less than that at equilibrium at the lower temperature. As a consequence calcite will precipitate from solution as the temperature is raised in order to maintain equilibrium.

Next, you simulate heating the groundwater to 80C with your geochemical reaction model. The result is that over 70% of the dissolved calcium and carbonate precipitate as calcite. Can you think of some clever way of either eliminating calcite precipitation or dealing with the precipitated calcite?

Once again, you could try to increase the solubility of the calcite at the higher temperature by lowering the pH or adding a complexing agent. Alternatively, you could allow the mineral to precipitate and filter it out from the solution. Whichever you use, it will probably add significantly to the operating costs of the system.

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#### ANSWERS TO CLASS EXERCISE NUMBER 3

#### ACID MINE DRAINAGE IMPACTS ON GROUNDWATER QUALITY

Under normal conditions, the sulfate concentration in groundwater is limited to about 2,500 mg/L because of the formation of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). What are some possible explanations for the sulfate concentration of almost 60,000 mg/L in the contaminated groundwater?

Gypsum solubility is enhanced by the high ionic strength of the contaminated groundwater which lowers the activity coefficients of the dissolved species. Also, magnesium forms strong complexes with sulfate thereby lowering the activity of sulfate.

Normally bicarbonate (HCO<sub>3</sub>-) and carbonate (CO<sub>3</sub><sup>2</sup>-) are major anions in groundwater. What parameter is used to denote these compounds in Table 3-1? Why is the value so low in the contaminated groundwater?

Alkalinity is a measure of the bicarbonate and carbonate concentrations of the water. At a pH of 3.1 the alkalinity of the water is zero.

What reaction(s) in the aquifer limit the rate at which the acid neutralization front moves relative to the groundwater flow rate? The primary reaction that consumes hydrogen in the system is calcite ( $CaCO_3$ ). Note that calcite is depleted in the acidic zone of the plume.

What chemical reactions add to the acidity (amount of  $H^+$ ) in the low pH plume? The hydrolysis of Fe<sup>3+</sup> produces hydrogen and adds to the acidity of the groundwater.

What are the sources of calcium  $(Ca^{2+})$  in the aquifer that can combine with sulfate to form gypsum?

Calcium is released from the dissolution of calcite and as part of the ion exchange reaction with the clay minerals (CaX).

If gypsum is the solubility-limiting solid phase for sulfate upgradient of the acid neutralizing front, how can you explain the large changes in sulfate concentration (50,000 to 2,500 mg/L) in this zone of the aquifer?

The change in concentration is due to the effect of ionic strength and complexation on the effective concentrations (or activities) of the components of gypsum. Gypsum is very soluble near the source because of the high ionic strength and the high concentration of magnesium, which complexes with sulfate. As you move away from the source the ionic strength and the magnesium concentrations decrease, lowering the solubility of gypsum and decreasing the concentrations of calcium and sulfate that can be in equilibrium with gypsum.

Figure 3-2 shows the results of a computer model used to simulate neutralization of the acid leachate solution. The simulation consisted of adding incremental doses of  $CaCO_3$  to the solution and calculating the resulting pH value as each increment of the neutralizing agent ( $CaCO_3$ ) was added. Considering the reactions shown on Figure 3-1, to what can you attribute the steep rise in the curve at a pH value of about 4.8?

The steep rise in the curve at a pH of 4.8 is due to the precipitation of iron as ferric hydroxide from the solution. As shown by the following reaction, this releases quite a bit of hydrogen from the water.

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$$

How could you use the information on Figure 3-2 to evaluate the rate of movement of the acid neutralizing front produced by this acid leachate in an aquifer?

Figure 3-2 shows how much acidity is present in the water in terms of calcium carbonate. In other terms, in shows the amount of calcium carbonate necessary in the solid form necessary to neutralize the acid leachate. Comparing the flux of water at a given acidity with the amount of calcium carbonate present in the solid phase in the aquifer can be used to determine the rate of advance of the acid front relative to the groundwater flow velocity. For instance, if each pore volume of water consumes half the neutralizing capacity of the aquifer in that pore volume, then the

acid front will move at a rate of 1/2 the groundwater velocity.

Figure 3-3 shows the results of another computer simulation in which the solubility of gypsum was calculated and compared to the dissolved magnesium concentration of contaminated groundwater from the acidic plume. The value K'' is not a true thermodynamic equilibrium constant. It represents the product of the total dissolved calcium and sulfate concentrations, i.e.

 $K'' = T_{Ca} + T_{SO4}$ 

where,

 $T_{Ca}$  = total dissolved calcium concentration

 $T_{SO4}$  = total dissolved sulfate concentration

Could Figure 3-3 explain the variability of sulfate concentration shown in Figure 3-1?

Yes, Figure 3-3 shows that the solubility of a mineral can vary dramatically depending on the other components in the groundwater.

If sulfate is a contaminant of concern at this site and its cleanup level in groundwater is 500 mg/L, what geochemical process will extend the cleanup time for this aquifer compared to simply removing the initial dissolved sulfate concentration?

The presence of the acid leachate in the aquifer has caused the precipitation of gypsum in the pore spaces. Not only will the dissolved sulfate have to be lowered in the aquifer to the cleanup level, but the solid gypsum will also have to be dissolved and removed because the solubility of gypsum is high enough that the sulfate level will exceed 500 mg/L if the water is in equilibrium with gypsum.

Does Figure 3-3, give you any ideas of ways that you could enhance the removal of sulfate from this system?

The solubility of gypsum can vary over an order of magnitude due to solution conditions. It is possible to enhance the removal of gypsum by adding complexing agents for calcium and sulfate to the water that is flushed through the aquifer.

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The initial cation/anion charge balance calculation for the acid leachate water given in Table 3-1 gave a value of about 40%. This meant that either the chemical analysis was poor or that an important cation was not being analyzed. On re-testing, it was found that aluminum was present in the leachate at very high concentrations of about 5,000 mg/L. How might the presence of aluminum affect the conclusions you came to regarding the acidity of the water (Figure 3-2) and gypsum solubility (Figure 3-3)? (Note that aluminum hydrolyzes according to the reaction  $Al^{3+} + H_2O = Al(OH)^+ + H^+$ , and aluminum forms strong dissolved complexes with sulfate.)

Aluminum hydrolyzes as the pH of the water is increased just as iron does. The result of this reaction is that the acidity of the water would be significantly increased because of the presence of 5,000 mg/L aluminum. Because aluminum forms strong complexes with sulfate, the effective concentration of sulfate will be lower in the presence of aluminum. As a result, the solubility of gypsum will be increased by the presence of aluminum.

Evaluate water quality results collected at the site in terms of redox chemistry for iron (oxidizing or reducing).

#### WATER QUALITY ANALYSIS I

SPECIES/PARAMETER	VALUE (mg/L)
Fe	10
SO4	500
ALKALINITY	
(mg CaCO <sub>3</sub> /L)	250
Mn	2
As	2.5
DOC	3
Eh (V)	-0.200
pH	7.5
REDUCING CONDITIONS, I	

**REDUCING CONDITIONS: Elevated concentrations of As,** Fe, Mn, and DOC.

#### WATER QUALITY ANALYSIS II

SPECIES/PARAMETER	VALUE (mg/L)
Fe	350
so <sub>4</sub>	15000
ALKALINITY	
(mg CaCO <sub>3</sub> /L)	0
Mn	5
As	50
DOC	0
Eh (V)	+0.800
pH	3.2

OXIDIZING CONDITIONS: Elevated concentrations of As, Fe, Mn, low pH, and low DOC.

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Evaluate water quality results collected at the site in terms of redox chemistry for iron (oxidizing or reducing).

#### WATER QUALITY ANALYSIS III

SPECIES/PARAMETER	VALUE (mg/L)
Fe	0.1
SO4	300
ALKALINITY	
(mg CaCO <sub>3</sub> /L)	110
Mn	0.05
As	0.002
DOC	0.2
Eh (V)	+0.250
pH	6.5

and a state of the second s

OXIDIZING CONDITIONS: Low concentrations of As, Fe, Mn, and DOC.

#### WATER QUALITY ANALYSIS IV

SPECIES/PARAMETER	VALUE (mg/L)
Fe	10
SO4	300
ALKALINITY	
(mg CaCO <sub>3</sub> /L)	110
Mn	1.5
DOC	10
As	0.75
Eh (V)	-0.220
рН	10.0

**REDUCING CONDITIONS: Elevated concentrations of As,** Fe, Mn, and DOC.

Kd VALUES FOR ARSENIC = 50 AND 0.50 ml/g.

```
GIVEN THAT Rd = 1 + <u>pKd</u>, where

n

Rd = RETARDATION FACTOR,

p = DENSITY (g/cm<sup>3</sup>),

n = POROSITY, AND

Kd = DISTRIBUTION COEFFICIENT (ml/g)
```

### CALCULATE Rd FOR THE FOLLOWING:

<u>SPECIES</u>	Kd(ml/g)	p/n	Rd
As	50	8	401
As	0.5	8	5

What water-rock interactions would account for the different Rd values for arsenic and iron?

Decreasing redox potential affects the stability of Fe(OH)<sub>3</sub> in which under reducing conditions, the solubility of Fe(OH)<sub>3</sub> increases significantly. Subsequently, desorption of As occurs as dissolution proceeds. Decreasing Rd values reflect dissolution of Fe(OH)<sub>3</sub> and desorption of As.

FIGURE 2.

UNDERSATURATED CONDITIONS OCCUR BELOW THE SOLUBILITY CURVE FOR Fe(OH)<sub>3</sub>; SATURATED CONDITIONS OCCUR ALONG THE SOLUBILITY CURVE; AND OVERSATURATED CONDITIONS OCCUR ABOVE THE SOLUBILITY CURVE.

ADSORPTION OCCURS WHEN A SOLUTION IS UNDERSATURATED WITH RESPECT TO A SOLID PHASE. PRECIPITATION OCCURS WHEN A SOLUTION IS OVERSATURATED WITH RESPECT TO A SOLID PHASE.

DECREASING REDOX POTENTIAL (Eh) RESULTS IN AN INCREASE IN  $Fe(OH)_3$  SOLUBILITY. THIS IS SHOWN BY SEVERAL DATA POINTS THAT PLOT ABOVE THE SOLUBILITY CURVE OF  $Fe(OH)_3$ CALCULATED AT Eh = 0.24 V.

#### FIGURE 3.

THE POSITIVE CORRELATION BETWEEN ARSENIC AND IRON IS RELATED TO ADSORPTION-DESORPTION AND PRECIPITATION-DISSOLUTION PROCESSES. AS Fe(OH)<sub>3</sub> DISSOLVES, ARSENIC IS RELEASED TO SOLUTION.

#### FIGURE 4.

BETWEEN Eh VALUES 0 AND +0.2 V, IRON CONCENTRATIONS IN EQUILIBRIUM WITH Fe(OH)<sub>3</sub> APPROXIMATELY INCREASE BY A FACTOR OF 2500. THIS CALCULATION SHOWS THAT Fe(OH)<sub>3</sub> SOLUBILITY CAN BE VERY SENSITIVE TO DECREASING REDOX POTENTIAL.

#### SITE REMEDIATION

#### pH, REDOX CONDITION

### ACIDIC, OXIDIZING

#### **ALTERNATIVE**

NEUTRALIZATION WITH CaCO<sub>3</sub>. PRECIPITATION OF Fe(OH)<sub>3</sub> ENHANCES ARSENIC REMOVAL. REMOVE ACIDIC SOURCES.

#### NEUTRAL, REDUCING ALKALINE, REDUCING

INJECTION OF SULFIDE SOLUTION. PRECIPITATE FERROUS SULFIDE, CO-PRECIPITATE ARSENIC. Section 15

# Geochemistry Processes Influencing the Fate of Organic Solutes in Ground Water

Lecture by: Patrick Longmire Los Alamos National Laboratory

# SECTION CONTENTS

 $= a_{12} + b_{13} +$ 

Sec. 1

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## GEOCHEMICAL PROCESSES INFLUENCING THE FATE OF ORGANIC SOLUTES IN GROUND WATER

### I. INTRODUCTION

## II. PHYSICO-CHEMICAL CONTROLS ON THE FATE OF ORGANIC COMPOUNDS

### III. EXAMPLES

- A. Petroleum hydrocarbons
- B. Aliphatic hydrocarbons
- C. Chlorinated Pesticides

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# Macromolecular Transport of Hydrophobic Contaminants in Aqueous Environments

by Carl G. Enfield and Göran Bengtsson<sup>a</sup>

#### ABSTRACT

The mobility of a model macromolecule, blue dextran, was compared under laboratory conditions to the mobility of tritiated water through a sandy soil. The blue dextran eluted from the soil prior to the tritiated water. The phenomenon was compared to exclusion chromatography where molecules are separated by size with the largest eluting first and each molecule flowing through a different portion of the total porosity. The porosity occupied by the macromolecule was 0.87 times the porosity occupied by water. When the soil was amended with a mixture of kaolinite and bentonite clay in a 1:1 ratio to weight fractions of 2% and 6% total clay, the porosity occupied by the macromolecule was decreased to 0.81 and 0.66 times the porosity occupied by water, respectively. The implications to hydrophobic chemical transport based on the presence and mobility of a macromolecule were evaluated from a theoretical basis. Macromolecules should increase the relative mobility of slightly mobile compounds more than they increase the relative mobility of highly mobile compounds. Very hydrophobic compounds should show greater mobility under natural conditions than predicted, ignoring the presence of dissolved organic carbon.

#### INTRODUCTION

The transport of organic pollutants in a saturated porous medium is determined by many physical, chemical, and biological processes. Mathematical models recently reviewed by Rao and Jessup (1983), Boesten and Leistra (1983), and Addiscott and Wagenet (1985) describe the importance of dispersion, advection, sorption, and transformation on the movement of chemicals in soils. Fairly extensive literature (e.g., Chiou *et al.*,

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1979; Karickhoff et al., 1979; Kenaga, 1980; Means et al., 1980; Briggs, 1981; Brown and Flagg, 1981; Karickhoff, 1981; and Schwarzenbach and Westall, 1981) has emphasized the relationship between sorption of nonpolar hydrophobic compounds, the organic carbon content of the soil, and the octanol:water partition coefficient of the sorbate. In summary, neutral organic chemicals are sorbed more strongly to soils with high organic carbon than to soils with low organic carbon. Several relationships have been developed which permit estimating a linear partition coefficient based on easily measurable properties of the chemical such as water solubility or octanol:water partition coefficient. These linear partition coefficients describe the equilibrium concentration sorbed to the organic carbon in the soil based on the concentration in the water. Multiplying the partition coefficient to the organic carbon in the soil by the weight fraction organic carbon in the soil yields the partition coefficient for the soil. Briggs (1981) proposed the relationship

$$k_d = 4.47 F k_{ow}^{0.52}$$
 (1)

to describe the soil:water partition coefficient  $(k_d)$ as a function of the weight fraction of organic carbon in the soil (F) and the octanol:water partition coefficient  $(k_{ow})$ . Roy and Griffin (1985) suggested that relationships such as equation (1) can be expected to predict the soil partition coefficient within a factor of ten. Recently, attention has been given to the possibility of binding of the organic compounds to dissolved organic macromolecules, micelles, or other colloidal materials in the pore water. These mobile macromolecules may greatly increase chemical mobility by sorbing compounds normally sorbed by stationary soil particles.

Several studies have addressed the partitioning between an organic compound of environmental concern and dissolved organic macromolecules

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(e.g., Poirrier et al., 1972; Hassett and Anderson, 1982; Carter and Suffet, 1982; Perdue, 1983; Wijayaratne and Means, 1984; Carlson et al., 1985; Caron et al., 1985; and Gschwend and Wu, 1985). Enfield (1985) suggested that macromolecules, or immiscible substances such as micelles or colloidal materials, moving along with a water carrier, may under certain circumstances enhance the movement of hydrophobic chemicals through soils. If hazardous chemicals partition to mobile macromolecules in subsurface environments, the current approaches of making environmental exposure and risk analysis, assuming partitioning between soil organic carbon and dilute aqueous solutions of the chemical, may significantly underestimate chemical mobility. Adverse environmental impact caused by the application of hazardous materials to the soil surface is more likely where there is a significant amount of recharge. The objective of this study was to determine the relative mobility of a model macromolecule in comparison to the mobility of water through a sandy soil and estimate, based on linear partitioning previously reported in the literature, the influence of mobility of the macromolecule on the mobility of pollutants.

#### THEORETICAL DEVELOPMENT

The movement of a conservative pollutant through saturated soil in the presence of macromolecules or other nonreactive organic substances can be described by dividing a representative elemental volume of the soil system into three phases: aqueous (a), solid (s), and mobile organic (o) phases. With notation given at the end of the paper, the following one-dimensional equations can be written to describe changes in mass concentration in the individual phases as a function of a dispersive flux, a convective flux, and mass transfer between adjacent phases assuming first-order kinetics.

$$\frac{\partial(\theta\rho_{a}C_{a})}{\partial t} = D_{a}\frac{\partial^{2}(\theta\rho_{a}C_{a})}{\partial x^{2}} - V_{a}\frac{\partial(\theta\rho_{a}C_{a})}{\partial x} - k_{a0}\theta\rho_{a}C_{a} +$$

$$k_{oa}\phi\rho_{o}C_{o} - k_{as}\theta\rho_{a}C_{a} + k_{sa}(1-n)\rho_{s}C_{s} \qquad (2)$$

$$\frac{\partial [(1-n)\rho_s C_s]}{\partial t} = -k_{sa}(1-n)\rho_s C_s + k_{as}\theta\rho_a C_a \quad (3)$$

$$\frac{\partial(\phi\rho_{0}C_{0})}{\partial t} = D_{0} \frac{\partial^{2}(\phi\rho_{0}C_{0})}{\partial x^{2}} - V_{0} \frac{\partial(\phi\rho_{0}C_{0})}{\partial x} - \frac{k_{0a}\phi\rho_{0}C_{0} + k_{a0}\theta\rho_{a}C_{a}}{k_{0a}\phi\rho_{0}C_{0} + k_{a0}\theta\rho_{a}C_{a}}$$
(4)

In writing the above equations, the aqueous phase was assumed to totally cover both the solid phase and the organic phase or macromolecule such that transfer of the pollutant from the organic phase to the solid phase requires passing through the aqueous phase. The total change in mass within an elemental volume can be written as the sum of equations (1) through (3) or

$$\frac{\partial(\theta\rho_{a}C_{a})}{\partial t} + \frac{\partial(\phi\rho_{0}C_{0})}{\partial t} + \frac{\partial[(1-n)\rho_{s}C_{s}]}{\partial t} = D_{a}\frac{\partial^{2}(\theta\rho_{a}C_{a})}{\partial x^{2}}$$
$$+ D_{0}\frac{\partial^{2}(\phi\rho_{0}C_{0})}{\partial x^{2}} - V_{a}\frac{\partial(\theta\rho_{a}C_{a})}{\partial x} - V_{0}\frac{\partial(\phi\rho_{0}C_{0})}{\partial x}$$
(5)

When local equilibrium, constant density, and constant volume fractions occupied by the different phases are assumed,

$$\mathbf{k_{ao}}\theta \rho_{a} \mathbf{C_{a}} = \mathbf{k_{oa}}\phi \rho_{o} \mathbf{C_{o}} \tag{6}$$

This yields a dimensionless organic:water partition coefficient or ratio of mass between the organic and aqueous phases as

$$k_{p} = \frac{k_{20}\theta\rho_{2}}{k_{02}\phi\rho_{0}} = \frac{C_{0}}{C_{2}}$$

Similarly,

$$k_{as}\theta\rho_a C_a = k_{sa}(1-n)\rho_s C_s \tag{7}$$

which yields a soil:water partition coefficient

$$k_{d} = \frac{k_{as}\theta \rho_{a}}{k_{sa}(1-n)\rho_{s}} = \frac{C_{s}}{C_{a}}$$

When field measurements are made, there is no attempt to separate the amount of chemical in the aqueous phase versus the amount associated with the macromolecules. To apply this theory to environmental situations, it is necessary to define a new variable C\* as the total mass concentration of the mobile pollutant over all phases

$$C^* = \theta \rho_a C_a + \phi \rho_0 C_0 \tag{8}$$

The total change in the elemental volume can be shown to follow the equation

$$(1 + \frac{k_{ao}}{k_{oa}} + \frac{k_{as}}{k_{sa}})\frac{\partial C^*}{\partial t} = (D_a + \frac{k_{ao}}{k_{oa}}D_o)\frac{\partial^2 C^*}{\partial x^2}$$
$$- (V_a + \frac{k_{ao}}{k_{oa}}V_o)\frac{\partial C^*}{\partial x}$$
(9)

By defining the variables

$$R^* = 1 + \frac{k_{a0}}{k_{0a}} + \frac{k_{as}}{k_{sa}}$$
(10)

which describes the retardation of the chemical relative to the velocity of the total fluid,

$$D^* = D_a + \frac{k_{ao}}{k_{oa}} D_o$$
(11)

the effective dispersion coefficient for the total fluid, and

$$V^* = V_a + \frac{k_{ao}}{k_{oa}} V_o$$
 (12)

the effective velocity of the total fluid, equation (9) becomes

$$R^* \frac{\partial C^*}{\partial t} = D^* \frac{\partial^2 C^*}{\partial x^2} - V^* \frac{\partial C^*}{\partial x}$$
(13)

Equation (13) is the same form that has been solved analytically for a variety of boundary and initial conditions. Several of these solutions have been summarized by van Genuchten and Alves (1982). The theoretical development presented includes retardation of the chemical due to partitioning between the phases and the influence of partitioning on the dispersive and advective transport of a hydrophobic chemical when macromolecules are present.

#### MATERIALS AND METHODS

The soil for the experimental portion of the study was obtained from the current surface horizon of an infiltration basin used at the Vomb water plant to treat surface water for the drinking-water supply of the cities of Lund and Malmo, southern Sweden. The infiltration basins are natural sand deposits. The system operates by intermittently applying lake water to the surface of the infiltration basin, and the filtered water is extracted using wells. The study soil sample had no visible structure in nature and was collected as a disturbed sample. The soil was air-dried and homogenized as much as possible prior to characterization or experimentation. The weight fraction total organic carbon of the soil was determined, on ten replicate samples, using a (Leco model CR-12) total carbon analyzer.

Blue dextran, a polysaccharide synthesized from sucrose by Lactobacillaceae, was selected as a model compound for the study. The size and hydrophilic characteristics of this compound are similar to natural microbial exopolymers found in soil and ground-water systems. This type of hydrophilic carbon compound is not normally identified in aqueous solutions even under rigorous GC-MS evaluations. The manufacturer, Pharmacia Fine Chemicals, reports the molecular weight of this compound to be approximately 2,000,000 g mole<sup>-1</sup>. The octanol:water partition coefficient ( $k_{ow}$ ) for blue dextran was determined by equilibrating 10 ml of ground water containing 0.05  $\mu$ mol (100 mg l<sup>-1</sup>) dextran with 10 ml of n-octanol for 24 hours. After equilibration, the mixture was centrifuged at 3000 g for 20 minutes. The amount of dextran in the octanol was measured, at a wave length of 630 nm, with a (Beckman DB-GD) grating spectrophotometer.

The experimental columns, made from stainless steel, were 5 cm in diameter and 3 cm in length. The top and bottom of the soil sample were supported with sintered stainless steel plates. The replicate columns were packed to a bulk density of 1.5 Mg m<sup>-3</sup>. Assuming a particle density of 2.65 Mg  $m^{-3}$  for the mineral soil, the porosity (n) would be 0.43. After establishing steady-state hydraulic conditions with ground water collected from one of the adjacent extraction wells near the infiltration basin where the soil was sampled, a solution containing 0.25  $\mu$ mol (500 mg l<sup>-1</sup>) of dextran and  $2 \mu \text{Ci} l^{-1}$  tritiated water, in ground water, was pumped through the soil for a period of 3.67 hours. The Darcy flow velocity was approximately 50 cm  $d^{-1}$ , corresponding to the average infiltration rate at the water treatment facility. The pulse of dextran and <sup>3</sup>H was followed by ground water for several additional pore volumes. The pulse length was selected such that the effluent concentration would equal the influent concentration prior to removing the pulse. Dextran and <sup>3</sup>H were monitored as a function of time in the column effluent. Samples were collected in glass tubes using a Fractovap fraction collector every 8 min. The volume of each sample was approximately 5.5 ml. One ml from each fraction sampled was mixed with Beckman CP cocktail in 7-ml polyethylene vials and counted for 10 min on a (Beckman model 1801) scintillation spectrophotometer. Dextran was measured in each sample as indicated earlier.

#### **RESULTS AND DISCUSSION**

Representative experimental breakthrough curves for the tritiated water and blue dextran are shown in Figure 1. Tritiated water is commonly used in laboratory experiments to describe water movement through soil columns. The experiment was designed such that water-filled porosity could be obtained directly from the experimental data without obtaining solutions to equation (13). The volume of water in the column (one pore volume) is equal to the volume of water required to increase the effluent tritiated water concentration from zero to 0.5 times the influent concentration with both influent and effluent concentrations corrected for background decays. The approach is valid for a conservative nonretarded chemical, such as tritiated

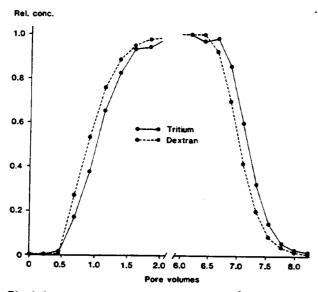


Fig. 1. Relative concentration of dextran and <sup>3</sup>H versus pore volumes. The pore volumes were determined gravimetrically assuming a particle density of 2.65. Corrections were made to minimize errors due to lengths of inlet and outlet tubing.

water, when the effluent concentration is allowed to reach the influent concentration prior to removing the chemical pulse. In Figure 1, the data were normalized to pore volumes and relative concentrations. One pore volume determined gravimetrically was consistent with volume required to reach a relative concentration of 0.5 for the tritiated water. The octanol:water partition coefficient for the blue dextran was experimentally determined to be 0.09. From equation (1), one can estimate, based on the octanol:water partition coefficient and the measured weight fraction of carbon in the soil  $(0.002 \pm 0.0003 \text{ or } 0.2 \text{ percent})$ , that the soil:water partition coefficient should be approximately 0.0026. If the blue dextran is miscible with water and does not behave as a separate phase, the retardation factor from equation (10) reduces to

$$R = 1 + [(1 - n)\rho_s/n\rho_a]k_d$$
(14)

The estimated retardation factor for blue dextran in the study soil becomes 1.009, and one would anticipate the blue dextran to elute from the column slightly behind the tritiated water. The blue dextran, nevertheless, eluted from the column prior to the tritiated water. The experiment was repeated three times on four different soil columns packed to the same bulk density. A relative concentration of 0.5 was observed at  $0.87 \pm 0.01$  pore volumes as shown, for one data set, in Figure 1. Apparently the large dextran molecule was excluded from the smaller soil pores and forced to move through only the larger pores. This suggests that the effective pore volume for this macromolecule soil combination was approximately 13 percent less than for the tritiated water, and the resultant average interstitial velocity of the blue dextran would be greater than for the water. The observations are similar to those in gel chromatography (Giddings and Mallik, 1966) where chemicals are separated by size with the largest molecules being eluted first, followed by successively smaller molecules.

To further test the hypothesis that the macromolecules were being excluded from the smaller pores, subsamples of the Vomb soil were amended with commercial samples of kaolinite and bentonite clay. One sample of soil was amended such that it contained 2 volume percent clay; 1 volume percent each of kaolinite and bentonite. A second sample of soil was amended such that it contained 6 volume percent clay; 3 volume percent each of kaolinite and bentonite. The soils were homogenized, by tumbling, prior to packing. After establishing hydraulic and ionic steady-state conditions with ground water assumed after 100 pore volumes, similar tests were performed as described above except the Darcy flow velocity was reduced to 14.7 cm d<sup>-1</sup>. The blue dextran obtained a relative concentration of 0.5 at 0.81 and 0.66 pore volumes, respectively, for the clay amended soils. The data collected demonstrates that large hydrophilic molecules can be excluded from smaller soil pores and thus appear to move with a higher average velocity than the water. The data presented are not sufficient to determine the size of pore that is excluded by this macromolecule or suggest that all macromolecules of the same weight would behave in a similar manner. The experimental data demonstrate a phenomenon which should be considered when performing exposure assessments.

Two theoretical figures were developed to elucidate the significance of the presence of the macromolecule and the differences in interstitial velocities between fluid phases for the transport of trace organic pollutants. Several simplifying assumptions were made in the development of the figures including: (1) dispersion in equation (13) was ignored which yields

$$R^* \frac{\partial C^*}{\partial t} = -V^* \frac{\partial C^*}{\partial x}$$
(15)

(2) the density of the macromolecule equals the density of the water; (3) the partition coefficient to the macromolecule organic carbon is the same as the partition coefficient to the soil organic carbon  $(k_{oc})$ ,  $k_p = k_{oc}$  times the weight fraction of carbon occupied by the macromolecules; (4) the weight fraction occupied by the organic carbon (F) is 0.02; (5) the soil partition coefficient can be described by equation (13); (6) the total porosity (n) of the soil is 0.5; and (7) the particle density of the soil is 2.65.

The importance of the macromolecule on the mobility of hydrophobic compounds is estimated in Figure 2. If the interstitial velocity of the macromolecule and the water are the same ( $V_a = V_o$ ), the octanol:water partition coefficient versus the relative chemical mobility (mobility of hydrophobic compounds with macromolecule / mobility without macromolecule) can be presented. A group of chemicals with different  $k_{ow}$  are shown on the

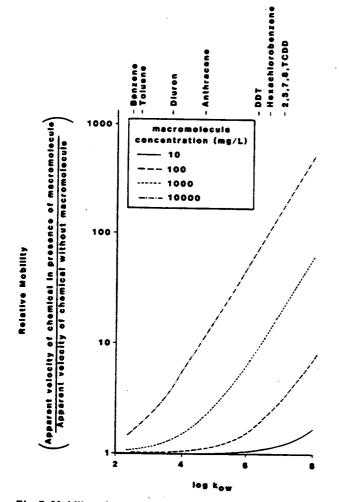


Fig. 2. Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule as a function of octanol-water partition coefficient and amount of organic carbon in the mobile phase.

figure for reference purposes only. Figure 2 displays the change in mobility of hydrophobic chemicals due to the macromolecule rather than the mobility of the chemical. Macromolecules in the mobile phase can significantly alter the relative mobility of extremely hydrophobic compounds even when the amount of macromolecule is in concentrations typical of ground water or agricultural soil solution (1 to 10 mg l<sup>-1</sup> dissolved organic carbon of unknown composition). This might be one explanation of why hydrophobic pesticides such as DDT have been reported to move farther under field conditions than model projections (e.g., Enfield et al., 1982). The importance of the macromolecule rapidly diminishes as the octanol:water partition coefficient goes down. At municipal or industrial waste sites where relatively high concentrations of macromolecules might exist, the importance of the macromolecule to chemical mobility could be significant even for chemicals with log kow of 3 or less. Hydrophilic macromolecules similar to dextran at carbon concentrations of 100-500 mg  $l^{-1}$  may change the relative mobility of hydrophobic compounds by an order of magnitude in low carbon soils.

The significance of differences in interstitial velocities of the two mobile phases are shown in Figure 3. It was assumed, in Figure 3, that the carbon concentration of the macromolecule was 100 mg  $l^{-1}$ . It is possible to plot relative mobility of the macromolecule  $(V_0/V_a)$  versus the relative mobility of the trace compound for different interstitial velocities of the mobile phases. The increased velocity of the macromolecule itself may increase the mobility of hydrophobic trace compounds by a factor of 5 or 10. It can be seen from the figure that if the velocity of the macromolecule drops to 10 percent of the water velocity, the importance of the macromolecule in accelerating transport approaches zero. Therefore, chemical transport will be facilitated only by macromolecules which behave as hydrophilic compounds (have high mobility).

The soil selected for study was a sandy soil and expected to have only a small proportion of its pores that could not be penetrated by the macromolecule. The observed decrease in effective porosity of the natural soil would not have a major impact on the mobility of chemicals at this site. However, under conditions where there is a high percentage of small pores, as would be anticipated in clay liners used in the construction of lagoons, there could be a significant increase in the mobility of chemicals due to a reduction in effective porosity

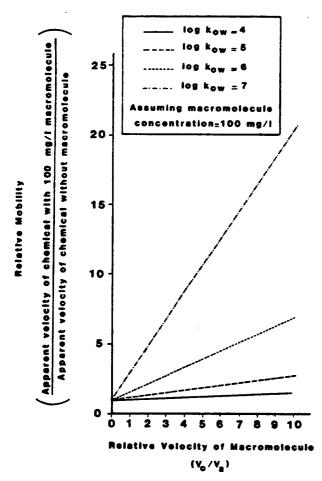


Fig. 3. Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule versus the velocity of the macromolecule relative to the velocity of the water where the concentration of the macromolecule is 100 mg  $l^{-1}$ .

to the macromolecule, as demonstrated by the additions of clay to the Vomb soil. This could have significant implications at industrial holding ponds and lagoons. Even when the macromolecule does not move faster than the water, it should dramatically increase the mobility of chemicals. There are two important implications to the macromolecule: (1) When a municipal landfill which produces large amounts of dissolved organic carbon is codisposed with toxic hydrophobic chemicals, the large amounts of DOC produced by the natural degradation processes will create conditions favorable to the transport of hydrophobic materials normally considered to be immobile. (2) At locations where the soils are already contaminated with hydrophobic materials, the addition of macromolecules to the system potentially will reduce the time required to remove the hydrophobic material from a contaminated aquifer.

#### NOTATION

- $C_a$  Mass concentration in aqueous phase,  $g g^{-1}$ .
- $C_0$  Mass concentration in immiscible phase,  $g g^{-1}$ .
- $C_s$  Mass concentration in solid phase,  $g g^{-1}$ .
- C<sup>\*</sup> Mass concentration of mobile phase,  $g g^{-1}$ .
- $D_a$  Dispersion in aqueous phase, m<sup>2</sup> d<sup>-1</sup>.
- $D_0$  Dispersion in immiscible phase, m<sup>2</sup> d<sup>-1</sup>.
- $D^*$  Lumped dispersion coefficient,  $m^2 d^{-1}$ .
- F Fraction of organic carbon associated with the soil.
- kao First-order transfer coefficient aqueous to immiscible phase, d<sup>-1</sup>.
- k<sub>as</sub> First-order transfer coefficient aqueous to solid phase, d<sup>-1</sup>.
- k<sub>d</sub> Soil:water partition coefficient.
- $k_{oa}$  First-order transfer coefficient immiscible to aqueous phase,  $d^{-1}$ .
- koc Organic carbon:water partition coefficient.
- kow Octanol:water partition coefficient.
- k<sub>p</sub> Mobile carbon:water partition coefficient.
- $k_{sa}$  First-order transfer coefficient solid to aqueous phase,  $d^{-1}$ .
- n Volume fraction of soil voids (porosity), m<sup>3</sup> m<sup>-3</sup>.
- R Retardation factor.
- R\* Lumped retardation factor.
- t Time, d.
- $V_a$  Interstitial velocity of aqueous phase, m d<sup>-1</sup>.
- $V_0$  Interstitial velocity of immiscible phase, m d<sup>-1</sup>.
- V\* Lumped interstitial velocity of mobile phase, m d<sup>-1</sup>.
- x Distance along flow path, m.
- $\theta$  .Volume fraction occupied by the aqueous phase, m<sup>3</sup> m<sup>-3</sup>.
- $\rho_a$  Density of aqueous phase, Mg m<sup>-3</sup>.
- $\rho_0$  Density of immiscible phase, Mg m<sup>-3</sup>.
- $\rho_{\rm s}$  Particle density of the soil, Mg m<sup>-3</sup>.
- $\phi$  Volume fraction of the immiscible phase, m<sup>3</sup> m<sup>-3</sup>.

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# Adsorption and Movement of Organic Pollutants

#### by Arthur W. Hounslow

#### Introduction

Over the last three decades, it has become increasingly apparent that the organic and inorganic constituents of the soil and deeper subsurface play an important part in the retardation of introduced organic chemicals. Early work centered about the movement of pesticides and herbicides in this environment. In recent years, the movement of other pollutants in this zone has become a primary concern, not only from the aspect of estimating pollutant movement but also because the greater the retardation of a contaminant, the greater will be the time during which biotic or abiotic degradation may occur.

The purpose of this paper is to describe adsorption, outline the methods used to quantify it and to show how it is incorporated in the mass transport equations used to describe and/or predict pollution movement.

#### Mass Transport Equation

The primary purpose of the mass transport equation is to determine the concentration of a pollutant at a specified place after a specified time. Four different processes are incorporated into this equation:

1. Advection, or the transport of the pollutant at the ground-water velocity;

2. Dispersion, or the spreading of the concentration front because of aquifer inhomogeneity and molecular diffusion;

3. Biodegradation, or the disappearance of the solute because of microbial action;

4. Adsorption, or retention of the solute in the soil phase because of partitioning between the solid and liquid phases.

The only term to be discussed in this paper is the last one, adsorption.

#### Adsorption term

The total mass of solute per unit volume of porous medium is the sum of the solute in solution plus that adsorbed on the soil.

If the porous medium is 100 percent saturated with solution, the volume of solution per unit volume of porous media is equal to the effective porosity,  $\theta$ . Further, the mass of soil per unit volume of porous medium is  $\rho_{\rm B}$ , the bulk density.

Thus if the total mass of solute per unit volume is  $C_T$ then  $C_T$  (total) =  $\theta C$  (liquid) =  $\rho_B C_s$  (solid) (1) where C is the solution concentration and  $C_s$  is the adsorbed mass concentration.

In general,  $C_s$  is a function of C, that is, a relationship defined by the adsorption coefficient.

The change in the mass of solute adsorbed on the solid ( $C_s$ ) with time can be expressed as:

 $\delta C_s / \delta t = d C_s / d C$ .  $\delta C / \delta t$  (2) After combining (1) and (2), the change in total mass of solute per unit volume of porous medium with time is

$$\delta C_{T_{\delta}} = \theta. \ \delta \ C/\delta t + \rho_{B}.dCx/dc. \ \delta C/\delta$$
$$= \delta C/\delta t(\theta + \rho_{B}. dC^{s}/dC)$$

= 
$$\theta$$
.  $\delta C / \delta t (1 + \rho_B / \theta . dCs / dC)$ 

where the term

 $1 + \rho_{B}/\theta$ . dCs/dC (3) efined as the retardation coefficient R

is defined as the retardation coefficient R<sub>d</sub>. \_\_\_\_\_ Thus

$$\delta C_{T} / \delta t = Rd.\theta. \, \delta C / \delta t. \tag{4}$$

#### **Retardation Coefficient**

This coefficient as defined in (3) contains two readily obtainable terms:  $\theta$ , the effective porosity, and  $\rho_{\rm B}$ , the bulk density of the soil. The third variable is the ratio dC<sub>s</sub>/dC, which is derived from the adsorption

#### coefficient, Kd.

#### Thus the retardation coefficient

 $R_d = 1 + Kd \rho_B/\theta$ 

This represents a ratio of the velocity of the water over the velocity of the solute. Thus if a solute having a retardation  $R_d = 10$  has traveled 10 ft., the water has traveled 100 ft.

The reciprocal of  $R_d$ , which is the chemical  $R_F$  factor, is more readily understood because solute movement is defined in terms of the water movement. That is, during the time that water has moved a distance x, the solute has moved a distance  $R_F$  times x. Thus assuming an  $R_F$  of 0.1 and a water movement of 100 ft., the solute has moved 100 x 0.1 = 10 ft.

#### Chromatographic Movement

Chromatography is the process whereby a solution of a compound (mobile phase) moves through porous solid (stationary phase). As a solution flows through a porous media, some solutes appear to move more rapidly than others. The process that controls the rate at which a particular compound moves relative to that of the fluid is called adsorption or partition. Adsorption is the term used if the stationary phase is a solid, and partition if the stationary phase is a gel or a liquid (whose support may be an inert porous solid phase).

In analytical chemistry, chromatography is commonly used to separate compounds. It was first used in 1906 by Tswett to separate colored substances in plant materials, hence the name.

Although the flow of fluids through porous media has received considerable attention in both field and laboratory studies, the movement of the dissolved constituents through porous media has been little studied outside the analytical chemistry laboratory. The following discussion is based primarily on the chemical literature.

Chromatography is used extensively in the laboratory to separate constituents of a solution by making use of the fact that some solutes move more rapidly than others, that is, they distribute themselves between the mobile and the stationary phases in proportions that vary from one substance to another.

Chromatographic movement can thus be described according to:

- The nature of the stationary phase
  - Solid adsorption chromatography
  - Liquid (or gel) partition chromatography
- The composition of the mobile phase (Stock and Rice 1963)
  - Pure solvent elution chromatography
  - A solution added continuously frontal chromatography
  - A solution of a substance more strongly adsorbed than any of the compounds of the mixture - displacement chromatography.

#### **Stationary Phase**

The stationary phase may be an active solid (solid stationary phase) or a liquid supported by porous inert solids (liquid stationary phase).

The liquid stationary phase may be a true liquid supported by an inert (nonreacting) porous solid or, in some cases, a gel. The rate of movement of a dissolved constituent depends on the relative solubility of this solute in the stationary and in the mobile phases. This ratio is called a partition coefficient. During the movement of the mobile phase, the solutes undergo partition between the mobile and stationary phases and separation occurs because of the differences in partition coefficients. It should be emphasized that in this case, these separations are due to differences in solubility of a compound in two immiscible phases and are not surface effects. Partition coefficients are commonly linear up to their saturation points; that is, the coefficients are independent of the concentration of solute. Martin and Synge (1941) evolved a theory of chromatographic movement based on the analogy with distillation columns. Their theory assumes linear partition coefficients and they derived the position of maximum concentration of the solute relative to the volume of liquid that had flowed through the laboratory chromatographic column.

They concluded that if

- P<sub>s</sub> = the movement of position of maximum concentration of solute, and
- P<sub>m</sub> = the simultaneous movement of developing fluid in the empty part of the tube above the chromatogram,

then R = P<sub>s</sub>/P<sub>m</sub> = A/(A<sub>L</sub> +  $\alpha$ A<sub>s</sub>) = (A<sub>L</sub> + A<sub>s</sub> + A<sub>l</sub>)/(A<sub>L</sub> +  $\alpha$ A<sub>s</sub>) where  $\alpha$  = the partition coefficient = gsolute per mL of non-mobile phase g solute per mL of mobile phase.

A = area of cross section of column  $A_s$  = area of cross section of non-mobile phase  $A_L$  = area of cross section of mobile phase  $A_l$  = area of cross section of inert solid

Also if areas are known  $\alpha = S/(RA_s) - A_L/A_s$ 

This relationship was verified by determining  $\alpha$  from the band movement and also directly.

Subsequently, Thornthwaite, Mather and Nakamura (1960) developed the plate theory and proposed a mathematical model that allowed calculation of solute with depth. They applied their model to the movement of radiostrontium in soils. The theory was further extended by Fissel and Poelstra (1963). King and McCarty (1968) applied this model to the movement of organic phosphate pesticides in a variety of soils and added an additional term to cover pesticide degradation. Their model was confined to linear adsorption coefficients.

The solid stationary phase is an active solid that reacts with solutes in the liquid phase and results in the process known as adsorption chromatography. It refers to a surface effect that takes place at the boundary between the moving and stationary phases. tography (qv) of a single solute based on a differential equation for the adsorption process. He derived equations for the determination of solute concentrations with depth using linear and nonlinear adsorption isotherms, band widths, solute movement and shape of the adsorption band. Weil-Malherbe (1943) verified the Weiss theory experimentally and determined that the tailing of an elution curve is a function of the Freundlich exponential coefficient. That is, for linear adsorption isotherms the elution curve is virtually symmetrical, whereas if the exponent is less than 1, a tail develops on the eluted solute band.

#### **Mobile Phase**

Chromatographic movement can also be classified according to the manner by which the solute moves through the porous medium. The terms elution, frontal and displacement are used to describe the different types of conditions.

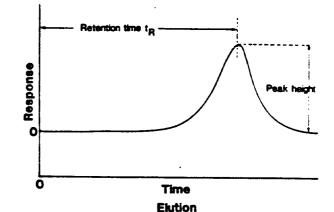
Elution chromatography refers to the transport of a solute previously added to a chromatographic column by means of the application of pure solvent (Figure 1). If it is assumed that there are no stationary phase-mobile phase interactions, then the more weakly adsorbed substances travel more rapidly than the more strongly adsorbed substances. A common phenomenon with this technique is that of tailing, which results in wider, diffuse and overlapping bands. In the other two processes this does not occur. A point source contaminated site leached by rainwater would be an example of this phenomenon.

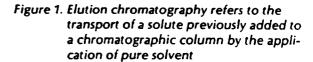
Frontal chromatography occurs when a solution of the mixture is added continuously. If there are a number of components in the mixture, each having different adsorption characteristics, a number of zones will be formed. The leading edge of each zone is called a front. The first (leading) zone will contain the least adsorbed solute, whereas the other zones will contain mixtures of the various solutes (Figure 2). Eventually, however, the effluent from the system becomes identical in composition to the sample entering the system. A land treatment disposal site could well illustrate this phenomenon.

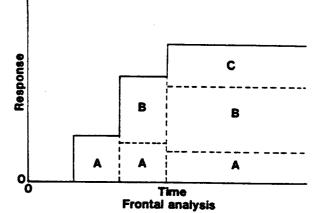
Displacement chromatography results when the mobile phase contains a substance more strongly adsorbed than any of the components of the mixture. This substance is known as the displacer. A mixture of solutes moves down the column at the same rate as the displacer is added and resolves itself into bands of pure components. The order of these bands is the order of the strength of adsorption on the stationary phase. Each pure band acts as a displacer of the less adsorbed component ahead of it (Figure 3). The regeneration of a water softener by sodium chloride illustrates this process.

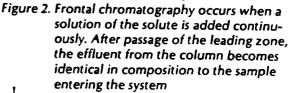
#### Adsorption

Adsorption describes the distribution of a solute between a liquid and a solid phase; it is of paramount importance in all chromatographic studies. It is generally









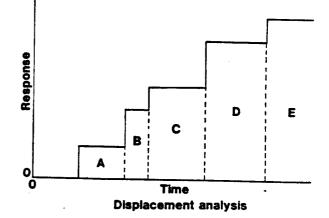


Figure 3. Displacement chromatography results when the mobile phase contains a substance more strongly adsorbed than any of the components of the mixture. The solute mixture resolves itself into bands, each band acting as a displacer of the less adsorbed component ahead of it

considered to be the result of either an affinity for the solid or a lack of affinity for the liquid (Weber 1972).

If the adsorption is a consequence of the lyophobic (solvent-disliking) character of the solute relative to a particular solvent, then the solute displays a low solubility in that liquid. This inverse relationship between adsorption and solubility is still invoked as the primary theory for explaining the movement of pesticides in soils. In aqueous systems this phenomenon is called hydrophobic adsorption. On the other hand, the solute may have a high affinity for the solid phase. Three types of surface phenomena must be considered.

1. Physical adsorption results from van der Waals forces; that is, fluctuations in electron distributions producing instantaneous dipoles. Adsorbed molecules are not fixed to a specific site but are free to move within the interface.

2. Chemisorption represents a chemical interaction with the adsorbent and the bonding occurs at specific sites on the surface of the adsorbent.

3. Exchange adsorption is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. The charge on the ion is the determining factor for exchange adsorption. Generally, the higher the charge and the smaller the ion, the stronger the adsorption. The molecular size or hydrated radius must, however, be the parameter considered.

#### **Adsorption Isotherms**

The adsorption coefficient is not always a constant and it may vary with the concentration of the solute in the liquid phase. The graph that allows the adsorption coefficient to be obtained at different concentrations is known as an adsorption isotherm.

An adsorption isotherm determined experimentally is a plot of the amount of material adsorbed per gram of adsorbant vs. the concentration of the adsorbate in solution. The result may be a straight line or an exponential curve (that is, a straight line on a log-log plot).

Linear adsorption isotherms result when the distribution coefficient is independent of concentration, that is:  $S = K_D C$ 

where: S is the amount of solute adsorbed by the solid phase

C is the concentration of solute in the liquid phase and

 $K_D$  is the distribution coefficient, (linear adsorption coefficient).

This is commonly the relationship observed where partition occurs between two liquid phases up to their solubility limit. Most chromatography models used for describing pollutant transport assume this model.

Freundlich isotherms are primarily an empirical attempt to describe nonlinear relationships. They are defined by the equation

 $S = KC^{N}$  (Figure 4),

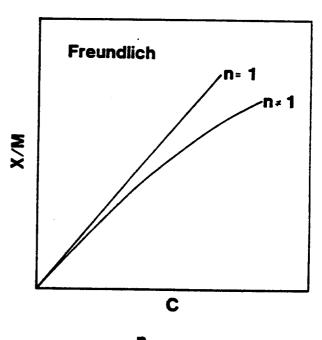
where K and N are constants. It is usually presented in the linear form:

 $\log S = K + N \log C,$ 

where N is the slope of the line and K the adsorption coefficient (Figure 5).

Although generally considered an empirical relationship, Sposito (1980) derived it theoretically for the trace adsorption of an ion participating in an exchange reaction.

Elution curves illustrating the phenomenon of tailing for isotherms where n = 1, n < 1 and n > 1 are shown in Figures 6, 7 and 8.



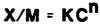
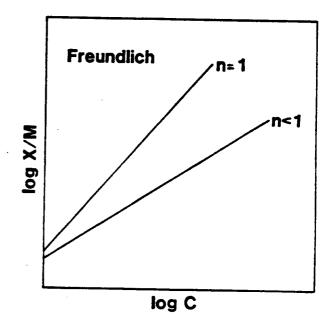
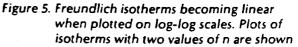


Figure 4. Freundlich isotherms, linear when n equals 1 and nonlinear when n does not equal 1



### $\log X/M = \log K + n \log C$



(1918) to describe the adsorption of gases by solids. It has a valid theoretical base and assumes monolayer adsorption, and that the solid possesses a finite number of adsorption sites. The general equation is:

$$S = (S_m bC) / (1 + bC)$$

where: S is the number of moles of solute adsorbed per gram of adsorbent,

 $S_m$  is the number of moles of solute adsorbed per gram of adsorbent in forming a complete single layer of adsorbed solute molecules on the surface of the adsorbent (monolayer)

C is the concentration of solute in the liquid phase,

### and d is a constant.

Expressed in linear form  $1/S = 1/S_m + 1/(bS_mC)$ where  $1/S_m$  is the intercept and  $1/bS_m$  is the slope (Figure 9).

B.E.T. isotherms were developed by Brunauer, Emmett and Teller (1938) to include systems in which a vapor is adsorbed as several layers of solute on the adsorbent surface (multilayers). They obtained the equation:

$$P/(V(P_{o}-P)) = 1/V_{m}C + P(C-1)/(P_{o}V_{m}C),$$

 $V_m$  is the volume adsorbed in the first completed monolayer,

 $P_o$  is the saturation pressure of the vapor C is a constant = exp ( $E_1$ -L)RT

where: E and L are the heat adsorption in the first layer and the latent heat of condensation, respectively. T is the absolute temperature and R is the gas constant.

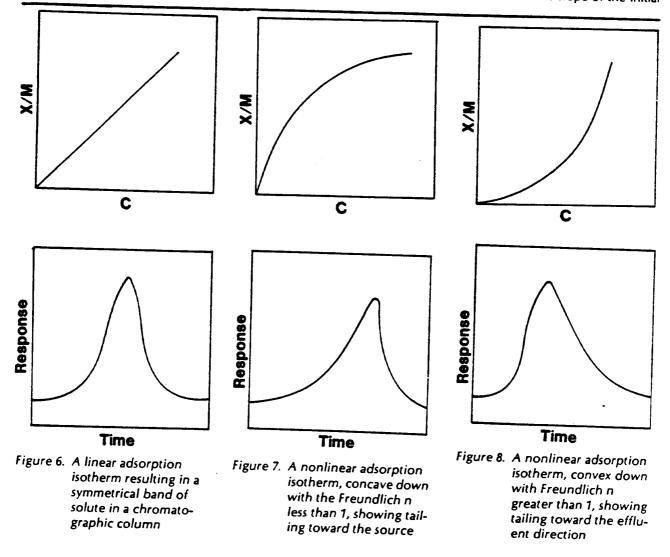
A plot of  $P/(V(P_o-P)$  vs.  $P/P_o$  should be linear.

#### Types of Isotherms

Studies of adsorption isotherms have indicated that their shapes may give some insight as to the nature and possibly the mechanism of the substrate-solute-solvent interactions (Giles et. al. 1960, Giles 1970). This is of prime interest to those studying natural systems where many of the parameters are poorly understood or even unknown.

It has been shown that for a given solute, differentshaped isotherms result from different combinations of solvent and substrate. The primary factors are the polar or nonpolar nature of the solvent and substrate, as well as of the polar nature or monofunctionality of the solute.

Giles et al. (1960) proposed a fourfold division of adsorption isotherms based on the slope of the initial



part of the curve, and a further subdivision according to the shape of the curve further from the origin.

The initial slope depends on the rate of change of site availability with increase in solute adsorbed. The plateau or inflection point on the curves represents the first degree of saturation; that is, further adsorption can only take place on new surfaces. If the adsorbed molecules of the monolayer are so oriented that the new surface they present to the solution has low attraction for more solute molecules, the curve has a long plateau. If they are oriented such that the new surface has high attraction for more solute, the curve rises steadily and has no plateau.

The four main classes of isotherms are:

• L-curves, the normal or "Langmuir" isotherms (Figure 9), are characteristically convex near the origin. Thus, the more solute taken up, the less chance that a solute molecule will find a suitable site on which it can be adsorbed. The types of systems that give this curve have one of the following characteristics:

 the adsorbed molecules are most likely to be adsorbed flat, or

adsorbed end on with little solvent competition,
 highly polar solute and substrate and a non-

polar solvent.

• monofunctional ionic substances with very strong intermolecular attraction.

• H-curves or high-affinity curves in which the solute has such a high affinity for the substrate in dilute solution that is completely adsorbed, or at least there is no measurable amount remaining in solution (Figure 10). This is usually indicative of chemisorption or ion exchange. The initial part of the isotherm is therefore vertical. The adsorbed species are either:

large units, such as ionic micelles or polymeric molecules, or

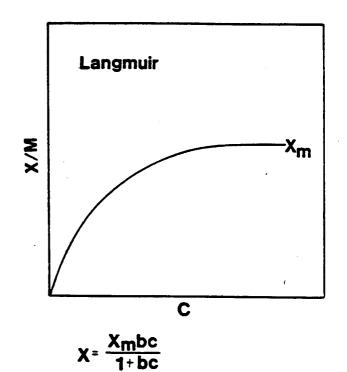
single ions with a high-exchange capacity.

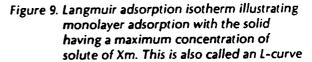
• S-curves describe those systems where the greater the amount of solute already adsorbed, the easier it is for additional solute to become adsorbed. They are characteristically concave near the origin (Figure 11) and are generally considered to indicate the vertical orientation of adsorbed molecules at the surface.

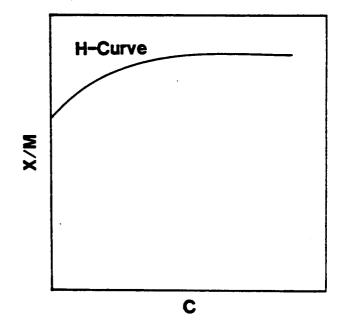
This is the characteristic adsorption isotherm for monofunctional solutes with moderate intermolecular attraction adsorbed on a polar substrate from a polar solvent. It indicates a tendency for large adsorbed molecules to associate rather than to remain as isolated units. This has also been called cooperative adsorption.

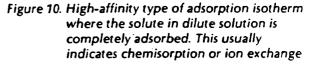
• C-curves, or constant partition curves, are linear isotherms where the availability of sites remains constant at all concentrations up to saturation (Figure 12). It is typical of the curve obtained for the partition of a solute between two immiscible solvents. The implication is that the solute is penetrating regions of the substrate that are inaccessible to the solvent.

It must be emphasized that isotherms may change in shape with a change in conditions. Thus the common organic chemical phenol, a monofunctional solute, will give an S-curve from polar solvents such as water on polar substrates, an L-curve on polar substrates from nonpolar solvents and a c-curve on hydrophobic poly-





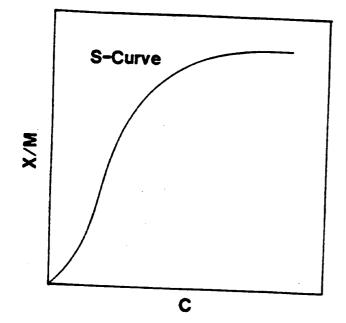


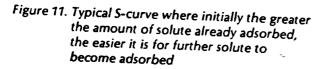


mers from an inert liquid (which does not swell the substrate).

#### **Retardation in the Soil-Sediment System**

Once a general understanding of adsorption chromatography is obtained, it must be applied to the



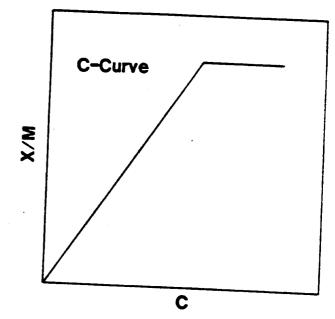


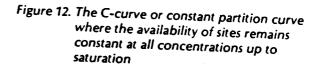
problem of predicting the rate of movement of chemical pollutants in the soil-sediment environment. The mobile phase is, of course, water, and the solid phase, soil. Soil is a complex multiphase system where components vary considerably from one area to another. The three solid-phase constituents most likely to be important in the adsorption reactions are soil organic matter, clay minerals and amorphous hydroxides of iron, aluminum and manganese.

Soil organic matter is a complex organic polymer of doubtful composition that is generally assumed to have a large number of phenolic -OH and carboxylic acid groups attached to it. It may be physically and chemically separated into three main components: alkali soluble fulvic, humic acids and insoluble humin. The interactions between the soil organic matter-clay minerals and amorphous hydroxides that may affect the adsorption charcteristics are essentially unknown.

A vast amount of literature has developed over the last three decades on the adsorption of organic compounds, primarily herbicides and pesticides, by soil constituents. One of the earliest papers reporting experimental data showing an unequivocal correlation between adsorption of a specific organic compound and soil organic matter was published by Sherburne and Freed in 1954. Since then, many papers have been written expanding the number of organic compounds for which this holds true.

It has become a fairly common practice to normalize adsorption coefficients obtained from soils to their organic matter or organic carbon content.





where  $K_{oc}$  is the normalized adsorption coefficient and K is the adsorption coefficient obtained using a soil containing OC% organic carbon.

The sorbing medium is thus considered to be the soil-organic matter rather than the total mass of soil. Lambert (1967), Furmidge and Osgerby (1967) normalize to %SOM whereas Karickhoff normalizes his distribution coefficient to percent of organic carbon. It has been found empirically that soil organic matter contains 58 percent organic carbon and thus  $K_{oc}$  can be derived from  $K_{som}$ .

It must be emphasized that although soil organic matter has been shown to be the primary factor in many adsorption experiments, it is not the only one. For example, 2-4D is strongly adsorbed by humic acid although the effect of illite may be important (Hague 1975). Similarly,  $\alpha$ -napthol is primarily adsorbed by soil organic matter although a high montmorillonite/soil organic matter ratio has a significant effect on the adsorption isotherm (Hasset et al. 1981).

Estimates of adsorption coefficients are commonly attempted using parameters, such as solubility, or simplified techniques, such as octanol/water partition coefficients rather than the difficult and time consuming determination of adsorption isotherms. Solubility estimates:

Cassidy (1951) notes that many investigators have noted that the solubility of a substance in a given solvent may be expected to affect its absorbility. He further cautions that correlations between solubility and adsorption onto a solid surface should not be expected unless the adsorbent does not play a role in the process.

Various equations have been prepared for this relationship. Lundelius, 1920 (Cassidy 1951) proposed that the Freundlich K is inversely proportional to S<sup>n</sup> where S was the solubility in a solute in question and n is the Freundlich exponent,

i.e., log K = A-n log S.

Kenaga and Goring (1978) collected data for 106 organic chemicals, primarily pesticides, and obtained a regression equation.

 $\log K_{oc} = 3.64 - 0.55 \log S.$ 

They estimated the results would be within  $\pm 1.23$ orders of magnitude from the actual value, assuming 95 percent confidence limits. S was reported in ppm.

Chiou et al. (1979) obtained a relationship between distribution coefficients and solubility for a large number of nonionic organic compounds. Their relationship covers more than seven orders of magnitude in S and four orders of magnitude in K<sub>or</sub>

They found that

 $\log K_{som} = 4.040 - 0.557 \log S$ 

where S is in micromoles/liter

assuming SOM = 58% oc;  $K_{oc}$  = 3.80 - 0.557 log S. Karickhoff et al. (1979) found the relationship to be log  $K_{oc}$  = 0.44 - 0.54 log S

where S is expressed as mole fraction. The compounds considered were hydrophobic compounds such as aromatic hydrocarbons and chlorinated hydrocarbons.

Means et al. (1980) found a relationship

 $\log K_{oc} = 4.070 - 0.82 \log S$  where S is mg/mL.

Karickhoff (1981) gives

 $\log K_{oc} = -0.197 - 0.594 \log S$  where S = mole fraction solubility.

He recommended the incorporation of a crystal energy term in the equation.

#### Octanol-water partition coefficients

The partitioning of a solute between water and an immiscible organic solvent has been used extensively to estimate biological concentration tendency solutes.

Ward and Holly (1966) found a linear relationship between amount of sorption and the degree of partitioning between cyclahexane and water of S-triazines. They showed this to be a better index of sorption for these compounds than their solubilities.

Generally, octanol-water partition coefficients are those most commonly measured, and an extensive compilation of them has been made by Leo et al. (1971).

Chiou et al. (1977) used octanol/water partition coefficients to obtain better estimates of solubility; that is,

 $\log K_{ow} = 5.00 - 0.670 \log S$ ,

where K<sub>ow</sub> = octanol/water partition coefficient and S = aqueous solubility in micro moles/L.

These equations were found to be valid over six orders of magnitude in  $K_{oc}$  (10 - 10<sup>7</sup>).

Karickhoff et al. (1979) examined 10 hydrophobic pollutants with water solubilities ranging from 1 ppb to 1,000 ppm and obtained excellent correlations of  $K_{oc}$  vs.  $K_{ow}$  and poor correlation between  $K_{oc}$  and solubility. The equation

 $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ 

or  $K_{oc} = 0.63 K_{ow}$  was suggested.

Means et al. (1979) obtained similar partition coefficients for pyrene and DMBA, namely  $K_{oc} = .53 K_{ow}$  and 0.50 K<sub>ow</sub> respectively.

Banerjee et al. (1980) correlated n-octanol/water partition coefficients with solubility and found log  $K_{ow} = 5.2 - 0.68 \log S$  with S in micro moles/L.

For solids with known melting points, they suggest log  $K_{ow} = 6.5 - 0.89 \log S - 0.015 (mp)$ .

Chiou and Schmedding (1980) state that most inaccurate data on water-solubility and partition coefficients are generated with impure compounds or solvents. They discuss methods of ensuring purity of phases and suggest at a minimum that a melting point of a solid phase is minimal and that poor phase separations or persistent emulsions are often an indication of undesirable solvents.

Experimentally they found for 36 organics that ranged more than six orders of magnitude that:

 $\log K_{ow} = -0.862 \log S + 0.710$ 

with S in moles/L.

Kenaga and Goring (1980) obtained the relationship  $\log K_{oc} = 1.377 + 0.544 \log K_{ow}$  for 45 organics.

Karickhoff (1981) obtained the equation for hydrophobic solutes

 $\log K_{oc} = 0.989 \log K_{ow} - 0.346.$ 

The near unity of the coefficients suggest  $K_{oc} = 0.411$  $K_{ow}$  to be a good approximation.

Briggs (1981) gives the relationship

 $\log K_{om} = 0.52 \log K_{ow} + 0.64.$ 

He presents the data of Felsot and Dahn (1979) in the form:

 $\log K_{om} = 0.52 \log K_{ow} + 0.78$ 

the data of Lord et al. (1978) as:

 $\log K_{om} = 0.53 \log K_{ow} + 0.98$ 

and his own earlier data

 $\log K_{om} = 0.52 \log K_{ow} + 0.62.$ 

Brown and Flagg (1981) found another empirical equation for nine compounds

 $\log K_{oc} = 0.937 \log K_{ow} - 0.006.$ 

#### Soil Thin-Layer Chromatography (TLC)

A direct method for determining retardation of pesticides in soil, termed "soil thin-layer chromatography," was proposed by Helling and Turner (1968). This quantitative index of relative pesticide mobility, which is based on  $R_f$  values, correlated well with published data on movement.

Further refinements of this technique were published by Helling (1971a) together with applications (Helling 1971b), as well as influence of soil properties (Helling 1971c). One correlation found was that pesticide mobility tended to be directly related to increased water flux.

A comparison of the various methods for determining the mobility of organic pollutants in the laboratory reveal that TLC is one of the least expensive techniques (Helling and Dragun 1980). menteriormance equili cinomatography (m ec)

McCall et al. (1980) suggested that the retention time on HPLC may be directly related to a  $K_{oc}$  value.

#### **Mass Transport Equation**

The primary objective of the preceding discussion is to describe chromatographic movement, the role of the adsorption coefficient and the various methods of obtaining this parameter. In this section the manner in which the adsorption coefficient is integrated into the mass transport equation is examined.

The retardation coefficient term in the mass transport equation contains the variable  $dC_s/dC$ , which is directly related to the adsorption coefficient. It equals Kd in the linear case but the relationship becomes more complex for nonlinear isotherms. In the linear case where

 $C_s = K_d C$ 

$$dC_{c}/dC = Kd$$

If the adsorption obeys the Langmuir isotherm, where:  $C_s = K_d C_m C/(1 + kC)$ 

 $C_m$  is the limiting concentration when the monolayer is filled,

 $dC_{s}/dC = K_{dr}C_{m}/(1 + k_{d}C)^{2}$ In the Freundlich case where  $C_{s} = K_{d}C^{n}$  $dC_{s}/dC = n.Kd.C^{n-l}$ 

#### Chromatographic R<sub>F</sub> Factor

 $R_F$  is defined as the velocity of the point of maximum concentration of the solute over the average linear velocity of the ground water (Freeze and Cherry 1979), that is:

 $R_{F} = V_{P}/V = 1/(1 + Kd\rho\beta/\theta)$ 

The reciprocal of  $R_f = V/V_p$  is the retardation coefficient, namely

 $R_d = (1 + Kd \rho_B / \theta)$ 

The  $R_f$  factor originally defined by Martin and Synge (1941) using linear isotherms is:

 $R_f = 1/(1 + Kd.A_s/A_1)$ 

where  $A_s$  and  $A_L$  are the cross sectional areas of the solid and liquid phase respectively, which equals  $\rho_B/\theta$ .

#### **Retardation Calculations**

Assuming linear isotherms, a pore fraction  $\theta$  and a bulk density  $\rho_{\theta}$ , the retardation

 $R_d = 1 + K_d \rho_{\beta'} \theta$ and as  $\rho_{\beta} = (1 - \theta)$ where  $\rho$  = specific gravity of rock minerals.

Koc is defined as 100 K<sub>D</sub>/%oc Therefore K<sub>D</sub> = %oc.Koc/100 the retardation R<sub>d</sub> becomes

 $R_d = 1 + (1-\theta)^{\rho}.K_{oc}$ %oc/(100. $\theta$ )  $R_f = 1/R_d$  As a guide, a number of organic chemicals with normalized adsorption coefficients ranging eight orders of magnitude are listed in Table 1. With these data are listed the calculated Kd value for 1% oc, retardation coefficients  $R_d$ ,  $R_f$  values and the amount they may be considered to have moved if the water moved a distance of 10 miles. It must be understood that linear adsorption is assumed, and that degradation and diffusion are ignored.

#### Summary

1. Chromatography is the name given to the movement of a dissolved chemical compound whose solution (mobile phase) moves through a porous solid (stationary phase). The process that controls the rate at which the compound moves relative to that at which the solvent moves is called adsorption if the stationary phase is a solid or partition if the stationary phase is a liquid.

2. Three types of solute movement can occur depending on whether or not the mobile phase is a pure solvent, a solution of the solute added continuously or a solution of a substance more strongly adsorbed than the solute(s) under investigation.

3. If the mobile phase is a pure solvent, the shape of the moving adsorption band depends on the Freundlich exponential coefficient. If this is less than 1, a tail develops on the eluted solute band.

4 If the solution of solute is added continuously, once equilibrium is attained, the effluent from the system becomes identical in composition to the solution entering the system.

5. When the mobile phase contains a substance more strongly adsorbed than any of the compounds of the mixture, the solutes resolve themselves into bands that move at the same rate as the mobile phase. The order of these bands is the order of the strength of adsorption and each band acts as a displacer of the less adsorbed component ahead of it.

6. Adsorption is generally considered to be the result of two processes, a lack of affinity of the solute for the solvent or an affinity of the solute for the solid. The first explains the inverse relationship between adsorption and solubility; the second includes the various types of surface phenomena such as physical adsorption, chemisorption and exchange adsorption.

7. Experimental determination of adsorption result in a graph known as an adsorption isotherm, a plot of the amount of material adsorbed on the adsorbent vs. the concentration of the solute in solution. If the amount adsorbed is independent of concentration in solution it is termed a linear isotherm. Non-linear relationships are usually defined by an exponential function, the Freundlich isotherm.

8. The shapes of adsorption isotherms may give some insight as to the nature and possibly the mechanics of the adsorption interactions.

9. One of the more confusing issues that may confront an investigator trying to obtain an approximation to an adsorption coefficient is the diversity of units used in the various equations.

• The adsorption coefficient may be obtained from data using mass units or using mole units; if the

# Table 1 Examples of Retardation Coefficients

Organic chemicals having a wide range of K<sub>D</sub> values showing their retardation and R<sub>1</sub> values. The calculations assume a porosity of 0.2, a rock mineral density of 2.65 and 0.1% organic carbon

Кос	KD	R	x 52,800 ft	Rf
0.4	0.00	1	52,577	0.996
20.0	0.02	1	43,564	0.825
24.0	0.02	1	42,092	0.797
44.0	0.04	1	36,007	0.682
53.0	0.05	2	33,807	0.640
83.0	0.08	2	28,088	0.532
410.0	0.41	5	9,877	0.187
911.0	0.91	11	4,955	0.094
1,300.0	1.30	15	3,572	0.068
3,914.0	3.91	42	1,243	0.024
15,473.0	15.47	165	320	0.006
26,000.0	26.00	277	<b>1</b> 91	0.004
80,000.0	80.00	849	62	0.001
82,000.0	82.00	870	61	0.001
84,000.0	<b>84.0</b> 0	891	59	0.001
238,000.0	238.00	2,524	21	0.000
-		·		
1,200,000.0	1,200.00	12,721	4	0.000
			·····	
				7
	0.4 20.0 24.0 44.0 53.0 83.0 410.0 911.0 1,300.0 3,914.0 15,473.0 26,000.0 80,000.0 82,000.0 84,000.0 238,000.0	0.4         0.00           20.0         0.02           24.0         0.02           44.0         0.04           53.0         0.05           83.0         0.08           410.0         0.41           911.0         0.91           1,300.0         1.30           3,914.0         3.91           15,473.0         15.47           26,000.0         26.00           80,000.0         80.00           82,000.0         82.00           84,000.0         84.00           238,000.0         238.00	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

isotherm is linear it will not matter which, however, if n is not equal to 1 then:

$$\frac{K(\text{moles}) = K \text{ (mass) } x M^n}{M}$$

where M is the molecular weight of the compound (Osgerby 1970)

or log K (moles) = log K (mass) - (1-n) log M

• The adsorption coefficient may refer to the total weight of soil, or it may be:

- normalized to the organic matter content K<sub>som</sub> = K/(%SOM) or
- normalized to the organic carbon content

 $K_{oc} = K_{som}/1.724$ 

(assuming 58% oc in SOM).

• If the adsorption coefficient is to be derived from solubility data, then it should be determined what units the solubility data are in and what the correlation equation uses. They may be expressed in mg/L micromoles/L or mole fraction.

micromoles/L = mole fraction x 55.56 x  $10^3$  log S(micromoles/L) = log S (mole fraction) + 4.74

• As a guide, the various equations advanced for obtaining  $K_{oc}$  from solubility have the form:

 $log K_{oc} = A - B log S$ If S<sub>f</sub> S is in micromoles/liter A = 3.6 to 5 B = .54 to .59

• The equation for obtaining  $k_{oc}$  from the octanol-water partition coefficients have the form:

$$K_{oc} = C K_{ow}$$
  
where C = .4 to .6

10. The mass transport equation is that equation used to determine the concentration of a pollutant at a specified place after a specified time. The four processes incorporated in it are advection, dispersion, biodegradation and sorption.

11. The sorption term in this equation is defined as the retardation coefficient  $(R_d)$  that is

$$R_d = 1 + \rho_\beta / \theta. dCs/dc$$

where  $\rho_{\beta}$  is the bulk density of the soil  $\theta$  is the effective porosity

dC<sub>s</sub>/dC the change in adsorption with concentration of pollutant.

It is usually assumed that adsorption is linear and  $dC_s/dC = K_D$ 

where  $K_D$  is the linear adsorption coefficient Therefore  $R_d = 1 + \rho_B K_D / \theta$  velocity of the point of maximium concentration of the solute over the average linear velocity of the ground water

 $R_t = 1/(1 + Kd\rho_B/\theta)$ 

that is  $R_f = 1/R_d$  for linear isotherms.

13. For retardation calculations, several points should be considered:

bulk density  $\rho_{\rm B} = (1-\theta)\rho$ where  $\rho$  is the specific capacity of the minerals in the rock.  $K_{\rm D} = \%$  oc . Koc/100  $R = 1 + (1-\theta)\rho$ .Koc. % oc/(100. $\theta$ ).

14. A direct determination of the  $R_f$  value, the reciprocal of  $R_d$ , may be obtained using soil thin-layer chromatography.

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#### **Biographical Sketch**

Arthur W. Hounslow is currently a professor of geology at Oklahoma State University. He obtained his B.Sc. degree from the University of Melbourne (Australia) and M.Sc. and Ph.D. degrees from Carleton University (Canada). Prior to joining the staff at Oklahoma State University, he taught at Idaho State University, was employed as senior project mineralogist at Colorado School of Mines Research Institute and was a geochemist with the Ground Water Research Branch of the U.S. EPA. His current research interests include ground-water geochemistry including rock-water interaction and organic and inorganic characterization of subsurface materials.

#### **Questions and Answers**

Q. Most hydrochemical models are assuming equilibrium conditions, implying slow enough flow velocities to allow binding site saturations, etc., as well as assuming first order kinetic reaction rate constants; however, even for relatively fast reactions — such as acid-mine-drainage leaching of metals, these assumptions may be erroneous. What alternative approaches would you favor? Statistical thermodynamics? Empirical field-derived constants?

Joe Keely

A. In most mass transport models we also assume linear adsorption isotherms, another convenient fiction. It cannot be over-emphasized that we do not have the data even for this simplistic model let alone the more complicated albeit more realistic models.

**Q.** What do we need to overcome the current modeling deficiencies you described? More complex models? Better field data? More lab experiments? Can the process of VOC transport in ground water be satisfactorily modeled?

#### Mike Aggar

A. I believe the last thing we need at this stage is more complex models. We do need better field and laboratory data to input into the models we presently have. I have not done any research on VOC transport but I think the above comment applies equally well to

#### these compounds.

**Q.** Can you comment on the effects of biodegradation on mass transport? Are there simple approximations using rates or biological kinetics which you could include in the mass transport equations to account for biodegradation?

#### Wayne Chudyk

**A.** In most mass transport models there is a biodegradation term. The catch is to find the appropriate parameters to feed into it. Even less is known about biodegradation than about adsorption.

**Q.** 1. Do you know the normal range of organic carbon concentrations in saturated unconsolidated soils? 2. What is the accuracy of analytical techniques for organic carbon in soil?

#### Henry Lord

A. 1. Very little research has been done on the vertical distribution of organic matter in a soil column. I doubt if there is such a thing as a "normal range." The amount present at the various depths will depend on the organic matter content of the topsoil, the grain size of the sediment, the amount of elution that has taken place, the extent of microbial degradation, etc. Some of our research effort is directed toward determining some of these variables. 2. The analytical precision and accuracy is more than adequate. Representative sampling is of much greater concern.

**Q.** 1. From your formula relating  $K_{oc}$  to  $K_{D}$ , is it true that as organic matter in the soil approaches O, the  $K_{D}$  approaches infinity? 2. You said the linear adsorption isotherm is independent of concentration. Could you explain what you mean by this—since it appears there is a linear relationship with concentration?

#### A. Scott Andres

A. 1. As the % organic matter becomes small, so does  $K_D$  if this model is correct. Thus as % OM vanishes so too does  $K_D$  with the result that  $K_{OC}$  is also zero. 2. In the case of a linear isotherm  $X=K_DC$  or  $K_D=\bar{S}/C$ where  $K_D$  is the ratio of the concentration of solute in the solid to the concentration of solute in the liquid. This ratio remains the same regardless of the concentration.

Q. Do you have any data (or theories) on what effects the crystallinity clays or iron, manganese oxides have on retention of organics? If adsorption on organic matter is dependent on adsorption of solute onto charged functional groups, what meaning do % organic carbon or % SOM test have? Are they realistic? What test would be meaningful?

A. Scott Andres A. Adsorption in general is inversely proportional to grain size which is usually a function of the crystallinity. However, most hydrophobic organic pollutants are more strongly adsorbed on solid organic matter adsorption is not known and % OC or % SOM is a convenient approximation. A major part of our research effort is directed toward the elucidation of this phenomena.

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# Distribution Coefficient of Trichloroethylene in Soil-Water Systems

by Mohsen Mehran<sup>a</sup>, Roger L. Olsen<sup>b</sup>, and Bryan M. Rector<sup>c</sup>

#### ABSTRACT

The distribution coefficient of trichloroethylene (TCE) was obtained from field and theoretical methods. The field method was based on measuring TCE concentrations in the soil samples and in the adjacent ground water. The theoretical method was based on using the organic carbon content of the soil and the octanol/water partition coefficient for TCE. The average distribution coefficient for 19 field samples and four methods of calculation was 0.18 ml/g which is in agreement with literature data and octanol/water partition coefficients results. For soils containing greater than 0.1 percent organic carbon, the theoretical methods of calculating the distribution coefficient appear to be valid. For soils low in organic carbon content, laboratory determinations of the distribution coefficient can provide reasonable estimates for predicting actual migration rates. Field determinations of distribution coefficients are, however, preferred because they integrate the effect of various factors on partitioning of TCE.

#### INTRODUCTION

In the last two decades, the number of organic compounds used for various industrial and agricultural purposes has been increasing at a rapid rate. Accidental spills and underground leaks of these compounds, particularly the halogenated organic solvents, have caused degradation of the quality of soil and ground water in numerous sites (Weimar, 1980; Mackay *et al.*, 1985). The soil and ground-water contamination investigations for

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predicting the rate of migration and for designing remedial action alternatives require a thorough understanding of geochemical behavior of these compounds in the soil-water system. The geochemical reactions affecting the rate of migration of organic solvents are complex, and research efforts in this area are relatively recent (Wilson, 1983).

Widespread usage of trichloroethylene (TCE) in the past has caused contamination in a number of sites (Paigen, 1982; U.S. Environmental Protection Agency, 1984). Consequently, more emphasis has been placed on understanding the geochemical behavior of TCE in soil-water systems.

Migration of TCE in soil-water systems is governed by convection-dispersion processes and geochemical characteristics of the medium. The rate of migration of TCE is also affected by the distribution coefficient dictating the partitioning of TCE between the liquid phase and the solid matrix. One of the most significant reactions contributing to this partitioning is the sorption to and desorption from the solid matrix. Partitioning of solvents by organic molecules is another mechanism for adsorption. Under appropriate conditions and assumptions, the distribution coefficient can be used to define the retardation factor which expresses the velocity of TCE migration relative to the advancing water front.

Different methods have been used to arrive at sorption-desorption behavior of contaminants. The most common approach is laboratory column leach studies where effluent concentrations are measured in order to describe the overall interaction between the liquid phase and the solid matrix. The applicability of such laboratory tests to field conditions is often of question and concern.

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In this paper, the distribution coefficient of TCE obtained by two different methods is reported. The first method (field) is based on field measurement of TCE concentrations in the soil samples collected at various depths during drilling and also in the adjacent ground water. The second method (theoretical) calculates the distribution coefficient based on the total organic carbon content of the soil. The results obtained from the two methods are compared and, based on an average distribution coefficient, an average retardation factor for TCE is calculated. The calculated retardation factor is discussed in light of the results of other investigators. Under appropriate conditions, the average retardation factor for TCE can be used to predict the rate of migration of TCE in soilwater systems.

#### **BACKGROUND AND SITE CHARACTERISTICS**

Initial site investigation detected soil and ground-water contamination near the tank area. The locations of the storage tank and observation wells are shown in Figure 1. The site is located in the Central Coast range of California, consisting of alluvial sediments deposited in a series of coalescing fans emanating from the uplands drainage. Maximum thickness of the sediments may exceed 1,500 feet. In the vicinity of the site, basin ground waters are broadly divided into upper and lower aquifer zones, separated by relatively

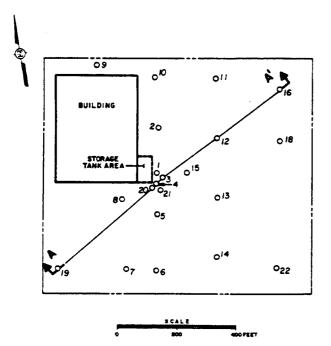


Fig. 1. Site plan and location of wells.

thick clay aquitards. Both the upper and lower zones are typically divided into two or more local aquifers that are separated by thinner and less extensive aquitards.

The site investigation included drilling borings to a depth of about 30 feet using a continuous flight hollow stem auger. Soil samples were collected at closely spaced intervals using a splitspoon sampler. The samples were placed in tightly sealed glass jars and shipped to the laboratory. Soil samples were tested for possible presence of TCE. The borings were converted to ground-water monitoring wells by installing either PVC or stainless steel casings.

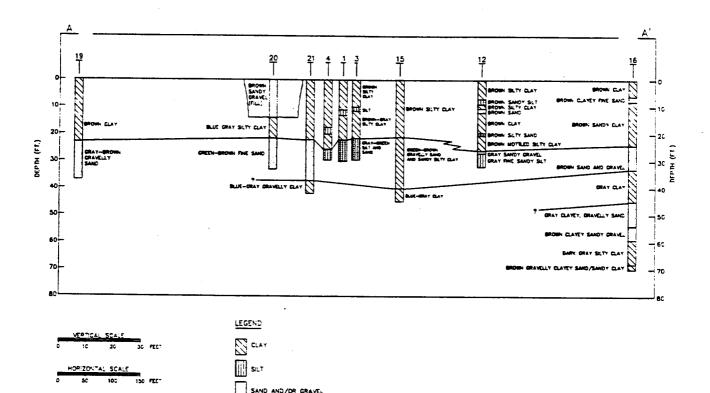
The shallow subsurface conditions encountered in the field are characterized by two waterbearing zones (A and B) separated by a thin aquitard. A typical representation of the stratigraphy of the site is shown in Figure 2, indicating a surface layer of clay or silty clay material on the order of 20 feet thick overlying the A waterbearing zone. This zone consists of sand, gravel, and variable amounts of silt and clay. The thickness of this zone varies from 5 to 20 feet. The A zone is underlain by a clay or silty clay aquitard, up to about 10 feet in thickness overlying the B water-bearing zone consisting of sand and gravel and variable amounts of silt and clay. The thickness of the B water-bearing zone is about 20 feet.

Ground water was encountered at a depth of about 25 feet. Soil samples were reported moist to wet at a depth of about 20 feet. The A zone is confined during wet conditions, and the B zone is always confined. Ground-water elevations in the A zone are usually one to two feet higher than in the B zone at corresponding locations.

Ground-water samples were obtained by purging the wells and evacuating at least four well volumes using clean bailers and techniques normally practiced for volatile organic compounds.

TCE was analyzed by gas chromatographic techniques. Specifically, the TCE was codistilled from the samples with water and isooctane and the extract was analyzed using a 2-m Carbopack B/1% SP-1000 column and electron capture detector. The detection limits were 0.1 mg/l in water and 0.1  $\mu$ g/g in soil. The identification and concentrations of TCE were verified by using (1) a 2-m 20% SP 2100/0.1% Carbowax 1500 column at 80°C and electron capture detector and (2) gas chromatography/mass spectroscopy (GC/MS) techniques following U.S. EPA Method 624 (U.S. Environmental Protection Agency, 1982). The results of the analyses are presented in Table 1.

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#### DISTRIBUTION COEFFICIENT AND RETARDATION FACTOR

The one-dimensional transport of a single sorbing solute in an homogeneous porous medium under saturated steady-state water flow conditions can be described as:

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 $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{n} \frac{\partial S}{\partial t}$ (1)

where C = solution concentration, mg/l; t = time, sec; D = dispersion coefficient, cm<sup>2</sup>/sec; x = distance, cm; v = average linear pore-watervelocity, cm/sec;  $\rho$  = soil bulk density, g/cm<sup>3</sup>; n = effective porosity; and S = adsorbed concentration, mg/Kg. In equation (1), the last term represents the interaction between the solid matrix and the liquid phase. Different mechanisms may be responsible for attenuation of different compounds in soil-water systems. Sorption, ion exchange, and coprecipitation are among the main mechanisms contributing to attenuation for inorganic compounds. In ground water, sorption may be a major mechanism determining the fate and movement of organic compounds (Bedient et al., 1982). The partitioning of these compounds between the solid matrix and the solution phase may follow a particular isotherm depending on the

properties of the material, interactions between the two phases, and their concentrations. In general, the partitioning between the two phases can be written as (Helfferich, 1962):

$$S = K_d C^N$$
 (2)

where  $K_d$  = Freundlich adsorption constant, and N = Freundlich exponent. Equation (2) is known as the Freundlich isotherm. For some pesticides and complex organic compounds, N in equation (2) is not equal to unity (Hamaker and Thompson, 1972; Rao and Davidson, 1979) indicating a nonlinear adsorption behavior. On the other hand, for a variety of hydrocarbons and under many circumstances N = 1 and thus equation (2) reduces to:

$$S = K_d C$$
(3)

which is referred to as the linear adsorption isotherm.  $K_d$  is a valid representation of the partitioning between the solution phase and the solid matrix only if the reactions that cause the partitioning are fast compared to the flow velocity and reversible and only if the isotherm is linear. Many organic compounds are reported to follow a linear adsorption isotherm. Examples include: several halogenated aliphatic hydrocarbons (Chiou *et al.*, 1979), polynuclear aromatic hydrocarbons (Means *et al.*, 1980), dibenzothiophene (Hassett *et al.*, 1980), benzene (Rogers *et al.*, 1980), and halogenated hydrocarbons and some substituted benzene compounds (Wilson *et al.*, 1981; Hutzler *et al.*, 1986). Based on the above studies, if the calculated  $K_d > 0$ , the chemical species will be retarded. Assuming equation (3) is valid, substitution of equation (3) in equation (1) yields:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x}$$
(4)

where R is the retardation factor expressed as:

$$R = 1 + \frac{\rho}{n} K_d = \frac{v}{v_c}$$
(5)

 $v_c$  in equation (5) represents the average velocity of the retarded constituent. The previous assumptions concerning the rapid rate and reversibility of reactions and linearity of the isotherm also apply to equation (5).

### METHODS OF Kd DETERMINATION

The  $K_d$  of TCE was determined using two different methods; one was based on field data and another was based on theoretical relations utilizing the organic carbon content of the medium.

#### **Field Method**

The field method of  $K_d$  determination was based on the TCE concentrations measured in the ground water and the adjacent soil.

Knowing the concentrations of TCE in the ground water and in the soil samples best corresponding to the ground water, Kd was calculated from equation (3). Technically, the sorbed concentration (S) in equation (3) should be based on analyses of a dry soil sample (i.e., only the TCE sorbed on the soil and not in the soil water should be considered). Because samples submitted for analyses are not dried (volatiles would be lost), a split of the sample should be analyzed for moisture content. The TCE concentration analyzed in the soil containing water should then be corrected for the TCE actually contained in the water fraction of the soil. The concentration of TCE in the soil moisture is usually assumed equal to the TCE concentration in the water taken from the same depth as the soil samples which may not necessarily be true. In addition, since the moisture content was not measured in the soil samples collected, the values reported for TCE concentration in the soil were used in equation (3) without correction (i.e., as if they were reported on a dry basis). This assumption yields higher values for Kd which leads to

conservatively lower estimates of chemical transport.

The results of the distribution coefficient and retardation factor calculations are presented in Table 1. As shown, Kd varies over a wide range from a minimum of 0.01 to a maximum of 4.0 ml/g. However, about one-half of the Kd values fall within the range of 0.1 to 0.25 ml/g. As previously stated, values of Kd are generally higher because the analytical results were not corrected for soil moisture. It appears that core materials from wells 2, 6, 9, and 15 were located in a relatively nontransmissive zone. Thus, it is possible that ground-water TCE concentrations were underrepresented producing higher values of Kd. If the Kd values from wells 2, 6, 9, and 15 are not considered, the average of the Kd values is calculated to be 0.20 ml/g.

As shown in Table 1, the water sample depth was not always the same as the depth from which the soil sample was collected. In most cases the screened interval from which the water was collected covered a larger distance than the soil sample. Therefore, in most cases it may not be possible to associate the calculated  $K_d$  with a distinct soil type.

To calculate the retardation factors using equation (5), the bulk density and effective porosity of the samples were estimated from their given identifying properties (Freeze and Cherry, 1979; Todd, 1959; Sowers and Sowers, 1970). Based on the values given in Table 1, the average retardation factor for 18 samples was calculated to be 2.48.

#### **Theoretical Method**

The methods of calculating K<sub>d</sub> are primarily based on the organic carbon content of the soil. Pioneering work of Lambert (1966, 1967) and coworkers (Lambert et al., 1965) has demonstrated that sorption of neutral organic pesticides is correlated with the natural organic carbon content of a given soil. Lambert also suggested that the role of organic matter is similar to that of an organic solvent in a solvent extraction process. Thus, partitioning of a neutral organic compound between soil organic matter and water should correlate well with its partitioning between water and an immiscible organic solvent. Chiou et al. (1979) showed that the transfer of nonionic organic compounds from water to soil could be due to partitioning in the soil organic matter. They demonstrated linear adsorption isotherms over a wide range of concentrations. Karickhoff et al. (1979)

	Water Soil				Soil cbaracteristics				
Well No.	TCE conc. (mg/l)	Depth (ft)	TCE conc. (µg/g)	Depth (ft)	K <sub>d</sub> . <sup>2</sup> (ml/g)	Туре	ρ <sup>b</sup>	n <sup>c</sup>	R <sup>d</sup>
1	3.0	20-30	trace <sup>e</sup>	23-24.5	0.03	silt	1.8	0.20	1.3
2	4.1	20-30	13.2	23-24.5	3.2	sandy silt	1.7	0.22	24.9
3	49.0	20-30	0.3	23-24.5	0.01	sandy silt	1.7	0.22	1.0
4	5.0	20-30	trace	23-24.5	0.02	gray-green clay	1.9	0.15	1.3
5	0.9	20-30	0.2	23-24.5	0.22	silty sand	1.65	0.23	2.6
6	trace	27-37	0.4	23-24.5	4.0	sandy clay	1.8	0.18	41.0
7	$0.8(1_5)^{f}$	25-32	0.2	23-24.5	0.25 (0.13)	silty sand	1.65	0.23	2.8 (2.0)
8	2.1 (2.0)	25-32	0.25	23-24.5	0.12 (0.13)	silty sand w/clay	1.7	0.20	2.0 (2.1)
9	1.7 (0.097)	25-32	0.16	23-24.5	0.09 (1.6)	sandy clay-sand	1.7	0.20	1.8 (15.0)
10	7.9	25-32	1.4	23-24.5	0.18	silty sand	1.65	0.23	2.3
11	5.8 (4.0)	25-32	2.5	23-24.5	0.43 (0.51)	silty sand	1.65	0.23	4.1 (4.7)
12	11.7	24.5-31.5	2.8	23-24.5	0.24	silty sand	1.65	0.23	2.7
13	3.3 (2.7)	26.5-31.5	1.03	23-24.5	0.31 (0.38)	fine sand	1.6	0.25	3.0 (3.4)
14	10.0	24.5-34.5	0.70	23-24.5	0.07	fine sand	1.6	0.25	1.4
15	trace (0.44)	27-30	0.2	23-24.5	2.0 (0.45)	sandy silty clay	1.8	0.17	22.2 (5.8)
16	1.2 (2.1)	20-30	0.2	18-19.5	0.17 (0.10)	sandy clay	1.7	0.18	2.6 (1.9)
18	21.6	24.5-32.5	3.2	23-24.5	0.15	sandy gravel	1.6	0.30	1.8
19	3.0	27-37	1.7	23-24.5	0.57	gravelly sand	1.6	0.30	4.0
20	20.0	26-33	14.0	23-24.5	0.70	fine sand	1.6	0.25	5.5
21	12.0	25-35	0.1	23-24.5	0.01	fine sand	1.6	0.25	1.0
22	0.25	28-55	0.03	23-24.5	0.12	-	1.6	0.25	1.7
Avera					0.205		1.66	0.23	2.48

Table 1. Distribution Coefficients and Retardation Factors for TCE Obtained from Field Data

 $\overset{a}{\cdot}$  K<sub>d</sub> = [TCE in soil] /[TCE in water].

Densities from "Introduction to Soil Mechanics and Foundations," Sowers & Sowers, pg. 30. Average value for each material assuming density of clay = 110 lb/ft<sup>3</sup>.

n = effective porosity from "Ground Water Hydrology," Todd, pg. 16.

 $d R = 1 + \rho K_d/n.$ 

1.11

1

ř.

1

trace = 0.1 mg/l and 0.1  $\mu$ g/g.

f () = reanalyses of same sample.

<sup>g</sup> Excluding samples from wells 2, 6, 9 (1.6 value), and 15 (2.0 value).

investigated the role of particle size and organic matter on sorption of a number of aromatic and chlorinated hydrocarbons. The correlation of sorption with sorbate aqueous solubility and octanol/water distribution coefficient was also studied by these authors. The role of organic carbon fraction has also been studied by Schwarzenbach and Westall (1981).

The distribution coefficient  $K_d$  is related to organic carbon content fraction according to:

$$K_{d} = (K_{oc}) (f_{oc})$$
(6)

where  $K_{oc}$  is the adsorption constant based on organic carbon content, and  $f_{oc}$  is the fraction of total organic carbon content in terms of grams of organic carbon per gram of soil.  $K_d$  defined in equation (6) is also referred to as partition coefficient. Karickhoff *et al.* (1979) showed that  $K_d$  for pyrene and methoxychlor in a given soil varies linearly with organic carbon fraction. They further demonstrated strong correlation between  $K_{oc}$ , water solubility, and octanol/water distribution coefficients.

In the present study, four different relations for calculating  $K_{oc}$  are utilized. The first relation is suggested by Kenaga (1980) expressed as:

$$\log K_{oc} = 3.64 - 0.55 \log W_1 \tag{7}$$

where  $W_1$  is the water solubility of the chemical in mg/l. The solubility of TCE in water is 1,100 mg/l at 20°C (Pearson and McConnell, 1975).

The second relation was suggested by Chiou et al. (1979) and is based on data from a number of chlorinated hydrocarbons (e.g., 1,2-dichloroethane, 1,1,1-trichloroethane) in a silty loam soil, as follows:

$$\log G = 4.04 - 0.557 \log W_2 \tag{8}$$

where G is the soil organics/water distribution coefficient, and  $W_2$  is the water solubility in mmole/l.

G and  $K_{oc}$  are empirically related by the following equation:

$$K_{oc} = \frac{G}{1.724} \tag{9}$$

The third relation used in calculating  $K_{oc}$  is as follows:

$$\log K_{ow} = 2.29 (U.S. EPA, 1979)$$
 (10)

where

$$K_{oc} = 0.63 K_{ow}$$
 (Karickhoff *et al.*, 1979) (11)

and K<sub>ow</sub> is the octanol/water partition coefficient. The fourth relation used is as follows

(Karickhoff et al., 1979):

$$\log K_{\rm oc} = 5.3 - 0.54 \log W_3$$
 (12)

where  $W_3$  is the water solubility of the chemical in terms of mole fraction multiplied by 10°. For TCE,  $W_3$  is equal to 150,700. The value for the intercept shown in the reference is 0.44; however, the data from which the value was calculated yield an intercept of 5.3.

Utilizing equations (6) through (12),  $K_d$  values for five soil samples were calculated. The soil type, organic carbon content, and corresponding  $K_d$  values are presented in Table 2.

Table 2 shows that highest  $K_d$  values were obtained when the Karickhoff *et al.* (1979) method was used. The lowest  $K_d$  values relate to the method given by Chiou *et al.* (1979). The average  $K_d$  value obtained from all methods on all samples is 0.23  $\pm$  0.26 ml/g. If calculations from equation (12) and from Sample No. 2 are not included,  $K_d$  is 0.17  $\pm$  0.11 ml/g. Exclusion of equation (12) may be appropriate because equations (11) and (12) were developed from the same set, and Karickhoff *et al.* (1979) state that equation (11) was a much better estimator. Sample No. 2 contained the least amount of organic carbon, which indicates that application of any of the equations may not be valid. It is possible that at very low organic carbon content concentration, the mineral surfaces play a more important role in adsorption of organic solvents. Recent data indicate that the critical organic carbon content, below which the inorganic fraction dominates the adsorption, is approximately 1000 mg/kg.

#### DISCUSSION

The average Kd values calculated from two different methods are: field method, 0.20 ml/g with a standard deviation of 0.19 ml/g; and theoretical method, 0.17 ml/g with a standard deviation of 0.11 ml/g. The average K<sub>d</sub> for the two methods is 0.18 ml/g. The variation of  $K_d$ using two different methods appears to be small. However, as shown by the standard deviation, the variation within each method is large. The field method has the largest variation with a coefficient of variance of 95 percent. Much of this variance is associated with the analyses of soil samples. The relative percent deviation between split or duplicate soil samples is usually relatively high because of the heterogeneous nature of soils and the relatively small sample analyzed. This source of variation could be reduced by extracting the TCE from a larger quantity of soil or from a series of soil samples and then combining the extracts before analyses. A similar source of variation is due to the small sampling interval of the soil (usually representing an interval of 1.5 ft) with respect to the relatively large interval (usually 10 feet) represented by the water sample (see Table 1). This source of variation could also be reduced by the approach outlined above. In this

<b>.</b> .					- K <sub>d</sub> (ml/g) -	$K_d$ (ml/g)		
Sample No.	Depth (ft)	Soil type	TOC <sup>2</sup> (mg/kg)	A <sup>b</sup>	BC	Cd	D <sup>e</sup>	
1	18.5-19.5	silty clay	1400	0.13	0.06	0.17		
2	31-32	silty clay	220	0.02	0.009		0.45	
3	<del>44-4</del> 5	blue-gray clay	3400	0.32	0.14	0.03	0.07	
4	81.5-83	silty clay	1200	0.11	0.05	0.42	1.09	
5	105-106	silty clay	1700	0.16	0.03	0.15 0.21	0.38 0.54	

Table 2. Calculated Distribution Coefficients of	TCE Based on Total Organic Carbon Content
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<sup>a</sup> TOC = Total Organic Carbon.

Kenaga, 1980.

d Chiou et al., 1979.

Karickhoff et al., 1979 and U.S. EPA, 1979.

e Karickhoff et al., 1979.

case, soil samples would be selected at uniform intervals over the entire 10-foot interval. The extracts of these samples would then be combined before analyses.

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Assuming an average bulk density of 1.6 g/cm<sup>3</sup> and porosity of 0.25, and utilizing the average distribution coefficient of 0.18 ml/g, equation (3) provides an average retardation factor of 2.2. This indicates that the velocity of advancement of TCE is about one-half of the average linear pore-water velocity.

Previous studies on different geologic media support the retardation factor presented here. Four field observations reported by Wilson *et al.* (1981) show that a clayey sand with organic carbon content of 0.01 to 0.25 percent exhibits an average retardation factor of about 2.4. The results of laboratory and theoretical methods presented by Wilson *et al.* (1981) provide similar retardation factors ranging from 1.5 to 2.0. The overall average retardation factor using field observation, laboratory experiment, and calculated values reported by Wilson *et al.* (1981) is 2.0 which is in satisfactory agreement with the data presented in this study.

The distribution coefficient calculated from different methods and comparison with results of previous investigators show that field, laboratory, and theoretical methods are sufficiently reliable to arrive at realistic values for the distribution coefficient of TCE. Knowing the soil characteristics (bulk density and porosity), a reasonable retardation factor can then be calculated in order to describe the rate of TCE migration relative to the water front. Therefore, for ground-water contamination studies, it appears sufficient to sample the soil and analyze the sample for organic carbon content, bulk density, and porosity from which the distribution coefficient and retardation factors can be calculated. However, in materials containing low organic carbon content, laboratory determination of  $K_d$  appears to be a better approach because for these materials, the clay and silt fractions play a more dominant role in adsorption (Karickhoff et al., 1979). However, field determination of distribution coefficient would be more representative of the actual field conditions.

In the analyses presented here, it was assumed that adsorption of TCE follows a linear isotherm. However, further studies are needed to verify this assumption for the entire range of concentrations of concern. Although limited distribution coefficient data are available for sorption of TCE on the soil matrix, the TCE desorption behavior is not well understood (Wilson, 1983). Further research in this area would provide a better estimate of time required for removal of TCE in aquifer restoration projects.

Ordinarily, in soil/ground-water quality investigations, soil samples are collected only from the unsaturated zone. Once the water table is encountered, ground water is usually analyzed as a measure of water quality. To provide a more realistic basis for geochemical characterization, it is suggested that during field investigations, soil samples be routinely collected from the saturated zone (below water table) and analyzed for the chemical species of concern. Chemical analysis of soil samples in conjunction with ground-water analysis will provide field distribution coefficients for migration analysis and remedial action purposes.

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# A Natural-Gradient Tracer Study of Dissolved Benzene, Toluene and Xylenes in Ground Water

by G.C. Patrick and J.F. Barker

#### Abstract

A solution containing a known mass of dissolved mono-aromatic hydrocarbons (benzene, toluene and xylenes) and chloride was injected as a slug into an unconfined shallow glaciofluvial sand aquifer. Transport of the constituents has been monitored using a dense array of multilevel sampling piezometers and a series of five three-dimensional 'snapshots' of the plumes have been obtained.

Vertically averaged concentrations of the chemical constituents have been used to define the horizontal aspect of the plumes and calculations of the centers of mass for each constituent have been performed. Results indicate that the hydrocarbons are all retarded relative to the chloride tracer, and the substantial mass losses of all hydrocarbon constituents have occurred. The losses, which are more than 90 percent for all but benzene, have occurred under aerobic conditions within the aquifer and can be attributed to biotransformations. The degree of retardation is similar to that which can be predicted using octanol-water partition coefficient formulations with benzene the least and xylenes the most retarded. The constituents are relatively mobile, however, in the low organic carbon content aquifer. Retardation factors range from only 1.1 for benzene to approximately 1.4 for xylenes.

Vertically, the plumes have assumed a distribution that reflects the heterogeneities of the aquifer material. The vertical scale of heterogeneity is of the order of 0.01 m, and hydraulic conductivity contrasts of up to an order of magnitude exist among layers. Retardation has occurred along individual layers with the result that concentration-depth profiles at individual locations appear erratic. These profiles illustrate the potential difficulties in monitoring contaminant migration in heterogeneous systems.

#### Introduction

Aquifer contamination by organic chemicals frequently results from the accidental spill or loss of a product to the soil. Because most organic fluids are soluble to some extent in water, a plume of dissolved constituents can form that may eventually occupy a significant volume of the aquifer. The rate at which the plume migrates and is attenuated is determined by many processes that, for organics, may include transport by the bulk movement of the ground water, dispersion, sorption, volatilization and, chemical and biological transformations.

Our present understanding of the behavior of many organics in ground water is relatively vague. The natural migration of organic chemicals has been studied for the most part, at sites where the volumes and masses of the chemical constituents are not known, and where the hydrogeologic regime is not well defined. An alternative method of study is to perform a controlled injection experiment using known volumes and masses of constituents at a site where the hydrogeology is known. By monitoring the plumes, the location, size, shape and changes in mass of each constituent can be quantified to assess the migration and attenuation processes under natural conditions.

This latter approach was used to assess the migration of dissolved benzene, toluene and the three xylene isomers (BTX) in ground water in a shallow sand aquifer at Canadian Forces Base Borden, Ontario. These organics are all relatively soluble in water and are common constituents of refined petroleum products such as gasoline. In water supplies they are of concern both for public health reasons (benzene and toluene are EPA priority pollutants) and because they impart foul tastes and odors to water at very low concentrations.

#### The Borden Tracer Site

The tracer test site is located in a shallow sand pit downgradient of an abandoned landfill at Canadian Forces Base Borden in southern Ontario. A fine to medium grained glacio-fluvial sand extends from the surface to a depth of about 9m, and overlies a relatively impervious clay. The sand is saturated below a depth of about 0.5m to 1.0m, forming an unconfined aquifer at the site. The lower 3m to 4m of the aquifer is occupied by an anoxic leachate plume from the nearby landfill, while the upper 5m is unaffected by the leachate and is aerobic. The upper zone generally contains 1 mg/L to 7 mg/L dissolved oxygen, although concentrations less than 1 mg/L are occasionally observed. The sand exhibits significant small scale horizontal bedding, and has a low organic carbon (0.02 percent) and clay (less than 1 percent) content (Mackay et al. 1985).

The upper five meters of the aquifer is instrumented with a dense array of Teflon® multilevel piezometers installed for a previous injection experiment (Mackay et al. 1983, 1985). The piezometers are placed at 1m to 3m intervals on a regular grid pattern, and extend approximately 50m downgradient from the original injection site. Each multilevel typically consists of 140.003m diameter Teflon tubes affixed to a common 0.013m diameter PVC center stalk. The tube ends are screened, and spaced vertically every 0.2m. The multilevels are easily sampled using a manifold system described by Mackay et al. (1983). A peristaltic pump creates a common vacuum enabling sample collection from up to 14 tubes at a time. The samples are retrieved in 18mL sealed glass hypovials leaving no entrapped air space.

For the present study, a single 0.051m diameter PVC injection well screened from 2.2m to 2.8m was installed within the sampling network. Several additional multilevels containing either 7 or 23 polyethylene tubes were also installed in the vicinity of the injection well to improve the sampling density of the network. A schematic showing the injection well and the various types of multilevels at the site is presented in Figure 1.

## The BTX Injection, Snapshot Sampling and Analysis

A continuous flow system was used for the BTX injection. A spike solution of BTX and chloride was metered into and mixed with ground water pumped from a 2,000L reservoir, and the dilute solution was injected through a single well into the aquifer. The entire system was sealed to inhibit volatilization losses. The injection began on August 9, 1984, and continued for 21 hours at a flow rate of 1.4L per minute producing a total slug input of 1,800L. The injection water was

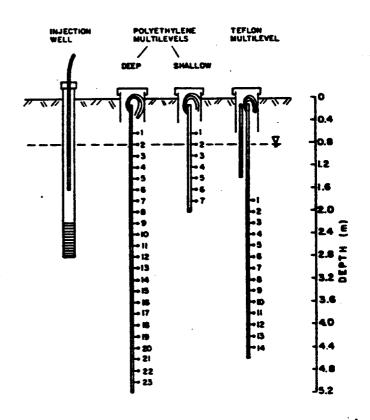


Figure 1. Schematic of the injection well and multilevel piezometers. Sampling points are vertically spaced at 0.2 m intervals.

sampled every 15 minutes at the well. Average chemical concentrations were determined to be 2,360  $\mu$ g/L benzene, 1,750  $\mu$ g/L toluene, 1,080  $\mu$ g/L p-xylene 1,090  $\mu$ g/L m-xylene, 1,290  $\mu$ g/L o-xylene and 1,280 mg/L chloride. The average dissolved oxygen concentration of the injection water was 1.4 mg/L.

The entire slug of constituents was sampled three days following the injection, and at approximately monthly intervals thereafter for four months. Each sampling session was completed within one to two days providing a three-dimensional 'snapshot' of the organic and chloride plumes. Since the injection, more than 3,200 samples have been collected and analyzed. All water samples for BTX analyses were retrieved in full 18 mL hypovials and, with the exception of the first snapshot, were preserved with 0.1 mL of 10 percent sodium azide and stored in a cooler until laboratory analysis. Sodium azide was added to inhibit microbial activity after it was observed that complete losses of BTX could occur within four to six days due to biodegradation at storage temperatures of 4 C.

In the laboratory, the organic samples were solvent extracted within the hypovials using modified methods described by Mackay et al. (1983) and Glaze et al. (1983). Using separate syringes, one mL of sample was removed and 0.5 mL of hexane containing m-fluorotoluene as an internal standard was added to each vial. The vials were shaken and allowed to stand for at least 10 minutes prior to injection into either a model 5790 or 5840 Hewlett-Packard gas chromatograph equipped with a Supelcowas 10 column (0.32 mm id., 60m length, 0.25m stationary phase thickness) and a flame ionization detector. Sample run times were rapid (5 minutes) and excellent resolution of all constitutents was obtained. Detection limits for each constitutent were about 1  $\mu$ g/L. Details of the procedure are described by Patrick et al. (1985).

Prepared standards having approximately 85  $\mu$ g/L of each organic were run every 10th sample for laboratory quality control, and a limited number of field replicates were also analyzed to assess overall precision. With the exception of the first snapshot data, the percent relative standard deviation for both the laboratory standards and field replicates were approximately 5 percent for each organic and chloride, and the biases of the laboratory standards from the true values were generally  $\pm$ 5 percent. Results from the first snapshot session were considerably poorer, most likely because azide was not added as a preservative to those samples.

#### Results and Discussion Horizontal Migration

Early attention was focused on defining the horizontal aspect of the plumes using vertically averaged concentrations of each constituent at each multilevel piezometer. Averaging was done by integrating each concentration profile using trapezoidal quadrature (Hornbeck 1975, page 146). Two dimensional contour plots of the averaged data were produced using a computerized contouring routine (Surface II). During execution, the averaged concentration data were interpolated to a regular dense grid and then plotted. The grid of values was stored for later use to assess retardation of the organic plumes.

Background chloride concentrations were generally 1 mg/L or less. Background BTX concentrations were below the detection limit, although corrections were required for data from the polyethylene multilevel piezometers. Polyethylene was found in the laboratory to reversibly sorb significant quantities of BTX. In addition, it was observed that dissolved BTX can be transferred through the tubing wall to sample water, and that this continues to occur after several flushings with fresh water. The samples at the polyethylene multilevels thus showed the false presence of BTX at locations below the BTX plumes. This effect was not observed at adjacent Teflon multilevels. Corrections to the data were made by eliminating the suspect data points. In any event, the difference between estimates of total mass of BTX in the ground, based upon the corrected and uncorrected data was approximately 5 percent.

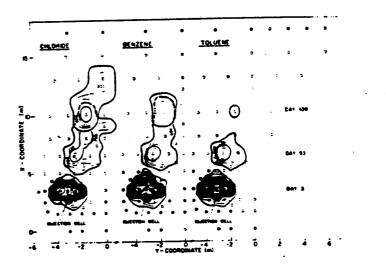
Plots showing the background corrected chloride, benzene and toluene plumes at three days, 53 days and 108 days after injection are presented in Figure 2. Chloride behaves conservatively and therefore illus-

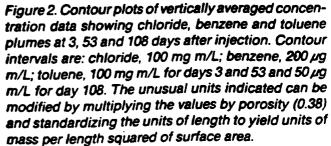
sonly the effects of advection and dispersion on

solute transport. The total mass of the chloride is constant through time. Apparent changes in mass are small, and are a function of the changing density of the sampling network, as well as a result of the effects of dispersion. As shown in Figure 2, dispersion is dominant in the direction of ground water flow producing an elongated plume, with relatively little lateral dispersion. This observation is consistent with the results of a previous tracer experiment in the Borden study area described by Sudicky et al. (1983).

All of the organic species exhibited some loss of mass through time. This is clearly illustrated in Figure 2 for toluene, which apparently lost more than 90 percent of its mass within four months. Similar losses were observed for the other hydrocarbons, although benzene, also shown in Figure 2, appeared to be affected the least.

These types of mass losses can result from a number of processes, including chemical and biological transformations, volatilization and irreversible sorption. No chemical transformations of BTX are reported in the literature to occur at significant rates under the range of conditions present in the aquifer. Losses due to volatilization can occur at the water table (Schwille 1981), although they were prevented during the study by injecting the BTX well below the water table out of contact with the soil gas phase. The mass losses were likely due to biological transformations, although irreversible uptake by the soil remains a remote possibility. Biological transformations of BTX compounds by microorganisms are known to occur in aerobic soil and water environments, including ground





water (Jamison et al. 1976), and the biochemical processes of the transformations are well understood (Hopper 1978; Gibson and Subramanian 1984). Dissolved oxygen levels were generally low (0.2 to 0.5 mg/L) but measurable within the plumes over the four months of monitoring. These low levels are below background and below the initial injection water concentration, suggesting that oxygen consumption through biotransformation was occurring. The rate of oxygen that diffused or mixed with the plumes may have been a controlling factor in the biotransformation process.

#### Sorption

Sorption of dissolved constituents by soil is a process in which the species are partitioned between solid and aqueous phases. The effect of sorption is to retard the velocity of a species relative to that of the ground water. For organics, the amount of solid organic carbon in soil is especially important in determining the extent to which sorption will occur, particularly when the dissolved species are non-polar and hydrophobic, and when the soil has a low clay content and an organic carbon content greater than about 0.1 percent (Karickhoff et al. 1979; Karickhoff 1984).

In general, the more hydrophobic an organic compound is, the stronger the sorption process will be. The degree of hydrophobicity can be estimated using parameters such as water solubility or the octanol-water partition coefficient. This has formed the basis of a number of predictive sorption equations which have recently been reviewed by Karickhoff (1984).

In the sand at the Borden site both the clay mineral content and the organic carbon content are low. One would therefore predict that compounds such as BTX, which are relatively water soluble and only moderately hydrophobic, to sorb very little. Insignificant sorption was previously observed for four different organic tracers at the Borden site (Sutton and Barker 1985). In that study, mass losses through time were attributed to biological transformations.

In a tracer study, sorption can be estimated by measuring the average velocity of the center of mass of the sorbing species,  $\bar{v}$ , relative to that of a nonreactive species such as chloride,  $\bar{v}c$ . Sorbed species will be retarded in proportion to the degree to which they partition between the solid and aqueous phases. The retardation factor, R, is defined by the ratio,  $\bar{v}c:\bar{v}$  and can, with certain assumptions, be directly included in the classic advection-dispersion equation to account for sorption (Bear 1979; Freeze and Cherry 1979).

Retardation factors were determined for BTX from the vertically averaged snapshot data. Centers of mass of each constituent were first estimated using the methods of Freyburg (1985), and velocities were then calculated between snapshots. The effects of continuous mass losses of BTX through time do not appear to have affecter the retardation process. Retardation factors calculated between the first and last set of snapshot data are presented in Table 1. Benzene was the least retarded, with a relative velocity (1/R) to that of chloride of about 90 percent, while the xylenes were the most retarded with relative velocities of about 60 percent to 70 percent.

Table 1				
<b>Retardation Factor</b>	s, R, for BTX in Borden San	d		

Constituent	Predicted R*	R from Tracer Study		
Benzene	1.1	1.1		
Toluene	1.2	1.2		
O-xylene	1.4	1.4		
P-xylene	1.5	1.4		
M-xylene	1.6	1.6		

\* From equation of Schwarzenbach and Westall 1981

As a comparison, retardation factors were calculated using the regression equation of Schwarzenbach and Westall (1981), which correlates sorption with the octanol-water partition coefficients of organic species. Their equation was selected because data for methylated benzenes are included in the correlation. A soil organic carbon content of 0.02 percent, a porosity of 38 percent and a bulk density of 1.7 gm/cm<sup>3</sup> were used. These values were previously established as characteristic of the sand at the Borden site. (Patrick et al. 1985; Sudicky et al. 1983). The predicted retardation factors are given in Table 1. The tracer results and predicted values compare remarkably well, particularly when one considers the uncertainty associated with the correlation equation, and the probable uncertainty in determining the soil organic carbon content. The agreement suggests that the correlation equations may be useful in predicting sorption for certain organic species in soils with organic carbon contents less than 0.1 percent.

#### Vertical Distribution of BTX

To assess the vertical distribution of BTX in the aquifer, the concentrations were examined in detail at a single multilevel piezometer. A continuous undisturbed core of aquifer sand had been obtained prior to its installation. The multilevel was located approximately 3m downgradient of the injection well. In the laboratory the core was divided into 0.05m lengths, and hydraulic conductivities were determined for each length using a falling head permeameter test (Freeze and Cherry 1979). A profile of the vertical hydraulic conductivity is presented in Figure 3 together with depth profiles of chloride and p-xylene concentrations at 32 and 53 days after the injection.

In the hydraulic conductivity profile, contrasts of up to an order of magnitude are evident over distances of only a few centimeters. These contrasts are a result of the thin horizontally layered structure of the sand. The average layer thickness is about 0.01m. The sand, although variable over small distances, would be considered relatively homogeneous by most hydrogeologists.

The chloride concentration profile at 32 days appears erratic, although a plausible interpretation can be made, based upon the hydraulic conductivity profile. The concentrations shown in Figure 3 are high in layers having a hydraulic conductivity of about 1 x  $10^{-4}$  m/s, and are reduced in layers having lower (0.5 x  $10^{-4}$  m/s) hydraulic conductivity. This suggests that chloride had not yet arrived in the low hydraulic conductivity layers, but had already passed through the profile in the high hydraulic conductivity layers. To test this idea, the chloride profile was examined at a later time (51 days), and the profile of the retarded species, p-xylene, was examined at both times.

The chloride profile at 53 days is somewhat the reverse of that at 32 days. Chloride concentrations are relatively high in the low conductivity layers, and are low in all other layers. The chloride plumes had apparently passed through the profile at 53 days in all but the least conductive layers.

The concentration of p-xylene at 32 days is high only in the high conductivity layer, where chloride is absent. Because p-xylene is a retarded species it should appear at a later time than the chloride. It is likely, therefore, that chloride in this layer had already passed through the profile at 32 days, as was previously suggested. By 53 days, p-xylene is absent from the high conductivity layers, but is present in most of the low conductivity layers that chloride occupied at 32 days. The net effect of retardation in individual layers was to produce an apparently erratic concentration profile. The sequence of events was that chloride first entered the profile in a highly conductive layer, and was followed in that layer by the retarded species (eg. p-xylene). This sequence was repeated in other layers of lower hydraulic conductivity at later times.

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According to Gillham et al. (1984) the concentration profiles should become smooth as a result of the vertical diffusion of constituents from layers of high concentrations to low concentrations. The smoothing effect should be enhanced by heterogeneities in hydraulic conductivity in the horizontal direction. In the present study smooth profiles did not appear to develop with travel distances up to 7m. Perhaps longer travel distances are required for smoothing to become noticeable.

These results have important implications with respect to the design and implementation of field scale studies of contaminant transport in ground water. Heterogeneities, such as those produced by horizontal

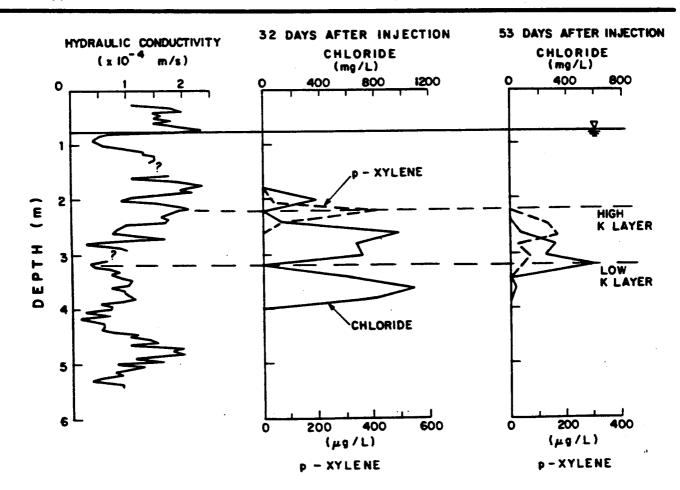


Figure 3. Vertical profiles of hydraulic conductivity, and chloride and p-xylene concentrations at 32 and 53 days after injection at a multilevel piezometer. The screened interval of the upgradient injection well is from 2.2m to 2.8m below surfactions and the screened interval of the upgradient injection well is from the screened interval of t

layering, can be important in determining the spatial distribution and migration patterns of dissolved species. For organic compounds, the heterogeneities may include factors such as the non-uniform distribution of the sorbing capacity and biotransformation potential of the soil, as well as small scale contrasts in hydraulic conductivity. This heterogeneity effect may account for some of the inconsistent organic/chloride and organic/organic ratios observed at different depths in multilevel piezometers monitoring a landfill-leachate plume at North Bay, Ontario (Reinhard et al. 1984; Barker et al. 1985). It may be valuable to first define the scale of the soil heterogeneities during the design phase of a study. By doing so, the scale of the investigation (eg. the density of the monitoring networks) can be made compatible with the spatial distribution of the heterogeneities, to yield more reliable and comprehensive information.

#### Conclusions

The results of the natural gradient tracer study demonstrates that both retardation and mass losses of dissolved BTX constituents can occur in shallow ground water environments. The losses, which amounted to a reduction of more than 90 percent within less than four months for all constituents but benzene, can be attributed to aerobic biological transformations. The observed retardation in the velocities of BTX relative to that of chloride were small but significant. Benzene and toluene were least retarded, with relative velocities of about 90 percent to that of the chloride, while the xylenes were slightly more retarded with relative velocities of about 60 percent to 70 percent. The retardation is attributed to a reversible hydrophobic partitioning process (sorption) between immobile organic matter in the aquifer and ground water. As such, the order and the extent of retardation agrees with predictions that are based upon the hydrophobicity of the organics.

Profiles of the BTX and chloride concentrations with depth appeared erratic, predominantly as a result of the differences in hydraulic conductivity among small scale (0.01m) horizontal layers of the aquifer sand. Retardation was also demonstrated along individual layers, which further contributed to the erratic nature of the profiles. These results suggest that an appreciation of the scale and magnitude of soil heterogeneities in an aquifer can be invaluable in implementing an organic ground water contamination study, and in evaluating its results.

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# Transport of Organic Compounds Dissolved in Ground Water

by Joan M. Newsom

#### Abstract

Organic compounds, such as trichloroethylene (TCE) and chlorobenzene, that have been found in drinking water supplies are of public concern because they are possibly carcinogenic. These substances can now be routinely detected in trace amounts with gas chromatograph mass spectrometers. There are some polar organic compounds, which are not detectable individually by common methods and therefore little is known about them.

The transport of organic compounds is more difficult to predict than the flow of ground water because:

• Trace amounts of pollutants are difficult to measure

• Transport is complicated if the compound is partitioned into several phases

• The concentration of organics in ground water may vary due to aquifer heterogeneity and other hydrologic factors

• Reactions with other organic compounds and reactions with the aquifer material (such as adsorption) may affect the mobility of the organics

Biodegradation may also affect net transport.

Adsorption is a factor in the attenuation of non-polar organics in aquifers with significant organic content (>0.1 percent organic carbon). The organic material adsorbs the non-polar organic chemicals. The mobility of a pollutant in such an aquifer depends on at least two parameters: the levels of dissolved organic matter and the content of organic carbon in the aquifer material. The partition coefficient of the chemical pollutant between the aquifer and water is commonly calculated as a function of the organic content of the aquifer and the partition coefficient between octanol and water.

Field and laboratory results reported in the literature indicate that the following organic compounds may be biodegradable under aerobic conditions: alkyl benzenes and chlorobenzenes. Under anaerobic conditions halogenated aliphatics, alkyl benzenes, several pesticides and phenolic compounds may be biodegradable. Halogenated aliphatics appear not to degrade under aerobic conditions and non-chlorinated aromatics and chlorobenzenes appear not to degrade under anaerobic conditions. Alkyl benzenes biodegrade more rapidly than their halogenated counterparts.

#### Introduction

Pollution of ground water by organic compounds is an important area of public concern, and hydrogeologists are increasingly required to evaluate hydrocarbon contamination in the subsurface. The methods of analysis have improved in recent years such that concentrations of less than one microgram per liter ( $\mu g/L$ ) can be determined. The ability to measure more organic compounds, especially polar organics, will increase the number of different contaminants detectable in water.

Some of the organic compounds found in water are believed to be harmful in trace amounts. The health risks of the synthetic organics, however, are difficult to determine mainly because of the uncertainty in extrapolating the results of laboratory carcinogen tests on lab animals to humans. The health risks are not likely to become known very rapidly. References on health aspects of synthetic organics are found in Pearson (1982a, 1982b), and Merian and Zander (1982).

Man-made hydrocarbons are used in a wide range of industries and in household products. They are for the most part a product of technology used since the 1940s. Their solubility in non-polar substances and poor solubility in water account for their common and widespread use as degressers. Trichloroethylene (TCE) is used, for example, to clean oil from industrial machines, to wash oils from airport runways, and to remove grease from clothes in dry cleaning.

#### Definitions

Hydrocarbon compounds, also called organic compounds, are composed of hydrogen and carbon. Aliphatic hydrocarbons are a group of hydrocarbons in which the carbon atoms are joined to form open chains. Aromatic hydrocarbons usually have structures that contain at least one benzene ring. Monocyclic aromatics, such as alkyl benzenes, have one ring. Polynuclear hydrocarbons possess more than one ring. This class of hydrocarbons can be divided into two groups. In the first, the rings are fused, which means at least two carbon atoms are shared between adjacent rings, e.g., naphthalene. In the second group, the aromatic rings are joined directly or through a chain of at least one carbon atom. e.g., biphenyl.

Many of the organic pollutants are halogenated:

that is, they contain halogen atoms in their molecular structure. Chlorine. bromine and fluorine are the most common halogens. Examples of halogenated aliphatics found in ground water include: trichloroethylene (C1CH:CCI2 commonly abbreviated TCE), which contains two carbon atoms joined by a double bond; 1.1.1trichloroethane (CH3CCI3), which contains two carbon atoms joined by a single bond: and tetrachloroethylene (C12C:CC12 commonly abbreviated PCE), which contains two carbon atoms joined by a double bond. Trihalomethanes (THMs) are a subgroup of the halogenated aliphatics that contain three halogens in the methane (CH4) molecular structure. Examples include chloroform or trichloromethane (CHC13), bromoform or tribromomethane (CHBr3). and dibromochloromethane (CHBr<sub>2</sub>C1). Halogenated aromatics found in ground water include: chlorobenezene (C1CeH3). dichlorobenezene (C12C6H4 abbreviated in this paper. DCB), and trichlorobenzene (C13CeH3 abbreviated in this paper. TCB).

Hydrocarbon compounds can also be generally divided into polar and non-polar groups. Polar molecules are electrically neutral molecules with concentrations of negative charge in one part of the molecule and of positive charge in another, producing an electric dipole.

#### Occurrence of Organic Pollutants in Ground Water

The extent of ground water pollution by organic compounds is difficult to estimate both for a given aquifer and in general. Specific studies are difficult to compare because of variations in analytical sensitivity and differences among the compounds studied. Even for a given aquifer, the extent of ground water pollution by organic compounds can only be estimated because such a small fraction of the ground water is usually sampled.

There are many sources of organic pollution. Contaminants may reach the aquifer by way of precipitation. by seepage of pesticides and herbicides from the surface. from pollutants in sanitary landfills, waste storage ponds, polluted streams and lakes, and from accidentally or deliberately spilled material. Organic pollution is found both in industrial areas and in rural areas.

Man-made compounds pose a ground water pollution problem in industrialized countries. One or two percent of ground water supplies in the United States are polluted based on estimates of point sources, but only a fraction of these are contaminated primarily by organic pollutants (Pye and Patrick 1983). The compounds that occur most frequently in ground water in the United States are the trihalomethanes (THMs), which are the halogenated organics produced by c.uorination of water containing humic materials (Bouwer et al. 1981). The problem of THMs, such as chloroform, has received considerable attention beginning in 1974 and the maximum contaminant level allowed by the EPA is 100  $\mu$ g/L total THMs (Cotruvo 1981).

The extent of ground water pollution by organics in the Netherlands was measured by sampling all 232 ground water pumping stations in the Netherlands between 1976 and 1978. The samples from 54 of the 232 locations. 25 percent of the locations, contained concentrations  $>0.1 \mu g/L$  of chlorinated hydrocatbons with 1 or 2 carbons (e.g., TCE) (Zoeteman et al. 1981). The Netherlands is at the end of the Rhine River and receives pollutants from countries upstream. The compounds detected most frequently at concentrations greater than 0.01  $\mu$ g/L in Dutch ground water include: TCE (67 percent), chloroform (60 percent), tetrachloromethane (43 percent), PER (19 percent), and 1,1.1-trichloroethane (17 percent). These compounds are on the Environmental Protection Agency list of priority pollutants. The concentrations at higher levels (>10 $\mu$ g/L) could always be associated with a specific source, i.e., local waste dumping. Concentrations at low levels (0.01 to 0.1  $\mu$ g/L) may be due to volatile organics in rain water. Levels of substances such as chloroform and TCE are less than 1  $\mu$ g/L in rain water in the Netherlands.

#### Measurements of Organic Pollutants

Accurate measurements of the concentrations of organic pollutants in ground water are essential for understanding the behavior of the pollutants in aquifers. The problems of sampling an aquifer are especially severe for volatile organics, which are easily lost to the atmosphere (e.g., Pankow et al. 1964). Problems can arise from the type of well construction and the type of casing used. A study of the leaching of trace organics (0.5 ppb naphthalene and 0.5 ppb p-dichlorobenzene) into water from five common plastics used in well casing showed the following results: Teflon® (no leaching detected). nonglued PVC (0 to 0.1 ppb). Polyethylene (0.1 ppb). Polypropylene (0.5 ppb), glued PVC (0.5 ppb), and Tygon (1.0 ppb) (Curran and Tomson 1983).

Analytical results may be suspect because of the difficulty of analyzing water for trace concentrations of organics. In a comparison of analyses among certified private, state and university labs, large variations were reported even for relatively simple measurements of total dissolved solids (Keith et al. 1983). The following procedures were used to control the analytical precision and accuracy during an extensive investigation of a PCB spill site (Roberts. Cherry and Schwartz 1982). The concentrations of PCBs were determined by several analytical techniques. A standard with PCB concentrations similar to the samples being analyzed was run approximately every ten samples. Blanks were run during a switch from analysis of high PCB concentrations to low concentrations to ensure that the residual response of the system had returned to background levels.

The occurrence of some polar organic compounds. in ground water has been much less studied than that of non-polar organic compounds. Very little is known about their health risk or their occurrence because they cannot be easily isolated and measured. The group parameter TOX (total organic halogen) provides a measure of the total amount of halogen in organic compounds and is determined by concentrating the organics by adsorption, and measuring halogen concentrations by titration, specific ion electrodes, or microcoulometer. TOX analyses are both relatively simple and quick compared to gas chromatography. The more polar, non-volatile and high molecular weight halogenated hydrocarbons presently can be detected by TOX and not by GC/MS (Jeckel and Roberts 1980). Field studies have shown that the TOX concentration is several times larger than the sum of halogenated organic compounds by gas chromatographic determination (Roberts, Schreiner and Hopkins 1982).

#### Transport Processes

#### Advection and Dispersion

The mechanisms of advection and dispersion have an important control on the transport of organic pollutants. Total solute flow in porous media is composed of the portion that travels with the average ground water flow (advection) and the portion that deviates from the average ground water flow (dispersion). Dispersion causes a dilution of the solute concentration and a spreading of the contaminated area. Seen as a plot of concentration vs. the time to reach an observation point. dispersion causes the S-shaped breakthrough curve to broaden. The characteristic length of the porous medium, which is known as the dispersivity length, when multiplied with the ground water velocity, has been shown in the lab to yield the dispersion coefficient. This coefficient is used to determine the flux due to dispersive effects (Anderson 1979).

There are two types of dispersion: dispersion that occurs at the pore scale (microdispersion) and dispersion that occurs at the field scale due to aquifer heterogeneity (macrodispersion). Microdispersion is usually of not much significance for transport in relatively fast-flowing ground water. On the other hand, microdispersion and molecular diffusion are important in underground waste isolation site studies. Macrodispersion is significant due to the heterogeneity of the aquifer (e.g., Sudicky et al. 1983).

Lab dispersivity measurements do not agree with dispersivity measurements determined by field tracer tests because of scale factors. Lab measurements of dispersivity values for calculating microdispersion consist of determining breakthrough times at the outlet of cylindrical columns packed with porous media and then using the solute transport equation to determine dispersivity values. The field measurements of longitudinal dispersivity (in the direction of flow), which are on the order of 10 to 100m, are at least three orders of magnitude larger than lab measurements. 10<sup>-4</sup> to 10<sup>-2</sup>m (Anderson 1979). Field tracer tests show that longitudinal dispersivity is not constant for a given aquifer, but increases as the distance between the injection and observation well is increased. At some point. dispersivity stops increasing. This increase in dispersivity with increased travel distance or travel time of the solute is referred to as the scale effect in the literature (e.g., Molz 1983; Sudicky et al. 1983).

The cause of the variable dispersivity is the heterogenity of the aquifer. leading to anisotropic distributions of horizontal hydraulic conductivity. Field data indicate that most compounds prefer to travel through more permeable pathways, such as through gravel lenses. The variation in concentration due to heterogeneity of the aquifer causes the distribution of the compound in a horizontal sense to sometimes deviate from the theoretical plume shape derived for homogeneous aquifer characteristics (e.g., Sudicky et al. 1983).

The problem of aquifer heterogeneity is as important on a vertical scale as on a horizontal scale. Field data have shown that when chemicals enter the aquifers do not mix to the full vertical extent of the ground water and are influenced by aquifer heterogeneities and density effects (Sudicky et al. 1983; Rea and Upchurch 1980; Schwartz et al. 1982). Even though some of the data in these studies are for ions and not organic compounds, one would expect the principles to apply. Organic pollutants dissolved in water infiltrated from the Glatt River into the upper approximately 9m of a 20m thick Quaternary glaciofluvial valley fill aquifer composed of sand and gravel (Schwarzenbach et al. 1983). The contaminated water was detected several kilometers from the Glatt River in the upper half of the aquifer, while water in the lower half originated from less polluted sources. Monitoring of a PERspill in glacial deposits in Michigan showed that the PER (density =  $1.62 \text{ g/cm}^3$  at 20 C), which was well below saturation, migrated downward as it traveled away from the source (Minsley 1983).

#### Adsorption

Most aquifers have less than 0.1 percent organic content. Quantitative relationships have not been well established between sorption and the controlling factors, although the specific surface area and the nature of the mineral surface influence the degree of sorption. Some adsorption of non-polar organic compounds was experimentally observed in columns containing materials that contain no organic carbon, such as clean sand. limestone and montmorillonite clay (Schwarzenbach and Westall 1981a). Sand and gravel aquifers are likely to contain insignificant amounts of organic matter. although this parameter is usually not measured. The aquifer near the Glatt River in Switzerland, for example, contains less than 0.1 percent organic content (Schwarzenbach et al. 1983). The retention of hexachlorobenzene. for example, was small between the aquifer next to the Glatt River and observation wells, which are up to 120m away from the river, despite the fact that hexachlorobenzene has a high log Kow of 6.06, and therefore, would be expected to be strongly retained in an aquifer with significant carbon content. The mobility of hexachlorobenzene indicates the low sorption capacity of sandy gravel aquifers with insignificant organic content (Schwarzenbach et al. 1983).

Aquifers comprised of deposits where former living matter is likely to have accumulated, such as from peat deposits. slow-moving streams, lakes or bogs, tend to have significant organic content. Studies have shown that at least 0.1 percent carbon content in the aquifer (0.001 g of organic carbon per gram sorbent) is needed for carbon adsorption to be significant (e.g., Schwarzenbach and Westall 1981a). Instead of solubility, the octanol:water partition coefficient (Kow) is often used as a measure of the partitioning of pollutants between water and organic phases. The Kow is the ratio of the concentration of a compound in octanol, a readily available alcohol that is relatively non-polar, to that in water. An inverse correlation between log Kow values (ranging between 1 and 6) and log solubility values, ranging between -3 to 5 in mg/L. has been found for non-polar organic compounds (Mackay 1980: Zoeteman et al. 1981). Kow values are also used to predict the partitioning behavior of compounds into soil that contains organic matter, as well as into the fat bodies of fish and other biota. Measured values of Kow can be found in: Chiou, Porter and Schmedding (1983): Banerjee, Yalkowsky and Valvani (1980): Kenaga and Goring (1980): and Hutzinger (1982): and estimated Kow values are found in Hansch and Leo (1979): and Leo. Hansch and Elkins (1971). In addition. chemical properties of organic compounds can be found in Verscheuren (1983), Hutzinger (1982, 1980), Weast and Astle (1982).

An example from California illustrates how the order of breakthrough of several organic compounds correlated with solubility and Kow such that the compounds that appear first have the highest solubility and lowest Kow. The order of appearance at an observation well 11m downstream from the injection well from first to last to appear was: chloride, chloroform, bromoform and dibromochloroform, 1.1.1-trichloroethane and chlorobenzene (Roberts, Schreiner and Hopkins 1982).

In another example from western Canada. TCB concentrations increased relative to that of PCB with depth as shown by the increase in the 1.2.4-TCB/PCB ratio from 0.02 in the surface fill to 0.19 in the underlying Regina clay (Roberts, Cherry and Schwartz 1982). The log Kow of 1.2.4-TCB is 4.05 (Leo, Hansch and Elkins 1971) while that of 2.4.5.2'.4'.5'-PCB is 6.72 (Schwarzenbach and Westall 1981a). The increased mobility of TCB is reflected by the lower Kow. Other indications of greater mobility are higher solubility, lower molecular weight and fewer chlorine atoms in the molecular structure in TCB compared with PCB.

Useful relationships have been found between the adsorption behavior of a pollutant and its Kow value and the organic content of an aquifer. Preliminary work indicates that the partitioning behavior of a pollutant and its residence time can be calculated for aquifers containing sufficient organic material. Karickhoff et al. (1979) demonstrated that the degree to which a compound is adsorbed in a soil, as measured by the partition coefficient (Kp), depends on the Kow and the "fraction organic content" (foc) of the soil by the relation:

$$Kp = 0.63 \text{ foc } (Kow)$$
 (1)

The equation was developed by examining the adsorption of 10 organic pollutants, whose log Kow ranged from 2 to 6, in river and pond sediments whose foc ranged from 0.1 to 3.3 percent. This equation applies when the pollutant concentration is less than half of the solubility limit in water. Based on surface and aquifer sediments, whose foc is greater than 0.001, Schwarzenbach and Westall (1981a) derived a similar equation:

$$K_{\rm D} = 3.2 \, \text{foc} \, (\text{Kow}^{0.72})$$
 (2)

This equation is also valid only for low concentrations of the pollutant. Means et al. (1980) derived a similar equation for PAHs. Figure 1 illustrates the relationship described by Equation 2 for four chlorinated benzenes with different Kow coefficients. The equations establish the similar dependence of the parameters foc and Kow on the partition coefficient between soil containing organic matter and water. These equations apply only for non-polar substances in material with greater than 0.1 percent carbon. Kow provides a better estimate of sediment-water partitioning than does solubility, which gives at best an order of magnitude estimate of the partitioning behavior of a chemical in the organic fraction of the sediment medium (Karickhoff et al. 1979).

Schwarzenbach and Westall (1981a) found that more than 85 percent of the adsorption of the pollutants took place on particles of size less than 0.125mm (fine sand) and Karickhoff et al. (1979) observed that most of the adsorption took place on the particle fraction smaller than 0.05mm (silt or clay). More organic

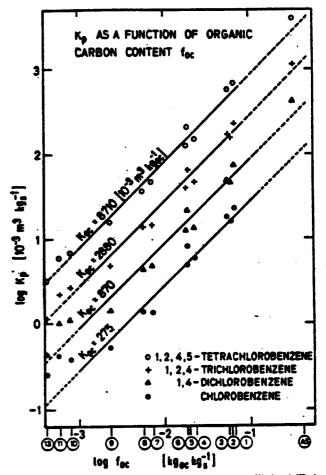


Figure 1. The sorbent to water partition coefficient (Kp) as a function of organic carbon fraction (ioc) for four chlorobenzenes (Schwarzenbach and Westdil 1981b). Eoc is the partition coefficient based on organic content and Koc = Kp/foc. The circled symbols indicate the sorbents on which the data were obtained: AS, activated sludge: 1. 4, sea sediments (coastal zone); 2, detritus; 3, 5, lethe sediments; 6, 8, river sediments; 7, 9, 10, 11, 13, aquiter material.

compounds were sorbed on the finer particle size fraction of sediments than on the coarse fraction principally because of the higher organic content as well as the larger surface area. Differences in sorption between silt and clay fractions depend on differences in foc rather than in sediment size (Karickhoff et al. 1979). Organic compounds also partition onto dissolved organic matter, such as fulvic and humic acids, such as in organic-rich water in landfill leachates (Cherry et al. 1984).

A pollutant that is adsorbed travels slower than the water containing the pollutant. The travel time of the solute divided by the travel time of the fluid is known as the retardation factor or the relative residence time (tr), which based on Equation 1 is:

tr = 1 + 0.63 foc (Kow)  $\rho/\epsilon$ 

where

 $p = average bulk density (g/cm^3)$ 

 $\epsilon = soil void fraction (unitless)$ 

(Roberts, Reinhard and Valocchi 1982)

A comparison among tr values, which are dimensionless, calculated from the equation and those derived from the field show that tr values diverge for increasing values of Kow. The tr values are 5 (field) and 6 (equation) for chloroform: 36 (field) and 41 (equation) for chlorobenzene: and greater than 200 (field) and 140 (equation) for 1.4-DCB (McCarty et al. 1981). Kow values for these three compounds are 93, 692, and 2.400 respectively and the calculations are based on an average bulk density of 2 g/cm<sup>3</sup>. $\epsilon$ = 0.22, and foc = 1 percent carbon (McCarty et al. 1981). Schwarzenbach et al. (1983) derived a similar equation but did not make a comparison with field results.

The common method of modeling the effects of sorption on solute transport is to assume that the solute and sorbent react in instant equilibrium. i.e., no kinetic effects, that the ratio of the sorbed solute to the solute dissolved in water is constant, i.e., linear isotherm, and that adsorption and desorption is a reversible process. The above equations are based on these assumptions.

Formulas for the calculation of limiting kinetic effects. non-linear isotherms and unequal sorption/desorption behavior are given in Miller and Weber (1984). Kinetic effects are important when the ground water velocity is too fast to allow equilibrium and the above equations are no longer valid. The ground water flow rate (approximately 0.014 cm/s) close to the Glatt River during storm water events was probably fast enough for kinetics to affect the transport of pollutants in the aquifer. Kinetic effects are also important when contaminants are newly introduced to a ground water system and when spike or plug contamination sources are appropriate. Under these conditions less material is sorbed onto the aquifer media and the material that is not sorbed travels farther. Kinetic effects were observed in column experiments when water containing chlorinated benzenes flowed through a column at a rate of 0.01 cm/s (Schwarzenbach and Westall 1981a. 1981b), which is well within the range of typical ground water velocities. The breakthrough times were faster than the breakthrough times of the same column experiment conducted at a velocity of less than 0.001 cm/s. The results of the column experiment at the slower rate (0.001 cm/s) matched those of an 18hour long equilibrium batch experiment indicating that sorption equilibrium occurred at the slower rate.

Although numerous studies have shown that trace levels of dissolved organic compounds follow linear isotherms. one exception are trace levels of PCBs (Cherry et al. 1984). Non-linear isotherms are most likely to occur when the concentration of the dissolved solute nears the solubility limit. For example, at low concentrations (well below the solubility limit) pesticides showed linear isotherms, but at high concentrations several organic pesticides have very non-linear isotherms (Cherry et al. 1984).

An important source of data on adsorption is the treatment of waste water by artificial recharge of an aquifer. The advantage of studies on waste water recharge is that the rate and length of time that a contaminant was injected or allowed to infiltrate into the aquifer is known, in contrast to most pollution studies.

In one study, approximately 92 percent of the organics were removed from the waste water (Tomson et al. 1979). The highest initial concentration was only 4.05  $\mu$ g/L and the range in final concentrations was between 0.1 to 1  $\mu$ g/L. Most removal rates for the 11

classes of compounds studied were between 90 to 100 percent, which included chloroaromatics and alkoxyaromatics, alkyl benzenes, naphthalenes, alcohols, ketones, indoles and indenes. Those groups whose removal rate was below 90 percent include the alkylphenols (85 percent), alkanes (71 percent), and chloroalkanes (70 percent) and phthalates (2 percent). The phthalates was the only group not to exhibit a dramatic decrease in concentration, and it was concluded the observed decline of only 2 percent was in error. A study of dune infiltration in northern Holland actually showed a dramatic increase in phthalate concentration (Piet et al. 1981). Perhaps PVC tubing contamination influenced the phthalate concentrations in both cases.

Adsorption and volatilization were thought to be the significant transport mechanisms for the pollutants studied by Tomson et al. (1981). Biodegradation had a minimal impact for two reasons: (1) The injected fluid was effluent from an activated sludge plant and compounds that easily biodegrade would not have been present. (2) Biodegradation does not occur for low pollutant concentrations. Tomson found that in the lab sewage bacteria reduced 2.3-dimethylnaphthalene from 1.3 mg/L to 40  $\mu$ g/L in one day and that there was no further degradation for several days.

Under equilibrium conditions the net ratio of the rates of adsorption and desorption do not change and the reaction is said to be reversible. Sorption was reversible in several column studies (Schwarzenbach and Westall 1981a: Karickhoff et al. 1979). The reversibility of the reactions indicated that the initial removal of the compounds from solution was due to sorption and not to other factors such as biodegradation, which would cause the amount removed to be greater than the amount desorbed. A study by Horzempa and Di Toro (1983), however, showed that sorption of PCBs is not readily reversible under field conditions. The amount of sorption correlated with sediment surface area and organic content. The sorption effects were not felt to be attributable to biodegradation because PCBs are not readily biodegraded.

The restoration of aquifers depends upon the ability to remove contaminants adsorbed onto the subsurface material. One method is to flush the aquifer via injection and extraction wells. If the ground water velocity is too fast for equilibrium to be established. the concentration of the pollutant in ground water will decrease below the equilibrium concentration. Once the flushing stops. equilibrium conditions may become established and the concentration of dissolved pollutants may increase as desorption takes place. In such a case, the concentration of the pollutant at the extraction well decreases as the aquifer is flushed and then increases when the flushing is stopped. In addition to desorption during flushing as an important mechanism, the concentrations may also be affected by biodegradation rates of adsorbed. in-phase and dissolved pollutants.

Polar organics appear to be more mobile than nonpolar organics. as shown by a study in an aquifer with significant amounts of organic carbon because they are poorly retained in the organic material in the soil (Roberts, Schreiner and Hopkins 1982). Piet et al. (1981) also found that the polar compounds were not as well adsorbed as non-polar compounds in soil column experiments using 50cm-long columns of soil composed of peat and sand layers. Those non-polar chlorine organics that were retained include: nitrobenzene. nitrotoluene and chloronitrobenzene. Similarly, studies with granulated activated carbon (GAC) exhibit less adsorption of the polar organics than the non-polar organics.

#### Redegradation

Biodegradation is the breakdown of chemical compounds by microorganisms and is controlled by such environmental parameters as temperature. pH, dissolved oxygen. Eh. salinity. nutrients. competing organisms, toxicity to organisms, and the concentrations of the organisms and compounds. Lab studies have shown that under steady-state conditions a pollutant must be present in concentrations of milligrams per liter to be broken down directly by microorganisms (McCarty et al. 1981). In a similar study it was found that the pollutant concentration must be at least 100  $\mu$ g/L to sustain a microbe population (Wilson and McNabb 1983). If the pollutant concentrations are not sufficiently high to sustain the microorganisms biodegradation will not occur (Kobayashi and Rittman 1982). Sewage bacteria reduced 2.3-dimethyinaphthalene from 1.3 mg/L to 40 µg/L and no further reduction was observed for several days (Tomson et al. 1981). A lower limit for biodegradation of  $10 \,\mu g/L$  has also been found by Wilson and McNabb (1983). Trace levels of a compound can sometimes be broken down as a secondary result of the breakdown of another compound, which is present at much higher concentrations (Rittmann et al. 1980: McCarty et al. 1979).

Biodegradation depends on essential metabolic requirements, such as oxygenated water for aerobic processes. Metabolism can deplete the oxygen or other metabolic requirements in ground water at pollutant concentrations greater than 1.000 to 10.000  $\mu$ g/L (Wilson and McNabb 1983). Thus, pollutants at high concentrations may be only partially degraded when oxygen is depleted.

Results of lab and field biodegradation studies under aerobic and anaerobic conditions for different classes of organic pollutants are presented below. Most of the priority pollutants have been shown to be biodegradable under laboratory conditions (Kobayashi and Rittman 1982). This does not, however, mean that these pollutants are necessarily biodegradable under field, conditions. Aerobic conditions generally occur in the unsaturated zone and may be found below the water table at shallow depths as well as at great depths (Winograd and Robertson 1982).

Halogenated Aliphatics. Field and lab results show that several halogenated aliphatics may biodegrade slowly under anaerobic conditions. but not under aerobic conditions. CH2Cl2 does, however. degrade under aerobic conditions (R. Schwarzenbach. personal communication 1983). Halogenated aliphatics at low concentrations in treated waste water decreased in concentration when injected into a coastal aquifer in California (Roberts, Schreiner and Hopkins 1982). THMs degraded 10 times faster than the other halogenated aliphatics although the rate of anaerobic degradation was slow for both. The THMs concentration declined from  $100\mu g/L$  to less than 0.1 µg/L at a rate of 0.03 per day. The decline was attributed to anaerobic biodegradation and not adsorption because the sorption capacity of the aquifer was saturated before the injection experiment began. Batch culture tests in the lab supported the field results that THMs degrade at low concentrations under anaerobic conditions (Bouwer et al. 1981). Similarly the THM bromodichloromethane degraded slowly under anaerobic conditions of a shallow fluvial squifer in Oklahoma (Wilson and Enfield 1983). Halogenated aliphatics that have been reported to biodegrade under anaerobic lab conditions include: TCE. trichlorethane. methyl chloride, chloroethane. dichlorobromoethane, vinylidiene chloride, PER. methylene chloride and the THMs chloroform. dibromochloromethane, bromodichloromethane (Kobayashi and Rittman 1982).

No degradation was observed in studies of several compounds under anaerobic conditions, but the rate of degradation may have been too slow to be detected during the period of investigation. Bouwer et al. (1981) observed THMs but not TCE or PER to biodegrade in batch culture tests in the lab under anaerobic conditions. Wilson et al. (1983) did not observe degradation below the water table for several aliphatics: 1,2dichloroethane. 1.1.2-trichlorethane. TCE or PER. but the period of study may not have been long enough to observe alow rates of degradation. Slow rates of degradation, therefore, cannot be ruled out. Similarly, Schwarzenbach et al. (1983) observed that TCE. PER. 1.1.1-trichloroethane. and hexachlorethane were persistent in the aquifer up to several kilometers away from the river, but the wide error bars on their figures may not rule out slow rates of degradation.

The decomposition of halogenated aliphatics under aerobic lab or field conditions has not been observed. No significant degradation of halogenated aliphatics (THMs, TCE, PER) was found under aerobic lab conditions (Bouwer et al. 1981: Bouwer and McCarty 1984). The persistance of chloroform, under aerobic conditions was reported in a study of ground water recharge. a study of chloroform passage through GAC columns, a study of bank filtration in Germany and a study of waste water percolation in soil columns (Bouwer et al. 1981). Wilson et al. (1983) in a field study in Oklahoma did not observe degradation of several halogenated aliphatics. 1.2-dichloroethane. 1.1.2-trichloroethane. TCE, or PER, above the water table.

Alkyl benzenes. Alkyl benzenes are known to degrade under aerobic conditions and may degrade under anaerobic conditions. Field observations show that toluene degraded rapidly in a shallow aquifer composed of flood-plain sediments in Oklahoma both above and below the water table (Wilson and Enfield 1979: Wilson et al. 1983). Schwarzenbach et al. (1983) observed a sharp decrease in non-halogenated compounds transported from the Glatt River to any of the ground water observation wells, the closest being 2.5m from the river. The alkyl benzenes included: toluene. 1.3-dimethyl benzene. and other 2 and 3 carbon benzene isomers. Acrobic respiration and nitrification occurred predominantly in the first few meters of infiltration, thus supporting the theory that the decrease in concentration was caused by biological processes under aerobic conditions. The biological processes that removed the organic compounds were efficient. considering the short residence time between the river and the closest well and the small retardation factors of the compounds. The decline was observed at different temperature throughout the year. including 5°C in winter. Alkyl benzenes degrade quicker than halogenated aromatics under aerobic conditions, probably because of the breaking of the halogen bond for halo-. genated aromatics is relatively slow.

Naphthalene and methyl-naphthalene also decreased in concentration but the decrease in naphthalene, however, may be due to adsorption based on the results of Ehrlich et al. (1982). Ehrlich et al. (1982) observed that naphthalene did not biodegrade under anaerobic conditions, but was slightly sorbed. Bouwer and McCarty (1984) observed that several non-chlorinated aromatics are removed under aerobic but not anaerobic conditions.

Chlorobenzenes. Chlorobenzenes have been observed to degrade under aerobic but not anaerobic conditions (e.g., Bouwer and McCarty 1984). The chiorobenzenes. 1.4-DCB, 1.2.4-TCB and 1.2.3-TCB decomposed under aerobic conditions in the aquifer near the Glatt River, and are suggested to have degraded to chlorinated phenols and catechols (Schwarzenbach and Westall 1981b). The rate of decrease was slower than for the alkyl aromatics, perhaps because the breaking of the halogen bond slows the process (Schwarzenbach et al. 1983). Halogenated aromatics do not degrade under anaerobic conditions. The concentrations of 1:4-DCB did not decrease in July and August of 1979, 1980 and 1981 between the river and 5m from the river, as it did the rest of the year because conditions were anaerobic during these summer months and the compounds did not decompose. During the rest of the year the conditions were aerobic and the chlorobenzenes decomposed. Chlorobenzenes in another Swiss study persisted for at least seven years under anaerobic conditions (Giger and Schaffner 1981). Chiorobenzenes (1.4-DCB. 1.2.4-TCB and 1.2.3-TCB) decomposed above, but not below the water table in a shallow fluvial aquifer in Oklahoma (Wilson et al. 1983). The failure of chlorobenzene to decompose in autoclaved (i.e., sterilized) lab samples established microorganisms as the likely agent of destruction.

**Pesticides.** Lab studies on sewer sludge indicated that pesticides such as lindane degraded more quickly under active anaerobic lab conditions than under corresponding aerobic conditions. probably due to bacteria (Hill and McCarty 1967). DDT. for example, converted rapidly to DDD under anaerobic conditions. but persisted as DDT under aerobic conditions of several mg/L of dissolved oxygen. Similarly, more than 20 species of bacteria were found to reductively dechlorinate DDT under anaerobic conditions. whereas aerobic conditions apparently did not promote dechlorination (Kobayashi and Rittman 1982). Other pesticides that were dehalogenated under anaerobic conditions in lab culture tests include: toxaphane by bacteria. lindane by soil bacteria and parathion by bacteria (Kobayashi and Rittman 1982). These lab results indicate that pesticides are easier to break down under anserobic than under aerobic conditions. The breakdown process is relatively easy once the halogen bond is broken.

Phenolic compounds have been shown to biodegrade under anaerobic conditions in an aquifer composed of glacial drift material in Minnesota (Ehrlich et al. 1982). Methane and  $CO_2$  were formed by the anaerobic bacteria breaking down the phenolic compounds. Lab studies supported the field results, and also indicated that principally biodegradation and not sorption account for the decline in concentration (Ehrlich et al. 1982). Glass column experiments showed that chlorophenols can biodegrade under aerobic conditions (Zullei 1981).

Biodegradation is an appealing cleanup method because expensive cleanup methods could be avoided and the pollutant is destroyed rather than transferred to another part of the environment, such as to the atmosphere via air stripping. In some cases, however, the degradation products could be as toxic or worse than the original compound. Management of some of the parameters that affect biodegradation, such as nitrate supply, may allow biodegradation to occur in situ in the vadose zone or aquifer. Limitations include the difficulty of managing environmental parameters that promote biodegradation and the difficulty in maintaining biodegradation as environmental conditions change.

#### Geological Considerations

The detailed structure and mineralogic composition of aquifers is critical to the transport of pollutants. One example is a PCB spill in a glacial till area in western Canada (Schwartz et al. 1962; Roberts, Cherry and Schwartz 1982). Between 6,800 and 21,000 liters of transformer oil containing PCBs and chlorobenzenes were spilled at a transformer plant. The PCBs traveled mainly in-phase because of the low solubility of PCBs (0.05 mg/L). The laboratory-determined conductivities of the till zone. between 10-5 and 10-9 cm/s. are too low to explain the observed vertical migration. Vertical movement is primarily through fractures in the clay, silt and till units, as indicated by the high PCB concentrations measured on fracture surfaces. Tritium was also found along fracture surfaces and used to calculate the rate of solute migration. This rate is a minimum because, unlike PCBs, some of the small tritium atoms diffuse into the sedimentary units. The geological units also have a low organic content. 0.2 to 0.9 percent carbon. minimizing the role of organic carbon in absorbing the PCBs.

#### **Conclusions and Recommendations**

Although progress is being made in understanding how organic compounds travel in the subsurface, large gaps and unknown important parameters exist. Several recommendations are given below on areas that need research.

• Some polar organic compounds are not commonly detectable by present methods. They appear to be persistent in ground water, able to travel significant distances and be resistant to degradation. Perhaps the increased ability to identify these polar organics will provide a better understanding of this type of contamination. Group parameter methods, such as TOX, may be attractive compliments to the commonly used GC/MS method because of the lower cost and because the measurements include classes of compounds, e.g., polar halogenated organics in the case of TOX, which are not readily identifiable individually.

• In cases where the aquifer might contain sufficient carbon for adsorption to be significant, the empirical relationships that have been developed may be useful for determining the partitioning behavior of organic pollutants. Further study of the effect of grain size, organic content, solute concentrations, dissolved organic matter and other controls on adsorption will help clarify how solutes are transported.

• Some elements, such as N. S. or P-compounds, when injected into pollution plumes may promote microbial degradation. The field conditions under which biodegradation of different compounds is promoted is not well understood. The phase in which the pollutant biodegrades might also be considered. i.e., dissolved in water, in-phase, or adsorbed onto the matrix.

• More work is needed to determine how flushing of an aquifer via injection and extraction wells affects those pollutants sorbed onto aquifer or soil material. Travel of solutes in-phase during flushing, such as troplets within the water, may be an important mechanism.

Ground water flow models in porous media are useful for understanding a flow regime and for planning the placement of wells. Solute transport models assume constant dispersivity values and the solute is assumed to be dissolved, which in some cases may not be reasonable assumptions. Resolution problems with numerical models may occur in some cases, such as for modeling trace concentrations of a solute, high concentration gradients, or radial flow from a pulse on a rectangular grid. The mechanisms of adsorption and biodegradation are not well enough understood to model satisfactorily. The effects of such mechanisms will probably be lumped together in models because their effects will be difficult to separate in practice.

Although the technology may exist to clean up polluted ground water and pollution sites, the costs are often high. A water policy is needed to encourage prevention and set priorities for what should be cleaned up. The cost of cleanup can be several orders of magnitude larger than that of preventive measures. Monitoring of areas containing organic compounds has begun only recently, and as monitoring continues the understanding of solute transport will improve.

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## A Field Evaluation of In-Situ Biodegradation of Chlorinated Ethenes: Part 2, Results of Biostimulation and Biotransformation Experiments

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#### Abstract

Results are presented from a field study that document the in-situ biotransformation of trichloroethylene (TCE), cis-dichloroethylene (cis-DCE), trans-dichloroethylene (trans-DCE), and vinyl chloride (VC) in a saturated, semiconfined aquifer. The enhanced biotransformation was accomplished by stimulating the growth of indigenous methane-oxidizing bacteria (methanotrophs), which transform chlorinated aliphatic compounds by a cometabolic process to stable, nontoxic end products. Experiments were performed in the presence and absence of biostimulation by means of controlled chemical addition, frequent sampling, and quantitative analysis. The degree of biotransformation was assessed using mass balances and comparisons with bromide as a conservative tracer. Biostimulation of the test zone was successfully achieved by injecting methane- and oxygen-containing ground water in alternating pulses under induced gradient conditions. After a few weeks of stimulation, methane concentrations gradually decreased below the detection limit within two meters of travel. Under active biostimulation conditions, 20 to 30% of the TCE was biotransformed during the first season of testing. Direct evidence for biotransformation of VC, trans-DCE, cis-DCE, and TCE was obtained in the second and third seasons of field testing. In the absence of biostimulation, the organic compounds concentrations at observation wells reached 95% of the injection concentration, demonstrating negligible losses due to abiotic processes. Biostimulation of the test zone resulted in a concurrent decrease in concentration of methane and the halogenated aliphatic compounds. The organic compounds were transformed within two meters of travel as follows: TCE, 20-30%; cis-DCE, 45-55%; trans-DCE, 80-90%; and VC, 90-95%. These results are in qualitative agreement with methane-utilizing, mixed-culture laboratory studies which indicate that the rate of biotransformation is more rapid when the molecules are less halogenated.

A biotransformation intermediate was observed which was identified by GC-MS analysis as trans-dichloroethylene oxide (trans-DCE epoxide), an expected intermediate based on laboratory studies. When methane addition was stopped, the concentration of the intermediate rapidly decreased, while halogenated compound concentrations slowly increased, indicating that active methane utilization was required for biotransformation to occur.

#### Introduction

The in-situ bioremediation of aquifers contaminated with halogenated aliphatic compounds, commonly used as solvents, is a promising alternative in the efforts to protect ground-water quality. This paper presents the results of a field study conducted to evaluate the feasibility of enhancing the growth of indigenous methane-oxidizing bacteria that would degrade chlorinated aliphatic compounds cometabolically.

Enhanced in-situ biotransformation was achieved by creating a biostimulated zone in the subsurface. This was done by supplying methane, as a primary substrate (electron

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donor), and oxygen (electron acceptor) to stimulate growth of the desired bacteria. Details of the experimental methodology, and the characterization of the test zone are discussed by Roberts et al. (1990) in the first paper of this series. This paper summarizes the results of biostimulation and biotransformation experiments performed over three seasons of field testing. The biotransformation of TCE by the methaneoxidizing consortia was assessed in the first season. In the second and third field seasons, the simultaneous biotransformation of TCE, cis-DCE, trans-DCE, and VC was evaluated.

#### Background

The in-situ method tested requires the biostimulation of an indigenous population of methane-oxidizing bacteria (methanotrophs), which can degrade contaminants by cometabolism. Cometabolism is a process in which microorganisms growing on one compound (primary substrate), produce an enzyme which fortuitously transforms another compound, from which they cannot obtain energy for growth (Brock et al., 1984).

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The basic objective of enhanced in-situ biorestoration by cometabolism is to increase rates of biotransformation in the treatment zone. One of the simplest models for the rate of cometabolism, when the contaminant concentration is low, is given by McCarty (1984):

$$dC_2/dt = -(k/K_s)X_sC_2 \tag{1}$$

where  $C_2$  is the concentration of contaminant;  $X_a$  is the microorganism concentration; and  $k/K_s$  is a ratio of constants that is equivalent to a second-order rate constant. One means of enhancing the cometabolism rate is to increase the concentration of the requisite microbial population. This process, referred to as biostimulation, is accomplished by adding an appropriate electron donor and electron acceptor for growth. In this field experiment, the biostimulation of an indigenous methanotrophic population required the addition of methane as an electron donor and oxygen as an electron acceptor.

The characteristics of methanotrophs and methylotrophs as a broader physiological group have been summarized in numerous reviews (Quayle, 1972; Anthony, 1975; Colby et al., 1979; Wolfe and Higgins, 1979; Hanson, 1980; Higgins et al., 1981; and Hou, 1984a, 1984b). Methanotrophs possess an enzyme, methane monooxygenase (MMO), which initiates the first step in the oxidation of methane when used as a sole source of carbon and energy for growth (Dalton et al., 1984).

The MMO enzyme complex has a low substrate specificity and as a consequence is able to initiate the oxidation of a wide variety of carbon compounds (Higgins et al., 1980), methylated and brominated alkenes, and chloro-, fluoro-, bromo-, and nitro-methanes (Patel et al., 1979, 1982; Patel, 1984). Wilson and Wilson (1985) reported that TCE was fairly completely oxidized to carbon dioxide in an unsaturated soil column to which an atmosphere of 0.6% natural gas (mainly methane) and air was added. Methanotrophs were suspected as promoting this degradation. Fogel et al. (1986), using enriched methane-oxidizing mixed cultures from sediments, found TCE, vinyl chloride, vinylidene chloride, and cis- and trans-1,2-dichloroethylene to be rapidly degraded. Henson et al. (1987, 1988) also found a range of both one- and two-carbon halogenated compounds were

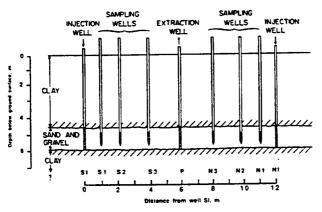


Fig. 1. Schematic of the well field used in the biostimulation and biotransformation experiments.

degraded by methane-utilizing mixed cultures. The rate of transformation was observed to be faster when the halogens were less substituted and more distributed on the molecule.

The field demonstration experiments described here were initiated to evaluate the potential for application of the methanotrophic biotransformation process. The main objectives of the first season experiments were to: (1) determine whether methane-utilizing bacteria (methanotrophs) could be easily biostimulated in the test zone; (2) assess the degree of TCE transformation under active biostimulation. The objectives of the second and third seasons were to: (3) evaluate the simultaneous biotransformation of VC, cis-DCE, trans-DCE, and TCE in response to biostimulation; (4) identify and quantify intermediate products produced, if any; and (5) study the effect of methane concentration on biotransformation.

#### **Experimental Methodology**

The field experimental site is located at the Moffett Naval Air Station, Mountain View, California. The test zone is in a shallow, semiconfined aquifer, consisting of sands and gravels. This test zone has many favorable features: high permeability; suitable ground-water chemistry; and the presence of indigenous methanotrophic bacteria (Roberts et al., 1990).

The experimental methodology and site instrumentation are discussed in detail by Roberts et al. (1990). Biostimulation and biotransformation experiments were performed under induced-gradient conditions created by the injection and extraction of ground water. The well field used for this purpose is presented in Figure 1. The target organic chemicals were dissolved in the injected fluid and continuously injected into the SI well. The chemically amended fluid was injected at rates of 1 1/min (first season) and 1.5 1/min (second and third seasons). Ground water was extracted at rates of 8 1/min (first season) and 10.0 1/min (second and third seasons) at well P, located 6 meters downgradient of the injection well. Partially penetrating monitoring wells (S1, S2, and S3, located at spacings of 1, 2.2, and 3.8 meters, respectively, from the injection well) were used to sample the ground water as it traveled through the test zone.

None of the compounds of interest—VC, cis-DCE, trans-DCE, and TCE—were detected in the native ground water. Regulatory approval was obtained to add these compounds to the injected fluid in the concentration range of  $150 \mu g/l$ , or less. The ability to add known amounts of the chlorinated aliphatic compounds of interest permitted controlled biotransformation experiments and required mass balances to be performed.

The experiments were performed as a series of stimulus-response tests. The stimulus was the continuous injection of measured concentrations of the chemicals of interest into the test zone, and the response was the concentration history of the chemicals in the ground water sampled from the monitoring wells and the extraction well. ۰.

Table 1 presents the sequence of field experiments and the processes studied. In the first field season, the test zone was first biostimulated by introducing methane and oxygen without TCE present. After biostimulation was achieved,

Experiment	Duration	Chemicals injected	Average <sup>a</sup> conc. (mg/l)	Process studied
First season Biostim l	9/05/86- 9/30/86	Methane DO Bromide	$5.9 \pm 1.1^{b}$ 20.8 ± 4.3 166 ± 4.5	Biostimulation of native methane- utilizing bacteria. Alternating pulse injection of methane and DO.
Biotranl	9/30/86- 10/21/86	Methane DO TCE	5.7 ± 1.2 22.2 ± 1.7 0.097 ± 0.024	Biotransformation of TCE with active biostimulation. Nonsteady-state conditions.
Biotran4	12/10/86- 12/31/86	Methane DO Bromide TCE	$5.2 \pm 0.9$ 23 ± 1.5 159 ± 16 0.051 ± 0.010	Biotransformation of TCE with active biostimulation. Steady-state conditions.
Second season				
Tracer8	7/06/87- 8/15/87	DO Bromide TCE cis-DCE trans-DCE	$\begin{array}{c} 14.3 \pm 1.3 \\ 78 \pm 6 \\ 0.048 \pm 0.010 \\ 0.110 \pm 0.036 \\ 0.112 \pm 0.039 \end{array}$	Transport and breakthrough of bromide, TCE, cis-DCE, and trans-DCE before biostimulation.
Biostim2	8/17/87- 10/26/87	Methane DO Bromide TCE cis-DCE trans-DCE	$5.3 \pm 0.9 \\ 23.4 \pm 2.0 \\ 44 \pm 4 \\ 0.036 \pm 0.006 \\ 0.091 \pm 0.025 \\ 0.092 \pm 0.026 \\ \end{array}$	Simultaneous biostimulation and biotransformation for TCE, cis-DCE, and trans-DCE.
Decmethl	10/27/87- 11/08/87	DO TCE cis-DCE trans-DCE	$\begin{array}{c} 24.5 \pm 1.1 \\ 0.045 \pm 0.005 \\ 0.136 \pm 0.022 \\ 0.095 \pm 0.013 \end{array}$	Test if biotransformation occurs without active methane utilization.
Third season				
Tracer 11	8/10/88- 10/10/88	Bromid <del>e</del> TCE cis-DCE trans-DCE	$72 \pm 50.047 \pm 0.0060.085 \pm 0.0130.050 \pm 0.007$	Transport and breakthrough of bromide, TCE, cis-DCE, and trans-DCE before biostimulation.
Tracer12	10/10/88- 10/20/88	Bromide TCE cis-DCE trans-DCE VC	$\begin{array}{c} 44 \pm 3 \\ 0.042 \pm 0.003 \\ 0.100 \pm 0.011 \\ 0.054 \pm 0.007 \\ 0.044 \pm 0.007 \end{array}$	Transport and breakthrough of bromide and vinyl chloride while continuing injection of TCE, cis-DCE, and trans-DCE.
Biostim3	10/20/88- 11/23/88	Methane DO Bromide TCE cis-DCE trans-DCE	$\begin{array}{c} 6.6 \pm 0.7 \\ 21.3 \pm 0.7 \\ 45 \pm 2 \\ 0.046 \pm 0.003 \\ 0.100 \pm 0.015 \\ 0.052 \pm 0.009 \end{array}$	Simultaneous biostimulation- biotransformation of TCE, cis-DCE, trans-DCE, and vinyl chloride.

#### **Table 1. Experiments and Processes Studied**

<sup>a</sup>Average values for methane, DO, are time-averaged due to pulsing.

<sup>b</sup>Standard deviation of the injection concentrations.

TCE was added, along with methane and oxygen, to assess biotransformation. In the second and third field seasons, the experimental sequence was changed to provide a more direct and convincing demonstration of in-situ biotransformation. This was accomplished by first adding TCE, cis-DCE, and trans-DCE (plus VC in the third season), and bromide before biostimulation to achieve nearly complete breakthrough of injected compounds at the first two monitoring wells. Complete breakthrough is defined as the normalized concentration of the chlorinated organics being unity, where the normalized concentration is the concentration observed at the monitoring well divided by the injection concentration. Normalized concentrations near unity at the end of the chlorinated organic addition experiment would indicate minimal losses from the system due to abiotic processes such as sorption, or biological processes.

The test zone was then biostimulated while continuing to add the halogenated organics. This sequence permitted the direct observation of the effect of biostimulation on biotransformation. Since concentrations of the chlorinated organics would be reduced due to biotransformation, desorption of the organics from the aquifer solids should also result in this stage of the experiment. Thus, biotransformation of both sorbed and injected organics would result.

The experimental methodology followed requires controlled chemical addition to the test zone over extended periods and frequent monitoring of chemical concentrations. Details of the system used to amend the injected fluids with the chemicals of interest, as well as the data acquisition and control system, and analytical methods and detection limits, are presented by Roberts et al. (1990) and Hopkins et al. (1988). An automated data acquisition and control system was used to continuously monitor the concentration of DO, methane, bromide, pH, and the chlorinated organics of interest in the injected and extracted ground water and the monitoring well samples. The system was capable of processing a sample from a preprogrammed location every 45 minutes. During the biostimulation and biodegradation experiments, the system provided approximately six complete analyses per day at each of the five sampling locations (injection, extraction, S1, S2, S3).

The performance of the injection and the analytical systems is indicated in Table 1, where the injection concentrations and their standard deviations are presented. The average coefficients of variation in the injection concentrations ranged from 15 to 20% for the chlorinated organics and methane, approximately 9% for oxygen, and 7% for bromide, demonstrating the ability to maintain constant injection concentrations and to precisely monitor the chemical concentrations of interest. Since the automated data acquisition system provided large numbers of analyses, the standard error for the mean of the measured values is only a few percent. This precision permits accurate estimates of the degree of transformation.

The degree of biotransformation achieved in the test zone was assessed using mass balance comparisons before and after biostimulation and direct comparisons with mass balances for bromide, used as a conservative (nonreacting) tracer during the biotransformation experiments. One method used was based on the ratio of the normalized concentration of organic solute to that of bromide tracer at each observation location, over a period of time where concentration remained constant, and quasi-steady-state conditions resulted. The percent biotransformed is then given by equation (2):

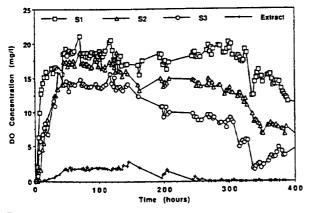


Fig. 2. Dissolved oxygen (DO) response at observation locations during the biostimulation experiment (Biostim1).

Percent biotransformed =  $(1 - C_{forg}/C_{fbr}) \times 100\%$  (2)

where  $C_{forg}$  is the mean normalized breakthrough of the oganic solute after biostimulation, and  $C_{fbr}$  is the mean normalized breakthrough of the bromide tracer over the same time interval. This equation does not account for the amount of organic solute that is desorbing from the aquifer solids, and thus it tends to underestimate the degree of transformation, especially if steady-state conditions are not achieved in the test zone.

#### **Results of the Field Experiments Results of the First Season of Field Testing** Biostimulation Experiment

The experiment (Biostim1) was conducted to evaluate: (1) the ease of stimulating methane-oxidizing bacteria; (2) the stoichiometric requirements for methane and oxygen; (3) the rate of growth; (4) the areal extent over which biostimulation could be achieved; and (5) the effectiveness of the pulsing method for distributing microbial growth.

Ground water containing either dissolved methane or dissolved oxygen was pulse injected alternately at the SI injection well as described by Roberts et al. (1990). The pulse cycle was varied during the course of the experiment, from less than 1 hr during start-up to ensure that pulsing would not interfere with growth, to a 12-hr period during the latter stages of the experiment to distribute growth over the test zone. The 1:2 pulse length ratio (methane:oxygen) resulted in time-averaged injected fluid concentrations of 5.9 and 20.8 mg/l respectively, for methane and oxygen. These concentrations are based on stoichiometric requirements for complete oxidation of methane. No additional nutrients (N or P) were added to the injected fluid.

Figure 2 shows the dissolved oxygen (DO) concentration as a function of time at the four observation locations: S1 (1 m), S2 (2.2 m), S3 (4 m), and P (6 m). During the first 140 hrs of the experiment, there was little evidence of DO consumption. Within 50 hrs of injection, DO concentrations reached maximum steady-state values, with some decrease with increasing travel distance. During this period, the bromide tracer and methane achieved the same degree of normalized breakthrough as DO, indicating the concentration decline with distance resulted primarily from dilution by the native ground water and not from microbial consumption. Dilution at the extraction well is due to the 1-to-8 ratio of the injection and extraction flow rates.

The first signs of incipient DO consumption were observed in the extraction well and the S3 observation well after approximately 200 hrs of injection. The concentration at the extraction well decreased below the detection limit after 300 hrs of injection. Owing to the increasing utilization removal by microorganisms with distance, the decrease in DO was greatest at the observation wells farthest from the injection well.

Figure 3 shows the similar response between methane and DO at the S2 observation well, decreasing as expected for methane oxidation by methanotrophs. At early time (0-50 hrs) methane and DO broke through similarly to the bromide tracer, indicating no retardation and minimal

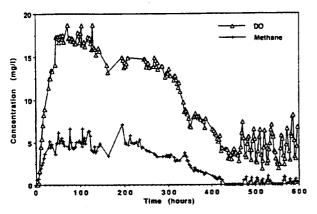


Fig. 3. Response of methane and DO at the S2 well during the biostimulation experiment (Biostim1).

consumption. The relatively rapid decrease in the methane and DO concentrations over the period between 200 to 430 hrs indicates fairly rapid microbial growth. Methane concentrations decreased below the detection limit (0.25 mg/l) after 430 hrs of injection, while a residual oxygen concentration of approximately 3.5 mg/l was maintained. Based on these values, the mass ratio of oxygen to methane consumed was approximately 2.5, which is significantly lower than the ratio of 4 that would be required for complete methane oxidation. The lower measured ratio was also expected, however, since some of the methane carbon removed was associated with biological growth.

The decrease of methane concentration below the detection limit at the S2 observation well after 430 hrs indicated that microbial growth was localized near the injection well. The pulse cycles were therefore lengthened to 12 hrs in order to prevent biofouling near the wellbore. The resulting response at the S2 observation well is shown in Figure 3: peak methane values increased from below detection to maximum values of approximately 1 mg/l. Peak methane concentrations occurred when minimum DO concentrations were observed, consistent with transport theory. These long pulse cycles were continued throughout the first year of experiments. Pulse cycle periods ranged from 6 hrs to 12 hrs. Based on some continued methane breakthrough at the observation wells, the pulsing is believed to have promoted a spatially distributed microbial population in the test zone. Biofouling of the near-wellbore region was thus limited by the pulsing methodology, as anticipated in the experimental design.

#### **Biotransformation Experiments**

Results of the first season's biotransformation experiments, discussed in detail by Semprini et al. (1988), will be summarized here. The initial biotransformation experiments were performed after the test zone was biostimulated. TCE was then continuously injected over a three-month period, initially at an average concentration of 97  $\mu$ g/l. The TCE concentration was then reduced to 51  $\mu$ g/l so that desorption from the aquifer solids would result, and thus sorptive uptake onto the aquifer solids would not be a potential explanation for the decreases observed in the test zone. Methane and oxygen were continuously pulse-injected during this period.

Upon reaching steady-state concentrations at the monitoring wells, the degree of transformation of TCE was determined by comparisons with bromide as a conservative tracer using equation (2). The degree of biotransformation at each location was as follows: S1, 17%; S2, 28%; S3, 23%; and extraction (P), 16%. Biotransformation was indicated only in the zone of active methane utilization. In the area between S2-S3 and the extraction well, no methane was present to support bacterial growth, and no additional degradation of TCE was observed.

The concentration of 1,1,1-trichloroethane (TCA), found as a background contaminant in the test zone, was also monitored during the biotransformation experiment. After normalizing for the degree of mixing of the injected fluid with the native fluid (based on bromide tracer test data), over 95% of the estimated TCA concentration was observed at the S1 and S2 observation wells. The estimate indicates minimal transformation of TCA. There is, however, a large error associated with this estimate due to the high concentration of TCA in the native ground water.

At the end of the first-year biostimulation experiment, TCE addition was stopped. Extraction and monitoring of the TCE elution was continued for an additional three months. The observations indicate a slow release of TCE sorbed onto the aquifer solids. A TCE and bromide mass balance over the complete biotransformation experiment showed 45% of the TCE injected during the course of this experiment was recovered by the extraction well, while over the same period, 65 to 70 percent of the bromide tracer was recovered. The lower recovery of TCE compared to bromide provides additional evidence for the conclusion that 25 to 30 percent of the injected TCE was biodegraded.

#### **Results of the Second Season of Field Testing** The Organic Addition Experiment

The second field season commenced with a long-term (five-week) organic transport experiment (Tracer8) to establish steady-state concentrations of TCE, cis-DCE, and trans-DCE in the test zone before restimulation, as well as to quantify the retardation of the organic solutes (Roberts et al., 1990). Operating conditions are presented in Table 1. Before continuously injecting the chemicals, a background contaminant was detected in the ground water that coeluted with trans-DCE during GC analysis. The background peak area of this background contaminant was equivalent to 16 to 27  $\mu$ g/l of trans-DCE and was identified by GC-MS analysis to be as 1,1-dichloroethane (1,1-DCA). Since 1,1-DCA was found not to be transformed to a great extent in the test zone, the concentration of trans-DCE was corrected for its presence by subtracting an average background concentration as measured in wells N1, N2, and N3 located outside the test zone.

Upon continuous injection of the target compounds, gradual increases at the monitoring wells towards the injected concentration (normalized breakthrough of unity) were observed for all the compounds. This is illustrated in Figure 4 by the response of TCE (the most retarded com-

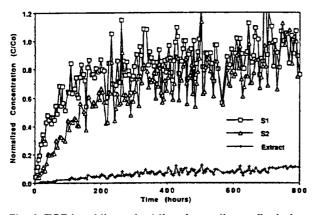


Fig. 4. TCE breakthrough at the observation wells during the organic addition experiment (Tracer8) at the start of the second season of field testing.

pound) at the S1 and S2 observation wells and the extraction well over the 40-day injection period. The slower approaches to steady-state values at the S2 observation well and the extraction well, which are farther from the injection well, can be seen. The breakthrough responses of trans-DCE and cis-DCE were similar to that of TCE. Possible reasons for the slow approach to injected values includes rate-limited sorption and aquifer heterogeneities (Roberts et al., 1990).

Table 2 summarizes the quasi-steady-state normalized breakthroughs achieved for bromide and the organic contaminants during the organic addition experiment. Complete bromide breakthroughs at the S1 and S2 observation wells were observed, indicating negligible dilution of the injected fluid by the native ground water. Mass balances indicated that  $100 \pm 5\%$  of the injected bromide was recovered at the extraction well. The more complete breakthrough and enhanced recovery, compared to the first season, permitted more accurate estimates of the extents of transformations achieved.

The organic solutes reached quasi-steady-state fractional breakthroughs of 94% at the S1 well, indicating negligible transformation by biotic or abiotic processes or losses due to continued sorptive uptake during this quasi-control stage before biostimulation. Cis-DCE reached the highest quasi-steady-state fractional breakthrough at the S2 observation well, followed by trans-DCE and TCE. This order is consistent with the degree of retardation, with TCE being the most strongly sorbed and cis-DCE being the least

Table 2. Tracer8 Experiment — Percentage Breakthrough of the Chlorinated Solutes and Bromide at the Observation Wells

Substance	Well SI	Well S2	Well S3	Extraction		
	(%)	(%)	(%)	(%)		
Bromide	$100 \pm 0.7^{2}$	$98 \pm 3$	$83 \pm 0.7$	$13.6 \pm 0.1 \\ 10.3 \pm 0.2 \\ 12.4 \pm 0.5 \\ 11.6 \pm N.D.$		
TCE	94 ± 2	$84 \pm 2$	$68 \pm 2$			
cis-DCE	94 ± 3	$94 \pm 3$	$72 \pm 3$			
trans-DCE	94 ± 3	$93 \pm 3$	$72 \pm 5$			

\*Standard error of the mean.

strongly sorbed (Roberts et al., 1990). Thus TCE, and to lesser extents cis- and trans-DCE, probably did not achieve maximum steady-state breakthrough concentrations at all locations before the start of the biotransformation experiment.

#### The Biostimulation-Biodegradation Experiment

The combined biostimulation-biotransformation experiment (Biostim2) immediately followed the organic solute addition experiment with operating conditions presented in Table 1. While injection of organic solutes continued, methane and oxygen were added in short pulses of 20 and 40 minutes, respectively. Average methane and DO injection concentrations were in the range of those used in the first season tests. Methane and DO uptake occurred very rapidly, with essentially no lag observed. The response indicated that some of the methane-utilizers stimulated in the first season were still present to immediately initiate methane utilization at the start of the second season, despite a sixmonth hiatus since the end of the previous biostimulation.

Figure 5 shows the simultaneous response of methane, DO, and trans-DCE at the S1 observation well. The decrease in all three components due to biological activity is apparent after about one day of injection. Methane decreased below the detection limit after 72 hrs of injection, while dissolved oxygen and trans-DCE showed a continued gradual decrease in concentration. The reduction in trans-DCE concentration, coincided with the consumption of methane, provides direct evidence for the in-situ biotransformation of this halogenated compound as a result of the biostimulation of the methane-oxidizing bacteria. Several of the initial normalized values of trans-DCE are greater than unity. This is an artifact of the normalizing method used. Because the observed values are divided by the most recent injected values in normalizing and several of the initial injection concentrations were lower than the field value, the resulting normalized values were greater than unity.

Figure 6 shows the S2 response of all three organics resulting from the biostimulation of the test zone. Bromide tracer results at the S2 well are also shown for comparison. A five-point running average is presented to clearly show the

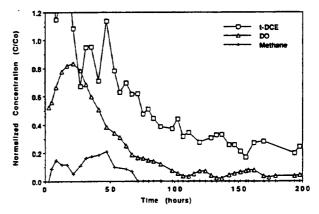


Fig. 5. Methane, DO, and trans-DCE response at the S1 well during the second season's biostimulation-biotransformation experiment (Biostim2).

trends for each compound. The decreases in concentration from normalized values near unity are apparent, especially for cis-DCE and trans-DCE. During this period, the bromide tracer breakthrough of unity was observed, demonstrating that decreases in the organic concentrations were not related to advective or dilution losses in the system, but were the result of biotransformation. Trans-DCE is shown to decrease in concentration most rapidly, followed by cis-DCE, and TCE. The more rapid decrease in trans-DCE concentration, compared to cis-DCE and TCE, is attributed to a faster rate of transformation.

#### Production of a Transformation Intermediate

Early in the second-year Biostim2 experiment, an intermediate product was detected during the chlorinated organic GC analysis. The sensitivity to electron capture detection indicated that this transformation product was halogenated. No peaks had appeared with a similar GC retention time during the previous years study with TCE, indicating that the intermediate was associated with either trans-DCE and/or cis-DCE transformation.

Janssen et al. (1987) and Leahy et al. (1987) reported the formation of a relatively stable trans-DCE oxide (epoxide) from the biodegradation of trans-DCE by a consortium of methanotrophic bacteria. Results of GC-MS analysis (Reinhard et al., 1989) confirmed that this intermediate observed in the field was indeed the trans-DCE oxide (epoxide).

Figure 7 shows the increase in the epoxide concentration, corresponding to the decrease in trans-DCE concentration resulting from biostimulation. The production of the epoxide appears to be associated with the transformation of trans-DCE. Quantification of the epoxide concentration was made using a synthesized external standard. There is some uncertainty in the accuracy of the epoxide concentration estimate, but still the epoxide represents only a few mole percent of the trans-DCE degraded.

#### Transient Methane Addition Experiments

At the end of the Biostim2 experiment, the methane-DO pulse time was increased to the standard 12-hr cycle, following which steady-state biotransformation conditions were achieved. A series of methane addition experiments (Decmeth1) were then performed to assess to what degree lower methane concentrations influenced biotransformation rates, and whether biotransformation continued after methane addition was temporarily ceased.

Figure 8 shows the response of TCE and cis-DCE to these changes, while the responses of trans-DCE and the epoxide are shown in Figure 9. During the period of 100-200 hrs, lower injected methane concentrations (average of 2.7 mg/l compared to 5.3 mg/l for 0-100 hrs) were produced by shortening the methane pulse length by a factor of two. No significant change in the degree of biotransformation resulted. Over the period of 275-475 hrs, methane addition was ceased. Gradual increases in cis-DCE, TCE, and trans-DCE towards injected concentrations resulted, indicating that biotransformation ceased. Sorptive retardation tends to promote the gradual increase in concentrations. This

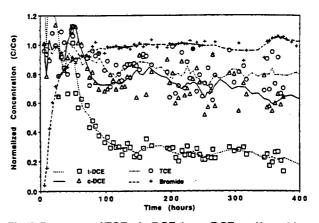


Fig. 6. Response of TCE, cis-DCE, trans-DCE, and bromide (as a conservative tracer) at the S2 well, during the biostimulation-biotransformation experiment (Biostim2).

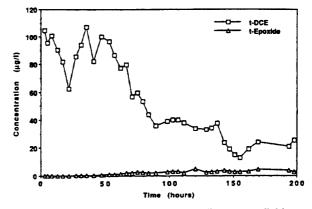


Fig. 7. Formation of the epoxide intermediate, trans-dichloroethylene oxide, in response to the biotransformation of trans-DCE during the Biostim2 experiment (well S1).

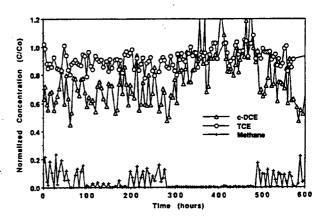


Fig. 8. Response of the cis-DCE and TCE at the S1 well to transient changes in methane addition in the experiment Decmeth1. Average methane concentrations 0-100 h, 5.3 mg/l; 100-200 h, 2.7 mg/l; 200-274 h, 5.3 mg/l; 275-475 h, 0, mg/l; >475 h, 5.3 mg/l.

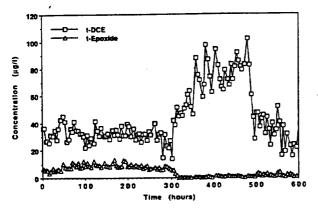


Fig. 9. Response of trans-DCE and the epoxide at the S1 well to changes in methane addition in the Decmeth1 experlment. (Methane concentrations as in Figure 8.)

makes it difficult to determine from organics data alone whether or not biotransformation stopped immediately after methane was no longer available.

The concentration of the epoxide, however, decreased in concentration soon after methane addition was stopped (Figure 9, t > 300 hrs), indicating that the biotransformation of trans-DCE quickly ceased. The rapid decrease in the epoxide concentration also suggests that the epoxide is much less strongly sorbed than trans-DCE, and/or that transformation of the epoxide continues after methane addition was stopped. After 475 hrs, methane addition was restarted to restimulate the test zone. A rapid decrease in concentration of the halogenated compounds to previous levels occurred as biotransformation commenced (Figures 8 and 9), and the epoxide intermediate reappeared (Figure 9). These data demonstrate that the biostimulated population of methane-utilizing bacteria required active methaneutilization for the biotransformation of halogenated aliphatics to occur.

### Degree of Biotransformation in the Second Season Experiments

The degree of biotransformation of the organic solutes was estimated after quasi-steady-state concentrations had been achieved in the test zone. The period evaluated was the first 200 hrs of the Decmeth 1 experiment shown in Figures 8 and 9. Estimates of the mean steady-state aqueous normalized concentration were computed by averaging over 40 measurements at each location over this period. Biotransformation was estimated using two methods. The first was based on comparisons with bromide as a conservative tracer using equation (2). The second method compares normalized breakthroughs of the organic solutes before and after biostimulation. In this case the normalized breakthrough of each chemical before biostimulation, as measured during the Tracer8 experiment (Table 2), is substituted for the bromide fractional breakthrough in equation (2).

The estimated percentage biotransformations, as a 95% confidence interval range, are presented in Table 3, for the chemical at monitoring locations. The minimum to maximum percentage biotransformation based on these two methods and considering only the information from the observation wells (S2 and S3) were as follows: TCE, 3 to 30%; cis-DCE, 46 to 58%; and trans-DCE, 58 to 76%. It is believed that the higher removal calculated by comparison with bromide provides the more accurate estimate. With TCE, a significantly lower removal resulted from the comparison with the Tracer8 results, perhaps because TCE had not reached its true steady-state level in that experiment.

Table 3 indicates essentially all of the biotransformation of trans-DCE occurred within the first meter of travel in the zone between the injection and the S1 observation well, where active methane utilization occurred. Cis-DCE and TCE appear to have undergone additional transformation between the S1 and S2 wells. The TCE results are consistent with the first season's results.

The extent of transformation of trans-DCE during the steady-state portion of the experiment, evaluated above, is lower than the 80% transformation achieved during the earlier stage shown in Figure 6. Cis-DCE, however, shows the opposite result. It is not clear what caused these changes. The main difference in the experimental conditions is the longer methane-oxygen pulse lengths that were used during the latter steady-state period.

The extent of biotransformation was also estimated from mass balances of TCE and cis-DCE injected over the course of the experiments compared to the amount removed from the system by the extraction well. Here, the extraction well concentrations were measured for a period of three months after organic addition was stopped, in order to account for mass sorbed on the aquifer solids. Biostimula-

Table 3. Percentage Biotransformation in the Second Season's Biostimulation-Biotransformation	n Experiments
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	Halogenated	Well SI	Well S2	Well S3	Extraction
	ethene	(%)	(%)	(%)	(%)
Comparison with bromide fractional breakthroughs <sup>45</sup>	TCE	10-14	21-25	23-30	20-26
	cis-DCE	34-30	50-58	50-58	55-72
	trans-DCE	61-67	70-76	67-73	(N.D.)
Comparison with fractional breakthrough before biostimulation <sup>b,c</sup>	TCE	0-10	4-12	3-11	-6-1
	cis-DCE	29-37	46-54	40-48	51-69
	trans-DCE	55-64	62-72	58-66	(N.D.)

Percentage biotransformation estimates (95% confidence interval shown).

Values over a time interval of first 200 hrs of the experiment Decmeth1 shown in Figures 8 and 9.

'Fractional breakthrough before biostimulation given in Table 2.

tion conditions were maintained throughout this period. These mass balances indicate 30% of the TCE and 54% of the cis-DCE injected were not recovered by the extraction well. This lower recovery suggests biotransformation, and not hydraulic losses, since 100% recovery of injected bromide was achieved during the course of these experiments. The additional mass balances are in good agreement with those given in Table 3.

#### **Results of the Third Season of Field Testing**

The third season's experiments used the same experimental sequence as the second season's tests, but in addition, vinyl chloride was studied. Based on the mixed culture studies of Fogel et al. (1986), and soil column studies performed in our laboratory (Lanzarone et al., 1989), we anticipated that vinyl chloride would be rapidly transformed.

A hall detector was added to the automated data acquisition system to increase the sensitivity in VC, trans-DCE, and cis-DCE detection. With the Hall detector, the coeluting background 1,1-DCA contaminant peak area represented less than 2% of the trans-DCE injection concentration peak area, permitting more accurate quantification of the trans-DCE concentration.

In the third season's organic transport experiments, oxygen was not added to the injection water. Table 4 presents the quasi-steady-state normalized breakthroughs of bromide and the chlorinated aliphatics achieved at the end of the Tracer12 test. The chlorinated aliphatics reached 86% to 100% of their respective injection concentrations at the S1, S2, S3 wells, after adjusting for dilution by indigenous ground water based on the bromide tracer data. TCE, the most strongly sorbed compound, had the lowest degree of fractional breakthrough, consistent with the second season's results. The extraction well generally had the lowest degree of fractional breakthrough, indicating that steady-state conditions had not been achieved in all areas of the test zone before the biostimulation experiment was initiated. The nearly complete breakthrough at the S1 for all compounds indicates minimal losses due to sorption, or abiotic or biotic processes in the absence of biostimulation.

The operating conditions of the Biostim3 experiment were similar to those used in the second season of field testing. Methane and DO addition were initiated using a 3-hr pulse cycle, slightly longer than that of the previous year. Methane was utilized immediately upon addition.

Table 4. Tracer12 Experiment — Percentage Breakthrough of Chlorinated Solutes and Bromide at the Observation Wells

Well	Bromide (%)	VC (%)	1-DCE (%)	c-DCE (%)	TCE (%)	
SI	$100 \pm 0.6^{b}$	95 ± 1.8	$100 \pm 1.2$	$100 \pm 1.2$	95 ± 0.9	
S2	99 ± 0.8	92 ± 2.0	$96 \pm 1.6$	99 ± 1.5	88 ± 1.3	
S3	$100 \pm 0.5$	$100 \pm 1.8$	97 ± 1.6	98 ± 1.3	86 ± 1.2	
Ext	$15 \pm 0.5$	92 ± 2	97 ± 3	91 ± 2	70 ± 2	

<sup>a</sup> Chlorinated organics adjusted for dilution by native ground water based on the bromide fractional breakthrough presented in column 1.

Standard error of the mean.

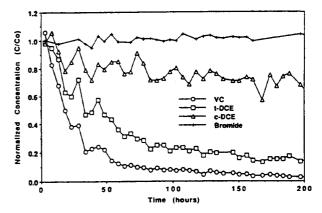


Fig. 10. Response of VC, trans-DCE, and cis-DCE at the S2 well during the third season's biostimulation-biotransformation experiment (Biostim3).

Methane concentrations at the S1 well remained below 0.5 mg/l after one day of injection, indicating even a greater number of methanotrophs were initially present than at the start of the second season of testing. The pulse cycle was therefore increased to 12 hours to distribute methane over the test zone.

Figure 10 shows the simultaneous decreases of vinyl chloride, trans-DCE, and cis-DCE at the S2 well in response to biostimulation. Biotransformation started immediately upon the addition of methane and DO, consistent with the previous season's results. Bromide tracer breakthroughs were complete during this period; thus the decreases in the organic solutes concentrations result from biotransformation. Vinyl chloride was the most rapidly transformed, followed by trans-DCE, and cis-DCE. TCE (not shown) was the most slowly transformed. The concentrations of vinyl chloride and trans-DCE decreased most rapidly within the first 50 to 80 hrs of biostimulation, followed by more gradual decreases at later times. Cis-DCE concentrations decreased more gradually. The rank order of rates of biotransformation-trans-DCE > cis-DCE > TCE-is consistent with the second season's results. The decrease in trans-DCE concentration was more rapid than observed in the second season. This result is consistent with the more rapid methane uptake, and the likelihood that more methane-utilizing bacteria were initially present in the test zone, resulting in faster removal rates.

#### Degrees of Biotransformation in the Third Season

The degrees of biotransformation achieved in the third year are presented in Table 5. Vinyl chloride was more than 95% biotransformed within two meters of travel in the biostimulated test zone. The lower degree of biotransformation of VC based on the extraction well estimates probably results from not having achieved steady-state conditions at that location during the 200-hr evaluation period following methane addition. The vinyl chloride concentration was reduced to approximately 1  $\mu g/l$ , demonstrating that drinking-water standards might be satisfied by this process.

Ninety percent of the injected trans-DCE was biotransformed in the biostimulated zone, which is greater than the

	Halogenated	Well SI	Well S2	Well S3	Extraction
	ethene	(%)	(%)	(%)	(%)
Comparison with bromide fractional breakthroughs <sup>4</sup>	TCE	7-13	15-19	16-22	24-30
	cis-DCE	28-34	38-44	41-45	46-52
	trans-DCE	83-87	89-91	89-91	68-72
	vinyl chloride	81-90	94-98	93-97	85-91
Comparison with fractional breakthrough before biostimulation	TCE cis-DCE trans-DCE vinyl chloride	2-10 25-37 81-89 78-90	1-9 36-44 86-94 92-98	6-14 38-46 86-94 91-99	-9-9 33-53 64-76 84-91

#### Table 5. Percentage Biotransformation — Third Field Season

\*Percentage biotransformation estimates (95% confidence interval shown).

70 to 80 percent achieved in the second season. The difference may have resulted from the large error associated with the second year's estimate, due to the presence of the coeluting 1,1-DCA contaminant. The estimated cis-DCE and TCE transformations are in the range found in the second year's tests. For cis-DCE, steady-state conditions were probably not achieved during the 400-hr evaluation period, and thus removals are probably underestimated.

In general, the responses to biostimulation observed in the third season tests agree well with the second season's responses demonstrating the reproducibility of the field experiments. The tests also demonstrated that VC was rapidly transformed as anticipated from laboratory studies.

#### **Discussion of Results**

The results of this field evaluation indicate that enhanced in-situ biotransformation of chlorinated aliphatic compounds is a potential method for aquifer restoration. Native bacteria in the subsurface if present can be readily stimulated to degrade these compounds when the proper conditions are provided in the subsurface. The experiments demonstrated that these conditions can be promoted in-situ in a controlled manner.

Biostimulation here did not require the addition of biological nutrients (N and P). A high background concentration of nitrate in the ground water (30-60 mg/l) was available as a nitrogen source. Phosphate concentrations in the ground water, however, were very low, less than 0.1 mg/l, and were near the solubility limit with respect to minerals such as hydroxylapatite. Dissolution of phosphate minerals, as phosphate in the ground water was removed by the microorganisms, may have acted as a source of phosphate.

The ease of biostimulation of the aquifer is consistent with the results of batch soil column laboratory experiments using aquifer solids from the test zone. Studies by Wilson et al. (1987), Mayer et al. (1988), and Lanzarone and McCarty (in press) indicate methane utilization occurred within a few weeks after addition to the columns. These results indicate that such laboratory studies may be quite useful in determining the presence and ease of stimulating a particular class of microorganisms for restoration purposes.

The oxygen to methane uptake in the test zone was significantly lower than required for the complete oxidation of methane, indicating that a portion of the methane added is used for cell synthesis. Anthony (1979) suggests cell yields ranging from 0.5 to 1 mg cells per mg CH<sub>4</sub>, and stoichiometric ratios ranging from 2.5 to 3 mg  $O_2$  per mg CH<sub>4</sub>. These ratios are consistent with the field measurements.

The alternating pulsed addition of methane and oxygen served to prevent biofouling in the area near the injection well and helped distribute the biological population through the test zone. An alternative method of achieving a similar effect (which may be simpler in practice) would be to add the methane and oxygen at separate wells and allow them to mix by dispersion in the treatment zone.

The different methods of assessing the degree of degradation-including mass balances on the amounts injected and extracted, comparison of normalized breakthrough concentrations with pseudo-control experiments, and comparisons with bromide as a conservative tracervield reasonably consistent results. These estimates of the degree of biotransformation are based on the measured ground-water concentrations, and do not directly account for degradation of the sorbed contaminant. The experimental methodology used, however, minimized sorption effects by continuously injecting the target chemicals and conducting experiments for sufficiently long periods so steady-state conditions were closely approached. Of the compounds studied, sorption is most likely to influence the estimate of the transformation of TCE, the most strongly sorbed and the least degraded compound.

The results indicate a similar degree of transformation for TCE over the three seasons of field testing. Thus, over the study period, there was no apparent increase in the ability of the microorganisms to degrade TCE.

Several experimental observations indicate that the stimulation of methane-utilizing bacteria was responsible for the biotransformation of the chlorinated aliphatic compounds: (1) the simultaneous decrease of chlorinated organics with the onset of methane utilization, (2) the appearance of the epoxide intermediate for trans-DCE, and (3) the increase in chlorinated organic concentrations and the disappearance of the epoxide intermediate when methane addition was stopped. Observations (1) and (3) indicate a direct association with methane utilization. The formation of an epoxide as a first step in the biotransformation of these compounds has been suggested by Henry and Grbic-Galic (1986) and Little et al. (1988). Janssen et al. (1987) and Leahy et al. (1987) identified an epoxide intermediate in laboratory studies of trans-DCE transformation by methane-utilizing mixed cultures. Moore et al. (1989) also observed the formation of the trans-DCE epoxide, from the transformation of trans-DCE by methane-utilizing organisms in a laboratory aquifer simulator. The formation of epoxides is also a wellknown step in the oxidation of aliphatic compounds by methanotrophs (Patel et al., 1982). The observations of the epoxide intermediate product in these experiments therefore support the argument that aerobic transformation was occurring, and provided an immediate indication when the biotransformation process ceased, as was the case when methane addition was stopped.

An argument might be made that anaerobic conditions resulting from the oxygen consumption required for methane utilization were responsible for biotransformation of these compounds. There is no evidence that this was the case. Intermediate products of anaerobic transformations, as discussed by Vogel and McCarty (1985), were not observed in the field. The rates of transformation were also faster for the less chlorinated compounds, consistent with an aerobic transformation process but inconsistent with anaerobic transformation (Vogel et al., 1987).

An increase in the organic carbon content of the aquifer solids due to biostimulation of methane-utilizers, and a resulting increase in the sorption capacity does not explain our observations. An estimate of the increase in the microbial mass due to biostimulation by Semprini and McCarty (1989), indicates a slight increase (<2%) in organic carbon content would have occurred, compared to that contained in the aquifer solids. Thus, no significant increase in sorption capacity was likely.

The greater extents of transformation of VC, and cisand trans-DCE, compared to TCE and TCA, are in qualitative agreement with both laboratory investigations and theoretical considerations previously discussed. Thus, the structure of the molecules being degraded is an important consideration for in-situ restoration with methane-oxidizing bacteria. A compound that is less halogenated, such as vinyl chloride, is rapidly degraded, and thus more amenable to treatment, than a compound such as tetrachlorethylene (PCE) which is more highly chlorinated and hence less rapidly degraded.

Another important factor which controls the rate of biotransformation of the compounds in the test zone is the biomass of methane-utilizing bacteria stimulated. The biomass size was limited by the low solubilities of methane and oxygen in the injected fluid. The greater extent of TCE biotransformation observed in some laboratory studies (Wilson and Wilson, 1985) probably results from the higher microbial concentrations. Based on an empirical correlation by Wilson and White (1986), a reduction in TCE concentration of approximately 35% would be expected for 6 mg/l of methane consumption. This is in fairly good agreement with the field observations. Thus, it appears that a major limitation on the biotransformation achieved was the amount of methane and oxygen that could be delivered under saturated conditions, limiting the biomass of methane-utilizing bacteria that could be supported.

Several other factors may influence the degree of trans-

formation obtained: (1) competition between methane and the chlorinated organics for the methane monooxygenase enzyme, (2) requirement to adapt to the chlorinated organic before degradation occurs, (3) unfulfilled minor nutrient requirements, and (4) sorption of the organics onto the aquifer solids. There is limited experimental data to determine which of these factors may have the most effect on the rates of transformation.

Results of soil column experiments by Lanzarone and McCarty (in press) and mixed cultured studies of Henry and Grbic-Galic (1987) suggest that high concentrations of methane may inhibit TCE degradation. Hou et al. (1979) and Patel et al. (1982) found methane to inhibit the rate of utilization of other hydrocarbons. This may explain why no change in the degree of transformation resulted when the methane concentration was temporarily lowered (Figures 8 and 9). Directed evidence of such inhibition was observed in our field experiments (Semprini et al., 1989). The effect of sorption on biotransformation is not well understood. In the field test, vinyl chloride, cis- and trans-DCE were less strongly sorbed than TCE, and were degraded at a faster rate. But here, sorptive effects cannot be easily separated from structural effects.

Active methane utilization was required for biotransformation of the chlorinated organics under the field conditions studied, which is consistent with laboratory studies by Little et al. (1988), but not those of Lanzarone and McCarty (in press). The biostimulation may have enriched a population which requires active methane utilization for biotransformation to occur. In-situ restoration would be more easily and effectively accomplished if biotransformation could continue for some period after methane addition was stopped. More studies are here needed. Also, additional research is needed in order to obtain a better understanding of the biotransformation process and how it might be optimized for use as a viable in-situ restoration method.

#### Conclusions

The field experiments have shown that microbial transformation processes observed in the laboratory can be promoted and effectively tested in-situ, under conditions typical of many contamination incidents. Stimulation of a specific population of indigenous bacteria that degrade selected compounds of interest can be accomplished when the proper conditions are promoted in the subsurface. In this study the population of methanotrophic bacteria was enhanced by the addition of methane as a primary substrate for growth.

The biostimulation and biodegradation experiments demonstrated that:

1. A specific class of microorganisms, the methanotrophs, which are indigenous to the subsurface environment, can be successfully biostimulated to promote the degradation of certain chlorinated aliphatic compounds.

2. Partial transformation of VC, 90 to 95%; trans-DCE, 80 to 90%; cis-DCE, 45 to 55%; and TCE, 20 to 30%, occurred over a relatively short flow path of one to two meters in a field test with fluid residence times of one to two days. 3. The rate of biotransformation was dependent on the structure of the chlorinated organic compounds, with less chlorinated compounds more rapidly transformed.

4. An intermediate transformation product, trans-DCE oxide, was produced and resulted from trans-DCE oxidation, which is consistent with the proposed transformation pathway.

5. Active utilization of methane in the test zone was required for chlorinated aliphatic biotransformation to occur.

Overall, the field results confirmed the existence of a natural population of methane oxidizers that could be stimulated by introducing methane and oxygen. Moreover, it was demonstrated that quantitative comparisons could confirm the extent of transformation within five percent. Finally, it was observed that substantial transformation of TCE, cis- and trans-DCE, and VC occurred within a distance of a few meters and residence times on the order of several days.

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## GEOCHEMICAL PROCESSES INFLUENCING THE FATE OF ORGANIC SOLUTES IN GROUND WATER

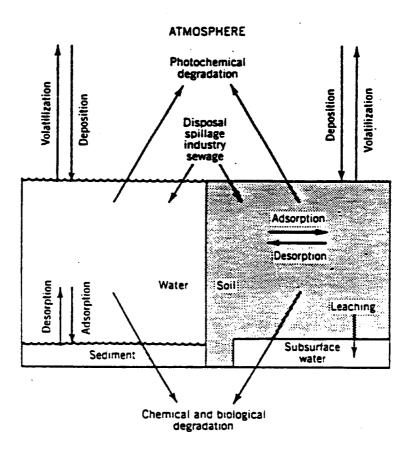
- Introduction
- Physico-chemical controls on the fate of organic compounds
- Petroleum hydrocarbons and aliphatic hydrocarbons
- Summary

NWWA

## GEOCHEMICAL PROCESSES CONTROLLING THE MOBILITY OF ORGANIC COMPOUNDS IN GROUND WATER INCLUDE

- Sorption/Partitioning
- Oxidation/Reduction
- Volatilization
- Complexation

Sorption/partitioning is a measure of the distribution of a given compound in two phases and is expressed as a concentration ratio. Partition coefficient values are useful in describing the environmental behavior of the organic compound of interest. Many organic compounds can either accept or donate electrons, forming reduced or oxidized species. This is environmentally significant since the oxidized and reduced forms of an organic compound many have totally different biological and ecological properties. The transport of a compound from the liquid to the vapor phase is called volatilization and it can be an important pathway for chemicals with high vapor pressures or low solubilities. Naturally occurring organic compounds (humic and fulvic acids) can undergo complexation reactions with metals and pesticides. Complexation reactions can increase the solubility of metals including iron, aluminum, copper, nickel, and lead.



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Fate and transport of organics in the environment. (James M. Montgomery, 1985)

The concentration, behavior, and eventual fate of an organic compound in the aquatic environment are determined by a number of physico-chemical and biological processes. These processes include sorption-desorption, volatilization, and chemical and biological transformation, solubility, and vapor pressure. The partition coefficient of a compound determines its concentration and residence time in water. Solubility data, however, are lacking for many compounds. Equilibrium vapor pressure is a measure of the solubility of the compound in air from liquid phase.

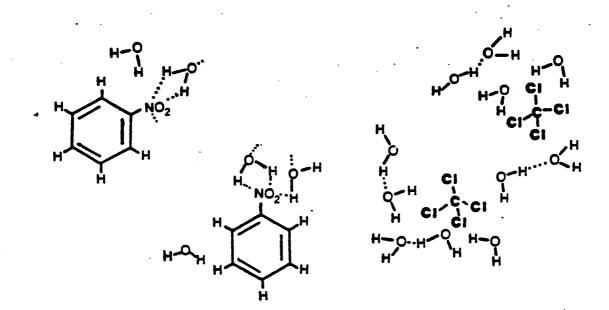
# **HYDROPHOBIC SORPTION**

unce acid and class are minor role

- Hydrophobic sorption involves the sorption of organic molecules onto organic coated minerals or solid-organic matter in soil and aquifer material
- Hydrophobic compounds are readily soluble in many nonpolar organic solvents, but are sparingly soluble in water
- The relatively lower solubility in water is the result of a lack of electrostatic attractions between the nonpolar organic solutes and the dipolar molecules of water

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#### Nitrobenzene

#### Carbon Tetrachloride

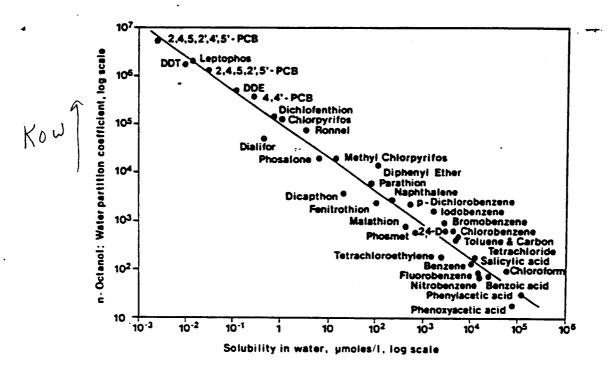
Schematic representations of the electrostatic interactions or hydrogen bonding between the dipolar nitrobenzene and water and the lack of interaction between carbon tetrachloride and water. The aqueous solubilities of nitrobenzene and carbon tetrachloride are 2000 and 800 mg/L, respectively.

#### ADSORPTION OF ORGANIC COMPOUNDS

A SOLVENT SYSTEM THAT HAS BEEN EXTENSIVELY USED TO QUANTIFY HYDROPHOBIC SORPTION IS THE N-OCTANOL-WATER SYSTEM.

- Solubility of octanol in water is 300-540 mg/L
- Octanol imitates the fatty structures in plants and living tissues
- Linear relationship between aqueous solubility of organic compounds and their octanol-water partition coefficients
- kow data can be used to estimate the relative strength of "hydrophobic bonding" in biological systems

In general, the more hydrophobic "water disliking" the organic compound is, the more likely the organic will be adsorbed onto the sediment. The solubility of an organic compound depends primarily upon the sorption-desorption characteristics of the organic compound in association with the soil or sediment. The physico-chemical characteristics of the adsorbent (surface area, nature of charge, charge density, presence of hydrophobic areas, and organic matter such as humic and fulvic acids) and the adsorbate (water solubility) determine the extent and strength of sorption.



Water solubility and octanol partitioning for organic solutes.

This figure shows the relationship between n-octanol: partition coefficient (kow) and aqueous solubility. Organic compounds such as benzene and carbon tetrachloride are moderately soluble in ground water (1,780 and 800 mg/L, respectively) and have kow values of 135 and 437, respectively. Other organic compounds of lower aqueous solubility such as DDT have a kow value of  $1.58 \times 10^6$ . DDT is relatively nonmobile in most aqueous solutions.

For neutral organic compounds, the sorption was shown to correspond to the organic content of the soil or sediment. Koc (kp/fraction of organic carbon) correlates well with water solubility and kow (k for octanol/water mixture). This table shows some empirical equations describing adsorption of organic compounds. The relationship between kp and koc, however, has limited predictability since many neutral organic compounds are also adsorbed by materials with little or no organic content. Chemical data for several organic compounds are provided in this lecture material.

Basis	General Form	Estimates of Constants			References	
ہ ہے جانے کے ایک کر ایک کے ایک کی سے جانے ایک کی کر ایک	ج ک نہ وہ نہ جہ چہ ج ن ن ن کی کر ج ک کے نے ک کے نے ک کر نے ک 	<u>A</u>	<u>B</u>	<u></u>		
Aqueous solubility	$\log K_{oc} = A + B \log S$	4.273	-0.686	(mg/L)	Means et al. (1980)	
Nuccus Constructory	- 00	3.64	-0.55	(mg/L)	Kenaga (1980)	
		3.95	-0.62	(mg/L)	Hassett et al. (1983)	
K <sub>ow</sub> data	log K <sub>oc</sub> = A + B log K <sub>ov</sub>	-0.21	1.00		Karickhoff et al. (1979)	
OW	~ OC • 0₩	-0.317	1.00		Means et al. (1980)	
		0.49	0,72		Schwarzenbach and Westall (1981)	
		0.88	0.909		lassett et al. (1983)	

Proposed empirical equations correlating K (Freundlich adsorption constant divided by the organic carbon fraction) with aqueous solubility and n-octanol-water partition coefficients.

SOURCE: Griffin and Roy, 1985

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COMPOUND:	BENZENE
FORMULA:	С <sub>6</sub> Н <sub>6</sub>
AQUEOUS SOLUBILITY :	1,780 mg/L AT 20C
DIELECTRIC CONSTANT :	
LOG KOW:	2.13
LOG KOC:	1.93
(FROM SOLUB	ILITY)
LOG KOC:	2.01
(FROM KOW)	
MOBILITY CLASSIFICATION:	HIGHLY MOBILE
REMARKS : BENZENE IS USED	EXTENSIVELY BY THE
PETROLEUM INDU	STRY AND SOLVENT

**RECOVERY PLANTS** 

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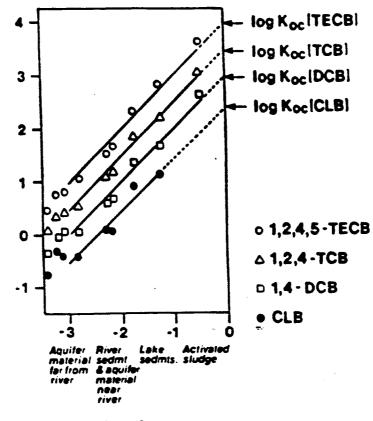
Higher Koc = Lower Mobility	2	
SOLVENT	Кос	MOBILITY CLASS
methanol, acetone, methyl ethyl ketone, pyridine, ethyl acetate, isobutyl alcohol, diethyl ether, cyclohexanone, n-butyl alcohol, o-cresol, p-cresol, methyl isobutyl ketone, methylene chloride		Very Highly Mobile
m-cresol, carbon disulfide, benzene	100	Highly Mobile
trichloroethylene, 1,1,1-trichloroethane		
carbon tetrachloride	200	-
toluene		
tetrachloroethylene chlorobenzene	300	_ Medium Mobility
		•
o-xylene		
	400	
	- 500	
p-xylene		
m-xylene	600	- ·
ethyl benzene		
euryi benicine	700	- Low Mobility
	800	
o-dichlorobenzene	900	
SOURCE: Utah Water Research Laboratory		

Mobility classification of the 37 organic solvents based on their soil-water partition coefficients (Koc) using a classification system proposed by the Utah Water Research Laboratory (1983).

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ml/g

Log Kp, cm<sup>3</sup>l/gs



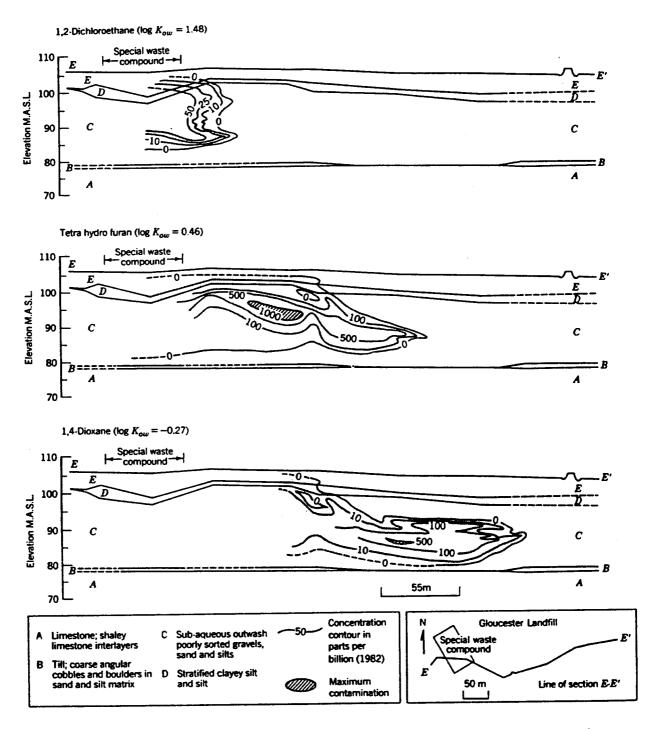
Log foc

Variation in log  $K_p$  for selected organic compounds on various types of natural sediments.

This figure shows the relationship between the adsorption constant (kp) and the amount of organic carbon (foc) reported by Schwarzenbach and Westall (1981) where

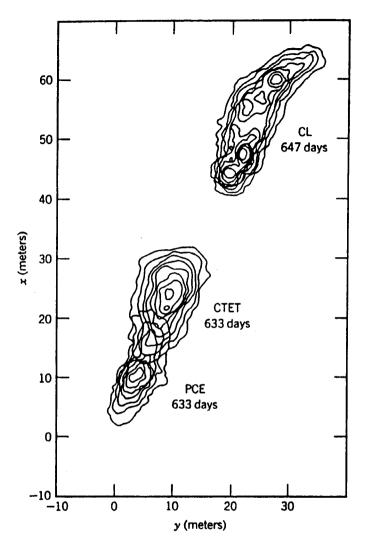
Log Kp = 0.72 log kow + log foc + 0.49

As the amount of organic carbon increases, the partition coefficient increases several orders of magnitude. CLB, DCB, TCB, and TECB mean chlorobenzene, dichlorobenzene, trichlorobenzene, and tetrachlorobenzene, respectively. Major controls on adsorption include % organic carbon, the amount of fine-grained material, and the aqueous solubility of the organic compound.



Sections illustrating the occurrence of three of the organic contaminants found at the Gloucester sanitary landfill near Ottawa, Ontario. Reprinted from Jackson and others, 1985. Contaminant Hydrogeology of Toxic Organic Chemicals at a Disposal Site, Gloucester, Ontario, 1. Chemical Concepts and Site Assessment. NHRI Paper No. 23, Environment Canada, 114 p.

A variety of organic contaminants were disposed of in shallow trenches in glacial drift. Diethyl ether, tetrahydrofuran, 1,4-dioxane, carbon tetrachloride, benzene, and 1,2-dichloroethane were the main contaminants. Plumes for some of the contaminants shown in the above figure illustrate the variable extent of spreading. The size of the plume for all compounds, however, is inversely related to the hydrophobicity of the compound as measured by the KOW. This relationship strongly suggests that hydrophobic sorption is a dominant process.



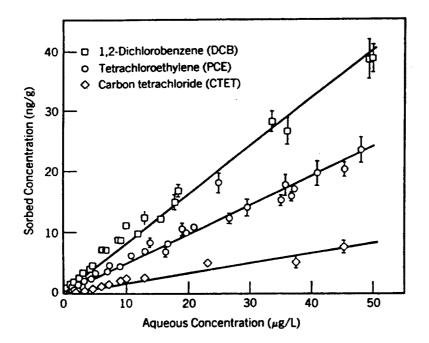
Retardation of carbon tetrachloride (CTET) and tetrachloroethylene (PCE) as compared to chloride (CL). Contour interval depicted for CL is 5 mg/L beginning at an outer contour of 10 mg/L. Contour intervals depicted for CTET and PCE are 0.1  $\mu$ g/L beginning at an outer contour of 0.1  $\mu$ g/L (from Roberts and others, Water Resources Res., v. 22, p. 2047–2058, 1986. A large-scale tracer experiment was conducted at Canadian Forces Base Borden using carbon tetrachloride (CTET), bromoform (BROM), tetrachloroethene (PCE), 1,2-dichlorobenzene (DCB), and hexachloroethane (HCE) by Roberts and others (1986). These contaminants sorb onto aquifer materials to a greater extent relative to chloride (CI<sup>-</sup>). The above figure shows the distribution of two of the lesser retarded contaminants (CTET and PCE) in relation to CI<sup>-</sup>. Roberts and others (1986) evaluated the sorptive behavior of these contaminants in terms of retardation factors estimated from the velocity ratios,  $V_{CI}/V_i$ , which are shown in the table below. The more hydrophobic compounds showed the highest amount of retardation.

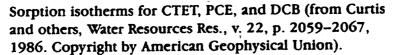
### Calculated retardation factors for five chlorinated hydrocarabons as a function of time\*

Time		<b>Retardation factors for</b>				
(days)	СТЕТ	BROM	PCE	DCB	НСЕ	
15	1.8	1.9	2.7	3.9	5.1	
30	1.9	2.0	3.1	4.6	6.1	
85	2.1	2.2	3.9	5.7	7.9	
250	2.3	2.5	4.8	7.3	Not quantifiable	
400	2.4	2.6	5.3	8.0	Not quantifiable <sup>1</sup>	
650	2.5	2.8	5.9	9.0	Not quantifiable <sup>1</sup>	

<sup>1</sup>Not quantifiable owing to disappearance of HCE.

\*From Roberts and others, Water Resources Res., v. 22, p. 2047-2058, 1986.





Batch and column experiments are conducted to quantify sorption and redox reactions. Batch sorption experiments provide isotherms that model the partitioning of a species between aqueous and solid phases. This figure shows that linear sorption is an important process. The species decrease in sorption as follows: DCB>PCE>CTET. Calculated distribution coefficients increased with increasing hydrophobicity as measured by the octanol/water partition coefficient (KOW) shown in the table.

	CTET	BROM	РСЕ	DCB	HCE
Number of data	11	10	25	24	52
Cmax, ng/cm <sup>3</sup>	47	13	49	50	34
K <sub>d</sub> , 95% CI R <sup>2</sup>	0.17 ± 0.03 0.972	0.17 ± 0.02 0.992	0.48 ± 0.02 0.994	0.81 ± 0.03 0.993	0.81 ± 0.03 0.981

#### Measured distribution coefficients' from batch sorption experiments\*

'(cm³/g)

\*From Curtis and others, Water Resources Res., v. 22, p. 2059–2067, 1986. Copyright by American Geophysical Union.

#### ORGANIC SOLUTE ADSORPTION BY AQUIFER MATERIAL

• As the kow of the solute increases, the importance of the organic matter increases

Same in the second

• The importance of organic matter decreases as the surface area of the mineral fraction increases

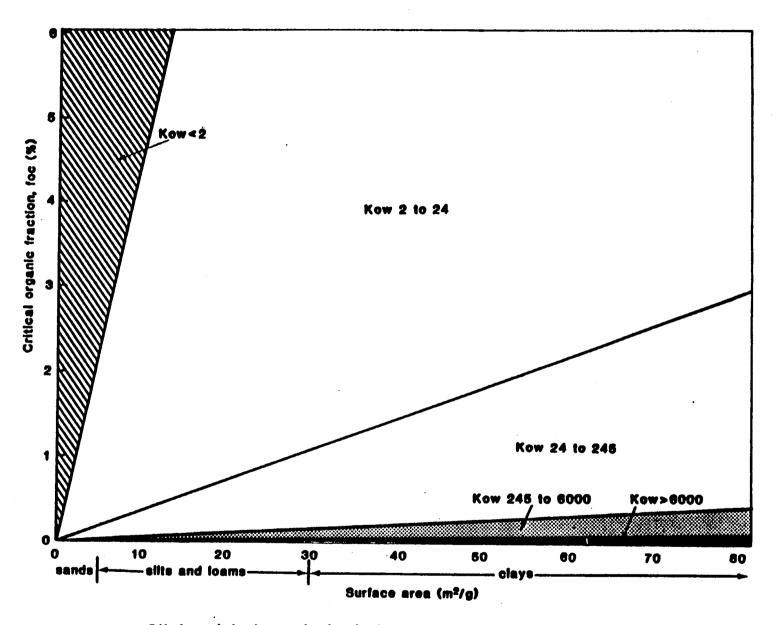
#### Critical organic fraction

The amount of organic matter present when sorption by organic and inorganic fractions are equal.

Studies using adsorbents such as montmorillonite without organic matter have demonstrated that hydrophobic compounds are also adsorbed by the inorganic fraction of soils and sediments. There is a critical level of organic matter in a soil at which adsorption by the organic and inorganic fractions are equal, and below which the organic matter is not dominant. This level is called the critical organic fraction, which is described by the following equation:

$$(foc)_i = \frac{S}{200} = \frac{1}{(kow)^{0.84}}$$

where (foc) = critical organic fraction, s = surface area, and kow = octanol-water partition coefficient of the solute.



Critical organic fraction as a function of surface area and the octanol-water coefficient (Kow)(Griffin and Rey, 1985)

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#### CRITICAL ORGANIC CARBON

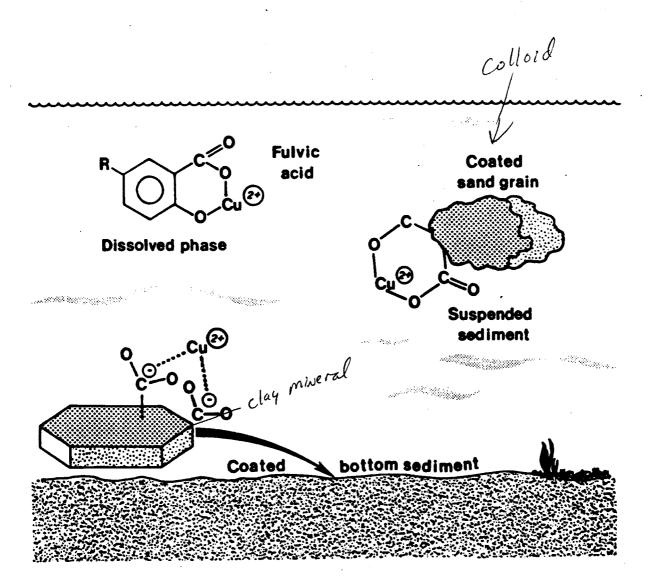
The previous figure shows the relationship between critical organic fraction and grain size. As the kow of the solute increases, the importance of the organic matter increases; but its importance decreases as the surface area of the mineral fraction increases. For compounds with kow values exceeding 6000 (PCB, DDT), the Critical Organic Fraction is less than 0.03%, even if clay minerals are present. For compounds with kow values between 245 and 6000 (aromatic, hydrocarbon, pesticides) the Critical Organic Fraction is less than 0.1% for clay minerals with surface areas less than 30 m<sup>2</sup>/g (kaolinite), which represents most soils and sediments. For compounds with kow values less than 245 (toluene, benzene, trichloroethylene) the Critical Organic Fraction rises rapidly, indicating an increased proportion of the adsorption occurring on mineral surfaces. If a soil has a very low organic content, it is possible that sand and clay-sized material may dominate the adsorption process, especially for soils with high clay content (high surface area) and very soluble organic compounds (kow values less than 24) such as methanol, acetone, and pyridine.

#### COMPLEXATION OF METAL IONS

# THE COMPLEXATION OF METAL IONS BY ORGANIC MATTER IS AN IMPORTANT ORGANIC-INORGANIC INTERACTION

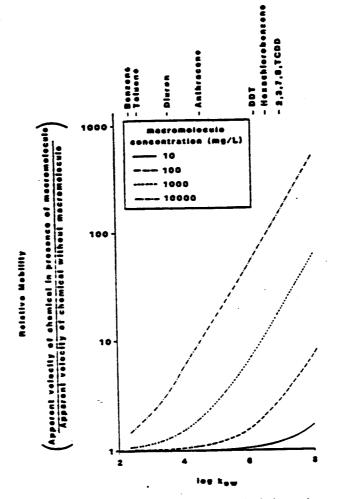
The following reaction types may occur

- Reaction between DOC and metal ions
- Complexation reactions of suspended organic matter and metal ions
- Bottom sediments (lake) and metal ions



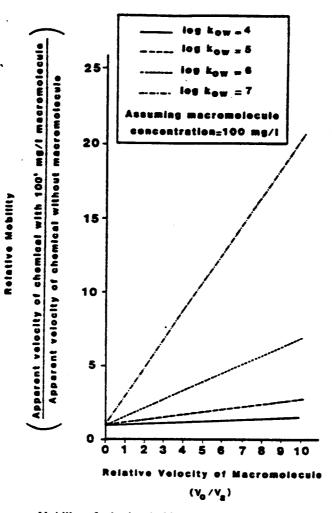
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Complexation of metal ions by organic matter in suspended sediment, bottom sediment, colloidal and dissolved phases(Thurmon, 1985).



Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule as a function of octanol-water partition coefficient and amount of organic carbon in the mobile phase( Enfield und Gengtsson, 1988).

Recently, attention has been given to the possibility of binding of the organic molecules such as pesticides to dissolved organic carbon, micelles, or other colloidal materials. This figure shows the importance of a macromolecule (blue dextran) on the mobility of hydrophobic compounds (benzene, toluene, diuron, etc.). These mobile macromolecules may greatly increase the chemical mobility of anthropogenic organic contaminants by cosolvent interactions. This figure shows the change in mobility of hydrophobic chemicals (pesticides) due to the macromolecule (dissolved organic carbon) rather than the mobility of the chemical. This figure may provide an explanation of why hydrophobic pesticides (DDT) have been reported to move farther under field conditions than model calculations. High-molecular weight organic compounds (benzene) by cosolvent processes.



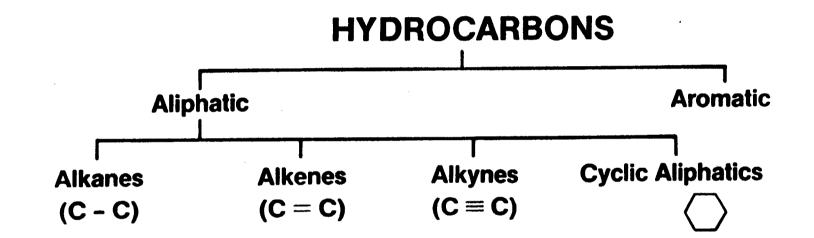
Mobility of a hydrophobic compound relative to the mobility of the same compound without the presence of a macromolecule versus the velocity of the macromolecule relative to the velocity of the water where the concentration of the macromolecule is 100 mg l<sup>-1</sup> (Enfield and Beng- $\pm$  SSON, 1988).

Macromolecules can migrate faster than the average linear ground water flow velocity because they do not migrate through pore spaces smaller than the size of the macromolecules. A decrease in porosity results. If these macromolecules contain anthropogenic organic contaminants, both organics will migrate faster than the average linear ground water flow velocity. The increase in flow velocity may increase the mobility of hydrophobic organic compounds by a factor of 5 or 10. When a municipal landfill containing high concentrations of DOC has toxic hydrophobic compounds, the hydrophobic compounds will migrate at faster rates relative to environments that do not contain high concentrations of DOC. Clay liners potentially may not be an effective barrier for the macromolecules and anthropogenic organic compounds if a reduction in effective porosity occurs relative to the migration of 'he macromolecules.

# **PETROLEUM HYDROCARBONS**

Petroleum is a naturally occurring oily, flammable liquid composed principally of hydrocarbons (50 - 98%) with the remainder consisting of organic compounds, oxygen, nitrogen, sulfur, and metals.

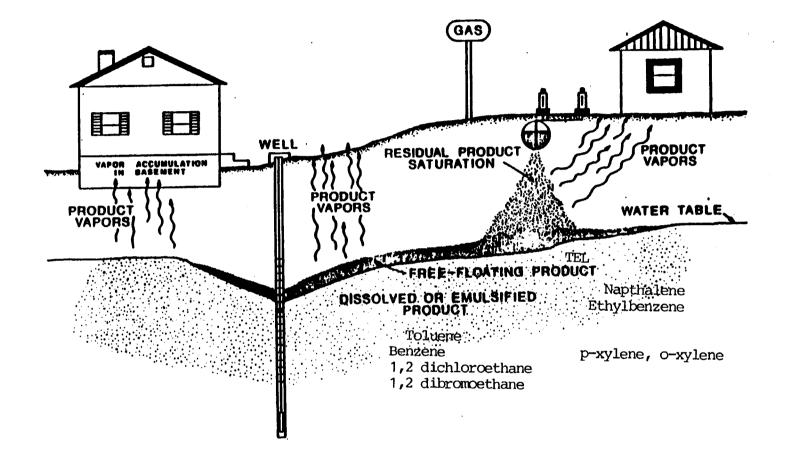
**NWWA** 



### AROMATIC HYDROCARBONS OF THE GASOLINE FRACTION OF PETROLEUM

Benzene Ethylbenzene Isopropylbenzene 1-methyl-3-ethylbenzene 1,3,5-trimethylbenzene Tert-butylbenzene 1,2,3-trimethylbenzene

Toluene Xylenes N-propybenzene 1-methyl-4-ethylbenzene 1-methyl-2-ethylbenzene 1,2,4-trimethylbenzene



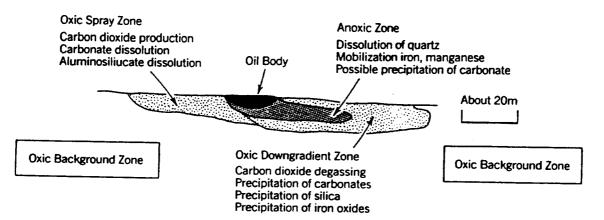
Overview of underground petroleum-product leakage and subsurface impacts (modified after API, 1980 and Yaniga, 1982).

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# GROUND WATER QUALITY DATA ALBUQUERQUE, NEW MEXICO

SPECIES AND PARAMETER	TYPE 1 UP- GRADIENT	TYPE 2 SOURCE AREA
Hq	7.40	7.14
Eh (mV)	-115	-150
Temp (C)	19	19
Fe (mg/L)	0.3	56
Mn (mg/L)	0.86	3.4
$HCO_3 (mg/L)$	381	869
AI (mg/L)	<0.25	27
Benzene (µg/L)	ND	3800
Ethylbenzene	ND	1000
(µg/L)		
Toluene ( $\mu$ g/L)	ND	3500
O-Xylene (µg/L)	) ND	2500
M-Xylene (µg/L	) ND	3800
P-Xylene (µg/L)	ND	1600
TDS (mg/L)	952	1540

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Redox environments related to a crude oil spill at Bemidji, Minnesota (from Siegel, 1987).

Based on detailed studies of major ions, some trace elements. pH, Eh, and dissolved oxygen, Siegel (1987) defined four redox environments related to a pipeline spill at Benidji, Minnesota. These processes are shown in the above figure. This study shows the importance of characterizing aquifer materials as well as the water chemistry, including inorganic and organic solutes. Microbial degradation was shown to be dominant process for removing organic contaminants from solution.

Siegel, U.S. Geological Survey Openfile report 87-109, p. C-13 - C15

# **BENZENE OXIDATION**

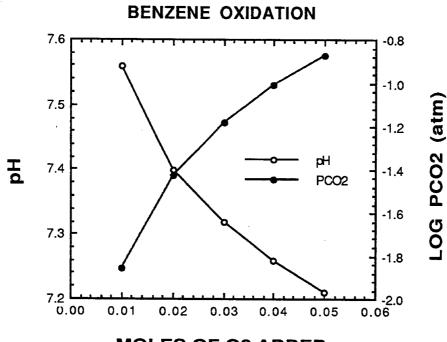
### **OXIDIZING HALF REACTION**

 $1/6C_6H_6 + nO_2 + 3H_2O = CO_3^2 + 7H + 5e$ 

ADD 0.005, 0.01, 0.02, 0.03, 0.04, AND 0.05 MOLES OF DISSOLVED OXYGEN.

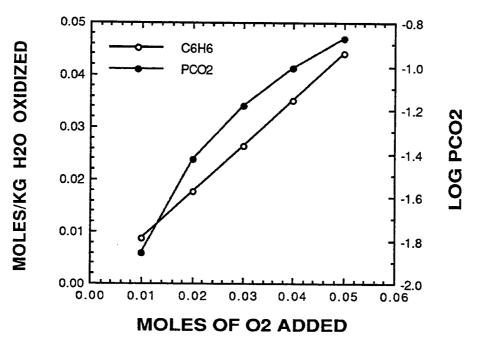
COUPLE BENZENE OXIDATION WITH Fe(OH)<sub>3</sub> REDUCTION.

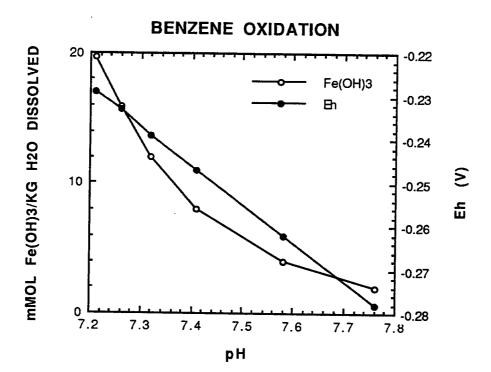
QUANTIFY WATER-ROCK INTERACTIONS WITH USE OF PHREEQE GEOCHEMICAL CODE.

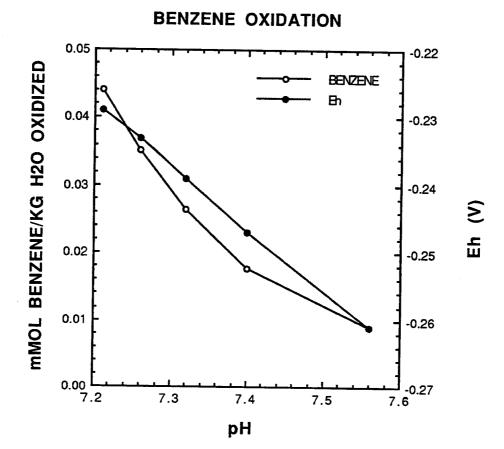


MOLES OF O2 ADDED

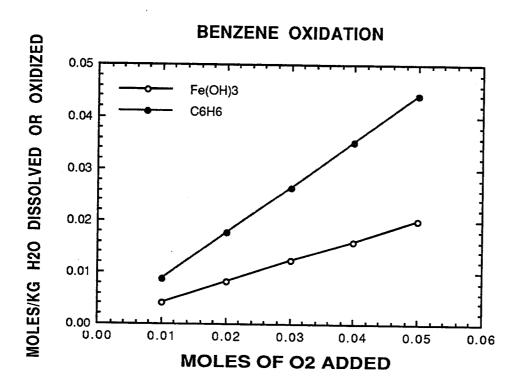
**BENZENE OXIDATION** 

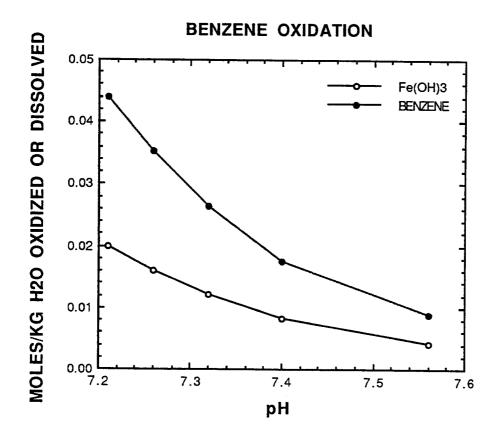






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#### PHYSICO-CHEMICAL CHARACTERISTICS OF PETROLEUM HYDROCARBONS

#### **ADSORPTION**

- Dependent on temperature and organic carbon content of sediment
- Aliphatics adsorb to a greater extent/than aromatic hydrocarbons (dependent on aqueous solubility)
- Desorption from sediments is slow

 $\Rightarrow$ 

diesel Fuel clean up is hard-

### PHYSICO-CHEMICAL CHARACTERISTICS OF PETROLEUM HYDROCARBONS

#### VOLATILIZATION

1

Henry's Law

- Dependent on the rate of aeration of water
- Effective for aromatic hydrocarbons, benzene, toluene, and xylenes

### Half-Lives for Volatilization of Some Typical Aromatic Monocyclic Compounds

COMPOUND	HALF-LIFE (t½)	
Benzene <sup>1</sup>	4.81 Hours	
Chlorobenzene <sup>1,2</sup>	9.0 Hours 10-11 Hours	
1, 2,-Dichlorobenzene <sup>1,2</sup>	<9.0 Hours 8-9 Hours	
1, 3,-Dichlorobenzene <sup>1</sup>	$\sim$ 10 Hours	
1, 4,-Dichlorobenzene <sup>1,2</sup>	<9 Hours 11-12 Hours	
Hexachlorobenzene <sup>3</sup>	$\sim$ 8 Hours	
Ethyl Benzene <sup>1</sup>	5-6 Hours	
Nitrobenzene <sup>1</sup>	$\sim$ 200 Hours	
Toluene <sup>1</sup>	5.18 Hours	
2, 4-Dinitrotoluene <sup>1</sup>	$\sim$ Hundred of Days	
2, 6-Dinitrotoluene <sup>1</sup>	$\sim$ Hundreds of Days	

Sources: 1-Versar 1979, 2-Garrison and Hill 1972, 3-Mackay and Leinonen 1975

(NWWA)

### **POLYNUCLEAR AROMATIC HYDROCARBONS**

- Environmentally significant
- Found in diesel and other types of fuels

### **ADSORPTION**

- Strongly adsorbed in soil and sediment

Low aqueous solubility High Koc Low vapor pressure Itish Districoef.

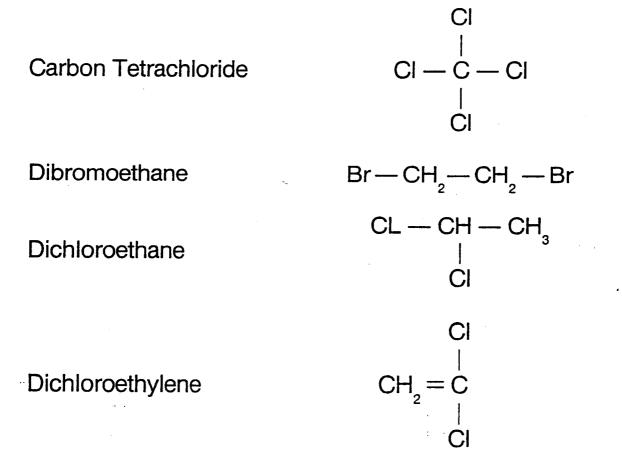
### VOLATILIZATION

Significant for 2-ring aromatic compounds (Naphthalene)

#### ALIPHATIC HYDROCARBONS

Aliphatic hydrocarbons constitute a diverse group of organic compounds characterized by an open-chain structure and a variable number of single, double, and triple bonds.

### **Examples of Aliphatic Hydrocarbons**



## Known and Suspected Aliphatic and Carcinogens Found in Drinking Water

KNOWN/SUSPECTED MUTAGENS	KNOWN/SUSPECTED CARCINOGENS
1, 1, 1-Trichloroethane	chloroform
Bromomethane	carbon tetrachloride
Chloromethane	1, 1-dichloroethylene
Bromodichloromethane	1, 1, 2-trichloroethylene
Dichloromethane	1, 1, 2, 2-tetrachloroethylene
Bromoform	1, 1, 2-trichloroethane
2-Chloropropane	dibromoethane
1, 2-Dichloropropane	2-bromoethylpropane
1-Chloropropene	1, 1, 2, 2-tetrachloroethane
1, 1-Dichloroethane	hexachlorobutadiene
1, 2-Dichloroethane	vinyl chloride
Chlorodibromomethane	-
1, 3-Dichloropropene	
Dibromomethane	
Hexachloroethane	

Sources: Kraybill 1980; Kraybill et. al. 1978; Sittig 1980.

### PHYSICO-CHEMICAL CHARACTERISTICS OF ALIPHATIC HYDROCARBONS

#### ADSORPTION

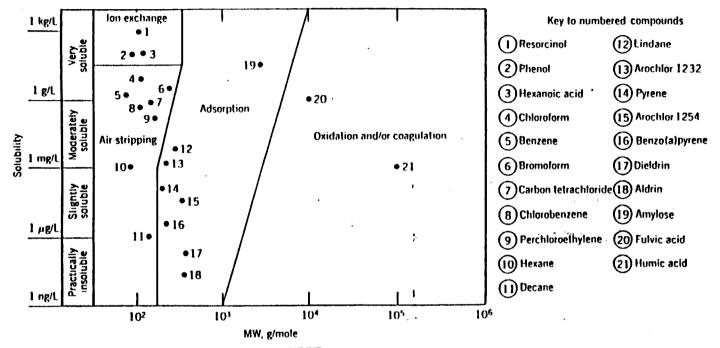
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 Chloromethanes have little affinity for surface interaction with sediment

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#### VOLATILIZATION

Chloromethanes volatilize from aqueous solution



TREATMENT PROCESSES FOR ORGANIC REMOVAL.

SOURCE: James M. Montgomery, 1985.

This figure presents an overview of the types of organic compounds to which different treatment processes, based on physico-chemical properties of the compound, that may be applied. The boundaries between each region of the diagram represent a generalization based on aqueous solubility and molecular weight of the different organic compounds. Ion exchange removes polar and ionized organic compounds, such as phenols, from aqueous solution. Air stripping effectively eliminates volatile organics, such as carbon tetrachloride, that are of low aqueous solubility and molecular weight. Adsorption removes pesticides and polynuclear aromatic hydrocarbons. Oxidation and/or coagulation are used to degrade and precipitate humic and fulvic acids.

# SUMMARY

Organic matter and fine-grained sediments influence the sorption of organic solutes

Octanol — water partitioning of organic solutes quantitatively describes hydrophobic sorption

Aqueous DOC can increase the solubility of organic solutes in natural systems

DOC provides binding sites for pesticides and metals

- DOG 71 mg/l - 7

NWWA

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# Data Compilation for Soil Sorption Coefficient

Results for soil sorption coefficient are presented for 336 hydrocarbon and organic chemicals.

..... by Chang Y. Jeng, Daniel H. Chen and Carl L. Yaws .....



The soil sorption coefficient  $K_{ex}$ , which determines the partitioning of an organic chemical between the soil/sediment and the aqueous solution, is an important en-

vironmental parameter. Kee affects the physical movement of pollutants, chemical degradation (photolysis and hydrolysis), biodegradation, acidity and buffered solution-phase concentration.

As a result, the soil sorption coefficient is widely used in river, runoff and soil/groundwater models for assessing the fate and transport of chemicals. With the value of  $K_{ex}$  known, the partition uptake of water contaminants for a particular soil/sediment or the degree of leaching of the pollutants into the groundwater can be estimated.

The amount of chemicals sorbed onto a soil or sediment depends on the concentration of chemicals and their equilibrium distribution coefficient (i.e.,  $K_{sc}$ ). For dilute aqueous solutions, the distribution coefficient can be adequately expressed with the Freundlich equation with 1/n equal to one.

$$x/m = K_{ec} C \qquad (Eq. 1)$$

x = weight of solute sorbed (mg)

C = equilibrium concentration of solute in aqueous phase (mg/L)

m = weight of sorbent, organic carbon in soil (kg)  $K_{sc} =$  soil sorption coefficient

From Equation 1,  $K_{ec}$  can be interpreted as the ratio of the solid phase concentration (normalized for the organic carbon content) to the solution phase concentration of the chemical at equilibrium. Therefore, in commonly used units,  $K_{ec}$  is:

$$K_{m} = \frac{\text{mg sorbed/kg organic carbon}}{\text{mg/L aqueous concentration}}$$
(Eq. 2)

The unit of  $K_{ex}$  can be abbreviated as L/kg. The average organic carbon content of a typical soil is from 0.5 percent to 3.5 percent. By basing the sorption coefficient on soil (or sediment) organic carbon, one can eliminate much of the variation between soils due to organic carbon content.

The cited experimental or predicted  $K_{se}$  values are intended for a normal environment (20°C, pH 4-8, etc.). Attempts to extrapolate far beyond these conditions may incur errors. In cases where the coefficient is expressed in terms of soil organic matter,  $K_{se}$ , the following equivalence can be used to obtain  $K_{se}$ :

$$K_{ec} = 1.72 K_{em}$$
 (Eq. 3)

POLLUTION ENGINEERING JUNE 15, 1992

This assumes the organic matter contains about 58 percent carbon.

The results for the soil sorption coefficient for organic chemicals in water are given in Table 1. Melting point (MP) and molecular weight (MW) data also are provided to facilitate predictions for other environmental properties. The tabulation is applicable to a wide variety of organic chemicals in contact with water at normal ambient conditions. The wide variety of substances include hydrocarbons, acids, alcohols, esters, ethers, ketones, fluorides, chlorides, bromides, amines, sulfones, nitros, amides, sulfides and phosphates. The tabulation is arranged by carbon number to help quickly locate data using the chemical formula.

In preparing the table, a database was compiled from many literature sources. The non-linear group contribution method was used to estimate the soil sorption coefficient when experimental K<sub>w</sub> values were not available. A comparison of calculated and experimental values for the soil sorption coefficient (Figure 1) shows general agreement of calculated and experimental values for different organic chemicals,

The compilation for the soil sorption coefficient is accurate enough for use in initial engineering and environmental impact studies involving organic compounds in water. Two examples are given.

Example 1. For aqueous concentration of benzene (C6H6) in contaminated river water of 10 ppm by weight, what will be the maximum uptake of benzene by the bottom sediment? The average organic carbon content of the bottom sediment can be taken as 3 percent. Refer to Equation 1,  $x/m = K_{er}C$ .

Calculate the amount of organic carbon per metric ton of bottom sediment:

 $\dot{m} = 1000 \times 3\% = 30$  kg organic carbon

Then substitute the soil sorption coefficient of benzene:

$$K_{ex} = \frac{83 \text{ (mg sorbed/kg organic carbon)}}{(mg/L \text{ aqueous concentration)}}$$
  
= 
$$\frac{83 \text{ (mg sorbed/kg organic carbon)}}{(ppm \text{ aqueous concentration)}}$$

Adding the aqueous concentration, C = 10 ppm, into Equation 1 gives:

 $x = 30 \times 83 \times 10 = 2.5 \times 10^4 \text{ mg} = 0.025 \text{ kg}$ 

Example 2. Atrazine (C8H14CLN5) is uniformly applied to a field and incorporated into the soil. The soil has a bulk density of 1.25 kg/L, 2 percent organic carbon and 25 percent each air and water by volume.

# Table 1 Soil Sorption Coefficient

<b> </b>	······································						
			MW	MP	K <sub>oc</sub> @20 C		
No.	Formula	Name	g/mol	С	L/kg		
1	CCL4	Tetrachloromethane	153.84	-23.16	1.22E+02		
2	СНСІЗ	Trichloro-methane	119.39	-111.16	7.68E+01		
3	CH2CL2	Dichloro-methane	84.94	-95.16	4.74E+01		
4	CH3NO2	Nitromethane	61.04	-28.16	1.76E+02*		
5	CH4N2O	Urea	60.06	132.70	1.40E+01		
6	CH12O3NPS2	Dimethoate	181.23	52.00	9.00E+00		
7	C2CL3F3	1,1,2-Trichlorotrifluoroethane	187.38	- 35.16	5.32E+01*		
8	C2CL4	Tetrachloroethene	165.85	-22.16	3.59E+02		
9	CICLE	Hexachioroethane	236.74	184.84	4.13E+02*		
10	C2HCL3	Trichloroethene	131.39	-86.16	1.37E+02*		
11	C2HCLS	Pentachloroethane	202.29	-29.16	3.07E+02*		
12	C2H2BR2	1,1-Dibromoethene	185.87	-	4.40E+01		
13	C2H2BR2	CIS-1,2-Dibromoethene	185.87	- 53.00	7.68E+01		
14	C2H2BR2	Trans-1,2-Dibromoethene	185.87	-6.50	7.68E+01		
15	C2H2CL2	1,1-Dichloroethene	96.94	- 117.16	8.02E+01*		
16	C2H2CL2	CIS-1,2-Dichloroethene	96.04	- 80.16	8.02E+01*		
17	C2H2CL2	Trans-1,2-Dichloroethene	96.94	- 50.16	8.02E+01*		
18	C2H2CL4	1,1,2,2-Tetrachioroethane	167.86	- 36.16	7.86E+01		
19	C2H3BR2CL	1,2-Dibromo-3-Chloroethane	222.33	-	2.22E+02		
20	C2H3CL3	Trichloroethane	133.42	-37.16	2.41E+02*		
21	C2H3NS	Methyl Isothiocyanate	73.12		6.00E+00		
22 23	C2H4BR2 C2H4CL2	Dibromoethane	187.88	9.84	6.24E+01		
24	C2H4C12	1,1-Dichloroethane	98.96	-97.16	8.02E+01*		
		1,2-Dichloroethane	98.97	-35.16	3.28E+01		
25 26	C3H4CL2	1,1-Dichloropropene	110.98	-	4.52E+01		
20 27	C3H4CL2 C3H4CLN5	1,3-Dichloropropene	110.98		4.63E+01		
28	C3H5BR2CL	Trietazine	145.56	103.00	6.00E+02		
29	CHS62CL CHSCL3	1,2-Dibromo-3-Chloropropane 1,2,3-Trichloropropane	236.36		1.29E+02		
30	C3H6BR2		147.43	-14.16	2.42E+02*		
31	C3H6CL2	1,2-Dibromopropane 1,2-Dichloropropane	201.89	- 55.16	6.97E+01*		
32	C3H6CL2	1,3-Dichloropropane	112.99	- 100.16 - 99.16	4.63E+01		
33	C3H6CL2	2.2-Dichloropropane	112.99	-34.16	1.41E+02* 1.41E+02*		
34	C3H8NO5P	Glyphosate	169.08	- 34.10	2.64E+02		
35	C4H8BR2	1.2-Dibromobutane	215.92	-65.16	1.22E+02*		
36	C4H8BR2	2,3-Dibromobutane	215.92	-34.16	1.22E+02*		
37	C5H2CL3N0	3,5,6-Trichloro-2-Pyridinol	253.36	-	1.30E+02		
38	C5H10BR2	2,3-Dibromo-2-Methylbutane	229.94	14.84	2.13E+02*		
39	C5H10N2O25	Methomyi	162.21	-	1.60E+02		
40	C6CL6	Hexachlorobenzene	284.80	229.84	3.91E+03		
41	C6F6	Hexafluorobenzene	186.06	4.84	1.83E+02*		
42	C6HCLS	Peatachiorobenzene	250.35	-45.60	5.44E+03		
43	C6HCL6O	Pentachlorophenol	301.81	174.00	9.00E+02		
44	C6H2CL4	1,2,3,4-Tetrachiorobenzene	215.90	47.50	1.16E+04		
45	C6H2CL4	1,2,3,5-Tetrachlorobenzene	215.90	54.50	2.73E+03		
46	C6H2CL4	1,2,4,5-Tetrachiorobenzene	215.90	140.00	1.25E+04		
47	C6H3BRCLNO2	3-Chloro-4-Bromobenzene	236.47	61.00	3.94E+02		
48	C6H3CL2NO2	3,4-Dichloronitrobenzene	192.01	43.00	3.35E+02		
49	C6H3CL2NO2	Dichloropicolinic Acid	192.01	-	2.00E+00		
50	C6H3CL3	1,2,3-Trichlorobenzene	181.46	54.00	4.03E+03		
51 52	C6H3CL3 C6H3CL3N2O2	1,2,4-Trichlorobenzene	181.46	17.00	8.62E+02		
53	C6H3CL3N2O2 C6H3CL3O	Picloram 2.4.5-Trichlorophenol	241.46		1.70E+01		
54 54	C6H3CL3O	2,4,5-Irichlorophenol 2,4,6-Trichlorophenol	198.05 198.05	69.00 69.00	5.13E+02 4.68E+02		
55	C6H3CL4N	2,4,0 Inchlorophenol	230.93	62.00	4.20E+02		
56	C6H4BRNO2	2-Bromonitrobenzene	202.02	43.00	2.60E+02		
57	C6H4BRNO2	3-Bromonitrobenzene	202.02	17.00	2.60E+02		
58	C6H4BRNO2	4-Bromonitrobenzene	202.02	127.00	2.60E+02		
59	C6H4CL2	M-Dichlorobenzene	147.01	- 25.16	3.13E+02		
60	C6H4CL2	O-Dichlorobenzene	147.01	52.84	2.92E+02		
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# Soil sorption coefficient is an important environmental parameter.

No. 61 62 63 64 65 66 67 68 69 70 71 72 73	Formula C6H4CL2 C6H4CL3NO C6H4CLNO2 C6H4F2 C6H4F2 C6H4F2 C6H5BR C6H5BRCLN C6H5CL	Name P-Dichlorobenzene 2-Methoxy-3,5,6-Trichloropyridine 6-Chloropicolinic Acid M-Difluorobenzene O-Difluorobenzene	MW g/mol 147.01 212.47 157.56	MP C -24.16 -	K <sub>oc</sub> @20 C L/kg 4.32E+02 9.20E+02
61 62 63 64 65 66 67 68 69 70 71 72 73	C6H4CL2 C6H4CL3NO C6H4CLNO2 C6H4F2 C6H4F2 C6H4F2 C6H4F2 C6H5BR C6H5BR	P-Dichlorobenzene 2-Methoxy-3,5,6-Trichloropyridine 6-Chloropicolinic Acid M-Difluorobenzene O-Difluorobenzene	g/mol 147.01 212.47 157.56	C -24.16 -	L/kg 4.32E+02
62 63 64 65 66 67 68 69 70 71 72 73	C6H4CL3NO C6H4CLNO2 C6H4F2 C6H4F2 C6H4F2 C6H4F2 C6H5BR C6H5BRCLN	2-Methoxy-3,5,6-Trichloropyridine 6-Chloropicolinic Acid M-Difluorobenzene O-Difluorobenzene	147.01 212.47 157.56	-24.16	4.32E+02
62 63 64 65 66 67 68 69 70 71 72 73	C6H4CL3NO C6H4CLNO2 C6H4F2 C6H4F2 C6H4F2 C6H4F2 C6H5BR C6H5BRCLN	2-Methoxy-3,5,6-Trichloropyridine 6-Chloropicolinic Acid M-Difluorobenzene O-Difluorobenzene	212.47 157.56	-	
64 65 66 67 68 69 70 71 72 73	C6H4F2 C6H4F2 C6H4F2 C6H5BR C6H5BRCLN	6-Chloropicolinic Acid M-Difluorobenzene O-Difluorobenzene	157.56	-	
65 66 67 68 69 70 71 72 73	C6H4F2 C6H4F2 C6H5BR C6H5BRCLN	M-Difluorobenzene O-Difluorobenzene		-	
66 67 68 69 70 71 72 73	C6H4F2 C6H5BR C6H5BRCLN		114.09	-24.16	9.00E+00 1.83E+02*
67 68 69 70 71 72 73	C6H5BR C6H5BRCLN		114.09	-34.16	1.83E+02*
68 69 70 71 72 73	C6H5BRCLN	P-Difluorobenzene	114.09	-13.16	1.83E+02*
69 70 71 72 73		Bromobenzene 3-Methyl-4-Bromoaniline	157.01	-31.16	2.97E+02*
71 72 73		Chlorobenzene	206.48 112.56	-215.16	1.80E+02
72 73	C6H5CL2N	3.4-Dichloroaniline	162.02	-45.16 72.00	2.17E+02
73	C6H5CLN	3,5-Dichloroaniline	162.02	52.00	1.93E+02 1.28E+02
	C6H5CLO	2-Chlorophenol	129.16	9.00	2.30E+01
	C6H5F	Fluorobenzene	96.10	- 39.16	1.82E+02*
74 75	C6H5NO2	Nitrobenzene	123.08	5.84	8.64E+01
75 76	C6H6 C6H6CL3	Benzene	78.11	5.84	8.30E+01
77	C6H6CL6	Methoxychlor Gamma-BHC	184.48	89.00	8.00E+04
78	C6H6CL6	Lindane	290.85 290.85		9.11E+02
79	C6H6N2O2	3-Aminonitrobenzene	138.12	113.00 114.00	1.08E+03
80	C6H6N202	4-Aminonitrobenzene	138.12	149.00	5.30E+01 7.50E+01
81	C6H6O	Phenol	94.11	40.84	2.70E+01
82 83	C6H7N C6H7N	2-Picoline	93.13	-66.16	4.42E+01*
84 84	C6H7N	3-Picoline	93.13	- 18.16	4.42E+01*
85		Aniline	93.13	-6.16	2.50E+01
86	C6H15N C7H4CL3NO3	Triethylamine	101.19	- 115.16	1.43E+02*
87	C7H4N2O4S	Triclopyr Asulam	256.48	-	2.70E+01
88	C7H5CL2NO2	Chioramben	212.18 206.03	-	3.00E+02
89	C7H5CL2NS	Chlorthiamid	206.03	· –	2.10E+01
90	C7H5F3	A.A.A-Trifluorotoluene	146.11	- 29.16	1.07E+02 3.16E+02*
91	C7H6CL2N2O	(3,4-Dichlorophenyi)Urea	205.05		3.06E+02
92 93	C7H6CL3	3-(Trichloromethyl) Aniline	196.49	-	2.27E+02*
94	C7H6O2 C7H7BRN2O	Benzoic Acid	122.12	122.84	7.91E+00*
95	C7H7BRN2O	(3-Bromophenyi) Urea (4-Bromophenyi) Urea	215.06	-	1.14E+02
96	C7H7CLN2O	(2-Chlorophenyi) Urea	215.06 170.60	=	1.13E+02 4.03E+01
97	C7H7CLN2O	(3-Chlorophenyi) Urea	170.60		
98	C7H7F	P-Fluorotoluene	110.13	- 57.16	1.02E+02 3.13E+02*
99	C7H7FN2O	(2-Florophenyl) Urea	154.14		1.01E+02
100	C7H7FN20	(3-Florophenyi) Urea	154.14	-	5.80E+01
101 102	C7H7FN2O C7H8	(4-Florophenyi) Urea	154.14	_	3.28E+01
103	C7H8CLNO	Toluene 3-Chloro-4-Methoxyaniline	92.14	-95.16	3.03E+02* .
104	C7H8NO2	Phenviurea	157.60	52.00	8.40E+01
105	C7H8O	Anisole	138.14 108.13	147.00 - 37.80	2.21E+01 3.40E+01
106	C7H8O	M-Cresol	108.14	-37.80	3.40E+01
107.	C7H8O	O-Cresol	108.14	30.84	3.60E+02*
108	C7H8O	P-Cresol ·	108.14	34.84	3.60E+02*
109	C7H9N	2-Methylaniline	107.15	-43.00	4.42E+01
110	C7H9N	3-Methylaniline	107.15	-64.00	4.42E+01
111 112	C7H9N	4-Methylaniline	107.15	-4.87	7.86E+01
113	C7H11CLN2O C7H12CLN5	3-(3-Chloro-4-Methylphenyl)-1-Methy	174.63	-	1.25E+02
314	C7H14N2O2S	Simazine Aldicarb	201.66	226.00	1.35E+02
115	C7H17O2PS3	Phorate	190.97 260.38	100.00	3.00E+01 3.20E+03
116	C8H5CL3O3	2,4,5-Trichlorophenoxyacetic Acid	255.49	0.00	5-30E+03
117	C8H6	Ethynyibenzene	102.14	- 30.16	5.19E+02*
118	C8H6CL2O3	2,4-Dichlorophenoxyacetic Acid	221.04	_	6.00E+01
119	C8H6CL2O3	Dicamba	221.84	115.00	4.70E+02
120	C8H6CL3NO	3-(Trifloromethyl) Acetanilide	238.51		5.56E+01
121	C8H7CL2NO	3,4-Dichloroacetanilide	204.06	-	2.17E+02
122 123	C8H7CL2NO2 C8H7CL3N2O	Chloramben	220.06	-	5.07E+02
124	C8H8	(3-Trifloromethyl) Phenylurea 1.3.5.7-Cyclooctatetraene	253.52	-	9.02E+01
125	Свна	Styrene	104.15 104.15	- 30.16	5.19E+02*
126	CBH8BRNO	2-Bromoacetanilide	214.07	99.00	5.19E+02* 1 1.01E+02
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No.	Formula	Name	MW	MP	K <sub>oc</sub> @20 C
			g/mol	C	L/kg
127	C8H8BRNO	3-Bromoacetanilide	214.07	87.50	1.01E+02
128	C8H8BRNO	4-Bromoacetanilide	214.07	168.00	1.01E+02
129	C8H8CL202	Chloreoneb	207.06	-	1.16E+03
130 131	C8H8CL2N2O C8H8CLNO	3-(3,4-Dichlorophenyi)-1-Methylurea	219.07	-	2.858+02
132	CBHBCLNO	2-Chloroacetanilide	169.61	- 1	3.76E+01
		3-Chloroacetanilide	169.61	<b>—</b> ·	7.17E+01
133	C8H8CLNO2	Methyl-N-(3-Chiorophenyl) Carbamate	185.61	-	1.40E+02
134 135	C8H8FNO	2-Floroacetanilide	153.15	-	7.84E+01+
135	C8H8FNO	3-Floroacetanilide	153.15		3.67E+01
137	C8H8FNO	4-Floroacetanilide	153.15		2.99E+01
138	C8H8N2O3 C8H8N2O3	2-Nitroacetanilide	180.16	94.00	8.62E+01
139	C8H8N2O3	3-Nitroacetanilide 4-Nitroacetanilide	180.16	155.00	8.62E+01
140	C8H8O	Acetophenone	180.16	216.00	8.62E+01
141	C8H9BRN2O	(3-Methyl-4-Bromophenyl) Urea	120.14	20.50	4.30E+01
142	C8H9CLN2O	3-(3-Chlorophenyi)-1-Methylurea	229.08	-	2.32E+02
143	C8H9CLN2O2	(3-Chloro-4-Methoxylphenyl) Urea	184.63 200.63	-	8.40E+01
144	C8H9FN2OF	(3-Methyl-4-Florophenyl) Urea	168.17	-	9.908+01
145	C8H9NO			-	5.96E+01
146	CBH9NO2	Acetanilide	135.16	114.30	2.66E+01
147	C8H10	Methyl-N-Phenylcarbamate	151.16	-	5.30E+01
148	C8H10	Ethylbenzene M-Xviene	106.17	-95.16	5.19E+02*
149	C8H10	O-Xviene	106.17	-48.16	5.19E+02*
150	CBH10	P-Xviene	106.17	-25.16	5.19E+02*
151	C8H10CL3O3PS	Methyl-Chloropyrifos	106.17 323.58	12.84	5.19E+02*
152	C8H10N2O	G-Methylphenyl Urea	323.58 150.18	-	3.30E+03
153	C8H10NO2	3-Phenyl-1-Methylurea	150.18	151.00	3.59E+01
154	C8H10O5PS	Methyl Parathion	249.21	36.00	1.90E+01
155	CBH11BRN2O2	isocii	247.10	158.00	9.80E+03
156	C8H14CLN5	Atrazine	216.70	172.00	1.30E+02 1.49E+02
157	C8H14N4OS				
158	C8H19O2PS3	Metribuzin	214.29	125.00	9.50E+01
159	C9H6CL2N2O3	Disulfoton Methazole	274.41	-	1.78E+03
160	C9H7CL303	Silver	261.07		2.62E+03
161	C9H7N	Ouinoline	269.52	181.00	2.60E+03
162	C9H10	M-Methylstyrene ·	129.15	15.60	5.70E+02
163	C9H10	O-Methvistvrene	118.18	-86.16	8.84E+02*
164	C9H10 .	P-Methylstyrene	118.18	-68.16	8.84E+02*
165	C9H10	CIS-Propenylbenzene	118.18	-34.16	8.84E+02*
166	C9H10	Trans-Propenylbenzene	118.18 118.18	-62.16	8.84E+02*
167	C9H10BRCLN2O2	3-(3-Chloro-4-Bromophenyl)-1-Methyl	293.56	- 29.16	8.84E+02*
168	C9H10BRCLN2O2	Chlorbromuron	293.56	_	3.76E+02 4.60E+02
169	C9H10CL2N2				
170	C9H10CL2N2	Diuron	217.10	158.00	4.00E+02
171	C9H10CL2N2O	3-(3,4-Dichlorophenyl)-1,1-Dimethyl	233.10	-	1.61E+02
172	C9H10CL2NO2	3-(3,4-Dichlorophenyi)-1-Methly-1-M	249.10	<b></b>	2.66E+02
173	C9H10CLNO2	Linuron 3-Chloro-4-Methoxyacetanilide	249.10	93.00	8.20E+02
174	C9H11BRN2O2	3-Chioro-4-Methoxyacetanilide 3-(4-Bromophenyl)-1-Methyl-1-Methox	199.64	-	8.23E+01
175	C9H11BRN2O2	3-(4-Bromopneny)-1-Metnyi-1-Methox Metobromuran	259.11		1.04E+02
176	C9H11CL3NO3PS	Chlorpyrifos	259.11	95.00	6.00E+01
177	C9H11CLN2O	3-(3-Chlorophenyl)-1,1-Dimethylurea	350.60	43.00	6.10E+03
178	C9H11CLN2O	3-(4-Chlorophenyi)-1,1-Dimethylurea	198.65 198.65		6.10E+01
179	C9H11CLN2O	Monuron	198.65	170.00	4.96E+01
180	C9H11CLN2O2	3-(3-Chloro-4-Methoxyphenyl)-1-Meth	214.65	175.00	1.00E+02
181	C9H11CLN2O2				6.85E+01
182	C9H11CLN2O2	3-(4-Chlorophenyi)-1-Methyl-1-Metho	214.65	-	1.53E+02
183	C9H11FN2O	Monoinuron	214.65	-	2.00E+02
184	C9H11FN2O	3-(3-Florophenyi)-1,1-Dimethylurea	182.19	-	5.31E+01
185	C9H11NO	3-(4-Florophenyl)-1,1-Dimethylurea 2-Methylacetanilide	182.19		2.66E+01
186	C9H11NO	3-Methylacetanilide	149.19	110.00	2.79E+01
187	C9H11NO	4-Methylacetanilide	149.19 149.19	65.50 148.50	2.79E+01
188	C9H11NO2	4-Methoxyacetanilide	165.19		2.79E+01 2.49E+01
189	C9H11NO2	Ethyl N-Phenylcarbamate	165.19	131.00	2.49E+01 6.54E+01
190	C9H12	1,2,3-Trimethylbenzene	120.19	-25.16	6.345+01 8.845+02*
191	C9H12	1,2,4-Trimethylbenzene	120.19	- 25.16	8.84E+02*
192	C9H12	Cumene	120.19	- 96.16	8.84E+02*
193					
193	C9H12	M-Ethyltoluene	120.19	-95.16	8.84E+02*
	C9H12 C9H12	O-Ethyltoluene	120.19	-81.16	8.84E+02*
		P-Ethyltoluene	120.19	-62.16	8.84E+02*
195		Pro- and how many a			
195 196	C9H12	Propylbenzene	120.19	- 99.16	8.84E+02*
195		Propylbenzene 1,1-Dimethyl-3-Phenylurea Fenuron	120.19 164.20 164.20	-99.16 	8.84E+02* 4.63E+01 2.70E+01

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# K determines the partitioning of an organic chemical between the soil/sediment and the aqueous solution.

No.	Formula	Nama	MW	MP	Koc@20 C
199		Name	g/mol	C	L/kg
200	C9H138RN2O2 C9H13CLN2O2	Bromacil Terbacil	261.13 .	158.00	7.20E+01
201	C9H13CLN6	Cyanazine	216.67	176.00	5.10E+01
202	C9H16CLN5	Propazine	241.71	167.00	2.00E+02
203	C9H16N4OS	Tebuthiuron	229.72 228.32	213.00	1.60E+02
204	C9H17N55	Ametryn	227.33		6.20E + 02 3.92E + 02
205	C9H19NOS	S-Ethyl Di-N, N-Propylthiocarbamate	189.32	-	
206	C9H22O4P2S4	Ethion	384.49	-13.00	2.40E+02 1.54E+04
207	C10HO5PS	Parathion	264.15	6.00	4.80E+03
208 209	C10H7N3S	Thiabendazole	201.25		1.72E+03
209	C10H8 C10H8	Azulene	128.17	174.00	1.50E+03*
211	C10H8CLNO3	Naphthalene Pyrazon	128.16	80.00	1.30E+03
212	C10H8F3N2O	3-(3-(Trifloromethyl)Phenyl)-1,1-Di	225.63		1.202+02
213	C10H80	Naphthol	229.18 144.16		2.99E+02
214	C10H9F3N3O4	Trifluralin	292.20	· 96.00 49.00	3.81E+02 4.30E+03
215	C10H11F3N2O	Fluometuron	232.20	164.00	1.75E+02
216	C10H12CLNO2	Chlorpropham	213.66	41.00	5.90E+02
217	C10H12N2O	3-Phenyi-1-Cyclepropyiurea	176.21	-	5.19E+01
218	C10H12N2O5	Dinoseb	240.21	_	1.248+02
219 220	C10H13CLN2O	3-(3-Chioro-4-Methylphenyi)-1,1-DIM	212.68	_	1.04E+02
221	C10H13CLN2O2 C10H13NO2	3-(3-Chloro-4-Methoxylphenyl)-1,1-D	228.68	-	5.44E+01
2222	C10H13NO2	Propham iso-Propyl-N-Phenylcarbamate	179.21	·	5.10E+01
223	C10H13NO2	n-Propyl-N-Phenylcarbamate	179.21	-	8.80E+01
224	C10H14	1,2,3,4-Tetramethylbenzene	179.21 134.22	-6.16	1.14E+02
225	C10H14	1,2,3,5-Tetramethylbenzene	134.22	-24.16	1.50E+03*
226	C10H14	1,2,4,5-Tetramethylbenzene	134.22	78.84	1.50E+03* 1.50E+03*
227 228	C10H14	Butylbenzene	134.22	-88.16	1.50E+03*
	C10H14	M-Diethylbenzene	134.22	-84.16	1.50E+03*
229 230	C10H14 C10H14	O-Diethylbenzene	134.22	-31.16	1.50E+03*
231	C10H14N2O	P-Diethylbenzene	134.22	-42.16	1.50E+03*
232	C10H14N2O2	3-(4-Methylphenyl)-1,1-Dimethylurea 3-(3-Methoxyphenyl)-1,1-Dimethylure	178.23	— ·	3.20E+01
233	C10H14N2O2	3-(4-Methoxyphenyl)-1,1-Dimethylure	194.23	-	5.19E+01
234	C10H16CL3NOS	Trialiate	194.23 304.67		2.49E+01
235	C10H17CL2NOS	Diallate	270.22	<b>—</b>	2.22E+03 1.90E+03
236	C10H18	Decahydronaphthalene, CIS	138.25	-43.16	2.928+03*
237 238	C10H18	Decahydronaphthalene, Trans	138.25	- 30.16	2.92E+03*
239	C10H18CLN5 C10H19N5O	Ipazine	243.74	87.00	1.66E+03
240	CI0HI9N55	Prometon	225.29	-	3.50E+02
241	C10H19N55	Prometryne	241.36	-	8.10E+02
242	C10H19O6PS2	Terbutyme	241.36	-	7.00E + 02
243	C10H21NOS	Malathion Pebulate	330.36 203.34	3.00	1.80E + 03
244	C11H10	2-Methylnaphthalene	203.34 142.19		6.30E + 02
245	C11H13F3N4O4	Dinitramine	354.31	34.60	8.50E + 03 4.00E + 03
246	C11H14CLNO	Propachior	211.69	71.00	4.002 + 03 2.65E + 02
247	C11H15BRN2O	3-(3,5-Dimethyl-4-Bromophenyl)-1,1-	271.16	_	3.35E + 02
248	C11H15NO .	Butyranilide	177.24	_	5.07E+01
249 250	C11H15NO2 C11H16	-n-Butylphenylcarbamate	193.24	— . l	1.80E + 02
251	C11H16	Pentamethylbenzene Pentylbenzene	148.25	54.84	2.52E + 03*
252	C11H16CLO2PS3	Carbophenothion	148.25 341.42	- 75.16	2.52E+03*
253	C11H16N2O	3-(3,5-Methylphenyl)-1,1-Dimethylur	192.25		4.54E+04
254	C11H21N55	Dipropetryne	255.38		5.32E + 01 1.17E + 03
255	C11H21NOS	Cycloate	215.35	_	3.45E + 02
256	C12H4CL6	2,2',4,4',5,5'-Hexachlorobiphenyl	361.90	103.00	1.20E + 06
257	C12H4CL6	2,2',4,4',6,6'-Hexachlorobiphenyi	361.90	103.00	4.17E + 05
258 259	C12H5CL5	2,2',4,5,5'-Pentachlorobiphenyl	326.45	75.00	5.00E + 05
260	C12H7CL3 C12H8CL2	2,4,4'-Trichlorobiphenyi	258.75	-	4.14E + 04
261	C12H8CL2	2,2'-Dichlorobiphenyl 2,4-Dichlorobiphenyl	224.31	-	8.25E + 03
262	C12H8S	2,4-Dichlorobiphenyl Dibenzothiophene	224.31 184.25		1.34E+04
263	C12H9C1	2-Chlorobiphenyl	189.86	98.00 34.00	1.12E+04
264	C12H9CL	3-Chlorobiphenyl	189.86	J-4.00 [	2.93E+03

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No.	Formula	Name	MW g/mol	мр С	K <sub>oc</sub> @20 C
265	C12H9CLF3N3O			<u> </u>	L/kg
266	C12H10	Norfluorazon Biphenvi	303.67	-	1.91E+03
267	C12H11CL2NO	Pronamide	154.21	71.00	4.23E+03*
268	CI2HIIN	Diphenylamine	256.13		2.00E+02
269	C12H11N02	Carbary	169.22 201.22	55.00	5.96E+02
270	C12H12	1,2-Dimethylnaphthalene	156.23	142.00	3.90E+02
271	C12H12	1,3-Dimethylnaphthalene	156.23	-1.16	4.23E+03*
272	C12H12	1,4-Dimethylnaphthalene	156.23	-4.16	4.23E+03*
273	C12H12	1,5-Dimethylnaphthalene	156.23	7.84 81.84	4.23E+03*
274	C12H12	1,6-Dimethylnaphthalene	156.23	- 14.16	4.23E+03*
275	C12H12	1,7-Dimethylnaphthalene	156.23	-13.16	4.23E+03*
276	C12H12	1-Ethylnaphthalene	156.23	- 14.16	4.23E+03* 4.23E+03*
277	C12H12	2,3-Dimethylnaphthalene	156.23	104.84	
278	C12H12	2,6-Dimethylnaphthalene	156.23	111.84	4.23E+03*
279	C12H12	2,7-Dimethylnaphthalene	156.23	97.84	4.23E+03*
280	C12H12	2-Ethyinaphthalene	156.23	-7.16	4.23E+03*
281	C12H12F3N3O4	Fluchoralin	319.24	-7.10	4.23E+03*
282	C12H15NO3	Carbofuran	211.17	151.00	3.60E+03
283	C12C16CL2N2	Neburon	275.18	131.00	1.30E+02
284	C12H16N2O	3-Phenylcyclopentylurea	204.26		2.30E+03
285	C12H17NO2	n-Pentyl Phenvicarbamate	207.26		8.40E+01 4.03E+02
286	C12H18	1,2,3-Triethylbenzene	162.27	-66,16	5.78E+03*
287	C12H18	1,2,4-Triethylbenzene	162.27	-66.16	· 5.78E+03*
288	C12H18	1,3,5-Triethylbenzene	162.27	- 66.16	5.78E+03*
289	C12H18	Hexamethylbenzene	162.27	165.84	
290	C12H18	Hexvibenzene	162.27	-61.16	5.78E+03*
291	C12H21N2O3P5	Diazinon	304.35	-01.10	5.78E+03*
292	C13H108RCL2O2P5	Leptophos	499.04	_	2.27E+02
293	C13H12N2O2	(4-Phennoxyphenyi) Urea	228.24	-	9.30E+03
294	C13H14	1-Propyinaphthalene	170.25	-8.16	3.59E+02
295	C13H14	2-Propyinaphthalene	170.25	-3.16	7.06E+03*
296	C13H14	2-Ethyl-3-Methylnaphthalene	170.25	70.84	7.06E+03*
297	C13H14	2-Ethyl-6-Methylnaphthalene	170.25	44.84	7.06E+03*
298	C13H14	2-Ethyl-7-Methyinaphthalene	170.25	44.84	7.06E+03*
299	C13H16F3N3O4	Benefin	335.28	66.00	7.06E+03* 1.07E+04
300	C13H18N2O	2-Phenylcyclohexylurea	218.29	00.00	1.16E+02
301	C13H19N3O6S	Nitralio			
302	C13H20	1-Phenylheptane	345.37	-	9.60E+02
303	C14H9CL5	4,4'-Dichlorodiphenyltrichloroethan	176.30	-48.16	7.06E+03*
304	C14H9CLF2N2O2	Diflubenzumn	354.50	109.00	1.50E+05
305	C14H10	Anthracene	310.69 178.22		6.79E+03
306	C14H10	Phenanthrene	178.22	216.00 101.00	2.60E+04
307	C14H16	1-Butyinaphthalene	184.28	-20.16	2.30E+04
308	C14H16	2-ButyInaphthalene	184.28		1.13E+04*
309	C14H16F3N3O4	Profluralin	347.29	- 5.16	1.13E+04*
310	C14H17CLNO2	Alachior	266.74		8.60E+03
311	C14H20N2O	3-Phenylcyclopentylurea	374.14		1.90E+02
312	C14H20N2O8S2	Paraquat	408.41		2.32E+02 1.54E+04
313	C14H21N3O4	Butralin			
314	C14H22	1,2,3,4-Tetraethylbenzene	295.33		8.20E + 03
315	C14H22	1,2,3,4-ieuaemyibenzene 1,2,3,5-Tetraethyibenzene	190.33	11.84	1.13E+04*
316	C14H22	1,2,4,5-Tetraethylbenzene	190.33	10.84	1.13E+04*
317	C14H22	1-Phenyloctane	190.33	9.84	1.13E+04*
318	C15H10O2	Anthracence-9-Carboxylic Acid	190.33	- 36.16	1.13E+04*
319	C15H12	9-Methylanthrancene	364.06 192.25		8.82E+02
320	C15H15CLN2O2	Chlorowron	290.74	82.00	6.50E + 04
321	C15H18	1-Pentvinaphthalene	198.31	- 22.16	3.20E+03
322	C15H18	2-Pentylnaphthalene	198.31	- 22.16 - 4.16	1.93E+04*
323	C15H18CL2N2O3	Oxadiazon	345.22	-4.10	1.93E+04*
324	C15H23N3O4	Isopropalin	309.36	- 1	3.24E+03
325	C15H24	1-Phenyinonane			<u>7.53E+04</u>
326	C16H10		204.35	-24.16	1.93E+04*
327	C16H22O4	Pyrene Dibutulabelata	202.24	156.00	8.40E+04
328	C16H26	Dibutylphthalate	278.34	-	4.50E + 02
329	C16H26	1-Phenyidecane	218.38	- 14.16	3.18E+04*
330	C17H21NO2	Pentaethylbenzene	218.38	54.84	3.18E+04*
331	C17H28	Napropamide	271.35	-	6.80E + 02
332	C18H12	1-Phenylundecane 1,2-Benzanthracene	232.41	-5.16	5.20E+04*
333	C18H12	1,2-Benzanthracene	228.28	162.00	6.50E + 05
	C18H30	letracene Hexaethylbenzene	228.28	332.00	6.50E + 05
334		TEADEUTYIDETIZETE	246.44	127.84	8.45E+04*
		9 10 Dimethylberranthereas			
334	C20H16 C21H36	9,10-Dimethylbenzanthracene 1-Phenylpentadecane	256.33 288.52	123.00 21.84	4.76E+05 3.53E+05*

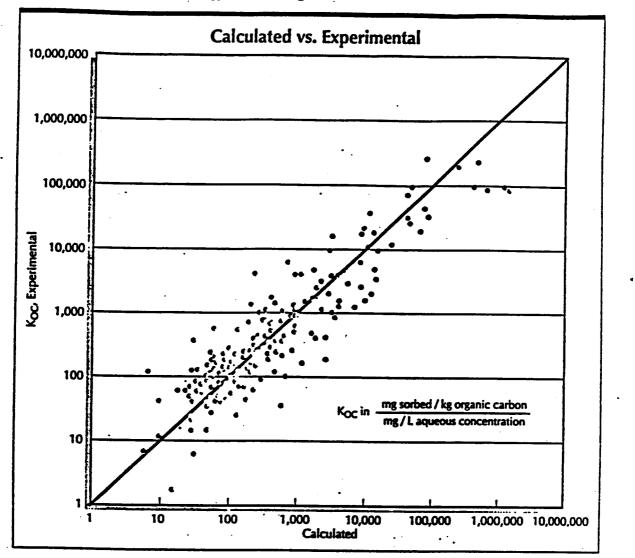
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Soil sorption coefficient is used in river, runoff and soil/groundwater models.



• Figure 1. Comparison of values for calculated and experimental soil sorption coefficients shows general agreement between the two.

Estimate the equilibrium distribution of the pesticide resulting from a 1 kg/hectare (1 hectare = 10,000  $m^2$ ) application incorporated to a 10 cm depth. Volatilization into the air is assumed to be negligible.

The amount of organic carbon in soil per hectare is:

From Table 1, the soil sorption coefficient of atrazine is:

$$K_{\infty} = \frac{149 \text{ (mg sorbed/kg organic carbon)}}{(\text{mg/L aqueous concentration)}}$$

Determination of the amount of atrazine in the soil phase per hectare requires a trial and error procedure. Trying x = 0.94 kg = 940,000 mg in Equation 1 gives:

C = 940,000/25,000/149 = 0.252 mg/L

The amount of atrazine in the aqueous phase per hectare is:

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#### 0.252 × 10,000 × 0.1 × 1000 × 25% = 63,000 mg = 0.063 kg

The total amount of atrazine is 1.003 kg/hectare. This is close enough to the application (1.003 vs. 1 application). The equilibrium distribution of atrazine is estimated to be 6.3 percent in water and 93.7 percent in soil.

Chang Y. Jeng, Daniel H. Chen and Carl L. Yaws are with Lamar University, Beaumont, Texas. Partial financial support for this project was provided by the Gulf Coast Hazardous Substance Research Center

#### Reader Interest Review

Please circle the	e appropriate number on th	e Reader Serv-
ice Card to indi	icate the level of interest in	i the article
High 471	Medium 472	Low 473

James W. Moore S. Ramamoorthy

# Organic Chemicals in Natural Waters

Applied Monitoring and Impact Assessment

With 81 Figures



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## Appendix A **Chemical Formulae of Compounds** Cited in this Book

NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
ACENAPHTHENE	C <sub>12</sub> H <sub>10</sub>	
ACENAPHTHYLENE	С <sub>12</sub> Н <sub>8</sub>	
ACETONE	с <sub>3</sub> н <sub>6</sub> 0	о сн <sub>3</sub> -с-сн <sub>3</sub>
ACETYLENE	C <sub>2</sub> H <sub>2</sub>	HC I CH
ACROLEIN	с <sub>3</sub> н <sub>4</sub> о	CH <sub>2</sub> = CH - CH = 0
ALDRIN	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub>	
m-ALKYLPHENOLS	RC <sub>6</sub> OH <sub>5</sub>	OH R
ALLYLALCOHOL	с <sub>3</sub> н <sub>6</sub> о	CH2 = CH - CH2 - OH
m-AMINOPHENOL	C <sub>6</sub> H7NO	NH <sub>2</sub>

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#### Appendix A

ANILINE

ANTHRACENE

BENZENE

BENZO (B)

BENZO (J)

BENZO (K)

BENZYLCHLORIDE

FLUORANTHENE

FLUORANTHENE

FLUORANTHENE

BENZ (A) ANTHRACENE CIB HI2

÷.

NAME

m-AMYLPHENOL

MOLECULAR FORMULA

C<sup>11</sup>H<sup>16</sup>O

C<sub>6</sub>H<sub>7</sub>N

C14 H10

C 6 H12

C7H7CI

C20 H12

C20 H12

C20H12

C<sub>R</sub>H<sub>6</sub>O

STRUCTURAL FORMULA

сн, - (сн,), - сн,











соон

### - CH2 - OH



BENZOIC ACID

BENZOFURAN

 $C_7 H_6 O_2$ 

	246		Appendix A	Appendix A		247
	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
	iso-BUTANOL	C₄ H <sub>IO</sub> O	СН <sub>3</sub>   СН <sub>3</sub> – С – ОН   СН <sub>3</sub>	BENZO (GHI) Perylene	C <sub>22</sub> H <sub>12</sub>	
	BUTENE	с <sub>4</sub> н <sub>в</sub>	сн <sub>3</sub> - сн = сн - сн <sub>3</sub>	BENZO (A) PYRENE	с <sub>20</sub> н <sub>12</sub>	
	BUTYLENE	С <sub>4</sub> Н <sub>В</sub>	СH3- CH = CH = CH3	BENZO (E) PYRENE	C <sub>20</sub> H <sub>12</sub>	
	I,4-BUTYLPHENOL	с <sub>ю</sub> н <sub>і4</sub> о	Сісн <sub>з</sub> ,	BENZOTHIOPHENE	с <sub>в</sub> н <sub>б</sub> s	
	CAPROLACTAM	с <sub>6</sub> н <sub>іі</sub> No	<sup>ل</sup> ُن <sup>•</sup>	BICYCLOOCTANE	С <sub>в</sub> н <sub>14</sub>	$\langle \downarrow \rangle$
15-109	CARBON TETRACHLORIDE (Tetrachloromethane)	CCI4	CI - CI CI - CI CI	BISPHENOL A	C <sub>15</sub> H <sub>16</sub> 0 <sub>2</sub>	но - С с
	CARBONYL SULPHIDE	COS	\$ = C = O	BROMODICHLOROMETHANE	CHCI <sub>2</sub> Br	H CI - C - Br CI
	CAROTENE	C <sub>40</sub> H <sub>56</sub>	0	BROMOETHYLPROPANE	C <sub>5</sub> H <sub>II</sub> Br	вг I HsC-C-CHs CH,CHq
	CHLORANIL	C <sub>6</sub> 0 <sub>2</sub> Cl <sub>4</sub>		BROMOFORM	CHBr <sub>3</sub>	H Br - C - Br Br
	CHLORDANE	с <sub>ю</sub> н <sub>б</sub> сі <sub>в</sub>		BROMOMETHANE	CH <sub>3</sub> Br	H – Ç – Br H

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	248		Appendix A	Appendix A		249
	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
	CHLOROETHYLENE	C <sub>2</sub> H <sub>3</sub> CI	Сн <sub>2</sub> • сн – с1	CHLORDENE	С <sub>10</sub> Н <sub>4</sub> СІ <sub>6</sub>	
	CHLOROETHYLVINYLETHE	R C <sub>4</sub> H70CI	CI-CH <sub>2</sub> -CH <sub>2</sub> -O-CH = CH <sub>2</sub>	CHLORDENE EPOXIDE	с <sub>ю</sub> н <sub>б</sub> сі <sub>б</sub> о	
	CHLOROFORM	снсіз	CI CI-C-H I CI	CHLOROBENZENE	с <sub>6</sub> н <sub>5</sub> сі	Ğ
	CHLOROMETHANE	сн <sub>з</sub> сі	н Н – С – Н С1	m-CHLOROBENZOIC ACID	с <sub>7</sub> н <sub>5</sub> сю <sub>2</sub>	СООН
	CHLOROMETHYLMETHYLET	THER C <sub>2</sub> H <sub>5</sub> OCI	CI-CH2-O-CH3	CHLOROBIPHENYL	C <sub>I2</sub> H <sub>9</sub> CI	C)
		С <sub>8</sub> Н <sub>9</sub> О <sub>2</sub> СІ с	CH3 OH OCH3	CHLORODECANE	с <sub>ю</sub> сі <sub>ю</sub> о	
	CHLOROMETHYL Phenol	с, н <sub>7</sub> осі		CHLORODIBENZOFURAN	с <sub>і2</sub> н <sub>8</sub> осі	
	CHLOROMETHYLVERATROL	E C9HIIO2CI	CI	CHLORODIBROMOMETHAN	E CH Br <sub>2</sub> CI	\ CI ' H CI-C-Br Br
	CHLORONAPHTHALENE	с <sub>ю</sub> н, сі	çı	CHLORODIFLUOROMETHAN	NE CHCIF <sub>2</sub>	H I CI-C-F F F
	o-CHLORONITROBENZENE	С <sub>6</sub> Н <sub>4</sub> СІ NO <sub>2</sub>	NO2	CHLOROETHANE	с <sub>2</sub> н <sub>5</sub> сі	н сн <sub>а</sub> -с-сі н

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NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME MOLECULAR FORMULA
o-CHLOROPHENOL	с <sub>6</sub> н <sub>5</sub> осі	OH CI	CYCLOHEXANONE C <sub>6</sub> H <sub>10</sub> 0
2-CHLOROPROPANE	C3H7 CI	сі і сн <sub>з</sub> – сн – сн <sub>з</sub>	CYCLOPENTANE C <sub>5</sub> H <sub>10</sub>
CHLOROPROPENE	С <sub>3</sub> Н <sub>5</sub> СІ	Сі-сн• сн-сн <sub>з</sub>	CYMENE C <sub>IO</sub> H <sub>14</sub>
CHRYSENE	C <sub>18</sub> H <sub>12</sub>		2,4-D (2,4-dichlorophenoxyacetic C <sub>8</sub> H <sub>6</sub> Cl <sub>2</sub> O <sub>3</sub> acid)
CORONENE	C <sub>24</sub> H <sub>12</sub>		D B H (4,4'-dichlorobenzhydrol) <sup>C</sup> 13 H <sub>10</sub> Cl <sub>2</sub>
CREOSOTE	mixture of phenols	~ ~	DBP (4,4'-dichlorobenzophenone) <sup>C<sub>13</sub>H<sub>8</sub>OCI<sub>2</sub></sup>
m-CRESOL ( methylphenol )	с <sub>7</sub> н <sub>8</sub> 0	он Сн,	D D A (4,4'-dichtorodiphenyl acetic C <sub>I4</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>2</sub> acid )
CYCLOHEPTANE	С <sub>7</sub> Н <sub>14</sub>	$\bigcirc$	D D C N (4,4'-dichlorodiphenylacetonitrile) <sup>C</sup> 14 <sup>H</sup> 9 <sup>N Cl</sup> 2
CYCLOHEXANE	C <sub>6</sub> H <sub>12</sub>	$\bigcirc$	DDCO (dichloro diphenyl carbonyl) <sup>C</sup> 13 H <sub>8</sub> OCI <sub>2</sub>
CYCLOHEXANOL	С <sub>6</sub> Н <sub>I2</sub> 0	<b>OH</b>	D D D (4,4'-dichlorodiphenyldichloroethane) <sup>C</sup> l4 <sup>H</sup> 10 <sup>Cl</sup> 4

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NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULI
D D E (4,4'-dichlorodiphenyldichloroethylend	e} <sup>C</sup> I4 H 8 CI4		DIBENZ (A, H)ANTHRACENE	C <sub>22</sub> H <sub>14</sub>	<u>JU</u>
D D M {4,4'-dichlorodiphenylmethane }	с <sub>із</sub> н <sub>іо</sub> сі <sub>2</sub>	сі — Сна- Срана сі	DIBENZOFURAN	C <sub>12</sub> H <sub>8</sub> O	
D D M S (4,4'-dichlorodiphenylchloroethane)	C <sub>14</sub> H <sub>11</sub> CI <sub>3</sub>		p-DIBROMOBENZENE	C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub>	er Br
D D M U (4,4'-dichlorodiphenylchloroethylene)	C <sub>14</sub> H <sub>9</sub> CI <sub>3</sub>	cı - C - C - C - C - C - C - C - C - C -	DIBROMOCHLOROMETHANE	CHBr <sub>2</sub> Cl	H CI-C-Br I Br
D D N S (4,4'-dichlorodiphenylethane )	C <sub>14</sub> H <sub>12</sub> CI <sub>2</sub>	сі - Сн - Сн - Сі сн - Сн - Сі	DIBROMOETHANE	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	Br - CH <sub>2</sub> - CH <sub>2</sub> - Br
D D N U (4,4'-dichlorodiphenylethylene )	C <sub>14</sub> H <sub>10</sub> CI <sub>2</sub>	cı - C - C - Cı	DIBROMOMETHANE	CH <sub>2</sub> Br <sub>2</sub>	Br – CH <sub>2</sub> – Br
D D T (4,4'-dichlorodiphenyltrichloroethand	<sub>e)</sub> C <sub>I4</sub> H <sub>9</sub> CI <sub>5</sub>	CI - CH - CH - CI	2,3-DIBROMOTOLUENE	CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Br <sub>2</sub>	CH3 Br Br
DECACHLOROBIPHENYL	C <sub>6</sub> CI <sub>10</sub>		2,4-DIBUTYLPHENOL	с <sub>14</sub> н <sub>22</sub> 0	
DECAHYDRONAPHTHALENE	С <sub>10</sub> Н <sub>18</sub>		DICHLOBENIL	с <sub>7</sub> н <sub>3</sub> сі <sub>2</sub> N	
DIBENZ (A,H) ACRIDINE	C <sub>21</sub> H <sub>13</sub> N	SC.S	m-DICHLOROBENZENE	C <sub>6</sub> H <sub>4</sub> CI <sub>2</sub>	CI CI

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NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMUL
DICHLOROBENZOFURAN	с <sub>в</sub> н <sub>з</sub> сі <sub>2</sub> о		DICHLOROMETHYL GUAIACOL	C <sub>8</sub> H702CI2	CI CI OH
4,4'-DICHLOROBIPHENYL	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub>	cı	DICHLOROMETHYLPHENOL	C7H60CI2	CH3 CI
DICHLOROBROMOMETHANE	CHCI <sub>2</sub> Br	H I Br - C - CI I CI	DICHLOROMETHYLVERATROLE	C <sub>9</sub> H <sub>10</sub> 0 <sub>2</sub> CI <sub>2</sub>	
DICHLOROCATECHOL	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> CI <sub>2</sub>		2,3-DICHLOROPHENOL	C <sub>6</sub> H <sub>4</sub> OCI <sub>2</sub>	
DICHLORODIFLUOROMETHANE	CCI <sub>2</sub> F <sub>2</sub>	F - C CI	1,2-DICHLOROPROPANE	C 3 H6 CI2	CH <sub>2</sub> - CH - CH <sub>3</sub> I I CI Cł
DICHLOROETHANE	C <sub>2</sub> H <sub>4</sub> CI <sub>2</sub>	сі-сн-сн <sub>з</sub> сі	1,3-DICHLOROPROPENE (dichloropropylene)	C3H4 CI2	CI – CH = CH – CH <sub>2</sub> – CI
DICHLOROETHYLENE	C <sub>2</sub> H <sub>2</sub> CI <sub>2</sub>	CI F CH <sub>2</sub> = C CI	2,4-DICHLOROTHIOPHENOL	C <sub>6</sub> H <sub>3</sub> SHCI <sub>2</sub>	CI CI
DICHLOROFLUOROMETHANE	CHCI2 F	H F - Ç - CI CI	DIELDRIN	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub> O	
DICHLOROGUAIACOL	C7H602CI2		3,5-DIETHYLPHENOL	C <sub>10</sub> H <sub>14</sub> 0	
DICHLOROMETHANE (methylene chloride)	CH2CI2	Н СI-С-Н СI	I,5-DIHYDRODIHYDROXY-BENZO (A) PYRENE	с <sub>20</sub> н <sub>14</sub> 0 <sub>2</sub>	
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NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
ETHYLENE OXIDE	C <sub>2</sub> H <sub>4</sub> O	CH <sub>2</sub> - CH <sub>2</sub>	ENDOSULFAN DIOL	C <sub>9</sub> H <sub>8</sub> CI <sub>6</sub> O <sub>2</sub>	
m-ETHYLPHENOL	С <sub>8</sub> Н <sub>Ю</sub> О	C <sub>2</sub> H <sub>5</sub>	ENDOSULFAN SULPHÂTE	C <sub>9</sub> H <sub>6</sub> CI <sub>6</sub> O₄S	$\begin{array}{c} C_1 \\
FENITROTHION	C <sub>9</sub> H <sub>12</sub> NO <sub>5</sub> PS	СН <sub>3</sub> 0 СН <sub>3</sub> 0 СН <sub>3</sub> 0 СН <sub>3</sub> 0 СН <sub>3</sub> 0	ENDRIN	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub> O	
FLUORANTHENE	C <sub>16</sub> H <sub>10</sub>		ENDRIN ALDEHYDE	C <sub>12</sub> H <sub>6</sub> CI <sub>6</sub> O	
FLUORENE	C <sub>13</sub> H <sub>10</sub>		EPICHLOROHYDRIN	C3 H5 OCI	$c_{H_2} - c_{H_2} - c_{H_2}c_{I}$
FLUOROTRICHLOROMETHANE	CCI3F	CI CI — CI F	ETHANE	C <sub>2</sub> H <sub>6</sub>	Сн <sub>3</sub> — Сн <sub>3</sub>
FORMALDEHYDE	н сно	о Н — С — Н	ETHYLBENZENE	С <sub>в</sub> Н <sub>ю</sub>	¢2 <sup>H</sup> 5
GLUCURONIC ACID	С <sub>б</sub> Н <sub>IO</sub> O7	соон он он он	ETHYLENE	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub> = CH <sub>2</sub>
GLUTATHIONE	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> 0 <sub>6</sub> S ⊮	<sup>1</sup> 2 NCHCH <sub>2</sub> CH <sub>2</sub> CONHCHCONHCH <sub>2</sub> COOH I I COOH CH <sub>2</sub> SH	ETHYLENE-I,I'-DIBROMIDE	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	Br - CH <sub>2</sub> - CH <sub>2</sub> - Br
GLYCERINE (GLYCEROL)	с <sub>3</sub> н <sub>в</sub> о <sub>3</sub>	носн <sub>е</sub> снон сн <sub>е</sub> он	ETHYLENE DIAMINE	C <sub>2</sub> H <sub>9</sub> N <sub>2</sub>	NH2 - CH2 - CH2 - NH2
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NAME MOLECULAR FORMUL	A STRUCTURAL FORMULA	NAME MOLECULAR FORMULA	STRUCTURAL FORMUL
2,4-DIMETHYL-3-ETHYLPHENOL C <sub>10</sub> H <sub>H</sub> O {ethylxylenol }		1, 4 - DIHYDROXYANTHRAQUINONE CIA H804	
2,4-DIMETHYLPHENOL (XYLENOL) C <sub>8</sub> H <sub>10</sub> O	он сн <sub>з</sub>	3,4-DIHYDROXY-5-CHLOROTOLUENE C <sub>7</sub> H <sub>7</sub> O <sub>2</sub> CI ( chloromethylcatechol )	сі сн, он
DINITROBENZENE C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	NO2 NO2	DIHYDROXYDIHYDROALDRIN C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> CI <sub>6</sub>	
2,4-DINITRO-6-METHYLPHENOL C7 H6 05 N2	CH <sub>3</sub> NO <sub>2</sub> NO <sub>2</sub>	1,3 - DIHYDROXINAPHTHALENE CIO H8 02	ОН
2,4-DINITROPHENOL C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub>	OH NO <sub>2</sub> NO <sub>2</sub>	2,3-DIHYDROXYTOLUENE C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> (methylcatechol)	СН3 ОН
2,4-DINITROTOLUENE C7H8204	CH <sub>3</sub> NO <sub>2</sub>	2,3-DIHYDROXY-1,4,5-TRICHLOROTOLUENE C7H502CI3	CI CI CI OH
DIPHENYLISODECYL C <sub>22</sub> H <sub>31</sub> PO <sub>4</sub> PHOSPHATE ESTER	ОС <sub>6</sub> Н <sub>5</sub> 1 С <sub>10</sub> Н <sub>2</sub> ) О – Р – ОС <sub>6</sub> Н <sub>5</sub> II О	9,10-DIMETHYLANTHRACENE C <sub>16</sub> H <sub>11</sub>	CH3 CH3
P-DODECYLPHENOL CI8 H30	он (сн <sub>2</sub> ), сн <sub>3</sub>	9,10-DIMETHYLBENZ (A) ANTHRACENE C <sub>20</sub> H <sub>16</sub>	CH <sub>3</sub>
ENDOPEROXIDE C <sub>16</sub> H <sub>14</sub> O <sub>2</sub>	CH3 CH3 CH3	2,4-DIMETHYL-6-tert-BUTYLPHENOL C <sub>12</sub> H <sub>18</sub> O	C(CH <sub>3</sub> ) <sub>3</sub> C(CH <sub>3</sub> ) <sub>4</sub> C(H <sub>3</sub> ) C(H <sub>3</sub> )
ENDOSULFAN C <sub>9</sub> H <sub>6</sub> CI <sub>9</sub> O <sub>3</sub> S	$\begin{array}{c} C \\ C $	7,14-DIMETHYLDIBENZ (A, H) C <sub>24</sub> H <sub>ib</sub> Anthracene c <sub>24</sub> H <sub>ib</sub>	CH <sub>3</sub>

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NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
METHYLETHYL KETONE	C4H80	о II сн <sub>3</sub> - с - сн <sub>2</sub> сн <sub>3</sub>
2-METHYL-4-ETHYLPHENOL	C <sub>9</sub> H <sub>I2</sub> 0 <sup>'</sup>	CH <sub>2</sub> CH <sub>3</sub>
METHYL GUAIACOL	С <sub>в</sub> н <sub>ю</sub> о <sub>2</sub>	CH3 OH
1-METHYLNAPHTHALENE	с <sub>іі</sub> н <sub>ю</sub>	CH <sub>3</sub> CH <sub>3</sub>
I-METHYLPHENANTHRENE	С <sub>15</sub> Н <sub>12</sub>	
METHYLSTYRENE	с <sub>э</sub> н <sub>ю</sub>	CH <sub>5</sub> - CH + CH
METHYLVERATROLE	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	CH3 OCH3 CH
MIREX	C <sup>10</sup> CI <sup>15</sup>	
NAPHTHALENE	C <sub>IO</sub> H <sub>8</sub>	
I-NAPHTHOIC ACID	C <sub>11</sub> H <sub>8</sub> O <sub>2</sub>	Соон

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NAME	MOLECULAR FORMU	ILA STRUCTURAL FORMULA
KETOENDRIN	C <sub>I2</sub> H9 OCI6	
MALEIC ANHYDRIDE	с <sub>4</sub> н <sub>2</sub> о <sub>3</sub>	°°°°°°°°
METHANE	CH4	н — С — н Н Н
9-METHYLANTHRACENE	C <sub>15</sub> H <sub>12</sub>	CH3
3-METHYL-4-tert-BUTYLPHE	NOL C <sub>II</sub> H <sub>IS</sub> O	CH3 C(CH3)3
METHYLCHLORIDE ( chloromethane )	сн <sub>з</sub> сі	H - C - CI
METHYL CHOLANTHRENE	C <sub>21</sub> H <sub>16</sub>	H <sub>s</sub> c
5-METHYL-2,6-dilert-BUTYLI	PHENOL C H 240	CH <sub>3</sub> ) <sub>3</sub> C CH <sub>3</sub>
METHOXYCHLOR	C <sub>16</sub> H <sub>15</sub> Cl <sub>3</sub> O <sub>2</sub>	н, со Сн-Сн-Сросн, ссі,
METHYLENE CHLORIDE (dichloromethane)	CH <sub>2</sub> CI <sub>2</sub>	н С1 — н С1

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	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
	HEXANE	С <sub>6</sub> Н <sub>14</sub>	Н Н Н Н Н Н 1 I I I I H – C – C – C – C – C – H I I I I H Н Н Н Н	HEPTACHLOR	C <sub>10</sub> H <sub>5</sub> CL <sub>7</sub>	
	P-HEXYLPHENOL	С <sub>I2</sub> Н <sub>I8</sub> O	OH CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	HEPTACHLOR EPOXIDE	C <sub>10</sub> H <sub>4</sub> OCI <sub>7</sub>	
	HYDROGEN SULPHIDE	H <sub>2</sub> S	H — S — H	P-HEPTYLPHENOL	C <sub>13</sub> H <sub>20</sub> 0	OH (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>
	2-HYDROXYBIPHENYL	C <sub>12</sub> H <sub>10</sub> O		HEXACHLOROBENZENE	C <sub>6</sub> CI <sub>6</sub>	
	HYDROXYDIELDRIN	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub> CI <sub>6</sub>		HEXACHLOROBIPHENYL	C <sub>6</sub> H <sub>2</sub> CI <sub>6</sub>	cicicici
15-	INDENO (1,2,3-cd) PYRENE	C <sub>22</sub> H <sub>12</sub>		HEXACHLOROBUTADIENE	C <sub>4</sub> CI <sub>6</sub>	CI CI CI CI CI CI CI CI CI C = C - C = C CI
117	ISOPRENE	с <sub>5</sub> н <sub>в</sub>	н н-с-н н   н н н-с=с-с=с-н	HEXACHLOROCYCLOHEXANE	C <sub>6</sub> H <sub>6</sub> CI <sub>6</sub>	
	di-ISOPROPYLETHER	С <sub>6</sub> Н <sub>I4</sub> 0	$\begin{array}{c} CH_{3} \\ H\\ CH_{3} \end{array} \stackrel{H}{\stackrel{l}{\longrightarrow}} \begin{array}{c} CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \end{array}$	HEXACHLOROCYCLOPENTADIENE	C <sub>5</sub> CI <sub>6</sub>	
	o-ISOPROPYLPHENOL	С <sub>9</sub> Н <sub>I2</sub> 0	CH (CH3)	HEXACHLOROETHANE	C <sub>2</sub> CI <sub>6</sub>	CI CI CI - C - C - CI CI CI CI CI
	KETODIELDRIN	C <sub>12</sub> H <sub>8</sub> OCI <sub>6</sub>		HEXADECANE	с <sub>16</sub> н <sub>з4</sub>	сн <sub>3</sub> (сн <sub>2</sub> ) <sub>14</sub> сн <sub>3</sub>

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	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMUL
	NITROBENZENE	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	NO <sub>2</sub>	PARAFFIN	C <sub>n</sub> H <sub>2n + 2</sub>	
	0-NITROPHENOL	C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>	OH NO2	PARATHION	C <sub>10</sub> H <sub>14</sub> NO <sub>5</sub> P <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> 0 C <sub>2</sub> H <sub>5</sub> 0 NO <sub>2</sub>
	m-NITROTOLUENE	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	CH3 NO2	PENTACHLOROANISOLE	с, н <sub>з</sub> о	
	NONYLPHENOL	mixture of alkyl pheno	bls	PENTACHLOROBENZENE	C <sub>6</sub> HCI <sub>5</sub>	
	OCTACHLOROBIPHENYL	С <sub>I2</sub> H <sub>2</sub> CI <sub>8</sub>		PENTACHLOROBIPHENYL	C <sub>12</sub> H <sub>5</sub> CI <sub>5</sub>	
15-11	OCTACHLORONAPHTHALENE	C <sub>IO</sub> CI <sub>8</sub>		PENTACHLOROETHANE	C <sub>2</sub> H CI <sub>5</sub>	CI CI I I CI-C-C-CI I H CI
00	OCTADECANE	С <sub>18</sub> Н <sub>38</sub>	СН <sub>3</sub> (СН <sub>2</sub> ) <sub>16</sub> СН <sub>3</sub>	PENTACHLOROPHENOL	с <sub>6</sub> сі <sub>5</sub> он	
	OCTANE	С <sub>в</sub> н <sub>ів</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	PENTANE	с <sub>5</sub> н <sub>і2</sub>	сн <sub>5</sub> -сн <sub>2</sub> -сн <sub>2</sub> -сн <sub>2</sub> -сн <sub>3</sub>
	P-OCTYLPHENOL	с <sub>14</sub> Н <sub>22</sub> 0	OH L CH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	p-PENTYLPHENOL	с <sub>II</sub> Н <sub>I6</sub> 0	
	OXYCHLORDANE	C <sub>5</sub> H <sub>6</sub> CI <sub>2</sub> O		PERYLENE	C <sub>20</sub> H <sub>12</sub>	

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NAME		MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
PHENANTH	ENE	C <sub>14</sub> H <sub>10</sub>		PROPACHLOR	C <sub>II</sub> H <sub>14</sub> CINO	(cH <sub>3</sub> ) <sub>2</sub> CHNC CH <sub>2</sub> CI
PHENOL		с <sub>6</sub> н <sub>5</sub> он	OH	PROPYLENE	C <sub>3</sub> H <sub>6</sub>	H <sup>2</sup> C = CH-CH <sup>3</sup>
O-PHENYLPI	ENOL	C <sub>12</sub> H <sub>10</sub> O		PYRENE	С <sub>16</sub> Н <sub>10</sub>	(CC)
PHOSGENE		COCI2	0 C – C1 C1	QUINONE	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	
PHOTOALDR	N	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub>		SALICYLIC ACID	с <sub>7</sub> н <sub>6</sub> 03	Соон
15 -1 PHOTODIELD 19	RIN	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub> O		SILVEX	C <sub>9</sub> H <sub>7</sub> CI <sub>3</sub> O <sub>3</sub>	СІ - СН3 сІ - С- СН - СО2 Н
PHTHALIC A	NHYDRIDE	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>		SODIUM DIOCTYL SULFOSUCCINA	NTE C <sub>19</sub> H <sub>35</sub> Ο <sub>7</sub> S Nα	<del></del>
PHYTOL		C <sub>20</sub> H <sub>40</sub> 0		STYRENE	С <sub>в</sub> Н <sub>в</sub>	C <sub>6</sub> H <sub>5</sub> CH = CH <sub>2</sub>
PICLORAM		C <sub>6</sub> H <sub>3</sub> CI <sub>3</sub> N <sub>2</sub> O <sub>2</sub>		2,4,5-T [(2,4,5-trichlorophenoxy) acetic acid]	C <sub>8</sub> H <sub>5</sub> CI <sub>3</sub> O <sub>3</sub>	сі сі - Сі - сн <sub>2</sub> - соон
PORHYRIN		C <sub>40</sub> H <sub>48</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub>	_	TERPENOIDS	approx. C <sub>10</sub> H <sub>16</sub> E up	

	268		Appendix A	Appendix A		269
	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
	TETRABROMOBENZENE	C <sub>6</sub> H <sub>2</sub> Br <sub>4</sub>	Br Br Br	TETRACHLOROPHENOL	C <sub>6</sub> H <sub>2</sub> OCI <sub>4</sub>	
	TETRACHLOROBENZENE	C <sub>6</sub> H <sub>2</sub> CI <sub>4</sub>		TFM (trifluoromethylnitropheno	I) C <sub>7</sub> H <sub>4</sub> F <sub>3</sub> NO <sub>3</sub>	о <sub>2</sub> N-
	TETRACHLOROBIPHENYL	C <sub>12</sub> H <sub>6</sub> CI <sub>4</sub>		THIOPHENOL	с <sub>6</sub> н <sub>6</sub> s	SH.
	TETRACHLOROCATECHOL	C <sub>6</sub> H <sub>2</sub> O <sub>2</sub> CI <sub>4</sub>		TOLUENE	С <sub>7</sub> Н <sub>В</sub>	CH <sub>3</sub>
51	TETRACHLORODIBENZO-P-DIOXI	N C <sub>12</sub> H <sub>4</sub> CI <sub>4</sub> O <sub>2</sub>		TOXAPHENE	approx. C <sub>IO</sub> H <sub>IO</sub> CI <sub>8</sub>	
1	TETRACHLORODIBENZOFURAN	C <sub>12</sub> H <sub>4</sub> CI <sub>4</sub> O		TRIALLATE	C <sub>10</sub> H <sub>16</sub> CI <sub>3</sub> NOS	CH <sub>3</sub> CH 0 H CI CH <sub>3</sub> N-CS-CC - CH <sub>3</sub> CH H
	TETRACHLOROETHANE	C <sub>2</sub> H <sub>2</sub> CI <sub>4</sub>	CI-CH-CH-CI CI CI	TRIBROMOBENZENE	C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub>	Br Br Br
	TETRACHLOROETHYLENE	C <sub>2</sub> Cl <sub>4</sub>	CI CI I I CI-C = C-CI	TRIBROMOMETHANE (bromoform	) CH Br <sub>3</sub>	H Br — C — Br I Br
	TETRACHLOROGUAIACOL	C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> CI <sub>4</sub>		TRICHLOROBENZENE	C <sub>6</sub> H <sub>2</sub> CI <sub>3</sub>	CI CI CI
	TETRACHLOROMETHANE ( carbon tetrachloride )	CCI4	CI CI-CI CI	TRICHLOROBIPHENYL	с <sub>і2</sub> н <sub>7</sub> сі <sub>3</sub>	

	270		Appendix A	Appendix A	
	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA	NAME	MOLECULAR FORMULA
	TRICHLOROCATECHOL	с <sub>6</sub> н <sub>3</sub> 0 <sub>2</sub> сі <sub>3</sub>		TRIMETHYLNAPHTHALENE	C <sub>13</sub> H <sub>14</sub>
	TRICHLOROETHANE	C <sub>2</sub> H <sub>3</sub> CI <sub>3</sub>	CH 2 - CH - CI I I CI CI	TRIMETHYLPHENOL	С <sub>9</sub> Н <sub>12</sub> О
	TRICHLOROETHYLENE	C2 HCI3	CI CI-C+CH-CI	TRINITROPHENOL	C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>7</sub>
	TRICHLOROFLUOROMETHANE	C C I <sub>3</sub> F	F CI - CI CI	TRINITROTOLUENE	C7H5N306
	TRICHLOROMETHANE (chloroform)	сн сі <sub>з</sub>	H 1 CI - Ç - CI CI	VINYL CHLORIDE (chloroethylene)	С <sub>2</sub> Н <sub>3</sub> СІ
15-121	TRICHLOROMETHYL GUAIACOL	C <sub>8</sub> H702CI3	CI CI CI OH	VINYLIDENE CHLORIDE (dichloroethylene)	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>
	TRICHLOROMETHYLVERATROLE	C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> CI <sub>3</sub>	CI CI CI CI OCH <sub>3</sub>	XYLENE	с <sub>в</sub> н <sub>ю</sub>
	TRICHLOROGUAIACOL	C7H502CI3	CI CI OH OCH	XYLENOL (dimethylphenol)	с <sub>в</sub> н <sub>ю</sub> о
	TRICHLOROPHENOL	с <sub>6</sub> н <sub>3</sub> сі <sub>3</sub> о			
	TRIMETHYL BENZENE	С <sub>9</sub> Н <sub>12</sub>	сн, сн,		

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STRUCTURAL FORMULA

сн,

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CH3 NO2

'nо,

H2C : CH - CI

ci H<sub>z</sub> c = c - ci

CH3 CH3

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	COMPOUND:	ACETONE
	FORMULA:	CH <sub>3</sub> COCH <sub>3</sub>
AQUEOU	US SOLUBILITY :	INFINITE
DIELECT	RIC CONSTANT :	20.7 AT 25C
	LOG KOW:	-0.24
	LOG KOC:	
	(FROM SOLUE	BILITY)
	LOG KOC: (FROM KOW)	0.015
MOBILITY CI	ASSIFICATION:	VERY HIGHLY MOBILE
REMARKS :	LOW CONCENTRATE CONCENTRATION ( INTER-LAYER SPA	CAN CAUSE COLLAPSE OF THE

CONDUCTIVITY)

COMPOUND: n-BUTYL ALCOHOL FORMULA: CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub> OH **AQUEOUS SOLUBILITY :** 70,800 mg/L AT 30C DIELECTRIC CONSTANT : 17.7 AT 25C LOG KOW: 0.88 LOG KOC: 0.94 (FROM SOLUBILITY) LOG KOC: 1.02 (FROM KOW) **MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE** NO TENDENCY TO BE ADSORBED BY SOILS **REMARKS** :

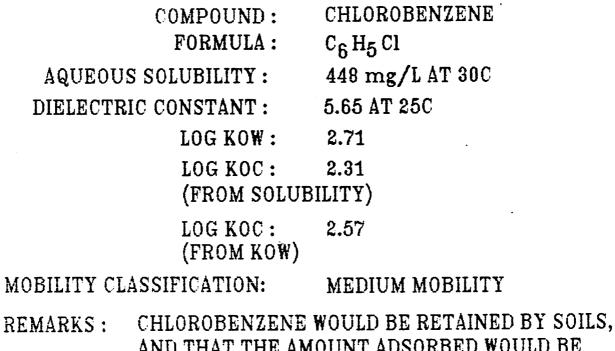
COMPOUND: CARBON DISULFIDE FORMULA: CS2 AQUEOUS SOLUBILITY: 2,940 mg/L AT 20C DIELECTRIC CONSTANT: 2.64 AT 25C LOG KOW: 1.84 LOG KOC: 1.80 (FROM SOLUBILITY) LOG KOC: 1.81 (FROM KOW)

MOBILITY CLASSIFICATION: HIGHLY MOBILE

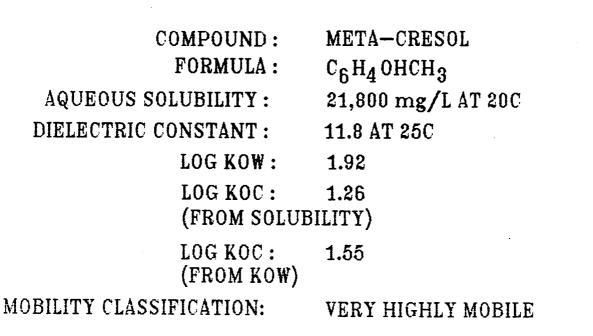
**REMARKS : NO TENDENCY TO BE ADSORBED BY SOILS** 

COMPOUND:	CARBON TETRACHLORIDE
FORMULA:	CCl <sub>4</sub>
AQUEOUS SOLUBILITY :	800 mg/L AT 25C
<b>DIELECTRIC CONSTANT:</b>	2.2 AT 25C
LOG KOW:	2.64
LOG KOC : (FROM SOLUB)	2.15 ILITY)
LOG KOC : (FROM KOW)	2.44
-MOBILITY CLASSIFICATION:	MEDIUM MOBILITY

REMARKS: CARBON TETRACHLORIDE TENDS TO SHRINK CLAYS AND SOILS RELATIVE TO THEIR PHYSICAL SWELLING BEHAVIOR IN WATER. CCI <u>4</u> MAY REDUCE THE HYDRAULIC CONDUCTIVITY OF CLAYS; HOWEVER, CCI<sub>4</sub> COULD CAUSE CLAYS TO FORM CHANNELS THAT WOULD INCREASE THE HYDRAULIC CONDUCTIVITY, AND THEREBY INCREASE ITS MOBILITY



AND THAT THE AMOUNT ADSORBED WOULD BE EXPECTED TO INCREASE WITH AN INCREASING ORGANIC CARBON CONTENT.



REMARKS : META-CRESOL IS NOT RETAINED BY SOILS AND ADSORPTION IS MINIMAL

#### **COMPOUND:** ORTHO-CRESOL FORMULA:

C<sub>6</sub>H<sub>4</sub>OHCH<sub>3</sub>

11.5 AT 25C

**AQUEOUS SOLUBILITY :** 24,000 mg/L AT 20C

**DIELECTRIC CONSTANT:** 

LOG KOW: 1.92

LOG KOC: 1.23

(FROM SOLUBILITY)

LOG KOC: 1.24 (FROM KOW)

**MOBILITY CLASSIFICATION:** 

**VERY HIGHLY MOBILE** 

**REMARKS**: ORTHO-CRESOL IS NOT RETAINED BY SOILS AND ADSORPTION IS MINIMAL

COMPOUND: PARA-CRESOL FORMULA: C<sub>6</sub>H<sub>4</sub>OHCH<sub>3</sub> **AQUEOUS SOLUBILITY :** 19,400 mg/L AT 200 **DIELECTRIC CONSTANT:** 9.9 AT 25C LOG KOW: 1.92 LOG KOC: 1.29 (FROM SOLUBILITY) LOG KOC: 1.27 (FROM KOW) **MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE** 

REMARKS : PARA-CRESOL IS NOT RETAINED BY SOILS AND ADSORPTION IS MINIMAL

- COMPOUND:
- **CYCLOHEXANONE**  $CH_2(CH_2)_4CO$

18.3 AT 25C

- FORMULA: 50,000 mg/L AT 30C
- **AQUEOUS SOLUBILITY :**
- **DIELECTRIC CONSTANT:** 
  - LOG KOW: 0.81

LOG KOC: 1.04

(FROM SOLUBILITY)

LOG KOC: 0.96 (FROM KOW)

**MOBILITY CLASSIFICATION:** 

**VERY HIGHLY MOBILE** 

**REMARKS** : CYCLOHEXANONE WOULD HAVE A VERY WEAK **TENDENCY TO BE RETAINED BY SOILS** 

DIETHYL ETHER **COMPOUND:**  $C_2 H_5 0 C_2 H_5$ FORMULA: 60,050 mg/L AT 25C **AQUEOUS SOLUBILITY:** 4.2 AT 25C **DIELECTRIC CONSTANT:** LOG KOW: 0.77 LOG KOC: 0.99 (FROM SOLUBILITY) 0.96 LOG KOC: (FROM KOW) -MOBILITY CLASSIFICATION: **VERY HIGHLY MOBILE** NO TENDENCY TO BE ADSORBED BY SOIL **REMARKS**:

# COMPOUND: ETHYL ACETATE FORMULA: CH<sub>3</sub> COO C 2 H5 AQUEOUS SOLUBILITY: 85,300 mg/L AT 20C DIELECTRIC CONSTANT: 6.02 AT 25C LOG KOW: 0.73 LOG KOC: 0.89 (FROM SOLUBILITY) LOG KOC: 0.91

(FROM KOW)

MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE REMARKS : NO TENDENCY TO BE ADSORBED BY SOIL

#### **ETHYLBENZENE COMPOUND:** FORMULA: C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>3</sub> 150 mg/L AT 20C **AQUEOUS SOLUBILITY: DIELECTRIC CONSTANT:** 2.41 AT 25C LOG KOW: 3.15 LOG KOC: 2.60 (FROM SOLUBILITY) LOG KOC: 2.87(FROM KOW) **MOBILITY CLASSIFICATION:** LOW MOBILITY

REMARKS: ETHYLBENZENE WOULD HAVE A STRONG TENDENCY TO BE RETAINED BY SOILS, AND THE AMOUNT ADSORBED WOULD BE EXPECTED TO INCREASE DRAMATICALLY AS THE AMOUNT OF ORGANIC CARBON IN THE SOIL MATERIAL INCREASES.

### **COMPOUND:**

FORMULA:

## CH<sub>3</sub>0H

**AQUEOUS SOLUBILITY:** 

**DIELECTRIC CONSTANT:** 

LOG KOW:

0.66

LOG KOC: **MISCIBLE IN WATER** (FROM SOLUBILITY)

**METHANOL** 

32.6 AT 25 C

**COMPLETELY MISCIBLE IN WATER** 

LOG KOC: -0.23(FROM KOW)

**MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE** 

**REMARKS**: NO TENDENCY TO BE ADSORBED BY SOIL

### COMPOUND:

## METHYLENE CHLORIDE CH<sub>2</sub>Cl<sub>2</sub>

FORMULA:

13,200 mg/L AT 200

9.1 AT 25C

DIELECTRIC CONSTANT :

**AQUEOUS SOLUBILITY:** 

LOG KOW: 1.26

LOG KOC : 1.40

(FROM SOLUBILITY)

LOG KOC: 1.40 (FROM KOW)

MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE

**REMARKS :** NO TENDENCY TO BE ADSORBED BY SOIL

#### **COMPOUND:** FORMULA: CH<sub>3</sub>COC<sub>2</sub>C<sub>2</sub>H<sub>5</sub> **AQUEOUS SOLUBILITY :** 270,000 mg/L AT 20C **DIELECTRIC CONSTANT:** 18.5 AT 25C LOG KOW: 0.26 LOG KOC: 0.58 (FROM SOLUBILITY) LOG KOC: 0.55 (FROM KOW) **MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE** NO TENDENCY TO BE ADSORBED BY SOIL **REMARKS**:

**METHYL ETHYL KETONE** 

COMPOUND:	NITROBENZENE
FORMULA:	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>
AQUEOUS SOLUBILITY :	2000 mg/L AT 20C
DIELECTRIC CONSTANT :	34.8
LOG KOW:	1.88
LOG KOC : (FROM SOLUB	1.90 SILITY)
LOG KOC : (FROM KOW)	1.79
RILITY OF A COLDICATION.	

-MOBILITY CLASSIFICATION: HIGHLY MOBILE

REMARKS : NITROBENZENE HAS BEEN SHOWN TO SHRINK CLAYS AND SOILS. THE HYDRAULIC CONDUCTIVITY OF KAOLINITE CAN DECREASE IN CONTACT WITH NITROBENZENE

## COMPOUND:

FORMULA:

AQUEOUS SOLUBILITY : COMPLETELY MISCIBLE IN WATER

DIELECTRIC CONSTANT :

12.3 AT 25C

**PYRIDINE** 

C<sub>5</sub>H<sub>5</sub>N

LOG KOW : 0.55

LOG KOC: MISCIBLE IN WATER (FROM SOLUBILITY)

LOG KOC: 0.84 (FROM KOW)

MOBILITY CLASSIFICATION: VERY HIGHLY MOBILE

**REMARKS : NO TENDENCY TO BE ADSORBED BY SOIL** 

## **COMPOUND: TETRACHLOROETHYLENE**

 $C_2Cl_4$ 

2.35

FORMULA:

150 mg/L AT 20C

DIELECTRIC CONSTANT :

**AQUEOUS SOLUBILITY:** 

LOG KOW : 2.88

LOG KOC : 2.60

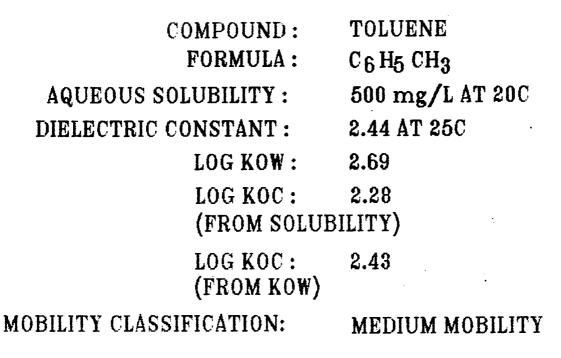
(FROM SOLUBILITY)

LOG KOC: 2.41 (FROM KOW)

**MOBILITY CLASSIFICATION:** 

MEDIUM MOBILITY

REMARKS: TETRACHLOROETHYLENE HAS A FAIRLY STRONG TENDENCY TO BE RETAINED BY SOILS, AND THE AMOUNT ADSORBED WOULD INCREASE AS THE ORGANIC CARBON CONTENT OF THE ADSORBENT INCREASES.



REMARKS: TOLUENE WHEN MIXED WITH ACETONE IS MORE MOBILE THAN IT WOULD BE IN WATER. MANY SOLVENTS ARE MORE SOLUBLE IN SIMILAR ORGANIC SOLVENTS THAN THEY ARE IN WATER.

## COMPOUND:

## 1,1,1 - TRICHLOROETHANE

- FORMULA:
- AQUEOUS SOLUBILITY : 700 mg/L AT 20C
- DIELECTRIC CONSTANT :
  - LOG KOW : 2.47

C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>

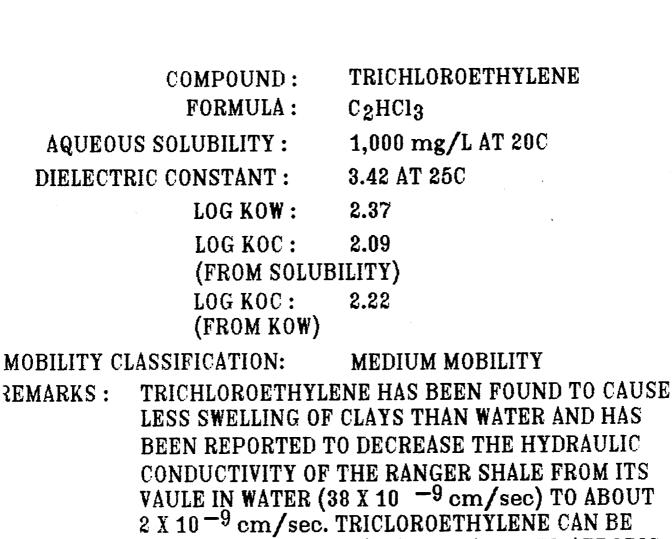
7.1 AT 0C

- LOG KOC : 2.19
- (FROM SOLUBILITY)
- LOG KOC: 2.27 (FROM KOW)

**MOBILITY CLASSIFICATION:** 

MEDIUM MOBILITY

REMARKS: 1,1,1 - TRICHLOROETHANE CAN BE BIODEGRADED UNDER ANAEROBIC CONDITIONS PRODUCING DICHLOROETHANE, WHICH IS MORE MOBILE THAN PARENT TRICHLOROETHANE (LOG KOC = 2.00)



CONDITIONS).

15-142

BIODEGRADED BY SOIL BACTERIA UNDER AEROBIC CONDITIONS (AND POSSIBLY UNDER ANAEROBIC

## COMPOUND:

FORMULA:

 $C_6H_4(CH_3)_2$ 

META - XYLENE

M - XYLENE: 2.44 AT 25C

- 175 mg/L
- DIELECTRIC CONSTANT :

**AQUEOUS SOLUBILITY:** 

LOG KOW : 3.20

LOG KOC : 2.56

(FROM SOLUBILITY)

LOG KOC: 2.91 (FROM KOW)

MOBILITY CLASSIFICATION:

LOW MOBILITY

REMARKS: XYLENE HAS BEEN IMPLICATED AS A SOLVENT THAT CAN INCREASE THE HYDRAULIC CONDUCTIVITIES OF CLAYS AND SOILS OR DECREASE THEM WHEN EXPOSED TO THE SOLVENT.

#### **ORTHO** – XYLENE **COMPOUND:** FORMULA: $C_6H_4(CH_3)_2$ **AQUEOUS SOLUBILITY:** 175 mg/L

**DIELECTRIC CONSTANT:** 0 - XYLENE: 2.57 AT 25C

> LOG KOW: 3.13

LOG KOC: 2.56

(FROM SOLUBILITY)

LOG KOC: 2.55 (FROM KOW)

**MOBILITY CLASSIFICATION:** 

**MEDIUM MOBILITY** 

**REMARKS**: XYLENE HAS BEEN IMPLICATED AS A SOLVENT THAT CAN INCREASE THE HYDRAULIC CONDUCTIVITIES OF CLAYS AND SOILS OR DECREASE THEM WHEN EXPOSED TO THE SOLVENT.

## COMPOUND:

FORMULA:

198 mg/L

DIELECTRIC CONSTANT :

**AQUEOUS SOLUBILITY :** 

P – XYLENE: 2.27 AT 25C

PARA - XYLENE

 $C_6H_4(CH_3)_2$ 

LOG KOW: 3.18

LOG KOC : 2.56

(FROM SOLUBILITY)

LOG KOC: 2.87 (FROM KOW)

MOBILITY CLASSIFICATION:

LOW MOBILITY

REMARKS: XYLENE HAS BEEN IMPLICATED AS A SOLVENT THAT CAN INCREASE THE HYDRAULIC CONDUCTIVITIES OF CLAYS AND SOILS OR DECREASE THEM WHEN EXPOSED TO THE SOLVENT.

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Section 16

# Degradation of Organic Solutes

Lecture by: Richard Meyerhein New Mexico Scientific Laboratory Division

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A PREDICTIVE MODEL FOR POLLUTION

FROM GASOLINE IN SOILS AND GROUNDWATER\*

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#### ABSTRACT

Gasoline and other petroleum products enter soils and groundwater from leaking pipelines and storage tanks, and from accidents involving tank trucks and railroad cars. This type of contamination has become a serious environmental problem in many states. In the unsaturated zone petroleum can penetrate downward rather quickly due to the relatively small amount of water present. In the capillary zone, where the water content steadily increases downward the percolating petroleum will begin to spread out forming a lens of free petroleum on top of the water table. Dissolved constituents can enter the aquifer at this interface and be transported over large horizontal distances in the saturated zone toward water wells away from the original source.

A predictive mathematical model describing the movement of a petroleum product, such as gasoline, in the soil will be obtained. This unique problem is one of multiphase transport (immiscible, air and water phases) with chemical reactions and microbial degradation.

The model has been applied to study the fate and transport of hydrocarbons found in petroleum products such as gasoline trapped in an unsaturated zone. This particular application can help assess the long term threat to underlying water resources posed by the fraction of the petroleum product which remains after remedial efforts have ceased. Thermodynamic equilibrium principles and the role played by oxygen in the biodegradation of hydrocarbons are incorporated into the model. The resulting system of equations is then solved using a finite difference scheme. The results predict the concentrations of each hydrocarbon in all

<sup>\*</sup> Some parts of this study were presented in IAWPRC Seminar on "Degradation, Retention and Dispersion of Pollutants in Groundwater", September 12-14, 1984, Copenhagen, Denmark, and published in the Proceedings.

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phases (water, air, immiscible, adsorbed) in space and time allowing the user to estimate the amounts of hydrocarbons which enter the underlying aquifer or which leave the soil via volatilization into the atmosphere. Such predictions will be presented for selected cases.

Understanding and prediction of gasoline and other petroleum products in soils and groundwater will advance effective recovery and clean-up methods of these contaminants as well as help to assess the risk of potential accidents to water supplies. This will insure the balance between industrial and environmental concerns.

#### INTRODUCTION AND PREVIOUS STUDIES

Gasoline and other petroleum products enter soils and groundwater from faulty storage tanks or leaking pipelines and from accidents involving tank trucks and railroad cars. Most groundwater contamination cases are caused by underground tanks from gasoline stations. Although, in general, the volumes involved at a particular station are not as great as volumes associated with spills beneath refineries and interstate pipelines, the frequency of occurrence and widespread distribution of such incidents are responsible for the concern. In New Jersey, for example, gasoline leaks from service station tanks are the most frequently reported type of groundwater contamination incident (Kramer, 1982). The Pennsylvania Department of Environmental Protection investigated over 200 hydrocarbon spills from 1972-1974 (Osgood, 1974). These are just a few examples among many other contamination cases reported across the United States.

Qualitative descriptions of the migration of the immiscible plume through the unsaturated zone and the entry of dissolved constituents in the saturated zone has been described by several researchers, among others, API (1972), Schwille (1976, 1981) Somers (1974). Holzer (1976) applied Hantush's theory for the movement of a fresh-water lens in an unconfined saline aquifer to the movement of an oil lens in fresh water to identify the probable source area of an oil spill of unknown origin. Van der Waarden et al. (1971) carried out experiments with an oil refinery product as a model for transferable components and with actual petroleum products such as gasoline and kerosene. In all the experiments they found evidence that water extractable components are leached out from an oil zone by trickling water at a rate which is determined by partition coefficients of the compounds and by the water/oil ratio. Van de Waarden et al. (1977) have shown that adsorption reduces concentrations and delays transport. Hoffmann (1970) has solved the classical onedimensional dispersion equation for various point sources of oil contamination with an assumption of a constant exchange rate and contact area. He did not consider the immiscible contaminant but rather considered only dissolved pollutant. Thus, it is no more than another solution of the one-dimensional hydrodynamic dispersion equation. Dracos (1978) has proposed an approach to estimate the spread of an oil slick in soils. By employing simple mass conservation principles, he presented expressions to calculate the maximum spread of the oil polluted area.

#### QUALITATIVE DESCRIPTION OF THE PHENOMENON AND FORMULATION

When significant volumes of petroleum products are introduced, the body of spilled oil can penetrate downward rather quickly through the unsaturated zone. As soon as it reaches the top of the capillary zone, the oil spreads out over the water table. As noted by Schwille (1981), the magnitude and form of the area of spreading depends among other things on the total quantity of oil infiltrated, the infiltration rate, the hydraulic gradient and the permeability of the soil. Another hazardous result of the spill occurs at the same time. Although the petroleum products are "immiscible" with water, this does not mean that the various constituents are absolutely insoluble in water. Solubility differences are observed among the many gasoline constituents. Gasoline and kerosene, for example, exhibit a higher total solubility than heavier products and crudes. In case of rainfall, the percolating water will solubilize some of the oil in the unsaturated zone and carry the dissolved constituents to the groundwater where they can be transported over large horizontal distances in the saturated zone. Very small concentrations of dissolved product make water unfit for domestic use. As noted by API (1972), experiments have shown that, although some of the dissolved constituents may be adsorbed by some types of soil in the saturated aquifer zone, they will be desorbed by relatively cleaner recharge water. The general principles outlined above are illustrated in Figure 1.

In the unsaturated zone transport of the contaminant can occur as solutes in the water phase, vapors in the air phase and as unaltered constituents in the immiscible phase. Phase transfers incorporated into the model are dissolution, adsorption and volatilization. Conservation

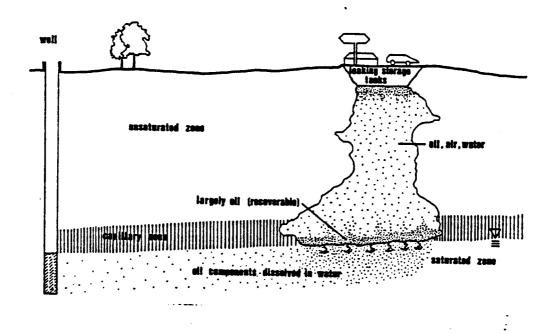


Figure 1. A Petroleum Contaminated Groundwater System

principles expressed in terms of quantifications of the physical, chemical and microbial processes described above lead to a system of governing equations. At the water table, the concentration of the dissolved constituents obtained by solving the system in the unsaturated zone which provides the boundary condition for the contaminant in the saturated zone. As noted above, a generalized mathematical model, incorporating the physical, chemical and biological processes which collectively describe the transport of a reactive and immiscible contaminant in soils and groundwater provide a model for predicting the long term effect of this type of contamination in a given soil/aquifer system. The problem is one of multiphase transport, that is, the contaminant can be transported as solutes in water, vapors in air and as unreacted constituents in an immiscible phase. Conservation principles lead to a system of nonlinear partial differential equations governing the phenomenon.

In the derivation of governing equations, we start from three dimensional macroscopic conservation of mass equations for each phase in the pores. Namely, water, air and immiscible (e.g., gasoline, kerosene) phases occupy the pore volume of the contaminated medium. The simultaneous flow of fluids not totally soluble in one another exhibit distinct fluid-fluid interfaces within the pores (e.g., gasoline, water and air). This type of flow is called immiscible displacement. Here the distinct fluids will be termed phases. The term immiscible phase will be used to refer to a largely unaltered industrial liquid. The immiscible phase, say gasoline, has various constituents like benzene, toluene, xylene, ethyl benzene, cyclohexane, etc. The constituent index, k, ranges from 1 to N. The chemical composition of this phase would differ somewhat from the petroleum product introduced to the ground due to the differing susceptibilities of the constituents composing the phase to various reactions occurring at the phase boundaries (for example, solubilization or microbial degradation). Corapcioglu and Baehr (1985) have obtained the system of governing equations to model the immiscible contaminant transport in soils and groundwater. After various states, they derived the total conservation of mass equation

$$\frac{\partial}{\partial t} \left[ C_{k} \theta_{w} + G_{k} \theta_{a} + I_{k} \theta_{i} + S_{k} \rho_{s} \right] = -\nabla \cdot \left[ \left( q_{w} C_{k} - D_{zkw} \nabla C_{k} \right) + \left( q_{a} G_{k} - D_{zka} \nabla G_{k} \right) + \left( q_{i} I_{k} - D_{zki} \nabla I_{k} \right) \right] - R_{bio}^{k}$$
(1)

where  $C_k$ ,  $I_k$  and  $S_k$  are the concentrations of the kth constituent of the contaminant in the water, air, immiscible and adsorbed phases, respectively,  $\rho_s$  is the soil bulk density,  $\theta_w$ ,  $\theta_a$  and  $\theta_i$  are the volumetric contents for water, air and immiscible phases, respectively,  $g_w$ ,  $g_a$  and  $g_i$  are respective specific discharges, and  $D_w$ ,  $D_a$ ,  $D_i$  the dispersion tensors for the respective phases and  $R_{k_i}^k$  denotes the total rate of microbial degradation.

Equation (1) yields N equations one for each constituent. Fortunately, the system presented above does not need to be solved in full generality to address some important environmental problems. Based on the problem of interest, it can be simplified for a solution. One problem is the transport and fate of an established gasoline plume trapped in the unsaturated zone. In this case, which is of interest in a water quality study, we shall make use of local equilibrium chemistry to express eq. (1) in terms of one dependent variable only. Then, the dependent variables,  $G_k$ ,  $C_k$  and  $S_k$ , can be expressed in terms of the dependent variable,  $I_k$ , so that the total conservation of mass equation can be written in terms of  $I_k$ .

Equilibrium partitioning of constituents between phases

$$G_{k} = \begin{bmatrix} H_{ai}^{k} & \left(\frac{1}{\omega_{k}\sum_{j=1}^{N} \frac{1}{\omega_{j}} \mathbf{I}_{j}}\right) \end{bmatrix} \mathbf{I}_{k}$$
(2)  

$$C_{k} = \begin{bmatrix} H_{wi}^{k} & \left(\frac{1}{\omega_{k}\sum_{j=1}^{N} \frac{1}{\omega_{j}} \mathbf{I}_{j}}\right) \end{bmatrix} \mathbf{I}_{k}$$
(3)  

$$S_{k} = \begin{bmatrix} H_{si}^{k} & \left(\frac{1}{\omega_{k}\sum_{j=1}^{N} \frac{1}{\omega_{j}} \mathbf{I}_{j}}\right) \end{bmatrix} \mathbf{I}_{k}$$
(4)

Then, Eq. (1) would yield to (Corapcioglu and Baehr, 1985)

$$\frac{\partial}{\partial t} \left\{ \left[ \theta_{w} H_{wi}^{k} + \theta_{a} H_{ai}^{k} + \theta_{i} (\omega_{k} \sum_{k=1}^{N} \frac{I_{k}}{\omega_{k}}) + \rho_{s} H_{si}^{k} \right] \left[ \frac{I_{k}}{\omega_{k} \sum_{k=1}^{N} \frac{I_{k}}{\omega_{k}}} \right] \right\}$$

$$= -\nabla \cdot \left\{ \begin{bmatrix} q_{w} H_{wi}^{k} & \frac{I_{k}}{N} & -\frac{D}{zkw} \nabla & \frac{H_{wi}^{k} I_{k}}{N} \\ & \omega_{k} \sum_{k=1}^{k} \frac{\omega_{k}}{\omega_{k}} & \omega_{k} \sum_{k=1}^{N} \frac{I_{k}}{\omega_{k}} \end{bmatrix} \right\}$$

+ 
$$\begin{bmatrix} q_{a}H_{ai}^{k} & \frac{I_{k}}{N} & -\frac{D_{a}}{2ka} \nabla & \frac{H_{ai}^{k}I_{k}}{N} \\ & \omega_{k} & \sum_{k=1}^{N} & \frac{I_{k}}{\omega_{k}} & -\frac{D_{a}}{2ka} \nabla & \frac{H_{ai}^{k}I_{k}}{W_{k}} \end{bmatrix} + [q_{i}I_{k} - \frac{D_{a}}{2ki} \nabla I_{k}] - R_{bio}^{k}$$
(5)

where  $H_{wi}^{k}$ ,  $H_{ai}^{k}$ , and  $H_{si}^{k}$  are the equilibrium partition coefficients for the kth constituent between soil water, soil air, solid phase and the immiscible phase, respectively, and  $\omega_{k}$  is the gram molecular weight of the kth constituent. Equation (5) is a highly nonlinear equation. It will give N equations, one for each constituent. The solution of this equation coupled with Darcy's law for each phase will provide an estimate of the fate of hydrocarbons trapped in the unsaturated zone under assumed equilibrium conditions. Specific discharge terms  $q_w$ ,  $q_a$ , and  $q_i$  will be obtained by solving the conservation of mass equation for water, air, and immiscible phases respectively. The microbial degradation term  $R_{bio}^{K}$  would couple the model with a conservation of mass equation for soll oxygen.

Modeling the microbial reaction rate for the kth constituent,  $R_{bio}^{\kappa}$ in a general manner is not a straight-forward task due to the overwhelming complexity of the microbial ecosystem. Dibble and Bartha (1979) discuss parameters affecting the biodegradation of oil sludges, and in addition to the all important oxygen supply  $R_{bio}^{\kappa}$  will also depend on the populations of all microbes utilizing the kth constituent, the hydrocarbon composition of the various phases (immiscible, water, air, adsorbed), the volumetric content of the immiscible and water phases, areas of contact between the phases, the availability of minerals and macronutrients, and temperature. The dependence of the rate of biodegradation on microbial population is fundamental. Corapcioglu and Haridas (1984) presented a mathematical model in which the equation for bacterial concentration is coupled with another transport equation for the bacterial nutrient seeping in the porous medium. The main emphasis in Corapcioglu and Haridas' model was the simultaneous transport of bacterial population and a nutrient.

As noted earlier, the microbial organisms in the soil will degrade hydrocarbons. In the context of microbial requirements hydrocarbons can serve as energy and carbon sources. Jamison <u>et al.</u> (1976), Raymond <u>et al</u>. (1976) and Huddleston and Meyers (1979) report field and laboratory data collected for studies on petroleum biodegradation and indeed demonstrate that such microbes naturally exist in soils.

Oxygen is required for significant microbial degradation of hydrocarbons which is carried out largely by aerobic bacteria, although degradation at much slower rates can occur under anaerobic conditions, particularly by sulfate-reducing bacteria (Davis, 1967). For the purposes of this model the activity of such anaerobes will be neglected and indeed this is a meaningful approximation to the hydrocarbon utilizing population (Raymond, 1983, personal communication). The optimum conditions of aeration, moisture content, and nutrient availability which hardly exist in nature can be approached artificially in remedial programs for groundwater supplies contaminated by gasoline or other petroleum products. In such programs nutrients and oxygen are added to the groundwater to increase the activity of the naturally occurring bacteria (Chaffee and Weimar, 1983). Researchers in the petroleum industry (Raymond, 1978) have documented success in applying this technique for rehabilitating gasoline contaminated aquifers. Schwille (1976) commenting on investigations of petroleum contamination incidents reports of microbial degradation of petroleum products and the associated reduction zone surrounding the plume where free oxygen is no longer available. This evidence suggests that oxygen, rather than the supply of hydrocarbon, is limiting in such an environment.

Raymond (1983) estimates that 3.5 lbs.of O<sub>2</sub> is required on the average to degrade 1.0 lb. of gasoline hydrocarbons. This is a requirement which precludes rapid biodegradation of hydrocarbons without

supplementing the oxygen which may replenish the contaminated subsurface environment under natural conditions. For a particular soil, other nutrients and minerals required by the microbes may also be limiting; however, the upper limit on degradation imposed by the oxygen shortage is universal.

Oxygen availability is modeled by introducing the conservation of mass equation for total oxygen. Here it is assumed that the free oxygen is partitioned between the air and water phases (oxygen dissolved in immiscible phase is assumed negligible) according to the equilibrium assumption. If the soil air is assumed to be at constant pressure (atmospheric) then the air phase may be assumed to be stationary, that is,  $q_a = 0$ . Then the conservation of mass equation for oxygen is,

$$\frac{\partial}{\partial t} \left[ \left( H_{O_2} \theta_w + \theta_a \right) G_{O_2} \right] + \nabla \cdot \left[ q_w H_{O_2} G_{O_2} - \sum_{z W_{O_2}} \nabla \left( H_{O_2} G_{O_2} \right) - \sum_{z a_{O_2}} \nabla G_{O_2} \right] = - \sum_{k=1}^{N} r_k R_{bio}^k$$
(6)

where  $G_{0}$  is the concentration of oxygen in air phase,  $H_0$  is the Henry's Law  $2^{\circ}$  coefficient relating  $O_2$  to the concentration  $2^{\circ}$  of free oxygen dissolved in water,  $D_w$  is the hydrodynamic dispersion tensor for free oxygen dissolved  $-O_2$  in the water phase,  $D_a$  is the hydrodynamic dispersion tensor for free oxygen in the air  $-O_2$  phase,  $r_k$  is the stoichiometric factor relating the mass of oxygen required to degrade the kth hydrocarbon constituent. In eq. (6), the hydrocarbon utilizing microbes appear as the only oxygen sink in the soil ecosystem. In addition to plants, protozoa, nematodes and earthworms, other microbial populations require oxygen for carrying out processes such as soil organic matter decomposition, nitrification, sulfur oxidation and nitrogen fixation. This activity is most intense near the soil surface, thus a possible technique to account for this significant oxygen demand would be to adjust the surface boundary condition associated with eq. (6), effectively subtracting off an estimate of this oxygen demand. This a tional oxygen demand will be directly dependent upon the biomass of the indigenous soil flora and fauna.

As noted earlier, the dependence of the rate of biodegradation on microbial population is fundamental; however, the inclusion of microbial populations in the model is not necessary to formulate a meaningful approximation to the upper bound for  $R_{bio}^{K}$  due to the critical role of the oxygen supply discussed above. Certainly the upper bound for aerobic degradation is given by the stoichiometric equivalent of the total available free oxygen, anticipating a numerical solution, a discretized version of this upper bound is,

$$R_{bio}^{k}(t) = \min \left\{ \frac{\beta_{k}}{r_{k}\Delta t} \left[ \left( G_{O_{2}}\theta_{a} + H_{O_{2}}\theta_{w} \right) \Big|_{t_{n}} \right], \\ \frac{\left[ \theta_{i}I_{k} + \theta_{w}C_{k} + \theta_{a}G_{k} + \rho_{s}S_{k} \right]}{\Delta t} \Big|_{t_{n}} \right\}$$

$$t_{n} < t < t_{n+1} ; \quad \Delta t = t_{n+1} - t_{n}$$

$$(7)$$

where  $\beta_k$  is a weighting factor for the kth constituent, allocating the available oxygen among the N constituents,

$$0 \leq \beta_{k} \leq 1 \qquad k = 1, 2, \dots N$$
  
subject to 
$$\sum_{k=1}^{N} \beta_{k} \leq 1 \qquad (8)$$

Note that eq. (7) selects for  $R_{bio}^k$  (t)  $\Delta t$  either the allocated stoichiometric equivalent to available oxygen (first argument) or the total amount of hydrocarbon present (second argument), whichever is less. If  $\sum_{k=1}^{N} \beta_k = 1$  then all of the available oxygen is consumed by microbes degrading hydrocarbons.

The value chosen for  $\beta_k$  will reflect the nature of the approximation. For example, the choice  $\beta_k = 0$  represents the most conservative estimate (no microbial degradation for the kth constituent) while  $\beta_k = 1$  would represent the most optimistic estimate (greatest possible microbial degradation for the kth constituent). The case  $\beta_k = 0$  for all k = $1,2,\ldots,N$  allows the model to predict the fate of the immiscible contaminant without considering microbial degradation at all. In this case eq. (7) can be eliminated from the system and  $R_{Lio}^{K} = 0$ ,  $k = 1,2,\ldots,N$ . This option may indeed be the best estimate for  $R_{Lio}^{K}$  for halogenated hydrocarbons (Wilson and McNabb, 1983) as well as for hydrocarbons. A choise of values for  $\beta_k$  so as to provide an intermediate estimate for microbial degradation can be based on data presented by Jamison <u>et al</u>. (1976). This data appears to be the only study which reports such an extensive list of constituent specific data for the microbial degradation of a petroleum product.

RESULTS AND DISCUSSION FOR A SPECIAL SUBPROBLEM

Upon discovery of a subsurface petroleum spill, the rehabilitation plan generally includes an effort to recover the petroleum product standing on top the water table. All of the spilled product is not recoverable, however, leaving behind a significant portion of the total spill as unaccountable or more precisely trapped in the soil. This trapped fraction, immobilized by capillary forces, may represent a long term threat to underlying water resources since over time constituents of the immiscible phase will selectively solubilize (the petroleum product will weather) and be leached down to the groundwater (Figure 1). For the purposes of assessing this long term threat, it is appropriate to assume that the immiscible phase is immobilized (i.e.,  $q_i = 0$ ) or that a

stationary immiscible plume has been established since the source (e.g., leaking tank) would be discontinued and the time required for the immiscible plume to be rendered stationary is small compared to the time for which contaminants remain trapped in the soil. The fate of constituents in the unsaturated zone is truly a three dimensional problem; however, the mass transport of major concern is in the vertical direction either downward towards the water table or upward towards the ground surface. Baehr and Corapcioglu (1985) address this important subproblem by solving the one dimensional (vertical) form of the model equations presented in this paper under the assumption of chemical equilibrium for homogeneous, isothermal soils. At the edge of a plume concentration gradients will exist and a one-dimensional model would be unable to describe the lateral spread of constituents due to diffusion. However, the one-dimensional approximation is a conservative one in that all of the initial mass remains confined to the initial plume boundaries, maximizing the leaching of constituents to the underlying water resource. Baehr and Corapcioglu (1985) have analyzed a finite difference scheme for their numerical solution.

Preliminary findings indicate that the fraction of the initial constituent mass which ultimately finds its way to the groundwater is sensitive to the diffusive properties of the soil (Baehr and Corapcioglu, 1985). Given this sensitivity, unless these properties are determined at a particular site one can only justify the most conservative case where only advective transport is allowed, insuring that all of the initial mass in the contaminated column finds its way to the groundwater. Figure 2 provides constituent fluxes for a hypothetical gasoline for an average recharge rate typical of precipitation rates in the northeastern U.S. (a very conservative estimate for recharge) under these conditions. Figure 3 illustrates the depth profile at given times for the same gasoline assuming the same recharge.

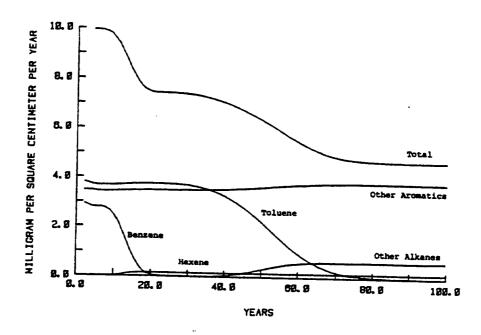


Figure 2. Flux into Aquifer

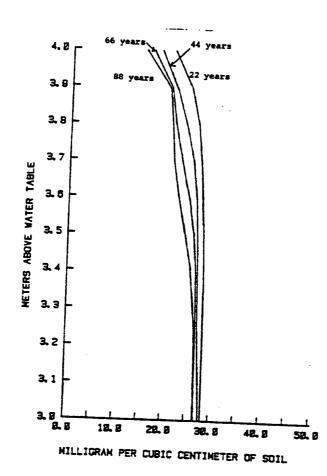


Figure 3. Total Hydrocarbons Remaining in Immiscible Phase

The biodegradation rate is also sensitive to the diffusive properties of the soil as illustrated by Figure 4. The larger the effective diffusion constant for the soil, the more oxygen recharge permitted, allowing for larger estimates of the upper bound for aerobic degradation. The low estimate is based on oxygen recharge dissolved in recharge water only, indicating that air phase oxygen recharge is required to generate significant biodegradation rates.

#### ACKNOWLEDGEMENT

This research has been partially supported by grants from National Science Foundation CEE-8401438, American Chemical Society/The Petroleum Research Fund PRF #15890-AC5, and U.S. Department of Interior G-897/02.

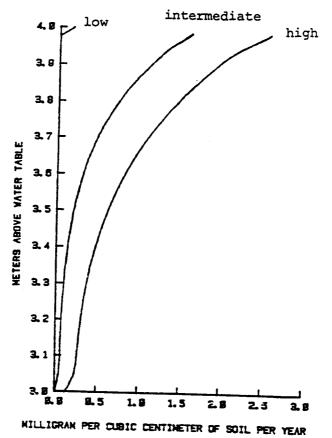


Figure 4. Initial Biodegradation Rate

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Biodegradation of Chlorinated Chemicals in

Groundwater by Methane Oxidizing Bacteria

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#### ABSTRACT

Low molecular weight, volatile chlorinated hydrocarbons are widely distributed in groundwater. The experiments described below were undertaken to demonstrate the feasibility of biodegrading chlorinated compounds in groundwater over a range of environmental conditions. The biodegradation and mineralization of trichloroethylene by methane oxidizing bacteria was demonstrated. Chloroform, vinyl chloride, methylene chloride, isomers of dichloroethylene and ethylene dibromide were also biodegraded. Similar experiments were conducted in groundwater containing both chlorinated compounds and non-chlorinated compounds such as benzene, toluene, acetone and tetrahydrofuran. In the presence of methane oxidizing bacteria, extensive biodegradation of both chlorinated and non-chlorinated chemicals was observed.

Biodegradation was also demonstrated in a saturated soil environment. A laboratory "aquifer simulator" was constructed to model the design of a proposed in situ treatment system which required the recirculation of contaminated groundwater through the aquifer. Trans-1,2-dichloroethylene was chosen as the test compound since it was rapidly biodegraded and produced an immediate product during methanotrophic biotransformation. The intermediate has been identified as trans-1,2-dichloroethylene epoxide and is readily identified during the same GC analysis used for the parent compound. The epoxide is chemically unstable with a half-life of 30 hours. These experiments showed that when methane was added to the aquifer simulator trans-1,2-DCE rapidly disappeared and the epoxide intermediate appeared immediately. The appearance of the intermediate is evidence of the in situ biodegradation in a saturated soil environment.

The development of biodegradation technology for chlorinated chemicals is currently in a field testing stage. A portion of a contaminated groundwater plume has been defined and will be treated with methane, mineral nutrients and oxygen to stimulate growth of methane oxidizing bacteria. Response in this treatment area will be compared to the untreated plume to determine degradation response.

#### 1. INTRODUCTION

#### Contamination of Groundwater by Halogenated Aliphatics

Low molecular weight volatile chlorinated hydrocarbons such as chlorinated ethenes, chlorinated ethanes and chloromethanes are common contaminants of groundwater. The use of these chemicals as solvents by commercial and industrial activities results in their frequent discharge to sewage treatment plants and to surface and ground waters, making their presence almost ubiquitous. These compounds are persistent in the environment and are transported rapidly in groundwater (Chiou <u>et al.</u>, 1979; Roberts <u>et</u> <u>al.</u>, 1978). Their presence in drinking water aquifers is of concern because of their toxicity and demonstrated or suspected carcinogenicity (Infante and Tsongas, 1982; U.S. EPA, 1980). Throughout the Northeastern United States alone, one hundred municipal water supplies have been closed as a result of contamination by these chlorinated hydrocarbons (U.S. EPA, 1983).

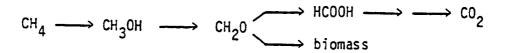
These substances are generally known to resist degradation by conventional biological wastewater treatment processes. As a result, chemicals such as trichloroethylene pass through activated sludge or trickling filter treatment plants and are released to receiving waters, groundwater or air. Removal of the chlorinated aliphatics from groundwater by the conventional methods of activated carbon adsorption and air stripping is often inefficient and expensive. For example, a mixture of vinyl chloride and trichloroethylene can be treated by activated carbon to remove trichloroethylene, but might require further treatment by air stripping to remove vinyl chloride.

#### Biodegradation of Chloroaliphatics by Methane Utilizing Bacteria

We have studied a bacterial mixed culture which grows by oxidizing methane and which can co-oxidize vinyl chloride, vinylidene chloride, all dichloroethylenes, and trichloroethylene (Fogel <u>et al.</u>, 1986). This discovery has significant potential for applications in the field of groundwater and wastewater treatment. In order to realize this potential, however, it was necessary to first demonstrate that these substances are indeed mineralized under proposed treatment conditions, and not simply converted to other toxic substances.

#### Biochemistry of Methanotrophs

Methane-utilizing bacteria oxidize methane first to methanol and then to formaldehyde which can be converted to biomass or to  $CO_2$ .



Most methanotrophs are capable of utilizing only methane and other one-carbon compounds as sole sources of carbon and energy, although a few facultative Methanotrophs have been reported which can also grow on more complex compounds (Lynch <u>et al.</u>, 1980).

The first step in methane oxidation is performed by the enzyme methane monooxygenase which obtains oxygen directly from molecular oxygen (Higgins and Quayle, 1981). Methane monooxygenase is a highly non-specific enzyme as evidenced by the fact that even obligate methanotrophs are able to insert an oxygen into a wide variety of "non-growth" compounds (Dalton and Stirling; 1982). Such oxygenations include hydroxylation of n-alkanes such as ethane, the epoxidation of n-alkenes such as ethylene, and dechlorinations of aliphatic and aromatic substances, including chloromethanes (Harbor et al., 1983; Hou et al., 1979).

### Non-toxic Nature of Biodegradation Products

One of the goals of our research was to determine whether degradation by methanotrophic bacteria is a safe treatment approach for these halogenated aliphatics. We investigated this by either identifying the products/intermediates of biodegradation or by demonstrating their complete mineralization to CO<sub>2</sub>. We evaluated the degradation by methane-utilizing bacteria of 211 halogenated aliphatic compounds which are widely found as contaminants of water supplies (Table I). For the 10 compounds which were oxidized by our bacterial culture, we compiled a list of compounds which might be intermediates or products of the oxidation of these substances, based on a literature review of known products of chemical, mammalian, and bacterial oxidation of chlorinated aliphatics.

	Table I
 Halogenated	Aliphatic Compounds Evaluated
	trichloroethylene tetrachloroethylene cis-1,2-dichloroethylene trans-1,2-dichloroethylene vinylidine chloride vinyl chloride chloroform methylene chloride 1,2-dichloroethene ethylene dibromide 1,1,1-trichloroethylene

#### Predicted Intermediates/Products of Biodegradation

In order to predict the products of biodegradation of chlorinated menes by methanotrophs, we assumed that they are first oxidized to the chlorinated epoxides, since the epoxidation of ethenes by methanotroms has been previously observed (Higgins <u>et al.</u>, 1980; Hou <u>et al.</u>, 1979). Methanotrophs oxidize ethylene by the addition of an oxygen atom across the carbon double bond:

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 $H_2C=CH_2 + 1/2 0_2 ----> H_2C-C_2 0_2$ 

Although ethylene oxide itself is relatively stable, the chlorinated ethylene epoxides are unstable and hydrolyze rapidly in water at neural pH with half-lives on the order of one minute for vinyl chloride epoxide and trichloroethylene epoxide (Guengerich <u>et al.</u>, 1979; Miller & Guengerich, 1982) and about ten minutes for tetrachloroethylene epoxide (Bronsted <u>et al.</u>, 1926).

The hydrolysis products of vinyl chloride epoxide and trichloroethylene epoxide have been previously determined (Guengerich <u>et al.</u>, 1979; Miller & Guengerich, 1982) and are a mixture of chlorinated and non-chlorinated compounds which can be further biodegraded. Vinyl chloride epoxide undergoes spontaneous rearrangement to form 2-chloroac taldehyde and dechlorination to form glycolaldehyde (Guengerich <u>et al.</u>, 1979). Trichloroethylene epoxide hydrolyzes at neutral pH to form a mixture of products: dichloroacetic acid, glyoxylic acid and formic acid (Miller and Guengerich, 1982, 1983; Henschler <u>et al.</u>, 1979). Chloral (trichloroacetaldehyde) is also formed from a rearrangement of an enzyme-bound trichloroethylene epoxide in rat liver (Miller and Guengerich, 1982). The hydrolysis of dichloroethylene epoxides will yield similar products. These hydrolysis products can be further degraded by methanotrophs and other soil microorganisms (Findlay et al., 1987; Leahy et al., 1987).

### Biodegradation in Groundwater

A second goal of our research was to determine whether the biodegradation of chlorinated compounds would occur in groundwater in the presence of other types of chemical contaminants. For this aspect, groundwater from a Superfund site was obtained and inoculated with methane oxidizing bacteria. Mineral nutrients, oxygen, and methane were added and the biodegradation of both chlorinated and non-chlorinated compounds measured over a wide range of concentrations.

### Biodegradation in an Aquifer Simulator

The third goal of our research was to design and operate a bench-scale simulator to demonstrate the biodegradation of trans-1,2-dichloroethylene under aerobic conditions by methane-utilizing bacteria in a soil/water environment. Trans-1,2-dichloroethylene was selected for this experiment because its biological oxidation produces a transient intermediate which

16-18

is readily analyzed by EPA Method 601 (Leahy et al., 1987). The production of this transient intermediate in the aquifer simulator was evidence that trans-1,2-dichloroethylene was actually biodegraded, rather than volatilized or absorbed to the soil (Moore et al., 1987). The use of the simulator allowed the effect of environmental conditions on the biodegradation of trans-1,2-dichloroethylene to be evaluated.

#### Demonstration of Biodegradation under Field Conditions

Our final research objective was to develop a commercial treatment process for biodegrading chlorinated solvents in situ. This effort is supported by EPA's Small Business Innovative Research Program and by internal funding from Cambridge Analytical Associates. The design features of the project are similar to those tested in the aquifer simulator.

### II. MATERIALS AND METHODS

#### Methanotroph Culture

The methane-utilizing culture used in this study (CL-M) was isolated from lake sediments enriched by growth on methane as sole carbon source (Fogel et al., 1986). The culture is capable of degrading trichloroethylene (TCE) and other chlorinated solvents.

The culture is a stable consortium composed of four morphologically distinct bacteria. Three of the bacterial types can be isolated as pure cultures and grown on either yeast extract or methane. These pure strains, however, are not capable of degrading TCE. The fourth strain forms pink colonies on agar plates but the colonies are always superimposed on one of the other colony types. This pink strain can not be isolated as a pure culture. Only the mixed culture containing this pink strain is capable of degrading TCE and <u>only</u> when grown on methane. This evidence indicates that the pink strain is the obligate methanotroph which degrades TCE. Other examples of methanotrophs unable to grow as pure cultures are documented in the literature (Wilkenson & Harrison, 1973; Lidstrom-O'Connor <u>et al.</u>, 1983). These strains are sensitive to the methanol and cell lysis products they produce. Such strains can only grow in the presence of other bacteria capable of acting as scavengers for the by-products that are toxic to the methanotrophs.

#### Culture Conditions

Culture were grown on a mineral salts media (Fogel <u>et al.</u>, 1986), with methane as the sole carbon source. Cultures were maintained in serum bottles capped with Teflon-faced silicon septa. Further details on individuals experiments are given in Results.

### Chemical Analyses

The halogenated aliphatic compounds were analyzed by gas chromatography using EPA method 601 (U.S. EPA, 1984). The analyses were carried out on a Hewlett Packard Model 5890 Gas Chromatograph, with a 6 ft. X 0.25 in. 0D glass column packed with 1% SP-1000 on 60/80 mesh Carbopac-B (Supelco, Inc., Bellefonte, PA). The gas chromatograph was interfaced to a halogen-specific Tracor Hall 700 electrolytic conductivity detector operated in the halogen-specific mode and a model LSC-2 automated purge and trap sample concentrator.

The concentration of CO<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> in the headspace of cultures were analyzed by gas chromatograph on a Hewlett Packard Model 5890 Gas Chromatograph with a 6 ft packed stainless steel Carbosieve column with thermal conductivity detection.

### III. RESULTS

## Biodegradation of Halogen Substituted Aliphatics.

The methanotrophic consortium is able to degrade 10 out of the 11 environmental pollutants tested. Further, the consortium tolerates and degrades these compounds at concentrations as high as 1 to 2 ppm. Most importantly, the concentrations of these compounds can be reduced to a few parts per billion or less as a result of this co-metabolic process. Such treatmeth down to very low concentrations can usually not be achieved by conventional biological treatment.

For each compound tested, cultures were incubated with the test compounds in the presence of 15% (v/v) methane in the headspace. Control cultures were killed with sodium azide to control for abiotic degradation and loss by volatilization. Acetylene, which is a specific inhibitor of the enzyme methane monooxygenase, was added to an additional culture to determine whether the biodegradation of these compounds was dependent on the activity of that enzyme. The data plotted in Figure 1 show the results of representative experiments. The results for the compounds tested are summarized in Table II.

All the test compounds listed in Table II, except tetrachloroethylene (TECE) which is not degraded and 1,1,1-trichloroethane (1,1,1-TCE) which is degraded very slowly, were degraded at concentrations above 1 ppm. Compounds which degraded very rapidly, such as trans-1,2-dichloroethylene can be degraded at concentrations well above 2 ppm. The biodegradation of the ten halogenated aliphatics was inhibited by the addition of acetylene, as shown in Figure 1, confirming that the first step in the biodegradation is the oxidation of the compounds by methane monooxygenase.

We have detected dichloroethylene oxides as transient intermediates in methanotrophic biodegradation of cis and trans-1,2-dichloroethylene

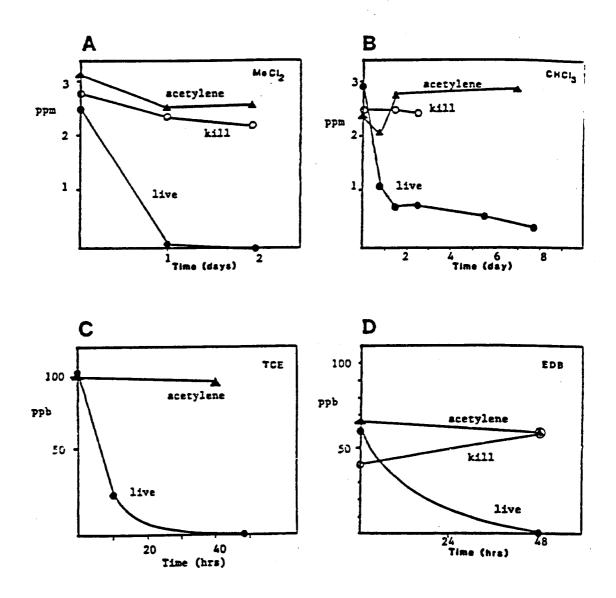


Figure 1. Biodegradation of Methylene Chloride, Chloroform, Trichloroethylene, and Ethylene Dibromide by a Methanotrophic Consortium. Live cultures •; killed cultures containing 20 ug/ml sodium azide, 0; live cultures containing 0.2% (v/v) acetylene.

## Table II

Biodegradation of Halogenated Aliphatic Compounds.

by Methanotrophic Consortium

Compound	Rate of Degradation	
	(nmole/mg/hour)	

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trichloroethylene	2.3
tetrachloroethylene	not degraded
cis-1,2-dichloroethylene	16.8
trans-1,2-dichloroethylene	25.8
vinylidine chloride	0.4
vinyl chloride	14.6
chloroform	5.9
methylene chloride	12.6
1,2-dichloroethene	16.0
ethylene dibromide	1.8
1,1,1-trichloroethylene	0.1

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(Findlay et al., 1987). The corresponding epoxides of trichloroethylene and vinyl chloride were not detected, as expected due to their extremely short half-lives. Mineralization studies of <sup>14</sup>C-radiolabeled trichloroethylene, chloroform, 1,2-dichloroethylene and ethylene dibromide have confirmed that mixed cultures of methanotrophs and soil microorganisms are capable of ultimately converting these halogenated compounds to carbon dioxide and biomass.

## Biodegradation of Mixed Solvents in Groundwater

Groundwater contaminated with chlorinated solvents frequently also contains non-chlorinated solvents. It was, therefore of interest to know whether methane oxidizing bacteria could biodegrade both classes of compounds. To investigate this, goundwater was obtained from an appropriate Superfund site, analyzed, and a treatability study performed. The results are shown in Table 3. The data show that, in addition to the usual array of chlorinated compounds acetone, toluene, benzene, and tetrahydrofuran were present. The results of the treatability study show that both classes of chemicals were biodegraded. Apparently, the methane dizing bacteria were responsible for biodegrading the chlorinated

> Table 3 Biodegradation of Volatile Organics in Groundwater

non-chlorinated compounds.

Compound	0 Hours	36 Hours	87.5 Hours	Killed Contro 184 Hours
methylene chloride	91	8.8*	•	86
1,1-dichloroethane	69	14.8	-	59
trans-dichloroethylene	253	nd	-	225
1,2-dichloroethane	112	nd	-	92
1,1,1-trichloroethane	131	86	-	113
trichloroethylene	477	nd	-	387
tetrachloroethylene	115	100	-	91
benzene	86	nd	-	64
toluene	54	nd	-	38
acetone	1,200	1,000	nd	1000
tetrahydrofuran	500	250	125	400

Concentration (ug/L)

\* blank = 6 ug/L (lab contamination)

nd = not detected

Analyses by EPA Method 601/602

7 chlorinated compounds by EPA Method 601

4 non-chlorinated compounds by EPA Method 602

## Biodegradation of Ethylene Dibromide at Trace Levels in Drinking Water

As mentioned previously, methanotrophic bacteria can reduce the concentration of halogenated compounds to a few parts per billion. We have demonstrated this reduction to less than one part per billion of ethylene dibromide in drinking water (Dooley-Danna et al., 1987). Methanotrophic bacteria, naturally occuring in drinking water contaminated with ethylene dibromide, were shown to degrade ethylene dibromide from 6 parts per billion to below 0.25 parts per billion. Parallel studies with 'C-radiolabeled ethylene dibromide confirmed that the contaminant was mineralized to carbon dioxide and biomass.

Methanotrophic bacteria degrade ethylene dibromide and other halogenated compounds by co-metabolism with methane. Since methanotrophs do not utilize the halogenated compounds as growth substates, these bacteria can degrade these compounds to very low concentrations, as long as methane is provided.

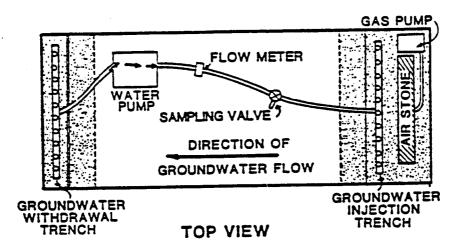
### Aquifer Simulator

This study demonstrated the biodegradation of trans-1,2-dichloroethylene by methanotrophic bacteria during simulated aquifer treatment (Moore <u>et</u> <u>al.</u>, 1987). Although biodegradation of this compound had already been demonstrated in mixed bacterial liquid cultures, it was important to demonstrate that the same process can occur in a saturated soil environment. A laboratory 'aquifer simulator' was constructed to model the design of a proposed in <u>situ</u> treatment system which involves the recirculation of contaminated ground water through the aquifer.

Trans-1,2-dichloroethylene was chosen as the target compound lince it is rapidly biodegraded and generates an intermediate, dichloroethylene oxide, which can be easily detected during methanotrophic biotransformation. This epoxide, which is unstable and degrades with a half-life of approximately 36 hours, provides a unique marker with which to follow biodegradation. Our approach was to add mineral nutrients, methane and bacteria to the aquifer simulator and demonstrate, by the appearance of the epoxide, the potential for in situ biodegradation of chlorinated aliphatic solvents.

A diagram of the bench-scale aquifer simulator used in these experiments is given in Figure 3. The system was designed to represent a portion of a saturated sand aquifer in which groundwater flow is controlled using two gravel-filled trenches, one for the withdrawal of groundwater and the other for re-injection of removed groundwater and dissolution of methane, oxygen, and mineral nutrients. The simulator was constructed from a 30 gallon aquarium filled with sand, pea stone and water to create a water-saturated sand zone underlying an unsaturated zone.

Simulated groundwater withdrawal and injection trenches were created by placing aluminum screens vertically near the ends of the aquarium. In the middle of the two trenches, vertical glass plates were placed to create



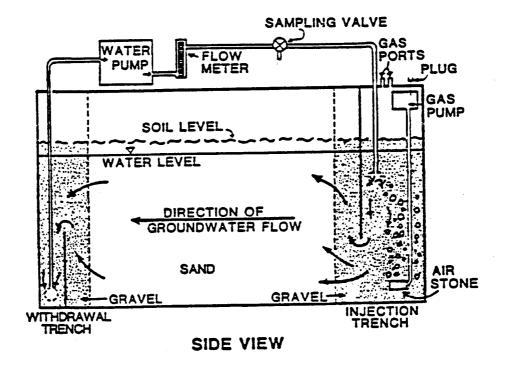


Figure 2. Aquifer Simulator

baffles to improve the uniformity of the water flow through the sand zone. The trenches were filled with pea stone. Tubing installed within the trenches was used to pump water from the withdrawal trench to the injection trench.

Dissolution of methane and oxygen in aquifer water was accomplished by sparging the headspace gas above the injection trench through an air stone in the injection trench and connected by plastic tubing to an aeration pump installed at the top of the injection gas compartment. The entire tank was sealed to minimize volatilization of trans-1,2-dichloroethylene and the epoxide intermediate from the tank. Ports were installed in the tank cover for gas sampling and in the circulation tubing for collection of aqueous samples for analyses.

### Simulator Operation

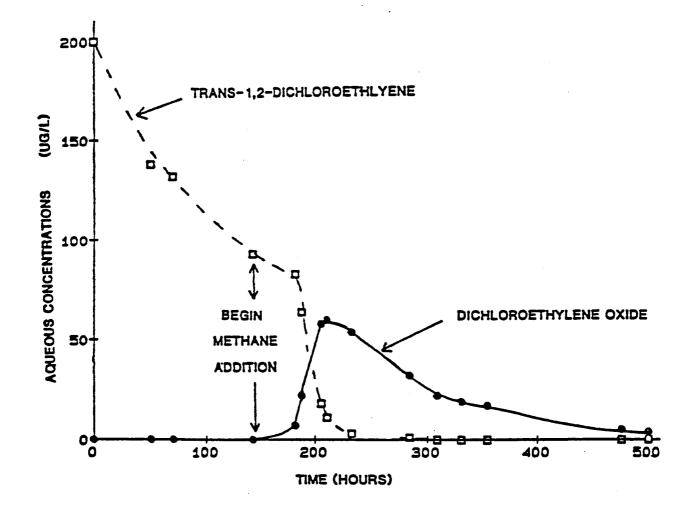
The tank was filled with water containing 1 mg/l of trans-1,2-dichloroethylene. The pump was set to recirculated the simulator water at a liquid hydraulic retention time of one day. The headspace gas was sparged into the trench at a rate of about one liter per minute.

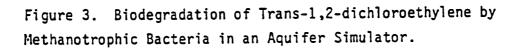
The aqueous concentration of trans-1,2-dichloroethylene in the simulator was monitored initially to determine the effect of volatilization and soil adsorption. The concentration of trans-1,2-dichloroethylene decrease over time to 200 ppb (parts per billion) with no epoxide intermediate formation. This point was arbitrarily picked as Day Zero of the experiment. On Day 6, a mineral nutrient solution was added to the tank. On the same day, methane gas (10 to 20% v/v) added was added to the dissolution compartment headspace. Methane concentrations in the recir ating headspace quickly decreased as methane dissolved into the water. On Day 7, methanotrophic bacteria were added to the tank through the injection trench.

Aqueous samples were taken periodically to monitor changes in trans-1,2-dichloroethylene and dichloroethylene oxide concentrations over time. The concentrations of nitrate and phosphate and the pH of the simulator water were also monitored. The headspace gas was analyzed for methane. Tygen and carbon dioxide.

### Simulator Results

Figure 4 shows the concentrations of trans-1,2-dichloroethylene and the dichloroethylene oxide biodegradation intermediate during the experiment. As this figure indicates, there were substantial losses of the trans-1,2-dichloroethylene from the aqueous solution even before the addition of methane or methanotrophs. These losses are presumably due to soil adsorption and volatilization into the aquarium headspace, as well as possible diffusion through the aquarium seals. However, when mineral nutrients, methane, and methanotrophs were added to the system at 140 hours, the rate of trans-1,2-dichloroethylene loss increased and the epoxide intermediate immediately began to appear. The appearance of this epoxide intermediate confirms the <u>in situ</u> biodegradation by the





### methane-utilizing bacteria.

These results showing epoxide intermediate production and trans-1,2-dichloroethylene reduction are clear indications of biodegradation of trans-1,2-dichloroethylene by the methane-utilizing bacteria in a saturated soil environment. These data are evidence that biodegradation of trans-1,2-dichloroethylene, trichloroethylene, and other chlorinated aliphatics in contaminated soil and groundwater is a feasible bioremediation method and should be attempted under full scale field conditions.

## Field Demonstration Project

We have begun a field demonstration of the application of the technology described in this report to the <u>in situ</u> bioremediation of groundwater and soils contaminated with chlorinated solvents. This project was initially supported by a Phase II U.S. EPA Small Business Innovative Research Grant and is currently supported by Cambridge Analytical Associates, Inc.

Our demonstration project is at a large industrial site which has areas of soil and groundwater contaminated with trichloroethylene, trans-1,2-dichloroethylene and several other chlorinated compounds. The site has an on-going groundwater withdrawal and air stripping remedial operation.

## Proposed Treatment System

Two parallel trenches have been constructed in a contaminated area of the aquifer, one for withdrawal of groundwater (downgradient) and one for injection (upgradient). These trenches are located perpendicular to the groundwater flow direction. Monitoring wells have been placed between the injection and withdrawal trenches (Figure 4).

Nitrogen, phosphorus, methane, and oxygen will be added to the recirculating groundwater to stimulate bacterial activity. We have performed experiments to determine the optimum amount of phosphate needed to overcome the soil adsorptive capacity and to prevent metal phosphate precipitation from occuring. Additional laboratory experiments have been performed to determine the optimal form and concentration of nitrogen. These mineral nutrients will be added from a stock solution tank with a metering or syringe pump to the recirculated ground water after gas absorption and before being injected into the ground. A conservative tracer will also be added to monitor the injected ground water flow.

The injection trench will receive the recirculating groundwater that has been supplemented with mineral nutrients, methane and oxygen. This water will flow downgradient through the contaminated soils and groundwater where methane oxidizing bacteria will degrade the chlorinated solvents contained in the groundwater and soils. Preliminary laboratory studies and test operations have been completed. System operation will commence after initial field measures have been made.

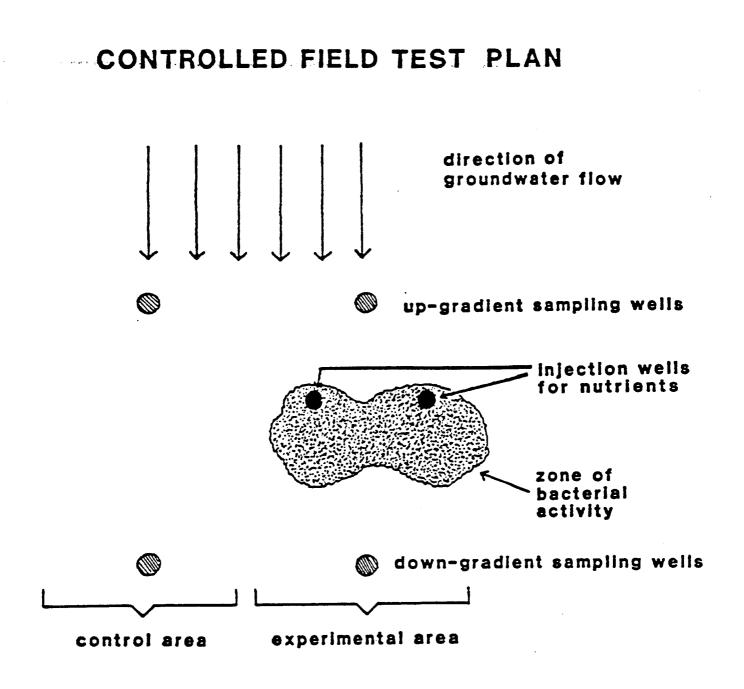


Figure 4. Field Demonstration Schematic.

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### Full Scale Aquifer Remediation

The controlled biodegradation of commonly occuring chlorinated compounds in groundwater holds great promise as a cost-effective in situ treatment technique. The work presented here was designed to demonstrate the technical feasibility and effectiveness of using methane oxidizing bacteria to biodegrade trichloroethylene and related compounds.

Full scale remediation of aquifers contaminated by halogenated solvents could be carried out by either of two strategies. The first, referred to as groundwater recirculation, was illustrated by\_our\_aquifer simulator experiment. This approach would be appropriate for clean-up of recent spills, in which the contamination was contained in a relatively small area.

An alternative approach, the Biological Barrier<sub>TM</sub>, is the subject of a patent application by CAA Bioremediation Systems. This technology would be applied in cases of extensive groundwater contamination involving a plume of dissolved solvent moving off-site or toward a drinking water source. A region of intensive methanotrophic activity would be created in front of the approaching contaminant plume. As the groundwater flowed through this "biological barrier<sub>TM</sub>", the chlorinated solvents would be degraded.

### Acknowl edgments

This material is based upon work supported by U.S. EPA Small Business Innovative Research Grants #68-02-4113 and #68-02-4147, National Science Foundation Small Business Innovative Research Grant ISI-8560700, and corporate funds of Cambridge Analytical Associates, Inc., Boston, MA.

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## Biographical Sketches

### SAMUEL FOGEL

Dr. Samuel Fogel is the Vice President of Bioremediation Systems, a Division of Cambridge Analytical Associates, (CAA). Dr. Fogel is responsible for the coordination of research and commercial development of biological treatment methods to remediate hazardous waste sites.

Prior to joining CAA, Dr. Fogel worked as a Senior Research Scientist at JBF Scientific Corporation where he served as Project Manager working on biodegradation and waste water projects.

His previous experience at ERT, Inc. and Process Research, Inc., includes public health, microbiology, water quality, and sludge management. Also, Dr. Fogel conducted courses at Harvard University and has worked at M.I.T. Dr. Fogel received a B.S. Degree in Pharmacy from Philadelphia College of Pharmacy and Science in Philadelphia, PA, and his Ph.D. in Microbiology/-Biochemistry from The University of Illinois at Urbana, Illinois. Dr. Fogel has authored 2 patents and has written over 25 published articles.

Dr. Fogel is an active member of the American Chemical Society, The Soil Science Society of America, The American Society for Microbiology, and The Society for Industrial Microbiology.

### MARGARET FINDLAY

Dr. Margaret Findlay is the Director of Research and Technology Development for Bioremediation Systems, a Division of Cambridge Analytical Associates, (CAA). Dr. Findlay is responsible for the investigation and development of new bioloigcal treatment systems for hazardous wastes. She directs research in aquifer restoration, as well as soil treatment and bioreactor treatment. She has been closely involved in developing the treatment processes for chlorinated solvents in groundwater and for coal tar in soil and bioreactor systems.

Prior to joining CAA, Dr. Findlay served as Scientific Director for Clivus Multrum, Inc., where she supervised and research on the treatment composting process and participated in product development. Dr. Findlay held a faculty position at Wellesley College where she taught cell biology, physiology, ecology, and marine ecology. She also taught at Harvard University.

Dr. Findlay received a B.A. degreee in Chemistry from Syracuse University, Syracuse, NY, and a Ph.D. in Biochemistry/Microbiology from the University of Illinois, Urbana, Illinois.

#### ALAN MOORE

Mr. Moore has an M.S. Degree from the University of Michigan in Water Resources and a B.S. in Chemistry and Environmental Studies from Trinity College in Hartford, CT. Mr. Moore is currently with Bioremediation Systems, a Division of Cambridge Analytical Associates (CAA) as a Project Engineer/Manager involved in several on-going projects.

Mr. Moore has several project responsibilites concerning environmental site investigations, assessments and remediation activities. He is the author of technical papers on the physical-chemical and biological treatment of contaminated waters and has nine years of experience as an Environmetnal Consultant. Prior to joining CAA, Mr. Moore was employed at Camp, Dresser & McKee as an Environmental Chemist. He is a memeber of the International Association for Water Pollution Control.

#### MAUREEN C. LEAHY

Dr. Leahy received her Ph.D. in Molecular Biophysics and Biochemistry from Yale University, New Haven, CT, and a B.S. degree in Chemistry from Fordham University, Bronx, NY. She is currently Senior Biochemist for Bioremediation Systems, a division of Cambridge Analytical Associates, Boston, MA.

Dr. Leahy has served as project manager for the development of technology related to the biodegradation of chlorinated solvents, petroleum hydrocarbons, and coal tar. Before joining the staff of CAA, Dr. Leahy worked at Yale University as an Associate in Research. She studied bacterial enzyme systems for the repair of DNA damage. Dr Leahy's research for her Ph.D. thesis at Yale was on the metabolic control of enzyme production in bacteria. Dr. Leahy has also worked on the development of assays for the detection of drugs by gas chromatography.

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# IN SITU BIORECLAMATION: A Case History

Gasoline Contamination in Northern Indiana his case history describes the result of a field demonstration of in situ bioreclamation at an area containing petroleum hydrocarbon contamination of soils and ground water created by a leak of approximately 80,000 gallons of unleaded gasoline. The project was conducted from May to November 1984.

The primary focus of the field project was to demonstrate that hydrogen peroxide could effectively supply oxygen to a contaminated aquifer and thereby enhance the natural biodegradation process. Therefore, the scope of the field test was limited to measuring the general efficiency of the bioreclamation process and did not attempt to determine the ultimate level of gasoline removal.

#### Site Description

The site, located in northern Indiana, is a petroleum hydrocarbon storage facility which was contaminated by a gasoline spill five years prior to this demonstration. The spilled gasoline spread rapidly, over a period of days, to cover an area of approximately 200-400 by 600-1,000 feet. Initial free product thickness was less than a foot. During the recovery of free phase material, fluctuations in the water table contaminated the soil over a depth of 6-8 feet. Levels of contamination of the soil ranged in concentration from 300-10,000 parts per million (ppm) gasoline...Leaching of the gasoline into the ground water resulted in a plume of soluble contaminants that extended several hundred feet downgradient from the spill site. The concentration of

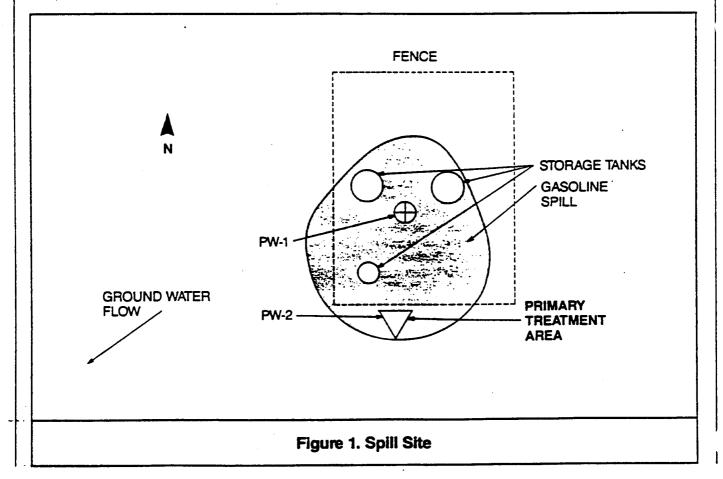
dissolved hydrocarbons was a maximum of 50-60 ppm. Most of the phase-separated hydrocarbon (free phase gasoline) had been recovered prior to the remediation demonstration.

The site is situated on a glacial outwash, consisting primarily of silt, sand and gravel deposits, which resulted from glacier melt and subsequent movement of a large prehistoric river that flowed through the area. On a large scale, there is a high degree of geological continuity, but extensive soil sampling identified significant inhomogeneity which presented some challenges to this project.

A small portion of the hydrocarbon plume was selected for the field demonstration. Selection of the specific location was based on its accessibility and its location away from both the plume edge and source, so that the site would be relatively homogeneous with respect to contamination. Figure 1 shows the spill site and location of the primary treatment area.

#### Procedures

The primary treatment area was hydrologically separated from the surrounding area to prevent migration of any remaining free phase gasoline into the test area. This was accomplished through the use of two concentric triangular injection galleries illustrated in Figure 2. Water from a recovery well (designated PW-2) located at the center of the test zone was injected into the inner triangle gallery. Water from a pumping well (PW-1 in Figure 1) located near the original leak site



and 470 feet upgradient of the test area was the source for the outer gallery. The original test design called for injection rates of 100 gallons per minute (gpm). The resulting hydrologic mounding was intended to protect the treatment zone from intrusion of gasoline and the movement of gasoline out of the test area. Thus, any change in contaminant level would be due to the bioreclamation process. Injection strategies, however, were modified during the test due to a combination of low permeabilities through the galleries and mineral precipitates.

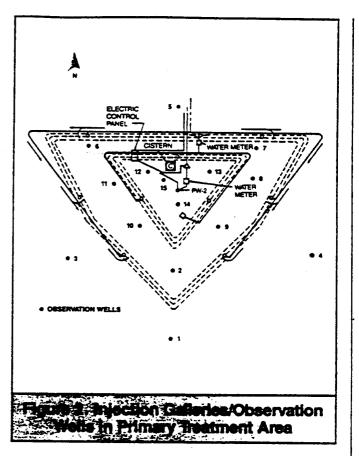
The results of sieve analysis classified the sand as a medium- to fine-grained, well-rounded quartz sand with minor silt and gravel. The silt, although a minor constituent, reduced the intrinsic permeability of the sands. This was especially critical since the highest percentage of silts was found in samples taken near the surface (5-7 feet). This silt had a deleterious effect on the transport of water which was injected just above this low permeability zone.

Another characteristic of the site geology and chemistry that affected the bioreclamation study was the presence of iron, calcium and magnesium in the formation. These materials appeared to form precipitates with the nutrient solution and caused further difficulty with the permeability of the formation.

Consequently, changes were made in the original design and operation. The initial amount of water that could be introduced into the inner gallery was 28 gpm. This decreased to 15 gpm after one month of operation. In order to increase flow to the inner gallery, recirculation water from pumping well PW-1 was introduced into observation wells 12-15 as well as to the cistern (see Figure 2). This increased the average injection rate to the inner gallery up to 20-30 gpm but altered flow patterns and reduced the amount of information that could be obtained from observation wells about the microbial activity. After one month, water addition to the observation wells was terminated, and the injection rate continued to decline.

second approach to improve infiltration rates was then tried. The remote pumping well PW-1 was shut down and water from recovery well PW-2 was pumped to the outer and inner galleries. It was assumed that infiltration in the inner gallery would be increased because more water was being removed from that zone. During this period, the total injection to both calleries dropped from 50 to 20 gpm, at which point, it stabilized. As a consequence of these changes, nutrients were recirculated to the outer gallery, and hydrogen peroxide was added to both galleries. Thus, the area between the galleries received approximately one half the total hydrogen peroxide and more nutrients than was initially anticipated. This is in addition to the indeterminate amounts of nutrients and hydrogen peroxide that moved outward from both galleries.

A third approach to increasing infiltration involved the installation of six injection wells. The new wells were



placed as shown in Figure 3 to have the greatest effect on the low permeability zone. These wells also had the effect of introducing nutrients and hydrogen peroxide more closely to the active zone. The wells were put into service on October 22 and used through November 15, 1984, the last day of the test. The water circulation during this period averaged 20 gpm.

Since none of the attempts to increase infiltration rates to design levels were successful, the original test period was extended to allow a sufficient volume of hydrogen peroxide and nutrients to circulate through the site for easily measurable results. In total, the test was conducted over 180 days. During 129 of those days, hydrogen peroxide addition was at its maximum level (500 ppm).

The progress of remediation was followed by monitoring water samples for both nutrients and microbial activity and by taking periodic core samples to determine hydrocarbon levels.

To provide a background for interpreting the test results, the site was extensively analyzed for residual hydrocarbon levels in the soil, background nutrient levels (ammonium and phosphate), residual dissolved oxygen (D.O.) and initial bacterial count. Soil contamination was determined by ultraviolet analysis of isoctane extracts of soil samples collected at three depths at numerous coring locations. The site was extensively cored during the test with 13 cores taken prior to start-up and 19 cores taken at the completion of the test. Two less extensive intermediate corings were confined to the inner gallery. Water samples were collected throughout the test from 15 observation wells located across the site (see Figure 2).

The test site was divided horizontally into zones (inner—A, between—B and outer—C) as shown in Figure 4. Soil contamination was also measured with depth. A statistical analysis of the initial hydrocarbon levels shown in Table 1 indicated that the gasoline soil contamination was uniformly distributed horizontally across zones A, B and C but not uniformly distributed vertically. The vertical distribution of the contamination was highest at about 25 feet, the average vater table depth for the site. The average hydrocarbon level at 24-26 feet (8,895 ppm) was statistically greater than the levels at 22-24 feet (3,575 ppm) or 26-28 feet (3,993 ppm), as shown in Table 1.

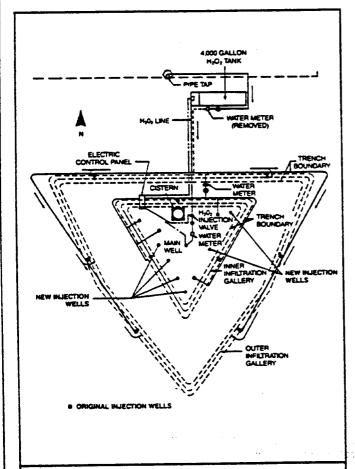
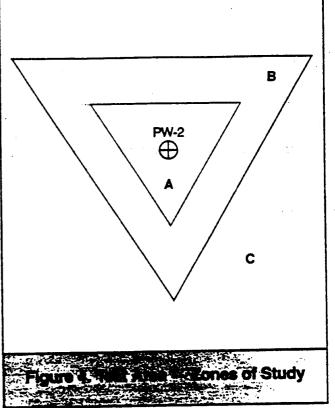


Figure 3. Location of New Injection Wells in Primary Treatment Area (Used Beginning October 22, 1984)

Based on soil analysis, it was estimated that the initial hydrocarbon contamination was 4,200 + /-840 pounds in the inner gallery and 13,400 + /-3,900 pounds between the galleries, or about 17,600 pounds for the total area inside the galleries. Background nutrient levels across the site were less than 1 ppm for both ammonia and phosphate. Residual D.O. levels



were less than 0.4 ppm across the site and averaged -0.2 ppm. Initial bacterial counts were generally low but uniform throughout the site. The total bacteria, as determined on nutrient agar, were on the order of  $1.2 \times 10^3$  colony forming units (CFU)/gram (gm) of soil. Gasoline-utilizing bacteria counted on mineral agar were an order of magnitude less,  $2 \times 10^2$  CFU/gm. There was no statistically significant correlation between bacterial counts and either depth or area. These low initial bacterial counts and oxygen.

After a short period of initial water circulation, microbial nutrients were batch fed to the water being introduced through the inner gallery. These were applied several times weekly by adding a blend of ammonium chloride, monosodium phosphate and disodium phosphate. Once the presence of ammonium and phosphate was observed throughout the area within the inner gallery, hydrogen peroxide was added continuously to the inner gallery feed.

Hydrogen peroxide was used as the oxygen source during the test. It is converted to oxygen through the decomposition process:  $H_2O_2 \rightarrow 1/2 O_2 + H_2O$ , in which one part of hydrogen peroxide supplies a half part of oxygen. Hydrogen peroxide was added continuously since oxygen concentration is typically the limiting factor in the natural degradation of petroleum products. The concentration of hydrogen peroxide was initiated at 100 ppm and gradually increased to a level of 500 ppm. Table 1. Mean Hydrocarbon Level in Contaminated Soil by Horizontal Zone and Vertical Depth

Horizontal Zone	Mean Hydrocarbon Level (ppm)			
A (Inner Gallery)	5,646			
B (Between Galleries)	4,823			
C (Outer Galleries)	6,331			
Vertical Depth				
22-24 ft	3,575			
24-26 ft	8,895*			
26-28 ft	3,993			
*Statistically greater than hydrocarbon levels at other vertical depths.				

## **Results**

he progress of bioreclamation can be followed by several direct and indirect parameters. The presence of nutrients. particularly nitrogen and phosphorus, and bacterial levels were determined as indicators that the subsurface environment had been. suitably modified to promote biodegradation. From initial concentrations of ~1 ppm, the nitrogen and phosphorus levels were increased 10- to 250-fold in the test areas shown in Table 2. The inner gallery area shows the highest concentrations of nutrients since they were added primarily through the inner gallery. Based on additional field experience acquired since this study, it is now recognized that these nutrient levels were excessive and that effective bioreclamation can generally be achieved at substantially lower nutrient levels.

Enumeration of microbial populations in soil and ground water samples demonstrates the impact of nutrient addition on microbial growth and thus indicates that metabolism is occurring. The bacterial counts increased dramatically during the test in response to the addition of nutrients and oxygen. As shown in Table 3, bacterial numbers were highest in the inner gallery where the primary injections of nutrients and  $O_2$ occurred. These bacterial enumerations indicate that significant stimulation occurred where the nutrients were effectively transported.

While measurement of nutrient levels and bacterial populations serve as good indicators of the response of the site to the bioreclamation process, such measurements do not give a direct indication of remediation. Remediation can be tracked only by measuring the change in contaminant level. This was achieved by monitoring the change in hydrocarbon level in soil coring samples. Table 4 summarizes this change in various sections of the test area, clearly showing that there was substantial removal of hydrocarbon contamination during the test. The most significant reduction occurred in the inner gallery. This was expected since this area received the greatest amount of oxygen and nutrients and showed the higher bacterial counts and nutrient levels.

The changes in hydrocarbon levels were statistically analyzed (>95 percent confidence level) to confirm that they were real and not simply due to the inherent variability of the initial gasoline levels. An analysis of variance procedure was used to compare data from all corings and to establish that the inner gallery (Test Area A) underwent a continued and statistically significant decrease in hydrocarbon level over the course of the study. Because of the lack of intermediate coring data for the zones between the galleries and the outer gallery, the initial and final coring results were used to show that the hydrocarbon reduction in these test areas was also statistically significant.

The utilization of hydrogen peroxide was measured as well since a key objective of the test was to examine the effectiveness of hydrogen peroxide as an oxygen source for bioreclamation. Because some of the hydrogen peroxide introduced into the inner gallery flowed toward the outer gallery, it is estimated that 10,800 pounds of hydrogen peroxide were utilized in the larger area between the galieries (Test Area B), and 6,400 pounds were utilized in the inner gallery (Test Area A). Table 5 shows a summary of the pounds of hydrogen peroxide utilized compared with the pounds of gasoline degraded for these two zones. Note that the ratios for the pounds of hydrogen peroxide to pounds of gasoline degraded were 2:2 for the inner gallery and 1:2 for the area between the galleries. These figures do not take into account gasoline degraded outside of both galleries; therefore, assessments of the degradation and utilization of hydrogen peroxide are conservative.

Table 2. Nutrient Levels During Test				
Test Area	Nitrogen, ppm	Phosphorus, ppm		
A (Inner Gallery)	100-250	100-250		
B (Between Galleries)	50-200	60-250		
C (Outer Galleries)	10- 50	1- 10		

Table 3. Bacterial Counts During Test				
Test Area	Total Bacteria CFU/gm Soil	Gasoline Utilizers CFU/gm Soil		
A (Inner Gallery)	13.8 X 10 <sup>6</sup>	1.1 X 10 <sup>6</sup>		
B (Between Galleries)	8.0 X 104	1.4 X 104		
C (Outer Galleries)	6.6 X 10 <sup>3</sup>	5.3 X 10 <sup>2</sup>		

## the L Hydrocarbon Lavest During Test

Test Area	Mean Hydrocarbon Level (ppm)		
	Initial	Final	Reduction
A (Inner Gallery)	5,646	665	88%
B (Between Galleries)	4,823	1,750	64%
C (Outer Galleries)	6,331	2,361	63%

Test Area	H <sub>2</sub> 0 <sub>2</sub> (lbs)	Gasoline Degraded (lbs)	Ratio of H <sub>2</sub> 0 <sub>2</sub> to Gasoline (lbs)
A (inner Gallery)	6,400	2,974	2:2
B (Between Galleries)	10,800	9,140	1:2

## Conclusions

**he use** of hydrogen peroxide is an effective means of supplying oxygen during an in situ bioreclamation process.

In situ bioreclamation is effective in reducing residual hydrocarbon soil contamination.

In situ bioreclamation requires close supervision and understanding of site hydrology and chemistry to ensure proper transport of nutrients through the contaminated zone.

> This paper presents data collected from a study by the American Petroleum Institute (API) and FMC Corporation. The report prepared in conjunction with this study is currently undergoing review by the API. As such, the interpretations and conclusions presented in this paper are not necessarily endorsed by the API. This case history has been prepared by Aquifer Remediation Systems, which was formed as an operating group of FMC Corporation in 1984 and was acquired by International Technology Corporation (IT) in 1986. IT/Aquifer Remediation Systems maintains offices at 30 Plainsboro Road, Plainsboro, NJ 08536.

# ENVIRONMENTAL DEGRADATION OVERVIEW

15-1

- \* CONTAMINANT REMOVAL (NOT ALWAYS GOOD)
- \* METHODS OF CONTAMINANT REMOVAL
- **\* ENVIRONMENTAL REACTIONS**
- **\* ENZYME KINETICS**
- **\* CHEMICAL DEGRADATION SCHEMES**
- \* MAJOR FACTORS AFFECTING BIOTRANSFORMATIONS
- \* LIMITATIONS OF THEORETICAL CALCULATIONS

15-2

## TOXICITY OF DEGRADATION PRODUCTS

F-CH<sub>2</sub>-COOH

CI-CH<sub>2</sub>-COOH

FLUOROACETIC ACID (TOXIC)

CHLOROACETIC ACID (NOT TOXIC)

# F-CH<sub>2</sub>-CH<sub>2</sub>-COOH

FLUOROPROPIONIC ACID (NOT TOXIC)

# F-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH

**FLUOROBUTYRIC ACID (TOXIC)** 

IT IS VERY DIFFICULT TO PREDICT THE TOXICITY OF AN ORGANIC MOLECULE BASED ON STRUCTURE. FLUOROACETIC ACID (2 CARBONS)(ALSO KNOWN AS "1080") IS VERY TOXIC - IT INTERFERES WITH THE ENERGY PRODUCTION IN THE TRICARBOXYLIC ACID (KREBS) CYCLE. CHLOROACETIC ACID IS NON-TOXIC BECAUSE THE CHLORINE ATOM IS TOO LARGE TO "FIT" INTO THE ENZYME INVOLVED. FLUOROBUTYRIC ACID (4 CARBONS) IS TOXIC BECAUSE IT IS EASILY CONVERTED INTO FLUOROACETIC ACID. FLUOROPROPIONIC ACID (3 CARBONS) IS NON-TOXIC BECAUSE IT IS NOT CONVERTED INTO FLUOROACETIC ACID.

LIKEWISE, DEGRADING TRICHLOROETHANES OR DICHLOROETHENES TO VINYL CHLORIDE IS NOT A DESIRABLE PROCESS.

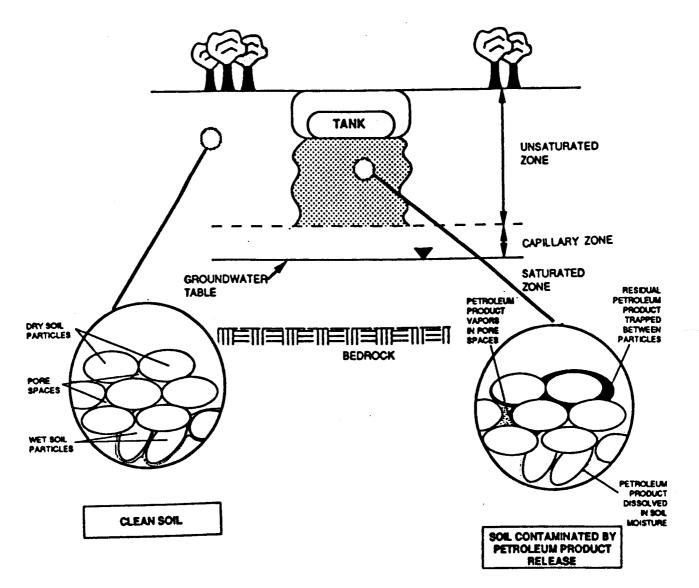
16-3

# PHYSICAL LOSS OF ORGANIC CONTAMINANTS

- **\*** EVAPORATION
- **\*** ADSORPTION
- **\*** DILUTION / DISPERSION

THERE ARE MANY FACTORS WHICH INFLUENCE THE PHYSICAL MOBILITY OF A CHEMICAL CONTAMINANT IN THE SUBSURFACE, INCLUDING WATER SOLUBILITY, VISCOSITY, DENSITY, AND VAPOR PRESSURE OF THE CHEMICAL CONTAMINANT; AND THE POROSITY, PERCENT CARBON AND/OR CLAY CONTENT OF THE SUBSURFACE ENVIRONMENT.

# THREE CONTAMINANT PHASES IN THE UNSATURATED ZONE

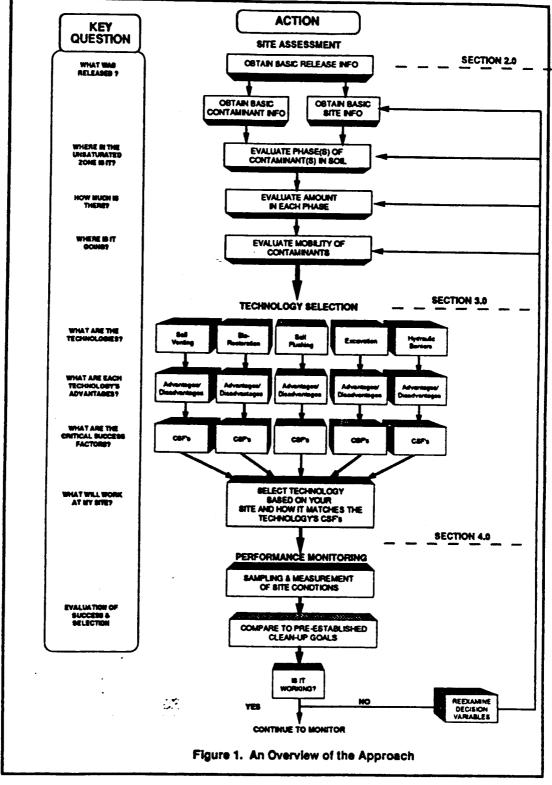


When petroleum products are released into the subsurface, they move primarily by gravity down through the unsaturated zone, with only a minor horizontal movement (away from the release source) due to dispersion and capillary forces. As the plume encounters the capillary zone above the water table, the weight of the plume depresses first the capillary zone and then the water table. The liquid product forms a pancake shape on top of the water table as the plume is drawn down by gravity. The floating plume will then be confined to horizontal flow, usually in the same direction as the groundwater.

15-4

15-5

# SELECTION OF REMEDIATION TECHNOLOGIES



(Lyman, et al., 1990)

15-6

# **DISTRIBUTION IN THE UNSATURATED ZONE**

FACTOR	UNITS	SITE OF			
RELEASE- RELATED		*			
• Amount Released	gellons		<b>3mai</b> (<100)	Medium (100-1000)	Large (>1000)
			0	0	0
• Rate Of Rolanse			Slow Release O	 0	Instantaneou Release O
• Time Since Release	months		Long (>12) O	<b>Moclum</b> (1 - 12) O	Short (< 1) O
SITE - RELATED	ang set y		i giby a constant anna		•
• Depth To Groundwater	metera		Shalow (< 1) O	Međum (1-5) O	Deep (>5) O
• Hydraulic Conductivity	cm/sec		High (>10 <sup>-3</sup> ) O	Medium (10 <sup>-4</sup> -10 <sup>-3</sup> ) O	Low (<10 <sup>-4</sup> ) O
• Reinfell Inflitration Rate	cm/day		High (s0.1) O	Medum (0.05 - 0.1) O	Low (⊲0.05) O
• Soll Temperature	<b>~</b> C		Warm (5-20) O	Medium (10 - 20) O	Cool (<10) O
• Sall Sorption Capacity (Surface Area)	m <sup>2</sup> Ag		Low (40.1) O	Medium (0.1 - 1) O	High (>1) O
CONTAMINANT- RELATED	1				
• Liquid Viscosity	cP		۲۵۳ (۷۶) 0	Medum (2-20) O	High (>20) O
• Liquid Deneity	g/cm <sup>3</sup>		High (>2) O	Medum (1-2) O	Low (<1) O
• Vapar Pressure	mm Hg		High (>100) O	Medium (10-100) O	Low (<10) O
• Water Solublity	mg/L		High (>1000) O	Medium (100-1000) O	Low (<100) O

(Lyman, <u>et al</u>.,1990)

15-7

- C

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Γ

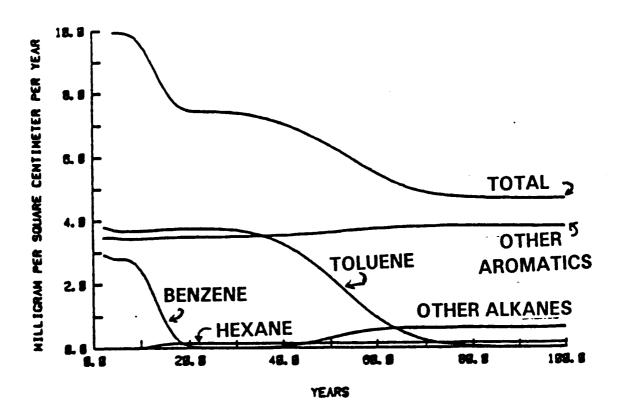
## CONTAMINANT VAPORS IN THE UNSATURATED ZONE

		CONTAMINANT UNSATURATED		G	
FACTOR	UNITS				
RELEASE- RELATED					
• Amount Released	gallons		Small (<100)	Medium (100-1000)	Large (>1000)
			0	0	0
• Rate Of Release			Slow Release O	 0	Instantaneous Release O
• Time Since Release	months		Long (>12) O	Medium (1-12) O	Short (< 1) O
SITE - RELATED					
• Depth To Groundwater	meters		Shallow (< 1) O	Međum (1-5) O	Deep (>5) O
- Air Conductivity	cm/sec		High (>10 <sup>4</sup> ) O	Međum (10 <sup>-6</sup> -10 <sup>-4</sup> ) O	Low (<10 <sup>4</sup> ) O
• Raintali Infiltration Rate	cm/dey		High (>0.1) O	Međum (.005-0.1) O	Low (<0.05) O
• Soil Temperature	<b>*C</b>		Cool (<10) O	Medium (10 - 20) O	Warm (>20) O
Sail Sorption Capacity     (Surface Area)	m²/g		Low (<0.11) O	Medium (0.1 - 1) Q	High (>1) O
CONTAMINANT- RELATED					
• Liquid Viscosity	сP		High (>20) O	Međum (2-20) O	لعب (ف) O
• Liquid Density	g/cm <sup>3</sup>		High (>2) O	Međium (1-2) O	Low (<1) O
• Vapor Pressure	mm Hç		Low (<10) O	Medium (10-100) O	High (>100) O
• Water Solubility	mg/L		High (>1000) O	Međum (100-1000) O	Low (<100) O

(Lyman, <u>et al</u>.,1990)



# **FLUX INTO AQUIFER**



(Baehr and Yavuz, 1984)

Baehr and Yavuz used theoretical equations to predict the flux into the aquifer of various components of "a hypothetical gasoline for an average recharge rate typical of precipitation rates in the northeastern U.S. (a very conservative estimate of recharge) under these conditions."

15-9

# **TERMS AND DEFINITIONS**

## **\* BIOTRANSFORMATION**

The transformation of an organic compound which has been biologically mediated. It could mean making an organic molecule larger, smaller or just changing the structure.

## \* **BIODEGRADATION**

Biodegradation generally means making an organic molecule smaller through biological activity.

## \* PARTIAL DEGRADATION

Partial degradation means to change an organic molecule while not completely degrading it to carbon dioxide and water.

## \* MINERALIZATION

Mineralization generally means the complete change of an organic compound to carbon dioxide, water, ammonia, etc.

## \* ULTIMATE DEGRADATION

Utimate degradation is the same as mineralization (the complete change of an organic compound to inorganic compounds.

15-10

# **TERMS AND DEFINITIONS**

## \* CONSORTIA

A consortia of microbes is the collective sum of all microorganisms (a mixed population). This is usually used when one doesn't know what microbes are present and/or actively doing the biodegradation.

## \* HETEROTROPHIC

Heterotrophic microbes require organic compounds for both their carbon source and for energy production.

## \* AUTOTROPHIC

Autotrophic microbes use carbon dioxide for their carbon source but use inorganic compounds or light for energy production.

## \* CO-METABOLISM (SECONDARY UTILIZATION)

Co-metabolism is a term used to indicate the metabolism of a compound along with the "primary" compounds used as a food source. Frequently this appears to be the "accidental metabolism of some compound which is structurally similar to the main food. This appears to be very important in the degradation of chlorinated and aromatic compounds which microbes do not normally use as their primary food source.

15-11

# BIOLOGICAL TRANSFORMATION OF ORGANIC CHEMICALS

# \* AEROBIC

Aerobic bacteria require molecular Oxygen as an electron acceptor for their metabolism and thus their survival. Strict Maerobes will die in the absence of oxygen. In general hydrocarbon fuels are relatively rapidly degraded under aerobic conditions. Most aerobic microbes do not easily degrade halogenated organic compounds.

# \* ANAEROBIC

Anaerobic bacteria can live in the absence of oxygen and use inorganic compounds or  $CO_2$  as electron acceptors in order that they might oxidize organic compounds for energy. Strict anaerobes will die in the presence of oxygen. Typically the metabolic rate for the degradation of hydrocarbon fuels by anaerobes is much slower than for aerobes. However, even though the rate is relatively slow many anaerobes seem to possess the necessary enzyme systems for the degradation of chlorinated compounds.

# \* METHANOTROPHIC - gerobec

Methanotrophic bacteria are a special class of aerobes which require methane as their carbon source and oxygen as their electron acceptor. This type of bacteria also seems to be very efficient in the degradation of <u>small chlorinated molecules</u>. Although they could not "live" on the chlorinated hydrocarbons they co-metabolize the chlorinated compounds with methane. There has been considerable interest in these microbes because it is possible to encourage the growth of these bacteria throughout a treated volume by saturating the soil alternately with oxygen and methane. This reduces the rampant growth of microbes near the wells supplying the nutrients, which tend to plug the infiltration wells.

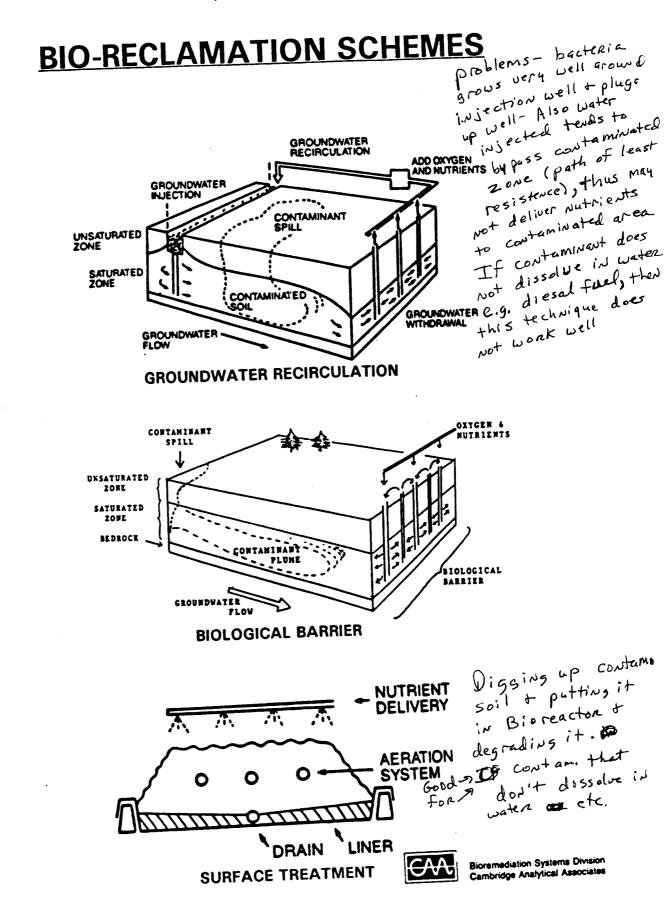
15-12

# AEROBIC DEGRADATION BY METHANOTROPHIC BACTERIA

<u>Compound</u>	Methanotrophic Degradation Rate <u>n moles/mg/hr</u>
trans-1,2-Dichloroethene	25.8
cis-1,2-Dichloroethene	16.8
Vinyl Chloride	14.6
Methylene chloride	12.6
Chloroform	5.9
Trichloroethene	2.3
Ethylenedibromide	1.8
1,1,1-Trichloroethane	0.1

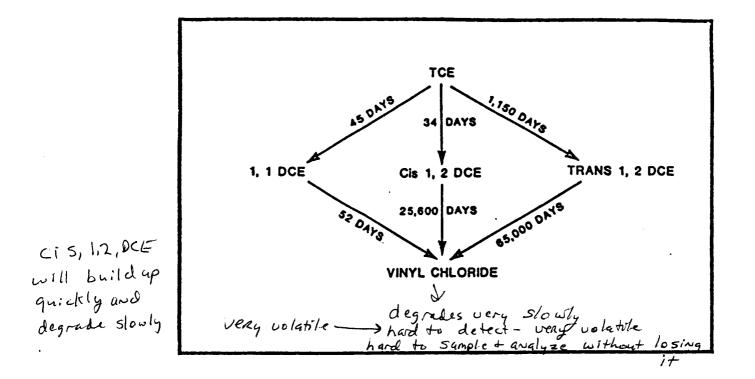
## **From Fogel**

Be cautions of using degradation rates from literature at your site. They are very site specific. Lab derived degradation rates will be optimum rates where ideal conditions 15-13



15-14

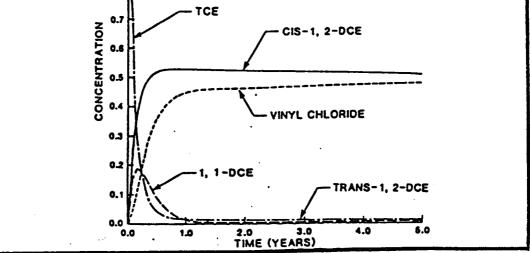
# A DEGRADATION REACTION OF TRICHLOROETHYLENE



#### EPA GROUND WATER MONITORING SERIES CERI-87-8

LANL is using I I to analyze TCE spill photo a constric analyzer - field analyze viny / chloride -(developed for a gualyzing viny 1 chloride in work environm) 405HA

Above is an example of the degradation of trichloroethylene with half lives for degrading to the various products. I have been unable to determine where the EPA obtained the half lives listed so the above times should be used only as an example of how a product plume might change in its composition and/or concentrations. Although one can find many reaction half lives in the literature, one should be very cautious in assuming that those times will apply in all/any situations. Frequently degradation schemes as above will vary depending on the type/abundance of microbes which can depend on soil moisture, oxygen and many other factors.

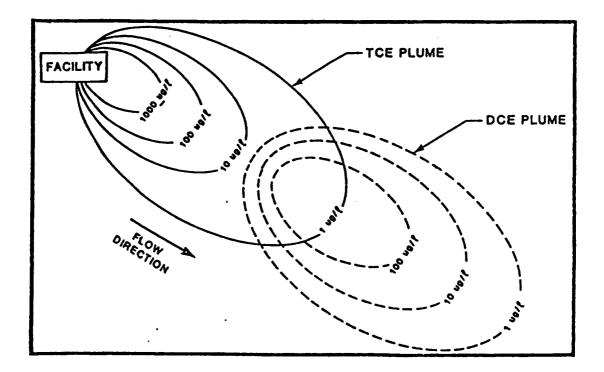


#### EPA GROUND WATER MONITORING SERIES CERI-87-8

Any time that a compound decays to a variety of different products at different rates the composition of the product plume will change with time. In some cases one would not be surprised to not find the original product after a period of time. It is often necessary to know and understand the decay scheme of chemicals in order to understand the analytical results as associated with the site history and geology. Again please don't assume that all sites will have the reaction rates shown above.

# CONTAMINANT PLUMES SHOWING MOVEMENT OF DEGRADATION PRODUCTS

15-15



#### EPA GROUND WATER MONITORING SERIES CERI-87-8

One should be aware that a plume of one compound will not move at the same rate as that of another compound. If there isn't a continuous source for the TCE plume (such as a lot of undissolved pure TCE) separate and distinct plumes will be generated for the various degradation products (TCE, DCE, & Vinyl chloride).

15-16

# **ENVIRONMENTAL REACTIONS**

Abiotic

- \* SUBSTITUTION
- \* DEHYDROHALOGENATION
- **\*** OXIDATION
- \* **REDUCTION**
- **\* DECARBOXYLATION**

The above classes of reactions can take place both abiotically and with biotic intervention. In general the reaction conditions (temperature, concentration, pH, etc. are sufficient for these reaction to take place without biological (enzymatic) help to increase the rate of the reactions.

15-17

# I SUBSTITUTION REACTIONS

Abiotic

\* SOLVOLYSIS (HYDROLYSIS)

ALKYL HALIDES Achide Group  $R-X^{L} + H_2O ----> R-OH + H-X$ 

NITRILES

 $R-CH_2-CN + H_2O ----> R-CH_2-COOH + NH_3$ 

**ESTERS** 

 $R-COOR' + H_2O ----> RCOOH + HOR'$ 

AMIDES

 $R-COONR'_2 + H_2O ----> RCOOH + HNR'_2$ 

15-18

# **HYDROLYSIS REACTIONS ABIOTIC**

# $R-X + H_20 ----> R-OH + H-X$

WHERE X = A HALOGEN (CI or Br) The greater the amount The greater the the of chlorise the half life longer the half life **R-** = AN ORGANIC MOLECULE and

COMPOUND HALF LIFE

- H<sub>3</sub>C-Cl ~ 1 MONTH
- H<sub>2</sub>CIC-CI ~ 700 YEARS

HCCl<sub>2</sub>-Cl ~ 3,500 YEARS

~ 7,000 YEARS Cl<sub>3</sub>C-Cl

IN GENERAL Br > CI and SH<sup>-</sup> > OH<sup>-</sup> and Hydrolysis is **pH DEPENDANT** 

15-19

# **II DEHYDROHALOGENATION REACTION**

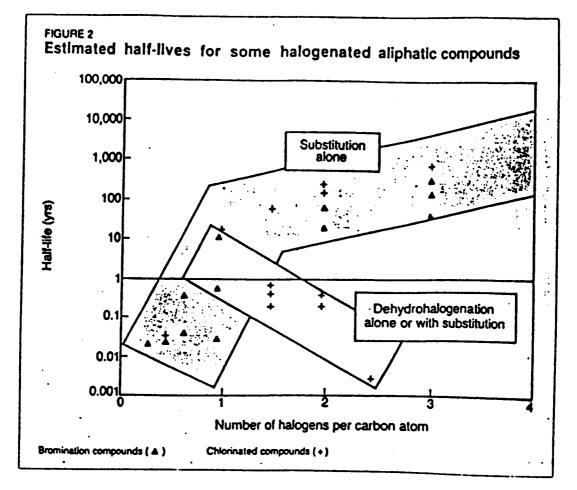
-C-C- ----> C = C + H-X / \ X H

Where X = Halogen

Generally this reaction proceeds very slowly with monochlorinated compounds, but polychlorination increases the rate. The rate for this reaction also increases with increasing hydroxide ion concentration (Ph). Even though one of the carbons (C-X; C oxidation state goes from +1 to 0) is reduced, and the other carbon (C-H; C oxidation state goes from -1 to 0) is oxidized, this reaction is not considered an external redox reaction. Also this reaction does not occur with vicinal (1,2-) dichloro- compounds.

15-20

# HYDROLYSIS Vs DEHYDROHALOGENATION



#### From Vogel

Dehydrohalogenation and hydrolysis are competing reactions in the degradation of chlorinated organic compounds. The figure above indicates that polychlorination tends to increase dehydrohalogenation while decreasing hydrolysis. Also note that brominated compounds are more reactive than the corresponding chlorinated compounds.

15-21

## **REDOX REACTIONS**

# **REDUCTION: GAIN OF ELECTRONS (H)**

# **OXIDATION: LOSS OF ELECTRONS (H)**

# MORE OXIDIZABLE COMPOUNDS PHENOLS AROMATIC AMINES OLEFINS (UNSATURATED) ALKYL SULFIDES

LESS OXIDIZABLE COMPOUNDS SATURATED ALIPHATICS HALOCARBONS ALCOHOLS ESTERS KETONES

15-21

# **III OXIDATION REACTIONS**

\* alpha-HYDROXYLATION

OH / -C-X + H<sub>2</sub>O -----> -C-X + 2H<sup>+</sup> + 2e<sup>-</sup>

\* beta-OXIDATION

 $RCH_{2}CH_{2}COOH + 2H_{2}O ---- > RCOOH + CH_{3}COOH + 4H^{+} + 4e^{-}$ 

\* <u>EPOXIDATION</u> X O X  $/ \ / \ / \ C = C + H_2O ----> C-C + 2H^+ + 2e^-$ O  $/ \ C = C + H_2O ----> C-C + 2H^+ + 2e^-$ 

\* **BIOHALOGENATION** 

HO X  $\setminus /$ C=C + X + H<sub>2</sub>O ----> C-C

# III OXIDATION REACTIONS (CONT.)

### \* OXIDATION OF ALKYL COMPOUNDS

 $RCH_3 + 2H_2O --> RCH_2OH ---> RCOOH + 6H^+ + 6e^-$ 

\* AROMATIC HYDROXYLATION (OXIDATION)

 $Ar + H_2O ----> ArOH + 2H^+ + 2e^-$ 

\* OXIDATIVE DEALKYLATION

 $ROCH_3 + H2O ----> R-OH + HCHO + 2H^+ + 2e^-$ 

\* OXIDATION OF SULFUR

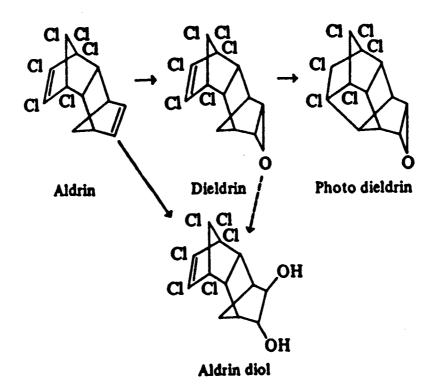
 $R_2S + 2H_2O ----> R_2SO ----> R_2SO_2$ 

\* OXIDATION OF AMINO GROUP

 $RNH_2 + 2H_2O ----> RNO2 + 6H^+ + 6e^-$ 

15-23

# **PHOTO-OXIDATION OF ALDRIN**



#### (Verschueren, 1983)

Above is the metabolic pathway of Aldrin and Dieldrin under oceanic conditions. Conversion of Aldrin to Dieldrin was 80% complete after 8 weeks in river water kept in a sealed jar under sunlight and artificial fluorescent light. The initial concentration was 10ug/l.

15-24

# **IV REDUCTION REACTIONS**

## \* HYDROGENOLYSIS

## $R-X + H^+ + 2e^- ---- > R-H + x^-$

## \* DIHALOELIMINATION

## \* COUPLING

2R-X + 2e<sup>-</sup> ----> R-R 2X<sup>-</sup>

15-25 FIGURE 6 -44 Half-life reduction potentials for reducing and oxidizing agents E\* (volts) -0.5 +0.5 0. ÷ DE' 0 +5 + 10 + 15 HCE to PCE EDB to E . 5 O<sub>2</sub> to H<sub>2</sub>O CT to CF - Reductions m electron PCE to TCE acceptors Costs erengy CF to MC -00 TCA IO 11-DCA . -011 TCE to DCE 011 11-DCA to CA -00 nitrate to nitrite sulfa:e to bisulfide DCE to VC 500 CO, to CH Hydrogenolysis lavorable Dichloro-H' IO H2 elimination lavorable Vitamin B-12 reduced to oxidized Ferredoxin reduced to oxidized 72 H- 10 H . Oxidations electron NACH to NAD donors Fe II to Fe(CH)<sub>h</sub> (amorph) Glutathione reduced to oxidized Cyto P450 (act) reduced to oxidized 110 Fe II to Fe III ceuterocorprin IX ۰. -50 ... Ò + 50 + 100 Free energy (kJ/mol of electrons transferred) ·•,• From Vogel 7 \*Base of arrows align with potential of half-reaction shown in volts, \*Energy for the combination of two half-reactions can be estimated from the difference between their free energy values, as indicated on the bottom aars

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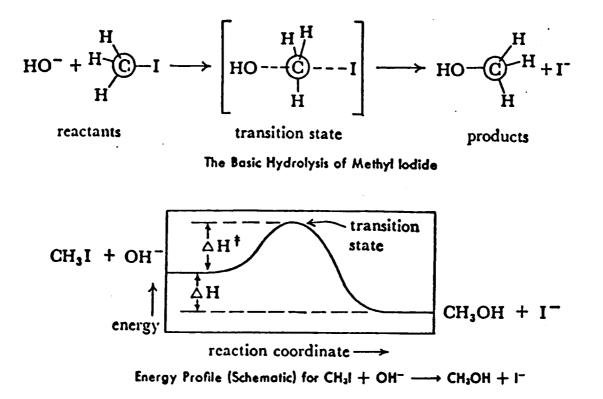
15-26

## **V** DECARBOXYLATION

# $RCOOH \dots > R-H + CO_2$

Oxidation/Reduction of Organic compounds takes a long time but will eventually happen thermodynamically will happen be cause the reaction results in a lower energy state

## A CHEMICAL REACTION WITH ENERGY PROFILE



THERMODYNAMICALLY A REACTION WILL OCCUR IF THE NET ENERGY OF THE PRODUCTS IS LESS THAN THAT OF THE REACTANTS. HOWEVER, THE RATE AT WHICH A REACTION WILL OCCUR IS DEPENDENT ON OVERCOMING A TRANSITION STATE ENERGY BARRIER AND HOW FREQUENTLY THE REACTANTS COME TOGETHER IN THE CORRECT CONFIGURATION. AN ENZYME CAN INCREASE THE RATE OF A REACTION BY HELPING TO STABILIZE THE TRANSITION STATE AND BY "HOLDING" THE REACTANTS IN THE CORRECT CONFIGURATION FOR THE REACTION TO OCCUR.

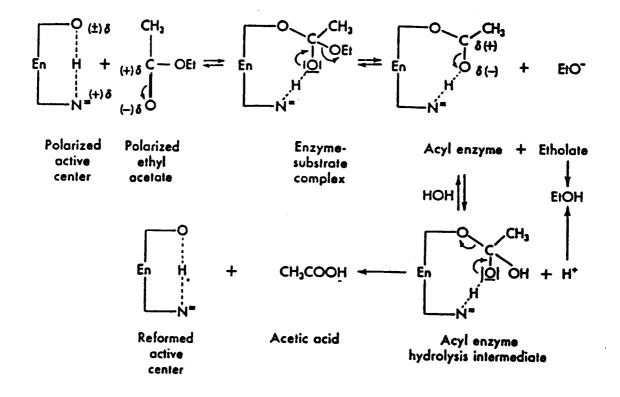
rate - K: Netically - how fast

ENZYMES Speed up the Kinetics of the reaction but don't Change the thermodynamics (lowers the transition state hump)

15-28

### ENZYMATIC HYDROLYSIS (ETHYLACETATE)

• -



15-29

X dup . of Naxt

# **ENZYME KINETICS**

#### bacteria degration rate



# AT HIGH [SUBSTRATE] r<sub>s</sub> = k X & high concentration of $\epsilon$

(high benzend), the reaction is very fast

## **AT LOW [SUBSTRATE]**

at low concentrations of benzeve in substrate, the reaction rate is slower + slower k

$$r_{s} = ---- X S = k_{2} X S$$
$$k_{s}$$

r<sub>s</sub> = RATE OF SUBSTRATE REMOVAL WHERE: X = MICROBIAL MASS/VOL SOIL S = SUBSTRATE CONCENTRATION  $\mathbf{k} = \mathbf{CONSTANT}$ 

**k**<sub>s</sub> = HALF SATURATION CONSTANT

15-30

# **ENZYME KINETICS**



At high substrate concentrations: first order with respect to biomass.

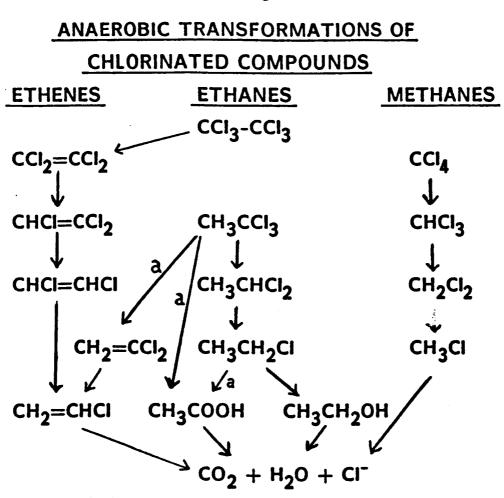
$$\mathbf{r}_{s} = \mathbf{k} \mathbf{X}$$

At very low substrate concentrations: first order with respect to substrate concentration and to biomass.

# **BIOTRANSFORMATION OF ALIPHATIC HYDROCARBONS**

.15-31

 $\begin{array}{c} H_{3}C(CH_{2})_{n}CH_{2}CH_{2}CH_{3} - --- H_{3}C(CH_{2})_{n}CH_{2}CH_{2}CH_{2}OOH \\ \downarrow \\ H_{3}C(CH_{2})_{n}CH_{2}CH_{2}CHO < --- H_{3}C(CH_{2})_{n}CH_{2}CH_{2}CH_{2}OH \\ \downarrow \\ H_{3}C(CH_{2})_{n}CH_{2}CH_{2}COOH - -> --> H_{3}C(CH_{2})_{n}CCH_{2}COOH \\ \downarrow \\ CO_{2} + H_{2}O < --- H_{3}CCOOH + H_{3}C(CH_{2})_{n-2}COCH_{2}COOH \end{array}$ 



a = abiotic

#### FACTORS INFLUENCING BIOTRANSFORMATION

- \* Inaccessibility of the Chemical
- Absence of Factor Essential for Growth
- \* Toxicity of the Environment
- \* Inactivation of the Requsite Enzyme
- \* Structural Characteristic of the Molecule
- Inability of the Community of Microorganisms to Metabolize the Compound because of some Physiological Inadequacy

#### MAJOR FACTORS AFFECTING BIOTRANSFORMATION

- 1. pH
- 2. Temperature
- 3. Water Content
- 4. Carbon Content
- 5. Clay Content
- 6. Oxygen
- 7. Nutrients
- 8. Nature of Microbes
- 9. Acclimation
- 10. Concentration

## . 15-34

# **pH INFLUENCE ON BIO TRANSFORMATION**

- pH 6.5 8.5 for most soil bacteria
- \* Fungi can tolerate more acidic conditions
- \* Enzyme activity affected by pH
- \* Percent of Substrate sorbed is affected
- \* Enzymes favor certain ionized forms of chemical

## TEMPERATURE INFLUENCE ON BIOTRANSFORMATION

- \* Microbes have temperature limits
- Microbial activity stimulated by temperature

Mesophiles25 - 35°Psychrophiles< 20°</td>Thermophiles45 - 65°

- \* Chemical Reaction Rate Proportional to Temperature.
- \* Adsorption Processes are Exothermic

If you can increase temp 10° you can double the rate of reaction

15-36

# WATER CONTENT INFLUENCE ON BIOTRANSFORMATION

- \* Moisture Required but Reduces Gas Exchange
- \* Optimum for Aerobics is 50 75% Soil Capacity
- Affects Soluble Chemical Concentrations

## CARBON CONTENT INFLUENCE ON BIOTRANSFORMATION

- Major Source of Microbial Food
- \* Strongly Sorbs Many Chemicals & make them inaccessible to bacteria
- \* Added Organics can cause Increase Or Decrease

## CLAY CONTENT INFLUENCE ON BIOTRANSFORMATION

- pH will affect this
- \* Many Chemicals Sorb to Clay & make them in accessible to
- \* Different Clays React Differently to Chemicals
- Clay Causes Increased Moisture, Decreased O 2

## **OXYGEN AFFECT ON BIOTRANSFORMATION**

- \* Terminal Electron Acceptor for Aerobes
- \* Required for Aerobes
- \* Toxic for Anaerobes
- \* Determines Mechanisms and Products Formed

15-38

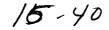
\* Soil Rarely Totally Aerobic

### NUTRIENT AFFECTS ON BIOTRANSFORMATION

- \* Required for Growth and Respiration
- \* Serve as Electron Acceptors
- \* May be Supplied by Chemical Being Degraded

#### NATURE OF MICROBIAL POPULATION

- \* Not All Chemicals degraded by all Organisms
- \* Population Size and Spacial Distribution Important
- Some Chemicals Degraded Sequentially by Different
   Species



#### ACCLIMATION AFFECTS ON BIOTRANSFORMATION

 Frequently a Biotransformation Lag Period Required Enzymes Induced
 Preferential Selection of Degrading Organism

### CHEMICAL CONCENTRATION AFFECT ON BIOTRANSFORMATION

- \* Too High a Concentration may be Toxic
- Too Low may not Support Growth

#### ESTIMATION OF RATE PARAMETERS

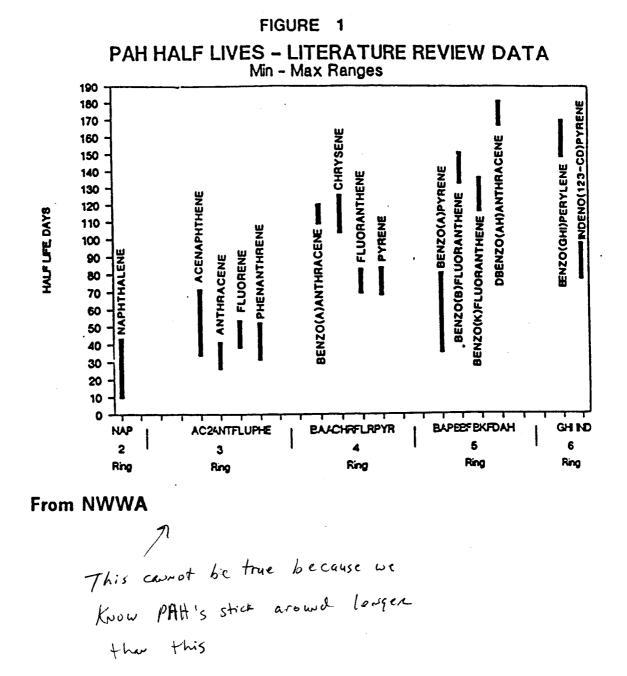
- Field Vs Lab Measurements very difficult to determine all the mechanisms that occurrings
- Measurement of Test Chemical Disappearance
- \* Lab Measurement of <sup>14</sup>C Production  $0 R^{13} C O_2^{\#}$
- \* Meassurement of Microbial Numbers & Biomass

hydrogen peroxide - e.g. can calculate how much oxygen is required to degrade gas to carbon dioxide

#### MEASUREMENT LIMITATIONS

- \* Abiotic Vs Biotic Processes
- \* Microbial Concentration
- \* Bound Chemical Residues
- \* Model Limitations
- \* Specificity of Constants
- \* Concentration Dependance of Constants
- Acclimation

15-43



15-44

#### ENVIRONMENTAL DEGRADATION OF ORGANIC COMPOUNDS

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# (Continued)

15-45

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16-46

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Section 17

# Geochemistry of Several Contaminant Sources

Lecture by: Patrick Longmire Los Alamos National Laboratory

## SECTION CONTENTS

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Passero, Ground Water, Vol. 28, No. 5, September-October 1990,	
pp. 728-737	-3

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### **CONTAMINANT MIGRATION -- INORGANIC SOLUTES**

- I. INTRODUCTION
- II. CASE HISTORIES
  - A. NITRATE CONTAMINATION
  - B. HEAVY METAL AND TRANSITION METAL CONTAMINATION
  - C. MUNICIPAL LANDFILLS

Nitrate Contamination

NO3 mobile in 5.6. under acidic conditions - Anionic sorption reduction to N2 Nitrogen as nitrote 10mg/L NO3 - N MCL  $NO_{3}^{-} + C_{\text{organic}} \rightarrow N_{2}(g) + CO_{2} + H_{2}O_{3}$ 

### pH and Redox Buffering Mechanisms in a Glacial Drift Aquifer Contaminated by Landfill Leachate

by Alan E. Kehew and Richard N. Passero<sup>a</sup>

#### Abstract

The KL Landfill in Kalamazoo County, Michigan was closed in June 1979 because of ground-water contamination. Study of water analyses from a monitoring-well network has provided insight into a variety of pH and pe buffering reactions within the contaminant plume. The reactions occur when contaminated ground water containing dissolved organic acids from the landfill reacts with carbonate minerals and other solid phases in a glacial drift aquifer. Concentrations of Total Inorganic Carbon (TIC) in the plume, measured as the difference between Total Carbon (TC) and Total Organic Carbon (TOC), are lower than those obtained by alkalinity titrations. The difference results from the dissociation of organic acids in solution, producing organic anions that are included in the erroneously high titration alkalinity values.

Organic acids cause dissolution of carbonate minerals in the drift and increased concentrations of calcium, magnesium, and bicarbonate in the plume. Geochemical modeling using WATEQF indicates that the plume is supersaturated with respect to calcite, dolomite, and siderite. The dissolution reactions buffer pH in the plume at near background levels.

Redox potentials are below the level of sulfate reduction in the contaminant plume. Therefore, redox buffering mechanisms, reactions that inhibit changes in redox potential in the presence of a strong reducing agent, are much less effective than pH buffering in this system. Possible redox reactions occurring along the flow path include oxidation of organic compounds coupled with reduction of nitrate to ammonium and reduction of ferric iron in oxyhydroxide phases to ferrous iron.

WATEQF simulations indicate that dissolved iron concentrations in the plume are well above saturation levels with respect to sulfide phases, moderately above saturation with respect to siderite, and below saturation with respect to iron hydroxide. It is likely that iron precipitates as sulfide phases until the dissolved sulfide is consumed. The concentration of dissolved iron is subsequently controlled by precipitation of siderite, which occurs when moderate levels of supersaturation are reached.

These redox buffering reactions are insufficient to maintain high pe levels, and pe values drop to the level of sulfate reduction in the contaminant plume. Together, pH and redox buffering reactions control the concentrations of most major chemical species in the KL Landfill contaminant plume.

### Introduction

Attenuation of contaminants in aquifers beneath general refuse landfills involves a variety of physical and chemical processes, including reactions between dissolved chemical species and aquifer solids. Landfill leachates often contain high concentrations of dissolved organic carbon, of which various organic acids make up a significant fraction (Chian and DeWalle, 1977; Baedecker and Back, 1979a, b). Despite the presence of these organic acids, the contaminated ground water is commonly in the neutral range of pH values, indicating that buffering of the pH is occurring.

Microbial decomposition of labile organic compounds in leachates and contaminated ground water tends to lower their redox potential. Decomposition continues as the leachate moves through the vadose zone beneath the landfill and into the saturated zone. Dissolved or solid oxidized compounds in the aquifer are reduced with oxidation of the organic compounds. These reduction reactions, such as the reduction of ferric to ferrous iron, occur in a specific sequence (Drever, 1988), and the redox potential of the contaminated ground water remains at a level determined by a particular reaction until the oxidized member of the reaction is reduced. Redox buffering, the tendency of a solution to maintain redox stability, is conceptually similar to pH buffering.

pH and redox buffering reactions taking place beneath and downgradient from the landfill alter the chemistry of the contaminant plume and influence attenuation reactions within it. This paper describes pH and redox buffering in a glacial drift aquifer contaminated by landfill leachate.

#### Site History

The KL Landfill, located approximately three miles west of the city of Kalamazoo, Michigan (Figure 1), was used as a township dump in the early 1960s. Although records do not exist for this period, it is likely that most refuse landfilled at this time was household and farm waste. In 1968, Kalamazoo County assumed management of the site and used it as a commercial landfill until 1979, when volatile hydrocarbons were detected in nearby residential

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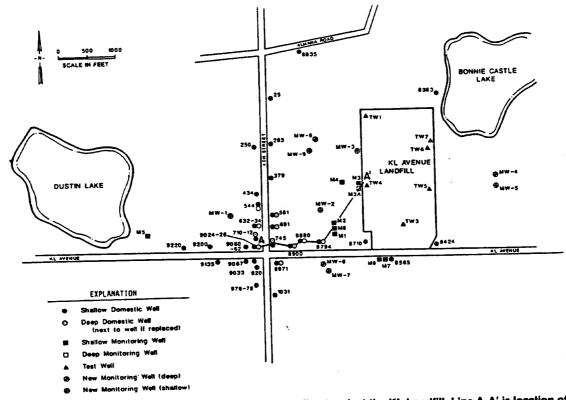
Fig. 1. Location of the KL Landfill.

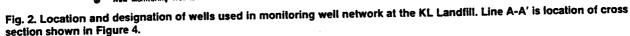
weils. The landfill was closed in June 1979, monitoring wells were installed on and off the site (Figure 2), and a hydrogeologic investigation was conducted (Passero et al., 1981). The closure plan included regrading, application of a final, bentonite-enhanced soil cover, installation of gas vents, and revegetation, followed by quarterly sampling of more than 50 monitoring and residential wells. Volatile hydrocarbons have been detected in residential wells as far as 2000 feet downgradient from the landfill. As part of the remediation effort, contaminated shallow residential wells were replaced with deep wells in a confined aquifer at the base of the drift and a water main was extended into the area.

In 1982, the site was added to the National Priority List (NPL) under the U.S. EPA Superfund program. During the Remedial Investigation Feasibility Study (RIFS), 12 new monitoring wells were installed and sampled (U.S. EPA, 1986a). Volatile organic scans and trace-metal analyses comprise the majority of the chemical data obtained from well samples, and most analyses are incomplete with respect to major cations and anions. Analyses adequate for modeling were, therefore, obtained from additional samples taken from selected wells in 1987 and 1988 (Table 1).

#### Hydrogeologic Setting

The geology and hydrogeology of the site were described by Passero et al. (1981). The landfill is located near the crest of the Kalamazoo Moraine, a prominent northeast-trending ridge deposited by the Lake Michigan Lobe (Figure 3). Topographic relief across the moraine is approximately 200 feet. The moraine is constructed of till units interbedded with glaciolacustrine and glaciofluvial sediments. In the vicinity of the landfill, the near-surface sediments consist of two discontinuous till units separated by glaciofluvial sand and gravel (Figure 4). Thicknesses of these units are: upper till, 0-30 feet; outwash, 0-20 feet; and second till, 13-60 feet. Beneath the second till is a thick (105-145 feet)





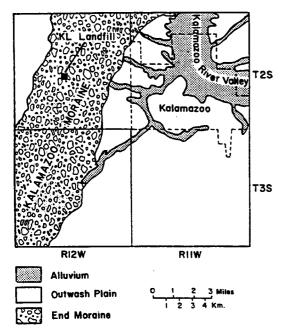


Fig. 3. Position of KL Landfill with respect to Kalamazoo moraine.

sand and gravel outwash unit known as the shallow aquifer, the principal aquifer for wells in the area. The shallow aquifer is underlain by a thin (5-10 feet), discontinuous glaciolacustrine bed, a third till unit (37-178 feet thick), a thin (10-30 feet) uncontaminated outwash unit (the deep

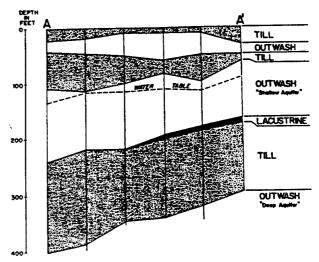


Fig. 4. Cross section along line A-A' (Figure 2). Contact between deep aquifer and Mississippian Coldwater Shale bedrock not shown.

aquifer), and the Mississippian Coldwater Shale. Depths to the water table beneath the rolling topography of the moraine range from about 23 feet to 138 feet in the vicinity of the landfill. The water table appears to be mounded beneath the landfill.

Regional ground-water flow in the area is to the northwest, away from a northeasterly trending divide just east of the landfill. West of the site, however, flow is complex (Figure 5) and includes westerly and southwesterly compo-

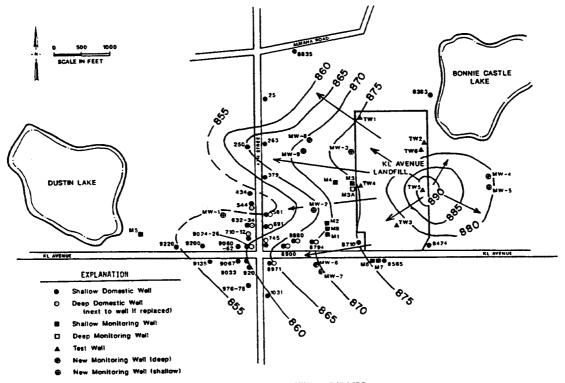


Fig. 5. Water-table surface contour map in the vicinity of the landfill on 3/31/88.

Table 1. Chemical Data (concentrations in mg/l) from KL Landfill Site

Well	Date	т °С	pН	TOC	TC <sup>2</sup>	TIC <sup>3</sup>	Total AIK	HCO <sub>3</sub> -	сг	SO4 <sup>2-</sup>	NO3 <sup>-</sup>	NH.	H <sub>2</sub> S	Ca <sup>2+</sup>	Mg <sup>:•</sup>	Na	ĸ	Fe	Ion ratio <sup>5</sup>
MW-5	5/18/87	12	7.0	<2	-	-	192	~	6.4	21	5.2	< 1.0	-	54.9	20.6	2.18	0.61	0.077	.93
TW4	3/11/87	9.2	7.5	1400	-	-	~	2200	233	<1	12.4	43.8	2.4	404	202	179	10.5	46.8	-
TW4	5/18/87	12.0	7.5	1440	-	-	1170	-	142	5.0	<0.1	61	-	446	192	154	12.6	37.6	-
TW4	3/29/88	11.0	7.63	890	990	<del>99</del>	-	-	186	<1	2.1	41.8	<4	267	158	114	12.6	52.3	2.74
мз	3/29/88	11.6	7.4	698	770	72	-	-	152	<1	1.4	38.6	<4	224	135	92.1	14.8	32.0	3.00
M4	3/11/87	5.0	7.74	91	-	-	-	350	32	<1	<1.0	7.2	-	51.6	27.9	30.1	3.46	0.11	
M4	3/29/88	10.3	7.85	130	190	61	-	-	44	<1	<1.0	2.8	<4	99.7	65.3	15.1	1.90	3.59	1.81
M₩•3	5/18/87	13.5	6.5	164	-	-	320	-	69	<3	<0.1	<0.1	-	93.6	61.1	17.4	7.31	5.60	-
MW-9	5/18/87	12.5	6.4	104	-	-	665	-	61	16	<0.1	9.6	-	100	61.6	97.6	9.82	11.8	-
MW-2	5/18/87	12	6.8	<2	-	-	328	-	6.4	<3	0.1	0.15	-	95.3	33.8	60.6	3.15	9.30	-
M8	3/11/87	ស	7.44	14	-	-	-	460	63	2	<1.0	45.9	<0.5	-	-	61.4	14.9	0.06	-
MW-7	5/18/87	11.0	6.6	3.4	-	-	256	-	26	<3	<0.1	0.15	-	61.7	25.7	10.8	2.05	0.252	-

<sup>1</sup> TOC - Total Organic Carbon, mg/l as C.

<sup>2</sup> TC - Total Carbon, mg/l as C.

<sup>1</sup> TIC — Total Inorganic Carbon, mg/l as C.

Total AlK - Total Alkalinity, mg/l as CaCO3.

<sup>5</sup> Ratio of inorganic cations to anions (milliequivalents per liter).

nents. A buried channel cut into the till unit that confines the deep aquifer was delineated by analysis of gamma ray logs, lithologic logs, and electrical earth-resistivity studies (Passero et al., 1981). This channel, which lies between Bonnie Castle Lake (a recharge lake northeast of the landfill) and Dustin Lake (a flow-through lake west to southwest of the landfill), is interpreted to extend beneath the landfill in a southwesterly direction toward Dustin Lake. The buried channel, which is filled with sand and gravel of the shallow aquifer, appears to focus contaminant migration from the southern part of the landfill in a southwesterly direction at an angle to the regional flow. The specific capacity of wells and contaminant data along this trend suggest that the channel-fill sediment has a higher hydraulic conductivity than the surrounding sediment of the shallow aquifer. A similar trend extends west-northwestward from the western boundary of the landfill (Figure 5), and a somewhat similar linear pattern of preferential contaminant movement also exists along this trend.

The glacial drift of southwestern Michigan consists of carbonate and noncarbonate sedimentary lithologies and a variety of igneous and metamorphic rock types (Shah, 1971). Carbonate lithologies constitute approximately 80% of clasts in gravel deposits of the Lake Michigan Lobe (Wingard, 1971). Dolomite is more abundant than calcite in many drift samples.

Ground water in drift aquifers in southwestern Michigan is moderately low in total dissolved solids (TDS). A mean TDS value of 259 mg/l was calculated for 28 analyses from Kalamazoo County reported by Allen et al. (1972). Ground water in Kalamazoo County is classified as calcium-magnesium bicarbonate type (Western Michigan University, unpublished data). At the KL Landfill, upgradient well MW-5 (Table 1) is assumed to approximate background quality, even though samples contain slightly elevated levels of chloride and nitrate.

### **Data Collection**

Geochemical processes in contaminant plumes can be investigated using chemical equilibrium models. Computer codes such as WATEQF (Plummer et al., 1976) require field-measured pH, temperature, and other parameters, if available, as well as concentrations of all major cations and anions. Minor chemical species increase the number of mineral saturation calculations that can be performed. Because most chemical analyses from the KL Landfill area do not include all major ions, more complete analyses were required for modeling ground-water chemistry in the plume. These came from two sources, one of which consists of data from U.S. EPA samples collected on May 18, 1987 as part of the RIFS (Table 1). RIFS wells were purged by manual bailing or by submersible pump. Field measurements included pH, temperature, and specific conductance. The other source includes samples obtained from four additional wells (TW4, M3, M4, and M8) specifically for this study. Wells TW4, M4, and M8 were sampled on March 11, 1987, and wells TW4, M3, and M4 were sampled on March 29, 1988 (Table 1). These four wells are fitted with dedicated deep rod pitcher pumps. Samples were collected after purging three to five well volumes. Temperature, pH, and specific conductance were measured immediately, and samples were field-filtered through 0.45 micron filters. One sample at each well was acidified for dissolved metal analysis and a second, nonacidified sample was collected for other parameters. Analyses for ammonia, nitrate, chloride, sulfate, and silica follow procedures described by the American Public Health Association (1985). Sulfide, calcium, iron, magnesium, manganese, potassium, and sodium were analyzed by methods given in U.S. EPA (1986b).

Alkalinity titrations to determine dissolved inorganic carbon were suspect for samples taken from the contaminant plume because organic acid anions accept protons added during the titration procedure (Baedecker and Back, 1979a). The reported alkalinity and bicarbonate values would therefore overestimate the true bicarbonate concentration. To test this hypothesis, Total Inorganic Carbon (TIC) was measured in the 3/29/88 samples (wells TW4, M3, and M4) as the difference between Total Carbon (TC) and Total Organic Carbon (TOC). TC and TOC were determined using a Dohrmann DC-52-D Carbon Analyzer. TIC values, reported as mg/l carbon, were then converted to bicarbonate concentrations. The results of these analyses, reported in Table 2, indicate that approximately 90 percent of the dissolved carbon occurs in organic compounds. Bicarbonate concentrations determined by the TIC procedure are therefore more accurate than titration values for ground-water samples taken from the contaminant plume.

### **Distribution of Contaminants**

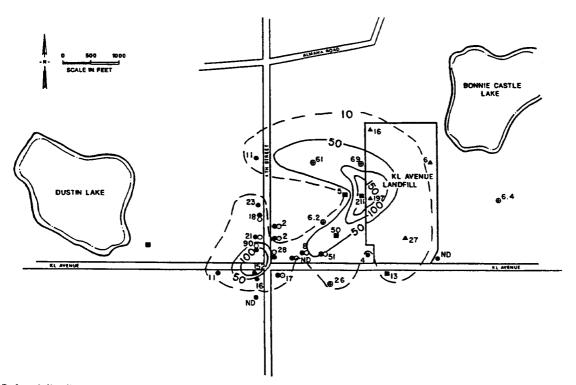
The general shape of the contaminant plume, which is restricted to the shallow aquifer, can be illustrated by the distribution of chloride (Figure 6). This map is based on ground-water samples from residential wells and monitoring wells sampled in May and September 1987, including the wells with MW designation shown in Table 1. Zones of preferential contaminant migration to the northwest and southwest are evident. Anomalously high chloride concentrations along KL Avenue, and particularly those near the intersection of KL Avenue and 4th Street, probably result from road-salt contamination.

Well TW4, completed just below the water table along the western edge of the landfill, yields the highest levels of most contaminants. Ground water at TW4 is highly reducing, rich in organic compounds (Table 1), and approximately neutral in pH. TOC is very high in well TW4 (Figure 7) and decreases downgradient to the northwest and southwest. The TOC value measured at well M8 in this study (14 mg/l) appears to be anomalously low. In data from the early 1980s (Passero et al., 1981), TOC values ranged between 150 and 200 mg/l for this well. TOC values in other wells, such as TW4, have increased over the same period.

The distribution of cations is similar to that of chloride. Calcium (Figure 8), iron (Figure 9), magnesium, sodium, potassium, and ammonium, conform to this pattern, although the downgradient rate of attenuation is different for each cation. Anionic species in the plume other than chloride include bicarbonate, dissociated organic acids, and

Table 2. Results	of Carbon Anal	lysis at KL Landfill Site
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Well	TC (mg/l as C)	TOC (mg/l as C)	TIC (mg/l as C)	Percent organic carbon	Calculated HCO3 <sup>-</sup> (mg/l)
TW4	990	890	99	89.9	503.3
M3	770	698	72	90.6	365.8
M4	190	130	61	68.4	309.9





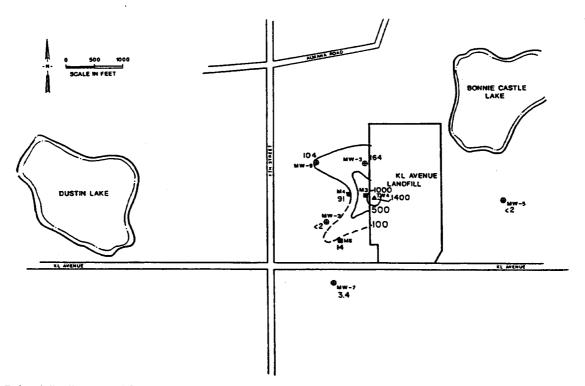
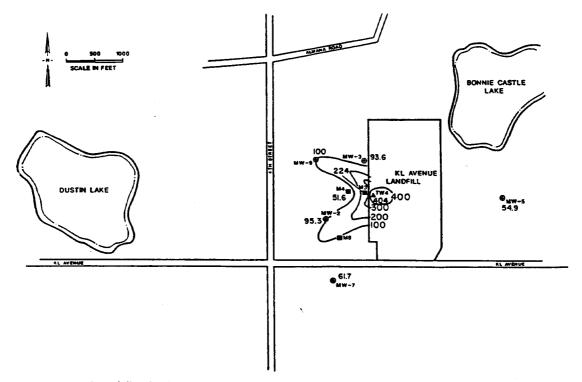


Fig. 7. Areal distribution of TOC at the KL Landfill site using data shown on Table 1. 100 mg/l contour in southwestern arm is dashed in assumed position because measured value for well M8 is anomalously low.



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Fig. 8. Areal distribution of dissolved calcium in the shallow aquifer at the KL Landfill site using data from Table 1.

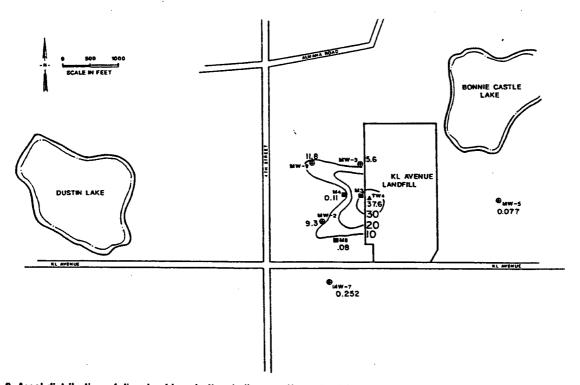


Fig. 9. Areal distribution of dissolved iron in the shallow aquifer at the KL Landfill site using data from Table 1.

sulfate. The distribution of bicarbonate cannot be mapped with available data because of the analytical problems discussed earlier. Sulfate concentrations are low in the plume relative to background. They are generally at nondetectable or very low levels along the southwesterly contaminant trend, and increase downgradient along the northwesterly trend.  $H_2S$  was detectable (2.4 mg/l) only in well TW4 on 3/11/87.

#### pH Buffering Processes

Buffering of pH refers to reactions that tend to stabilize pH in the presence of acids or bases. Although analytically difficult to identify and measure, it is likely that organic acids are abundant in most general refuse landfill leachates (Chian and DeWalle, 1977). Rudder (1988) identified numerous organic acids in the leachate-contaminated ground water at the KL Landfill (Table 3) using ion chromatography and Fourier transform IR spectrophotometry. Anomalously high ratios of inorganic cations to anions (Table 1) are additional evidence that the contaminated ground-water solution contains anions from dissociated organic acids. In TW4, for example, the sum of cations exceeds the sum of inorganic anions (using a bicarbonate value calculated from measured TIC) by approximately 23 meq/l, suggesting that organic acid anions make up the difference to balance the solution. Analyses reported by Passero et al. (1981) and U.S. EPA (U.S. EPA, unpublished data), which contain more inorganic parameters than Table I, confirm the lack of significant concentrations of other inorganic ionic species in the contaminant plume. The pH at

TW4 ranges from 7.0 to 8.0 in the presence of these organic acids, indicating that buffering is occurring.

Elevated concentrations of calcium, magnesium, and bicarbonate in the contaminant plume indicate that carbonate mineral dissolution is occurring and is an important buffering mechanism. Reactions (1) and (2) illustrate the dissolution of calcite and dolomite by reaction with acid.

$$CaCO_3 + H^2 - Ca^{2*} + HCO_3^{-1}$$
(1)

$$CaMg(CO_3)_2 + 2H^* \rightarrow Ca^{2*} + Mg^{2*} + 2HCO_3^-$$
 (2)

Acids produced in general refuse landfills include carbonic acid derived from CO<sub>2</sub> generated during the decomposition of organic wastes as well as various organic acids (Baedecker and Back, 1979a; Nicholson et al., 1983). These acids result

Table 3. Organic Acids Identified in Ground Water at KL Landfill Site (Rudder, 1988)

at KL Landill Site (Hudder, 1968)
 Acetic acid
Oxalic acid
Propionic acid
n-Valeric acid
Glutamic acid
Hexanoic acid
Malonic acid
Phenol
Pyrogallol
Resorcinol
Hydroquinone
Benzoic acid
Tannic acid

Well	Date	Mackinawite FeS	FeS (Amorph.)	Hematite F2O3	Goethite FeO(OH)	Calcite CaCO3	Dolomite CaMg(CO3)2	Siderite FeCO3	Fe(OH)3 (Amorph.)
TW4 <sup>1</sup>	3/11/87	3.68	2.01	6.14	0.31	1.06	1.91	1.92	-2.53
TW4 <sup>2</sup>	5/18/87	2.73	1.07	8.32	1.39	1.16	2.08	1.92	-1.41
TW4 <sup>3</sup>	3/29/88	3.01	1.35	9.29	1.88	0.89	1.68	2.01	-0.94
M34	3/29/88	2.61	0.94	7.62	1.04	0.49	0.90	1.47	-1.77
M4 <sup>5</sup>	3/29/88	2.39	0.73	8.35	1.42	0.60	1.12	0.96	-1.41

<sup>1</sup> Assumptions: TOC is 90% of total carbon; HCO<sub>3</sub><sup>-</sup> input as 790 mg/l. pe calculated by WATEQF from sulfide/sulfate distribution as -3.98.

<sup>2</sup> Assumptions: TOC is 90% of total carbon; HCO<sub>3</sub><sup>-</sup> input as 813 mg/l. pe input at approximate level of sulfate reduction (Eh = -0.17 V). H<sub>2</sub>S input at 0.1 mg/l.

<sup>3</sup> Assumptions: pe input at approximate level of sulfate reduction (Eh = -0.17 V); sulfate input at detection limit (1 mg/l); sulfide input at 0.1 mg/l.

<sup>4</sup> Assumptions: pe input at approximate level of sulfate reduction (Eh = -0.17 V); sulfate input at detection limit (1 mg/l); sulfide input at 0.1 mg/l.

<sup>5</sup> Assumptions: pe input at approximate level of sulfate reduction (Eh = -0.17 V); sulfate input at detection limit (1 mg/l); sulfide input at 0.1 mg/l.

in open system dissolution of carbonate minerals (constant  $CO_2$  partial pressure) in carbonate soils between the refuse and the water table in a landfill (Nicholson et al., 1983).

In this study, WATEQF (Plummer et al., 1976) was used to model carbonate mineral equilibria using chemical analyses from wells TW4, M3, and M4. The calculated saturation indices for various minerals are shown in Table 4, expressed as the log of the ratio of the ion activity product to the equilibrium constant (Log IAP/ $K_T$ ).

Supersaturation with respect to calcite, dolomite, and siderite (Table 4) may reflect slow precipitation kinetics or the complexing of calcium and iron with organic compounds. Calcite precipitation rates are low near saturation (Berner and Morse, 1974), and it may be necessary for saturation indices to rise appreciably above zero for significant calcite precipitation to occur (Suarez, 1977). In addition, calcite precipitation may be inhibited by competition between magnesium and calcium ions for nucleation sites and by blocking of nucleation sites by adsorption of polar organic molecules on calcite mineral surfaces in the aquifer (Baedecker and Back, 1979b). Baedecker and Back (1979b) also suggest that calcium is consumed in the formation of calcium salts of fatty acids (soaps) in a landfill environment and is thus unavailable for calcite precipitation. Rudder (1988) found evidence suggesting formation of complexes between iron and organic ligands in ground water from the KL contaminant plume. Complexation would retard the precipitation of iron carbonate and iron sulfide phases by keeping iron in solution beyond the point at which it would precipitate in the absence of organic ligands.

Exchange of ammonium in contaminated ground water for calcium and magnesium adsorbed on aquifer particle surfaces (Kehew et al., 1988) may also contribute to carbonate mineral supersaturation. In an analysis of the Borden, Ontario landfill, Nicholson et al. (1983) suggested that calcium and magnesium derived from ion exchange reactions provide a continuous source of calcium for calcite precipitation, once a sufficiently high level of supersaturation occurs.

The degree of supersaturation of carbonate minerals

calculated by WATEQF is dependent on the pH measurement. Wells TW4, M3, and M4 are equipped with dedicated pitcher pumps. Some degassing of  $CO_2$  may have occurred during sampling, but it is unlikely that  $CO_2$  degassing alone could account for the degree of oversaturation measured.

Although carbonate mineral dissolution reactions appear to play a major role in pH buffering within the contaminant plume, other reactions may also contribute to the consumption of hydrogen ions derived from carbonic and organic acids. These reactions include the reduction of ferric hydroxide and sulfate by organic carbon as shown below:

 $4Fe(OH)_3 + 8H^+ + CH_2O \rightarrow 4Fe^{2+} + 11H_2O + CO_2$  (3)

 $SO_4^{2-} + H^+ + 2CH_2O - HS^- + 2CO_2 + 2H_2O$  (4)

High dissolved iron concentrations are produced by reaction (3). The importance of sulfate reduction is difficult to assess because both sulfate and hydrogen sulfide are present in very low concentrations in TW4 and other downgradient wells. If a sulfate source is present in the refuse, it is possible that reduction to sulfide and precipitation as sulfide phases take place within or beneath the landfill.

The net result of the pH buffering reactions described is that pH remains in the range of 7 to 8 in the wells downgradient of the landfill. Large quantities of calcium, magnesium, and bicarbonate are released to ground water near the landfill from pH buffering reactions. Concentrations gradually decrease downgradient (Figure 8) as a result of precipitation and/or other attenuation mechanisms.

#### **Redox Buffering Processes**

Redox potential is often expressed as pe, the negative log of the electron activity. Redox buffering (Drever, 1988) refers to the ability of a solution to maintain a constant pe in the presence of electron donors. Organic compounds commonly serve as electron donors during microbial oxidation reactions, which yield  $CO_2$  under aerobic conditions, and  $CO_2$  and  $CH_4$  under anaerobic conditions. Methane is commonly produced in general refuse landfills (Baedecker and Back, 1979b) and has been detected both in gases (Passero et al., 1981) and ground water at the KL Landfill (Western Michigan University, unpublished data).

Electron acceptors in redox buffering reactions include a variety of compounds found in ground water and in aquifer materials. Specific redox reactions occur in a sequence defined by energy yields to microorganisms. This sequence includes, in order of decreasing redox potential, the redox couples  $O_2/H_2O$ ,  $NO_3^-/N_2$ ,  $MnO_2/Mn^{2+}$ ,  $Fe_2O_3/Fe^{2+}$ , and  $SO_4^{2+}/H_2S$  (Drever, 1988). Under reducing conditions, nitrate reduction may yield  $NH_4^+$  rather than  $N_2$ (Knowles, 1982; Kaspar et al., 1981).

Redox conditions are difficult to define and model. A "master" pe value for a ground-water solution, measured by a platinum electrode, may not accurately characterize the redox conditions because it includes the combined potentials of multiple redox couples in solution (Lindberg, 1984). Redox potentials based on the concentrations of both members of a redox couple can be calculated, but individual redox couples in solution commonly yield redox potentials that differ from other couples (Nicholson et al., 1983).

Field redox potentials were not measured in monitoring wells at the KL Landfill and detectable concentrations of oxidized and reduced members of potential redox couples in the plume were not obtained. Despite the lack of these data, interpretations of redox conditions can be made based on analytical results. The chemical composition of downgradient ground water indicates that the redox potential in the plume is very low and the capacity of the aquifer to buffer pe is lower than its capacity to buffer pH. This conclusion is consistent with the presence in solution of reduced forms of nitrogen, iron, and sulfur. Nitrogen exists primarily as ammonium, indicating that the pe is below the level at which denitrification occurs in the redox sequence. Elevated dissolved iron and manganese concentrations relative to background in the plume can be explained by reduction of iron and manganese in oxyhydroxide coatings on aquifer grains. Iron concentrations are much higher than manganese in the plume.

WATEQF simulations of the contaminated ground water were made using an assumed pe value at the level of sulfate reduction, approximately -3 (Drever, 1988). This value is reasonable near the landfill because the plume in this area contains very low to nondetectable sulfate concentrations. At this pe, the solution is significantly undersaturated with respect to amorphous Fe(OH)3 (Table 4), suggesting that other reactions control iron concentrations in the plume downgradient from the landfill. Siderite precipitation is a reaction that may control iron concentrations because saturation indices for this carbonate mineral are above the level of saturation (Table 4). According to Nicholson et al. (1983), siderite precipitation rates may be slower than calcite, thus allowing concentrations to rise to supersaturation prior to precipitation. Another possible explanation for siderite supersaturation is that some of the iron in solution is complexed with organic ligands (Rudder, 1988; Kehew et al., 1988). Dissociated organic acid anions such as tannic acid (Table 3) are known to form complexes with dissolved iron (Rudder, 1988). The presence of iron-organic complexes would lower free ferrous iron concentrations in solution and siderite would be closer to saturation than is indicated by WATEQF calculations made without accounting for complexation.

Detectable hydrogen sulfide was measured only in the sample taken from TW4 on 3/11/87. The sulfate concentration was below the detection limit of 1 mg/l in this sample. WATEQF was used to estimate the pe and sulfide mineral saturation indices based upon the sulfate/sulfide redox couple using the measured  $H_2S$  value (2.4 mg/l) and an assumed sulfate concentration at the detection limit (1 mg/l). At the calculated pe of -3.98, several iron sulfide phases were supersaturated (Table 4) including amorphous FeS, which precipitates first from solution (Berner, 1970). It is likely that precipitation of FeS or some other sulfide phase controls dissolved sulfide concentrations because iron concentrations are high and pe levels are in the range at which sulfide mineral precipitation is expected to occur. If some of the dissolved iron is complexed with organic ligands, however, the calculated saturation indices would overestimate the degree of supersaturation of sulfide phases.

Redox speciation data, therefore, suggest that redox buffering is not effective in maintaining pe levels in the KL Landfill plume. Utilization of all available electron acceptors does not provide the buffering capacity necessary to prevent low redox potentials downgradient of the landfill. Indeed, TOC and iron distributions (Figures 7, 9) suggest that several hundreds of feet of travel along the flow path is necessary before redox potential returns to background levels.

#### Conclusions

The reactions involved in pH and redox buffering are important in controlling the concentrations of many major and minor chemical species in the KL Landfill contaminant plume. Acid leachate causes carbonate mineral dissolution which, in turn, buffers the pH in the glacial drift aquifer at or near neutral background levels. Increases in calcium, magnesium, and bicarbonate concentrations result from these buffering reactions, thereby increasing the saturation indices of carbonate minerals in ground water. Supersaturation of carbonate minerals persists possibly because precipitation is retarded kinetically and/or inhibited by complexation of cations with organic ligands in solution or blockage of nucleation sites on mineral surfaces. Determination of saturation indices based on uncorrected titration alkalinities may overestimate carbonate mineral saturation levels because the resulting bicarbonate concentrations erroneously include organic acid anions.

Redox reactions in the contaminant plume include oxidation of dissolved organic compounds coupled with reduction of oxidized compounds in dissolved or solid phases. Redox buffering is inadequate to maintain background pe, which is below the level of sulfate reduction in the plume. Specific reactions include the reduction of iron and manganese contained in oxyhydroxide solid phases. Dissolved iron concentrations as high as 50 mg/l are attributed to this reaction. Siderite precipitation provides a possible solubility control for iron concentrations in the plume when the saturation index reaches a value of approximately 2.0. It is also possible that dissolved iron persists above saturation levels with respect to carbonate and sulfide phases because of complexation with organic acid ligands. Sulfide mineral precipitation may maintain sulfide concentrations in the plume at very low levels.

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\* \* \* \* \*

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## GEOCHEMISTRY OF SEVERAL CONTAMINANT SOURCES

INTRODUCTION

**CASE HISTORIES** 

NITRATE CONTAMINATION

HEAVY METAL AND TRANSITION METAL CONTAMINATION

**MUNICIPAL LANDFILLS** 

### GEOCHEMISTRY OF SEVERAL CONTAMINANT SOURCES

In this lecture we will discuss different inorganic contaminants, such as nitrate, lead, chromium, iron, arsenic, manganese, molybdenum, selenium, and organic contaminants associated with sewage treatment plants, metal extraction plants, and municipal landfills. Some of these contaminants are mobile in most ground water systems, whereas other contaminants are attenuated by precipitation and adsorption processes.

The purpose of this lecture is to apply the different geochemical processes that we previously have discussed to several types of contaminant sources. Lecture materials are taken from the articles and other sources provided in this handout.

### NITRATE CONTAMINATION

Nitrate is a serious cause of ground water contamination. Nitrogen is a major component of animal and human wastes and agricultural fertilizer. The EPA drinking water standard for nitrate is 10 mg/L as N. The dominant form of nitrogen is NO3°, which is very soluble and generally not affected by adsorption. Unconfined aquifers are susceptible to gradual long-term increases in nitrate concentrations, because of the widespread nature of nitrate and its mobility in aquiferss.

Dentitrification can reduce nitrate concentrations in ground water, and this process is represented by the following reaction:

 $NO_3^-$  + organic carbon

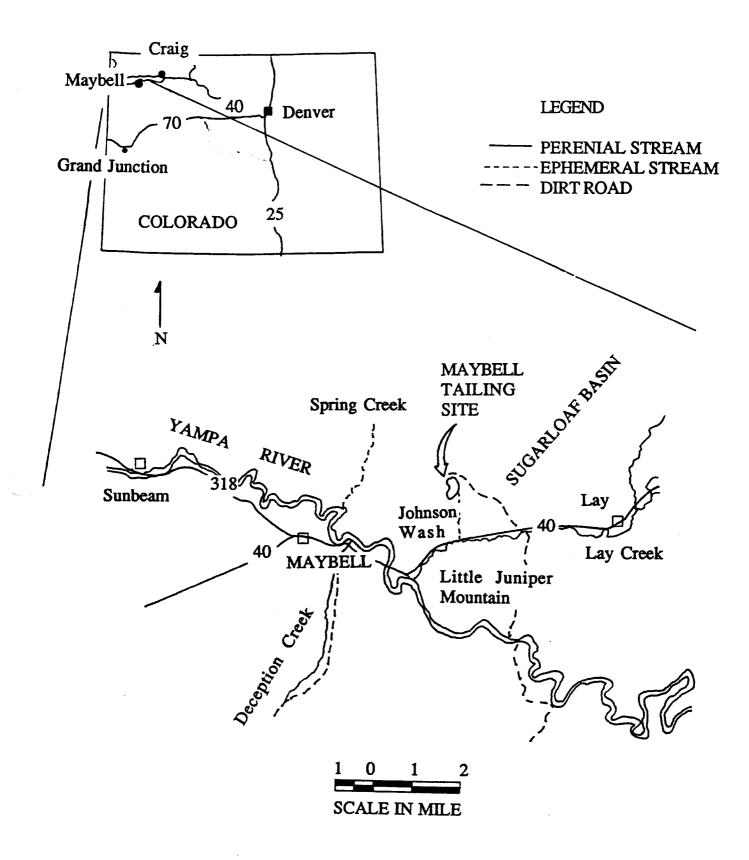
 $N_2$  (gas) +  $CO_2$  +  $H_2O$ 

Denitrification is expected to occur only in zones that are depleted in dissolved oxygen, namely anaerobic environments. Field studies, however, have shown that denitrification will occur in ground water zones where labile organic matter and denitrifying bacteria exist even if the ground water contains low concentrations of dissolved oxygen.

### Evidence for denitrification at a uranium-mill tailings site, Maybell, Colorado

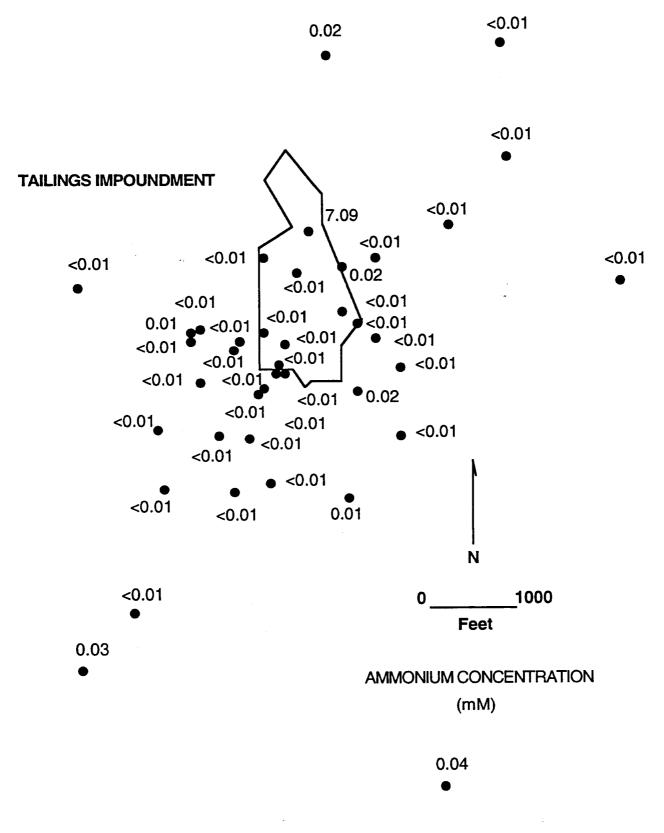
- P. Longmire<sup>1</sup> & B. M. Thomson<sup>2</sup>
- 1. Los Alamos National Laboratory, MS C346, Los Alamos, New Mexico 87545
- 2. University of New Mexico, Department of Civil Engineering, Albuquerque, New Mexico 87131

ABSTRACT: Sulfuric-acid leachate generated from surface disposal of uranium mill tailings at Maybell, Colorado has impacted groundwater quality within the Browns Park Formation. Groundwater contamination, however, is localized directly beneath the tailings impoundment. Tailings leachate at the site contains elevated concentrations of NO3, SO4, U, and other solutes. Groundwater quality data, microbiological studies, and geochemical modeling suggest that NO3 is being removed from solution through denitrification processes under reducing conditions. Presence of H2S, liquid and gaseous hydrocarbons, humic acids, and abundant pyrite have maintained reducing conditions subjacent to the impoundment. Denitrifying bacteria (Pseudomonas, Acinetobacter, and Flavobacterium) identified in sediment samples catalyze redox reactions with NO3. Subsequently, contaminant concentrations of NO3 decrease 1000 times over short lateral flow distances (300 m). Laboratory batch experiments using unconsolidated sediments from the Browns Park Formation, with NO3, glucose, and other nutrients added, resulted in a 40 to 60 percent decrease of NO3 concentrations over two weeks. Geochemical modeling of groundwater at the site suggests that denitrification is coupled with neutralization of acidic leachate by calcite. Application of biochemical and geochemical processes occurring at Maybell provide an excellent model for in situ aquifer restoration programs considered at other uranium tailings and NO3- contaminated sites.



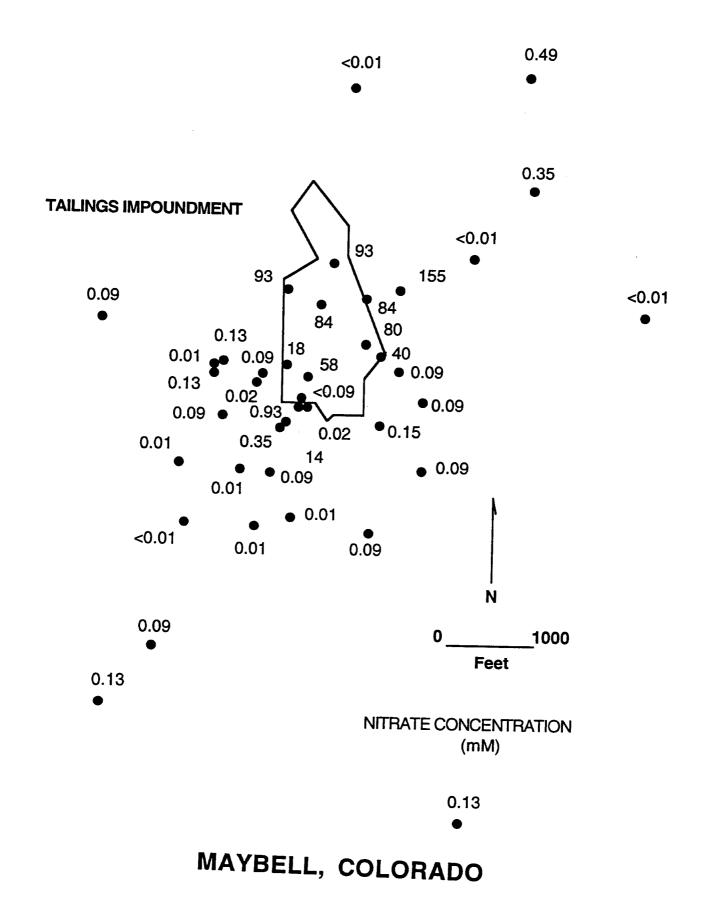
Species and Parameter	Lysimeter 082	Lysimeter 083
Mg	18.1	12.8
Ca	11.7	11.5
К	1.18	1.56
Na	4.96	5.13
SO4	116	84.4
CI	0.37	0.59
AI	26.7	13.0
Mn	15.8	6.36
Fe	6.79	10.0
NO <sub>3</sub> (N)	30.0	28.6
PO <sub>4</sub>	0.03	0.01
NH4 (N)	-	57.1
U	0.004	0.002
TDS (mg/L)	15300	11500
Temp (°C)	17.0	17.0
pH í í	2.87	3.26
Eh (field, mV)	+756	+686

### Table 1. Analyses of tailings-pore water, Maybell, Colorado. Sampled on March 17, 1989. (all concentrations in millimolar units unless noted).

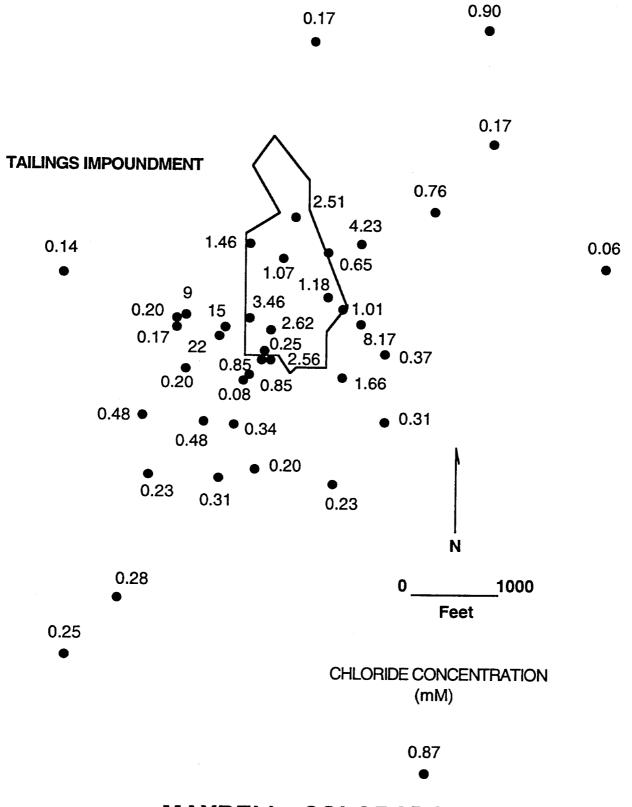




17-19



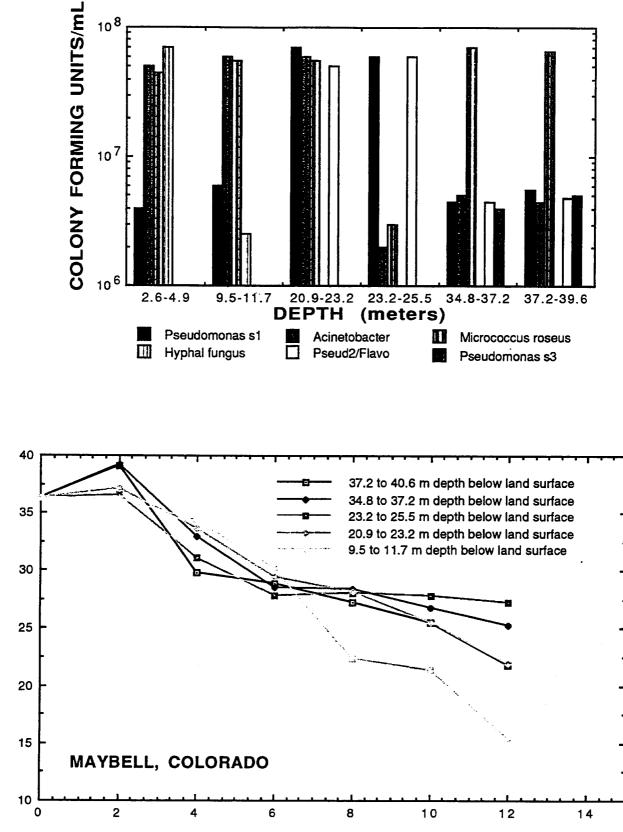
17-20



1

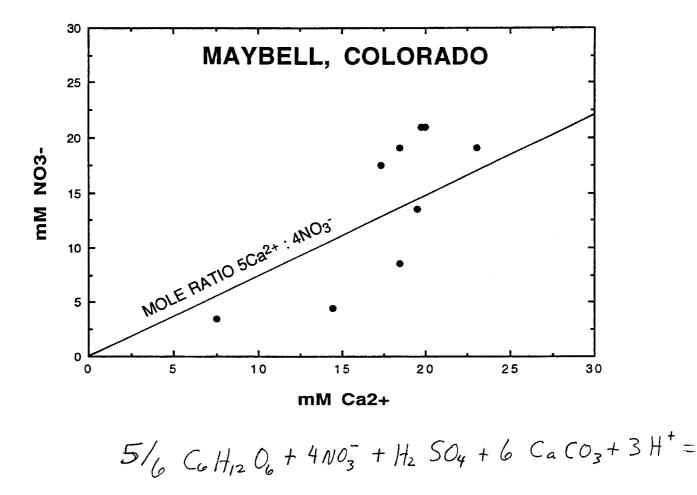


17-21



**MM NO3 (N)** 





 $CaSO_4 \cdot 2H_2O + 2N_2(g) + 11 NCO_3 + 5Ca^{2+}$ 

## CASE HISTORY: LONG-TERM FATE OF ORGANIC MICROPOLLUTANTS IN SEWAGE-CONTAMINATED GROUND WATER, BARBER ET AL.

HYDROGEOLOGICAL CHARACTERISTICS

NWWA

- Hydraulic conductivity 1.3 x 10<sup>-3</sup>
- Porosity 35%
- Ground water flow velocity 0.3 to 1.0 m/d

Source: Barber et al. (1988)

### VOLATILE ORGANIC COMPOUNDS IDENTIFIED IN SEWAGE EFFLUENT-CONTAMINATED GROUND WATER, OTIS AIR BASE, MA

001000	CONCENTRATION
COMPOUNDS	<u>(ug/L)</u>
BENZENE	1.6
p-DICHLOROBENZENE	0.60
o-DICHLOROBENZENE	0.67
DICHLOROETHENE	280
TETRACHLOROETHENE	1000

SOURCE: BARBER et al. (1988)

## **AVERAGE RETARDATION FACTOR**

R =  $r_z/r_w$  = 1 + 3.2 ffoc (KOW)<sup>0.72</sup> p(1-n)/n where

- R = Average retardation factor;
- r<sub>z</sub> = Solute residence time;
- r<sub>w</sub> = Water residence time;
- f = Material < 125 um;
- foc = Fraction of organic carbon on < 125 um material;
- p = Density of sediment; and
- n = Porosity

Source: Schwarzenbach et al. (1983)

NWWA

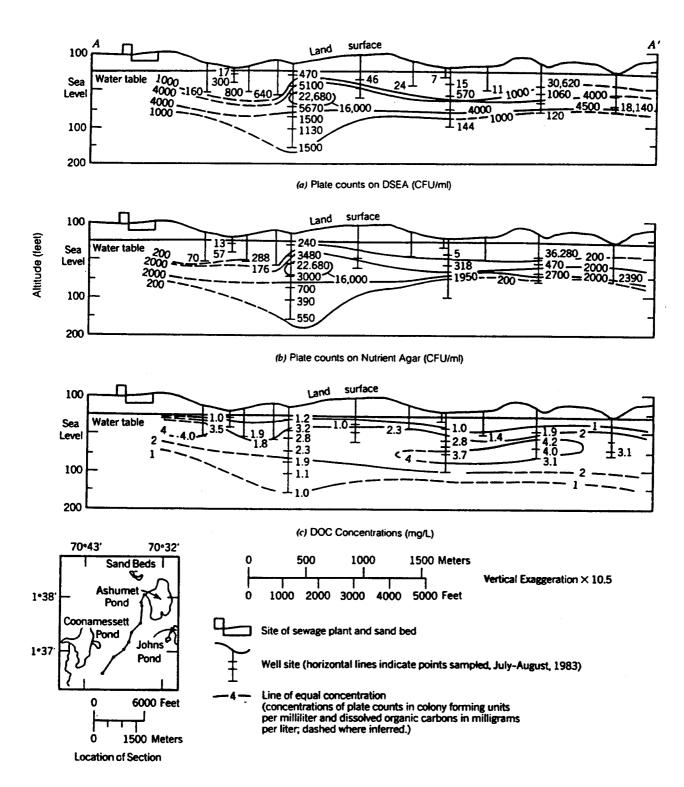
## **RETARDATION FACTORS**

COMPOUND	PREDICTED	OBSERVED
Trichloroethene	1.0	1.0
Tetrachloroethene	1.1	1.0
p=Dichlorobenzene	1.3	1.0

f = 0.05, foc = 0.001, p = 2.60 g/cm<sup>3</sup>, and n = 0.30

Source: Barber et al. (1988)

NWWA



### Bacterial distributions as reflected by plate counts and their relationship to dissolved organic carbon content (from Ceazan and others, 1984).

This study involved quantifying bacterial levels in water by counting the number of colony-forming units on both nutrient agar and dilute soil-extract media (Ceazan and others, 1984). The areas with elevated bacterial counts and the distribution of dissolved organic carbon (DOC) coincide with the position of the plume estimated using measured contaminant concentrations. The strong correlation between bacterial counts and distribution of DOC suggests that microbial processes are removing organic contaminants from the plume (Ceazan and others, 1984).

## **SUBSURFACE BEHAVIOR**

- Variations in source composition
- Variations in bed loading
- Adsorption
- Biological transformation
- Dispersion

NWWA

### SUMMARY

- The compounds TCE, PCE, and DCB are good indicators of sewage contamination:
  - Relatively unique to the sewage source
  - Mobile in low organic carbon sediments
  - not readily biodegradable
- Many trace organic compounds have persisted over 30 years
- Persistent organic compounds not removed by secondary treatment can contaminate large quantities of ground water by rapid infiltration into low-carbon, permeable aquifers

NWWA

### **HEAVY METAL AND TRANSITION METAL CONTAMINATION**

Heavy metal and transition metal contamination occur in situations where the pH is much lower or much higher than the normal range for ground water. Conditions of extreme pH in ground water are common in waste materials at metal mines or in ash disposal areas associated with coal-fired power plants. Selenium and arsenic, for example, have been reported at very high concentrations in ground water at fly-ash disposal sites in North Dakota in zones where pH levels are above 10. In contrast, similar investigations at fly-ash disposal sites in southern Ontario, where the ground water pH is between 7 and 9.5, have established that the concentrations of these elements are below EPA standards.

Field studies conducted at metal extraction-processing sites, where sulfuric and nitric acids are used, have shown that the contaminated ground water (with a pH below 4.5) invariably has high concentrations of many transition metals, heavy metals, non-metals, and in some cases radionuclides. The neutral pH zones of contamination that occur downgradient of the low-pH zones are characterized by lessor concentrations of contaminants, where some contaminant concentrations are below EPA standards (chromium, iron, manganese). Decreases in contaminant concentrations are the result of pH influence on decreasing solubility (except for arsenic, selenium, and molybdenum) and enhancement of adsorption of cationic species under increasing alkaline conditions. The hydrogeochemical nature of sandy aquifers that contain acidic leachate can be represented by three main zones: the acidic zone, the neutralization zone, and the neutral-pH zone, the hazardous contaminants are transferred from the water phase to the solid phase by precipitation and adsorption in the neutralization zone.

Sol

6H 8

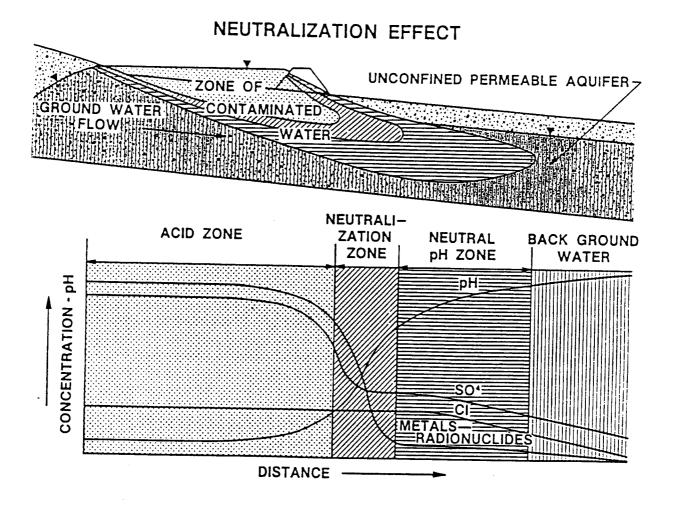
## HEAVY METAL AND TRANSITION METAL CONTAMINATION

- Occur in situations where waste leachate has a pH much lower or much higher than the normal range for ground water.
- Fly-ash disposal sites and metal extraction-processing sites are characterized by heavy metal and transition metal contamination.

17-32

 Contaminants typically found include arsenic, cadmium, chromium, molybdenum, and selenium.

**NWWA** 



The above figure illustrates the effect of neutralization on contaminant concentrations along the flow path and indicates the acid zone, neutralization zone, neutral pH zone, and background water (Shepherd and Brown, 1982).

#### CHARACTERISTICS OF ZONES

ACID	NEUTRALIZATION	NEUTRAL pH
ZONE	ZONE	ZONE
<ul> <li>ESSENTIALLY THE SAME AS TAILINGS WATER</li> <li>HIGH CONCENTRATION OF: HEAVY METALS TRANSITION METALS RADIONUCLIDES MAJOR CATIONS MAJOR ANIONS</li> <li>LOW pH: TO ≈ 3.5</li> </ul>	<ul> <li>pH INCREASES FROM ACIDIC (≃3.5) TO NEAR NEUTRAL (≃6.0) LEVELS IN A RELATIVELY SHORT DISTANCE</li> <li>RAPID DECREASE IN CONCENTRATION OF: RADIONUCLIDES HEAVY METALS TRANSITION METALS TOXIC NON-METALS SOIL CALCITE MINERALS</li> <li>ACTIVE PRECIPITATION OF GYPSUM</li> </ul>	<ul> <li>VERY LOW CONCENTRATIONS OF:</li> <li>RADIONUCLIDES HEAVY METALS TRANSITION METALS TOXIC NON-METALS</li> <li>HIGH TDS WATER PREDOMINANTES</li> <li>SOIL CALCITE UNREACTED</li> <li>ALL CONTAMINANT CONCENTRATIONS REDUCE DOWN GRADIENT</li> </ul>

The above table summarizes general chemical characteristics of the acid zone, neutralization zone, and neutral pH zone. The widths of these zones can vary, based on site-specific hydrogeological conditions and contaminant leachate characteristics (Shepherd and Brown, 1982).

## MOBILITIES OF SELECTED TRACE ELEMENTS IN GROUND WATER

Element	Form	PH Acid	Mobility Neutral	Alkaline
Aluminum Antimony Arsenic	AISO <sub>4</sub> <sup>+</sup> , AI <sup>3+</sup> , AI (OH) <sub>4</sub> <sup>-</sup> Sb(OH) <sub>3</sub> °, Sb(OH) <sub>6</sub> <sup>-</sup> H <sub>3</sub> AsO <sub>3</sub> °, H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> ,	high Iow	low high	high high
Cadmium Chromium	HAs $O_4^{2-}$ Cd <sup>2+</sup> , CdS $O_4^{\circ}$ , CdC $O_3^{\circ}$ Cr <sup>6+</sup> : HCr $O_4^{-}$ Cr $O_4^{2-}$ Cr <sup>3+</sup> : CrOH <sup>2+</sup> , Cr(OH) <sub>3</sub> °	low high low high	high Iow high Iow	high Iow high Iow

## MOBILITIES OF SELECTED TRACE ELEMENTS IN GROUND WATER

Element	Form	PH Acid	Mobility Neutral	Alkaline
Copper	Cu²+, Cu(OH) <sub>2</sub> º,			
Fluoride Iron	Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> F <sup>-</sup> , AIF <sub>2</sub> <sup>+</sup> , CaF <sup>+</sup> Fe <sup>2+</sup> : Fe <sup>2+</sup> , FeSO <sub>4</sub> <sup>o</sup> Fe <sup>3+</sup> : Fe(OH) <sub>2</sub> <sup>+</sup> ,	varies moderate	moderate high	moderate high
	Fe <sup>3+</sup> : Fe(ÓH) <sub>2</sub> +, <sup>4</sup>	moderate	moderate	high
Lead Manganese	Fe(OH) <sub>4</sub> - Pb <sup>2+</sup> , PbCO <sub>3</sub> º Mn <sup>2+</sup> , MnHCO <sub>3</sub> +	high moderate high	low moderate low	low moderate low

### MOBILITIES OF SELECTED TRACE ELEMENTS IN GROUND WATER

Element	Form	PH Acid	Mobility Neutral	Alkaline
Mercury	Hg, Hglɣ, Hg(OH)₂º	high	moderate	low
Molybdenum	H <sub>2</sub> MoO <sub>4</sub> <sup>0</sup> , MoO <sub>4</sub> <sup>2-</sup>	low	high	high
Nickel	Ni²+, NiHCO <sub>3</sub> +,			
	Ni(OH) <sub>3</sub> ⁻	high	low	low
Selenium	HSeO <sub>3</sub> <sup>-</sup> , SeO <sub>4</sub> <sup>2-</sup> ,			
	HSe⁻	low	moderate	high
Zinc	Zn²+, ZnCO <sub>3</sub> °,			
	Zn(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	high	low	high

Anions are generally adsorbed under relatively oxidizing conditions with acidic pH, because adsorbents such as clay minerals and iron oxyhydroxides have a net-positive surface charge. Antimony, arsenic, chromium, copper, fluoride, molybdenum, and selenium are adsorbed onto mineral surfaces under acid pH conditions. Cations are generally adsorbed under alkaline pH conditions, including cadmium, iron, lead, manganese, and zinc. Precipitation reactions also control the mobilities of the above elements.

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#### **LANDFILLS**

A serious cause of ground water contamination is leachate generated from municipal and industrial landfills. Investigations indicate that major constituents such as chloride, bicarbonate, sodium, calcium, and magnesium and minor constituents such as ammonium, iron, and manganese are mobile in landfill leachate. These constituents usually do exceed EPA and state standards. The pH of landfill leachates can vary from acidic to alkaline, whereas the pH of the contaminated ground water is neutral in most cases.

The leachate from municipal landfills has high concentrations of organic compounds. Complexing of trace elements, however, with organic compounds is reported by Cherry et al. (1984) to be insignificant and immobility of transition metals and non-metals is the rule rather than the exception. Humic and fulvic acids present in landfill leachate may, however, complex with metals as well as other organic contaminants.

Mineral dissolution can occur in contaminated ground water, because the landfill leachate migrating through the porous medium causes the reduction of iron and manganese oxyhydroxides. This is particularly the case when chemically-reducing landfill leachate reacts with iron and manganese-bearing minerals or solid phases stable under oxidizing conditions. These minerals or solid phases dissolve and their solubilities increase by many "orders of magnitude." Hydroxides and oxyhydroxides of iron and manganese are natural scavengers of inorganic and some organic contaminants. Their dissolution can cause the release of elements that have adsorbed onto the surface of the iron and manganese oxyhydroxides or hydroxides.

#### FACTORS AFFECTING LANDFILL LEACHATE COMPOSITION

#### **REFUSE COMPOSITION**

The amount of landfill materials available for leaching depends upon the physico-chemical characteristics of the waste, rates and extent of solid waste stabilization, and the volume of infiltration to the landfill. The total mass of refuse available for leaching may also be influenced by refuse surface area and contact time between the refuse and leaching solution.

#### REFUSE PROCESSING

Refuse processing refers to shredding and baling activities, which represent alternatives for refuse volume reduction for landfilling, and for material and energy recovery by many municipalities. The physical characteristics of refuse are changed after it undergoes a shredding process. These include an increase in surface area (greater contact of the refuse mass with percolating water); an increase in in-situ refuse density; a decrease in permeability of the refuse; a higher concentration of contaminants in the refuse; and accelerated refuse decomposition.

#### LANDFILL AGE

Variation in leachate composition and cumulative mass removal of contaminants in solid waste are dependent on age factors. Most leachate constituents exhibit concentration decreases over a 3 to 30 year period, including iron, zinc, phosphate, chloride, sodium, cooper, organic nitrogen, and total solids. The steady decreases can be attributed to continued flushing of the refuse by precipitation. Total organic carbon, however, can persist for many years (50) and still remain high. With increasing landfill age, humic and fulvic acids become more predominant. Volatile acids, including butyric acid, acetic acid, and propionic acid, are produced which corresponds to the first stage of anaerobic degradation during early stages of leachate generation.

The declining concentrations of specific organic classes of leachate (TOC) with increasing landfill age are also seen for organic degradation in natural environments. Based on research findings and available literature, Chian (1977) concluded that the resistance of organics to bacterial degradation follows the pattern: free volatile fatty acids < carbohydrates, proteins, and humic acids < aromatic hydroxyl, carboxyl, and fulvic acids.

The stability of organic compounds influences the solubility of trace metals, forming soluble complexes. Humic and fulvic acids are strong complexing ligands.

#### RATE OF WATER APPLICATION

The rate of water application can influence the mobility of the landfill leachate in a number of ways. A greater rate of water application will accelerate the attainment of landfill field capacity. Higher rates of water application to a landfill will produce a more dilute leachate than lower rates of water application.

#### DEPTH OF LEACHED BED

Refuse depth is a design variable which operates in conjunction with the rate of water application to influence leachate composition. In general, water percolating slowly through a landfill provides greater contact time between the solid and dissolved phases, and increases the chances for a high strength leachate to result. Increasing depth also results in a longer residence time and high strength leachate. For high infiltration rates, contact time is diminished between the two phases and a more dilute leachate is expected.

#### LANDFILL TEMPERATURE

Landfill temperature, a largely uncontrollable factor influencing leachate composition, has been shown to fluctuate with seasonally ambient temperature variation near the landfill surface, but significant changes are less pronounced with increasing landfill depth.

### FACTORS AFFECTING LANDFILL LEACHATE COMPOSITION

- **1. REFUSE COMPOSITION**
- 2. **REFUSE PROCESSING**
- 3. LANDFILL AGE
- 4. RATE OF WATER APPLICATION
- 5. DEPTH OF LEACHED BED
- 6. LANDFILL TEMPERATURE

### MUNICIPAL LANDFILL LEACHATE COMPOSITION (VALUES IN mg/L EXCEPT AS NOTED)

SPECIES/ PARAMETER	RANGE OF VALUES
pH (pH units)	3.7 - 11.5
Eh (VOLT)	-0.132 - +0.50
TOC	5.2 - 27,700
TDS	0 - 44,900
Alkalinity as CaCO <sub>3</sub>	0 - 20,350
NH₄	0 - 1,106
$NO_3^7 + NO_2$	0 - 27.2
Org-N	0 - 1,416
Fe	0 - 5,500
Mn	0 - 50
Cu	0 - 9.9
Cd	0 - 0.4
Pb	0 - 2.0
Hg	0 - 0.2
Se	0 - 2.7
Cr	0.01 - 18

SOURCE: Lu and others, 1985

#### NWWA

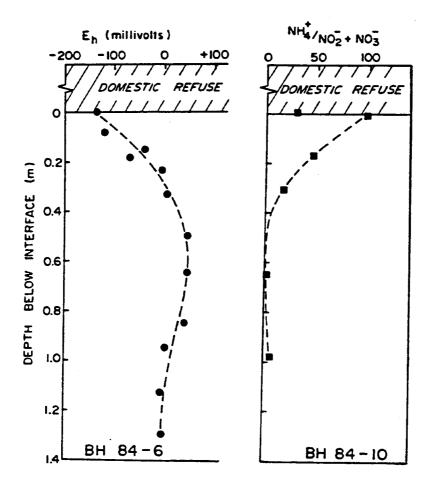
### PROCESSES INFLUENCING GENERATION OF LANDFILL LEACHATE

#### CARBON DIOXIDE AND ORGANIC ACIDS LOWER pH OF LEACHATE

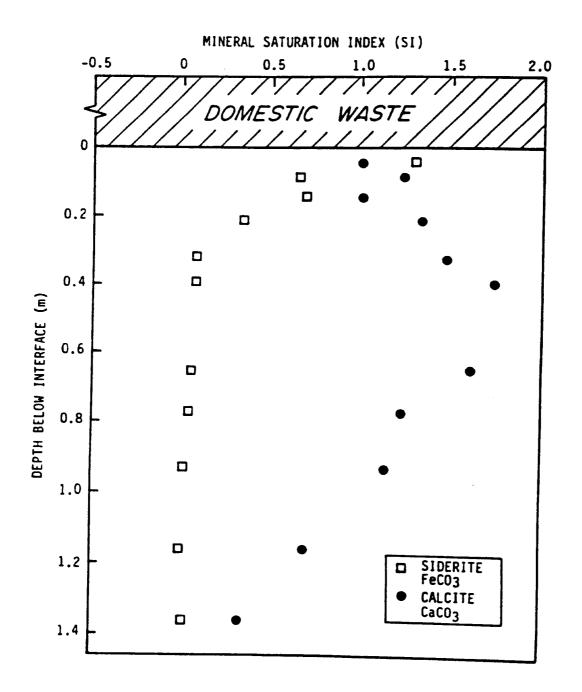
ACIDIC pH ENHANCES MINERAL DISSOLUTION

BIODEGRADABLE ORGANIC COMPOUNDS DEPLETE DISSOLVED OXYGEN CONCENTRATIONS AND CREATE ANAEROBIC CONDITIONS

REDOX POTENTIAL CONTROLS SOLUBILITY OF IRON AND MANGANESE OXIDES



Redox regime (Eh profile) in clayey subsoil and distribution of N-species ratio (Yanful, et al. 1988). Highly reducing conditions with Eh of -130 mV exist near the soil/waste interface and vary to +50 mV at about 50 cm below the interface at the Sarnia landfill, Ontario, Canada.

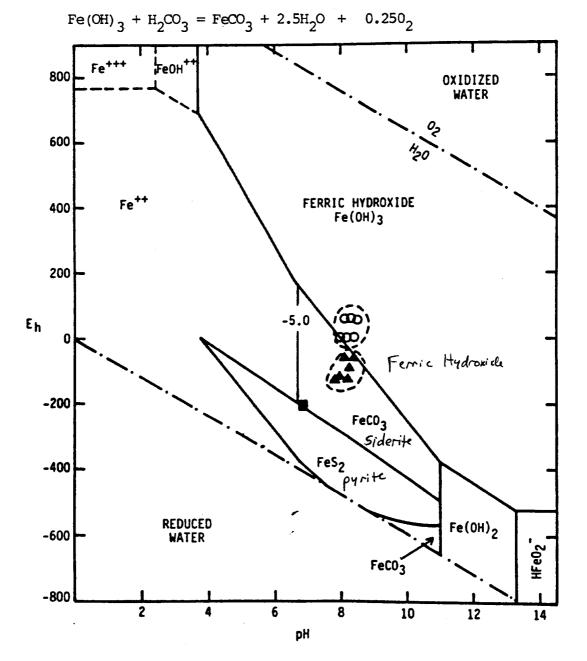


Mineral saturation indices vs. depth in pore waters in clay-rich zone at Sarnia landfill, Ontario, Canada (Yanful, et.al., 1988). Porewater is oversaturated with respect to  $FeCO_3$  in the top 20 cm of the profile. The degree of supersaturation decreases with depth. Porefluid is oversaturated with respect to calcite at all depths in the profile.

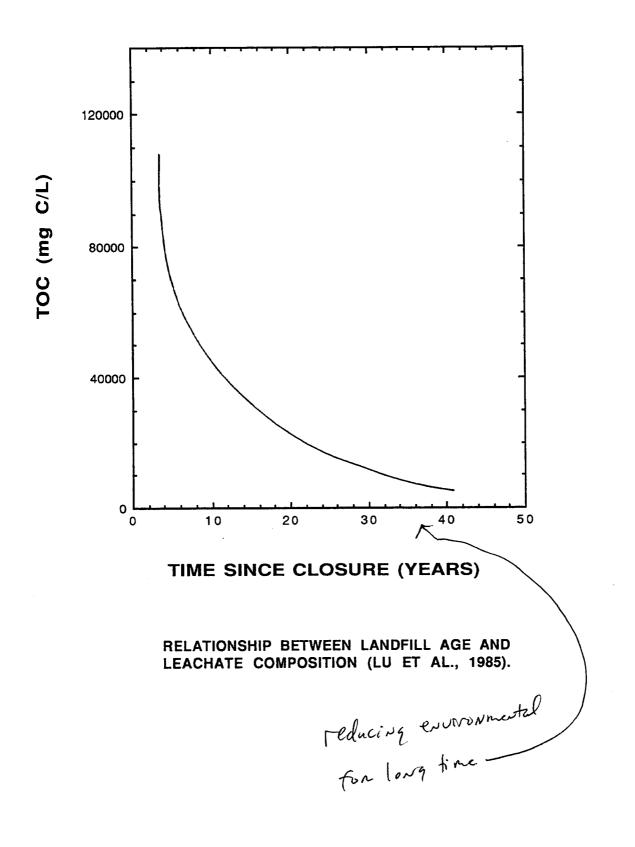
A sample of water collected from the waste (square dot) plots close to the pyrite - siderite boundary and the Eh conditions may be controlled by the reaction:

$$8e^{-} + FeS_2 + H_2CO_3 + 4H^{+} + 60_2 = FeCO_3 + 2SO_4^{2-} + 3H_2O_4^{2-}$$

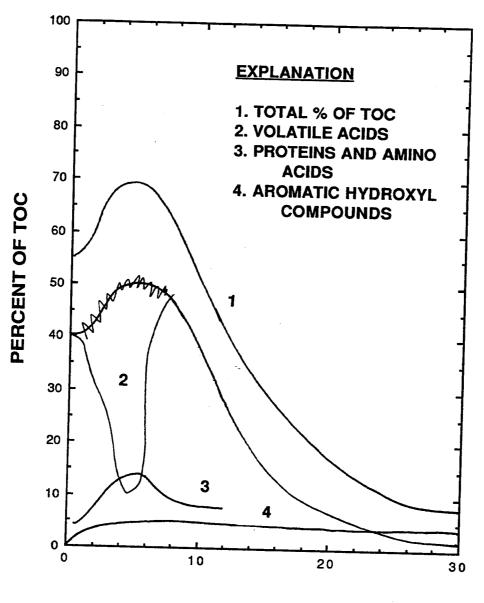
Water samples near the waste-subsoil interface (solid triangle) plot in the stability field for  $FeCO_3$ , indicating an increase in Eh and pH over conditions existing in the waste. Clay samples below the waste-clay subsoil interface (open circles) show higher Eh values, plotting close to the siderite -  $Fe(OH)_3$  boundary. Introduction of highly reduced aqueous species from <sup>3</sup> the waste into the subsoil results in reduction of subsoil  $Fe^{3+}$  to  $Fe^{2+}$  and precipitation of siderite:



Stability relations of iron hydroxides, sulphide and carbonate in water at 25°C and one atmosphere total pressure. Water sample in the waste,  $\blacktriangle$  soil samples near interface and  $\circ$  soil samples deeper in the profile.  $\Sigma S = 10^{-6}$ ,  $\Sigma CO_3 = 10^{-2}$ ,  $\Sigma Fe = 10^{-3.4}$ ,  $10^{-4.0}$ ,  $10^{-5.0}$ . (Vonful et al., 1988).



17-47



TIME (YEARS)

TRENDS IN TOC VERSUS LANDFILL AGE (CHIAN AND DEWALLE, 1977).

### ORGANIC COMPOUNDS OR CLASSES IDENTIFIED IN LANDFILL LEACHATES

ACETONE

SHORT CHAIN ALCOHOLS

SHORT CHAIN ACIDS

**ALKANES** 

**KETONES** 

**CHLORINATED SOLVENTS** 

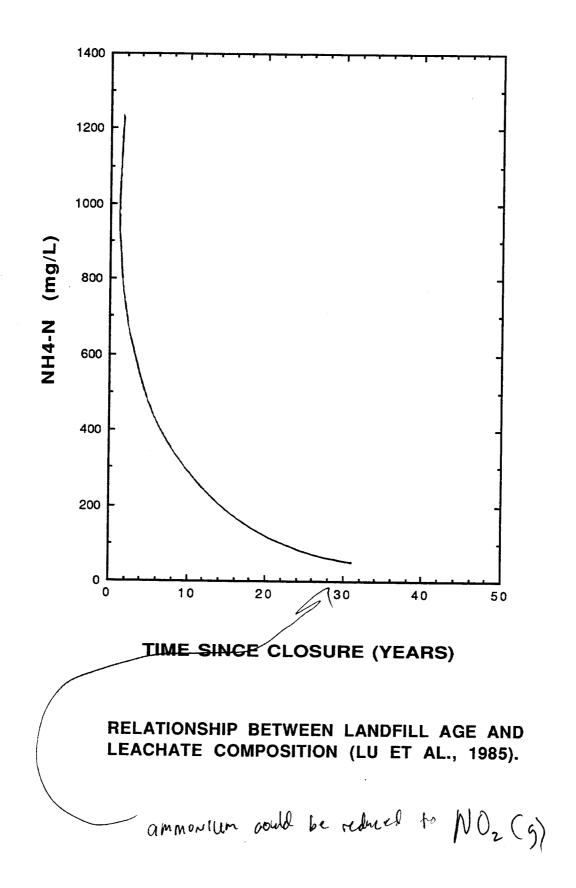
**AROMATIC SOLVENTS** 

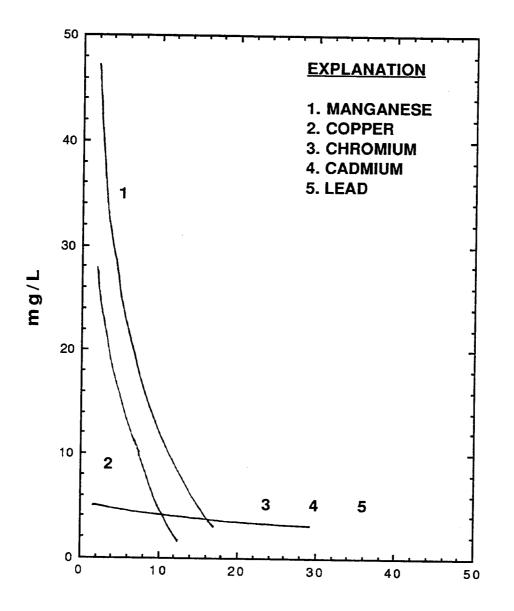
**PHTHALATE ESTERS** 

**HYDROCARBONS** 

**OTHERS** 

SOURCE: LU et al. (1985).







RELATIONSHIP BETWEEN LANDFILL AGE AND LEACHATE COMPOSITION (LU ET AL., 1985).

### LANDFILL LEACHATE AND ENVIRONMENTAL INTERACTIONS

**MIGRATION MECHANISMS** 

**DIFFUSION AND DISPERSION** 

DILUTION

**ADSORPTION** 

**PRECIPITATION/DISSOLUTION** 

COMPLEXATION

ION EXCHANGE

**REDOX REACTIONS** 

**BIOGEOCHEMICAL PROCESSES** 

### LANDFILL LEACHATE AND **ENVIRONMENTAL INTERACTIONS**

SOIL PROPERTIES AND COMPOSITION

**MINERALOGY** 

ORGANIC MATTER Kdorg = KOC(om) BIOLOGIC

**BIOLOGICAL ACTIVITY** 

TEXTURE

CATION EXCHANGE CAPACITY CEC at pH 6 and about AEC ~ 0. 10 CEC

**ANION EXCHANGE CAPACITY** 

### CASE HISTORY: HYDROGEOCHEMICAL STUDIES AT A LANDFILL IN DELAWARE

Baedecker and Apgar

#### ABSTRACT

Plume of leachate have migrated downgradient from the Army Creek landfill in Delaware, a site used for disposal of industrial and municipal refuse during the 1960's. A series of contaminantrecovery wells was installed in the early 1970's between the landfill and downgradient watersupply well to intercept and remove contaminated water. Beneath the landfill and immediately downgradient of the landfill large amounts of iron and manganese are dissolved, organic matter is oxidized and reduced, oxygen is consumed, ammonia is adsorbed, and nitrate is reduced. Farther downgradient some of the reactions are altered; iron and manganese precipitate, less organic matter is oxidized and reduced, and more ammonia is removed by ion exchange. Farther downgradient the water chemistry is controlled largely by mixing. Measurements of chemical constituents in water near the landfill show that most constituents have decreased in concentrations over an 8-year period (1973-1981). As leachate moves downgradient, the attenuation of contaminants is controlled by the following processes: (1) operation of the recovery-well system that removes contaminated water and reverses the local flow, (2) dilution of leachate with native groundwater, (3) mixing of anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and (4) interaction of contaminants with aquifer materials. Although the recovery-well systems have intercepted and removed most of the contaminated water and the quality of water from most downgradient monitor wells has improved, the leachate remains anaerobic, large amounts of gases are generated, and refractory organic compounds are present. Continued pumping of contaminant-recovery wells has lowered the head in the aquifer and wasted a large amount of uncontaminated groundwater.

### CONCLUSIONS

- Chemical reactions and processes in contaminated water do not remain constant with time.
- Early stage landfill leachate has high concentrations of carbon, nitrate, and sulfate.
- Late stage landfill leachate has high concentrations carbon, ammonium, hydrogen sulfide, methane, iron, and manganese.
- Under low flow conditions, geochemical attenuation occurs.

NWWA

### CONCLUSIONS

- Attenuation of leachate depends on:
  - Aquifer restoration system
  - Dilution of leachate with native ground water
  - Mixing of anaerobic leachate with oxygenated ground water (decomposition of organic matter and precipitation of metals)
  - Interaction of contaminants with aquifer materials

NWWA

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Shepherd, T.A. and Brown, S.B., 1982. A Generic Model of Contaminant Migration from Uranium Tailings Impoundments, <u>Symposium on Uranium Mill Tailings Management</u>, Fort Collins, CO, December 9-10, pp. 241-257.

Yanful, E.K., Nesbitt, H.W., and Quigley, R.M., 1988. Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada - 1. Thermodynamic Assessment and Chemical Interpretations: <u>Applied Geochemistry</u>, Vol. 3, pp. 523-533.

Yanful, E.K., Quigley, R.M., and Nesbitt, H.W., 1988. Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada - 2. Metal Partitioning and Geotechnical Implications: <u>Applied</u> <u>Geochemistry</u>, Vol. 3, pp. 623-629.

Section 18

C

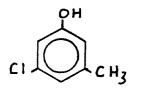
# **Organic Problem Session**

Lecture by: All Instructors

# SECTION CONTENTS

112.3

### CLASS EXERCISE NAME THE FOLLOWING ORGANIC COMPOUNDS.



NAME\_\_\_\_\_

 $H_{C1} = C = C_{H} = C_{H}$ 

NAME\_\_\_\_\_

# DRAW THE STRUCTURAL FORMULA FOR THE FOLLOWING ORGANIC COMPOUNDS.

PERCHLOROPROPANE

2-BROMO-1-CHLOROPROPANE

2, 2, 4-TRIMETHYLPENTANE

1, 1, 2-TRICHLORO-2, 2, 1-TRIFLUOROETHANE

ACETONE	C <sub>3</sub> H <sub>6</sub> O
ALDRIN	C <sub>12</sub> H <sub>8</sub> CI <sub>6</sub>
BENZENE	С <sub>6</sub> Н <sub>12</sub>
m-DICHLOROBENZENE	C <sub>6</sub> H <sub>4</sub> CI <sub>2</sub>
ETHYLBENZENE	С <sub>в</sub> Н <sub>Ю</sub>

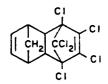
TOLUENE

NAME

 $C_7 H_8$ 

MOLECULAR FORMULA

о сн<sub>3</sub>-с-сн<sub>3</sub>









CH3

BASED ON MOLECULAR FORMULA, LIST ORGANIC COMPOUNDS IN ORDER OF DECREASING AQUEOUS SOLUBILITIES. STATE YOUR REASONS FOR THE ORDER.

ACETONE (C<sub>3</sub>H<sub>6</sub>O) /

ALDRIN (C<sub>12</sub>H<sub>8</sub>Cl<sub>6</sub>) (

**BENZENE (C<sub>6</sub>H<sub>6</sub>)**  $2^{-1}$ 

o-DICHLOROBENZENE (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>) 3

TOLUENE (C<sub>7</sub>H<sub>8</sub>) 4

ETHYLBENZENE (C<sub>8</sub>H<sub>10</sub>) 5

BASED ON MOLECULAR FORMULA AND WEIGHT, LIST THE ORGANIC COMPOUNDS IN ORDER OF INCREASING ORDER OF MOBILITY (FROM LOW (1) TO HIGH (9)).

ACETONE (M.WT.=58)	CH3-C-CH3	
BENZENE (M.WT.=78)	Ó	
TOLUENE (M.WT.=92)	CH,	
p-XYLENE (M.WT.=106)	CH, CH, CH,	,
ETHYLBENZENE (M.WT.=106)	CH2CH3	
p-CRESOL (M.WT.=108)	CH, OH	
NITROBENZENE (M.WT.=123)	NO <sub>3</sub>	
PARATHION (M.WT.=291)	$C_{2}H_{5}O \xrightarrow{S} P = O \xrightarrow{NO_{2}} NO_{2}$	
DDT (M.WT.=354)	ci	

USING THE INFORMATION GIVEN BELOW TO CALCULATE THE AMOUNT OF OXYGEN REQUIRED TO COMPLETELY OXIDIZE GASOLINE (ASSUME THE FORMULA FOR GASOLINE IS -CH<sub>2</sub>-) TO CARBON DIOXIDE AND WATER: If you know it is a redox equation Balance the half equations multiplying to balance TOTAL AMOUNT OF GASOLINE: 1000 LBS. Need to balance electrons THE HALF REACTIONS ARE AS FOLLOWS: -2 -2+4=66 (-CH<sub>2</sub>-)+ 2H<sub>2</sub>O --> CO<sub>2</sub> + 66<sup>-</sup> + 6H<sup>+</sup> (  $multipl_2$  by 2) to get commendence (-CH<sub>2</sub>-)+ 2H<sub>2</sub>O + 30<sub>2</sub> + 126<sup>-</sup> + 12H<sup>4</sup> -> 2 CO<sub>2</sub> + 126<sup>-</sup> + 12H<sup>4</sup> + 16H<sub>2</sub>O 2(CH<sub>2</sub>)+ 30<sub>2</sub> +> 2CO<sub>2</sub> + 2 H<sub>2</sub>O -> have lis  $O^2$  pen every C A. CALCULATE THE TOTAL POUNDS OF OXYGEN REQUIRED TO OXIDIZE THE 1000 LBS OF GASOLINE (ROUND OFF NUMBERS);

1000 16x 454 g × mole CH2 = 3.2 × 10 4 moles CH2 16 14 g

3.2 ×10<sup>4</sup> m Ettz × 1.5 m Oz x <u>32 8</u> × <u>16</u> = 4.9 × 10<sup>4</sup> 16 Oz mole Ettz mole Dz 454g

**B.** HOW MANY POUNDS OF WATER WOULD BE REQUIRED TO SUPPLY THE OXYGEN ASSUMING THAT THE WATER WAS IN EQUILIBRIUM WITH AIR (8 PPM  $O_2$ ).

$$\frac{816502}{10^{6}165 H_{20}} = \frac{4.9 \times 10^{4} 160_{2}}{7 165 H_{20}} = 4.3 \times 10^{8} 165 H_{20}$$

```
GIVEN THAT Rd = 1 + <u>pKd</u>, where

n

Rd = RETARDATION FACTOR,

p = DENSITY (g/cm<sup>3</sup>),

n = POROSITY, AND

Kd = DISTRIBUTION COEFFICIENT (ml/g)
```

CALCULATE Kd AND Rd FOR THE FOLLOWING:

SPECIES	КОС	00	Kd	p/n	Rd		
ACETONE	1.0	0.002		12			
CHLORO-							
BENZENE	372	0.002		12			
M-XYLENE	600	0.002		12			
NOTE. Kd =	NOTE. Kd = KOC X OC						
BELOW IS AN ISOCONCENTRATION MAP FOR A							
HYPOTHETICAL WASTE SITE WITH GROUND							
WATER CONTAMINATION. LABEL							
ISOCONCENTRATION LINES WITH							
APPROPRIA	ATE SPE	<b>CIES BA</b>	SED ON	Rd.			



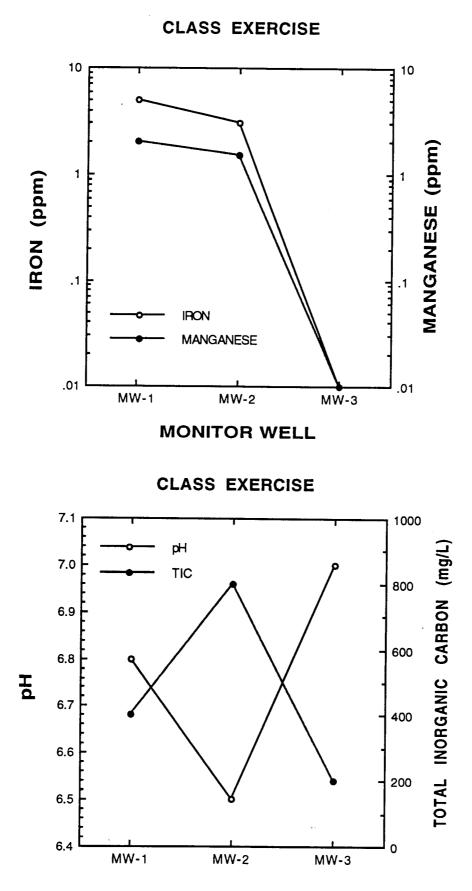
.

GIVEN THAT Rd = 1 + <u>pKd</u> , where					
		n			
Rd = RETA	RDATIO	N FACTO	DR,		
p = DENSIT	Ύ (g/cm³	),			
n = POROS	ITY, AND	)			
Kd = DISTR	BUTION	I COEFF	ICIENT (r	nl/a)	
CALCULAT					NG:
<b>SPECIES</b>		OC	Kd	p/n	Rd
CTET	275	0.001		10	
PCE	257	0.001		10	
1,1,1-					
ТСА	186	0.001		10	
TCE	166	0.001		10	
NOTE. Kd = KOC X OC					
BELOW IS AN ISOCONCENTRATION MAP FOR A					
HYPOTHETICAL WASTE SITE WITH GROUND					
WATER CONTAMINATION. LABEL					
ISOCONCENTRATION LINES WITH					
APPROPRIATE SPECIES BASED ON Rd.					



BASED ON CHEMICAL DATA PRESENTED IN GRAPHS, WHICH MONITOR WELLS ARE LOCATED UP GRADIENT, WITHIN THE SOURCE, AND DOWN GRADIENT FROM THE CONTAMINANT SOURCE?

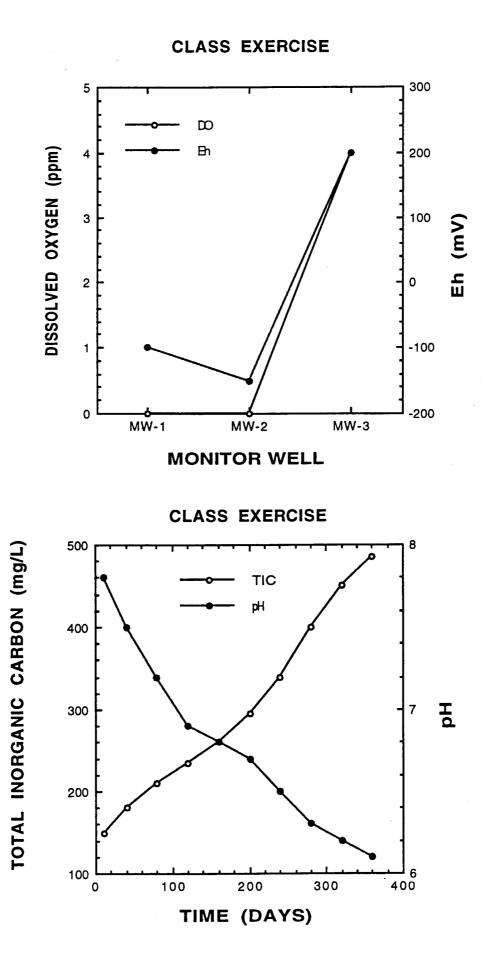
DESCRIBE CHEMICAL EVOLUTION OF GROUND WATER FROM PRE- TO POST-CONTAMINANT CONDITIONS. CONSIDER REDOX, MINERAL-SOLUTION INTERACTIONS, AND CONTAMINANT MIGRATION.



anta Ila

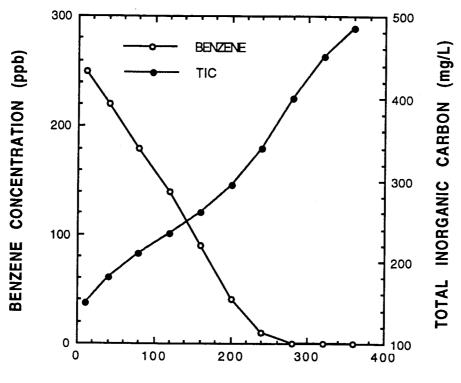
MONITOR WELL

18-9



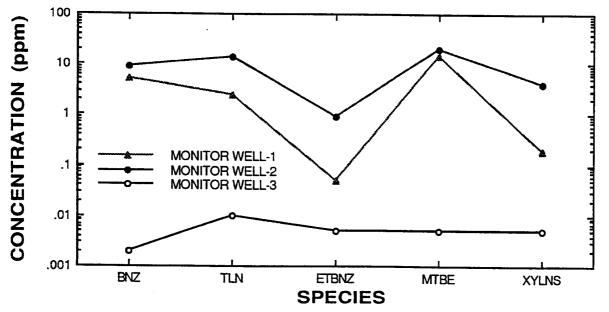
18-10

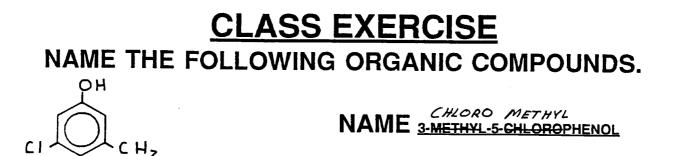




TIME (DAYS)

**CLASS EXERCISE** 



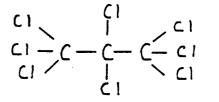


 $H_{C1} = C_{C1} = C_{H}$ 

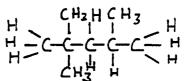
NAME<u>CIS-1. 2-DICHLOROPROPENE</u>

# DRAW THE STRUCTURAL FORMULA FOR THE FOLLOWING ORGANIC COMPOUNDS.

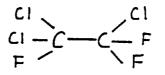
PERCHLOROPROPANE



2, 2, 4-TRIMETHYLPENTANE



1, 1, 2-TRICHLORO-2, 2, 1-TRIFLUOROETHANE



BASED ON MOLECULAR FORMULA, LIST ORGANIC COMPOUNDS IN ORDER OF DECREASING AQUEOUS SOLUBILITIES. STATE YOUR REASONS FOR THE ORDER.

ACETONE  $(C_3H_6O)$ ALDRIN  $(C_{12}H_8CI_6)$ BENZENE  $(C_6H_6)$ o-DICHLOROBENZENE  $(C_6H_4CI_2)$ TOLUENE  $(C_7H_8)$ ETHYL BENZENE  $(C_8H_{10})$ 

(HIGH SOLUBILITY) ACETONE > BENZENE > TOLUENE > ETHYL BENZENE > o-DICHLORO BENZENE > ALDRIN (LOW SOLUBILITY)

INCREASING MOLECULAR WEIGHT RESULTS IN DECREASING AQUEOUS SOLUBILITY.

OXYGEN ATOMS PRESENT IN ORGANIC MOLECULE INCREASES AQUEOUS SOLUBILITY (INCREASE IN POLARITY).

BASED ON MOLECULAR FORMULA AND WEIGHT, LIST THE ORGANIC COMPOUNDS IN ORDER OF INCREASING ORDER OF MOBILITY (FROM LOW (1) TO HIGH (9)).

- ACETONE (M.WT.=58) ORDER OF MOBILITY = 9 Miscible with water; log P<sub>oct</sub> -.24 Mobility Relative to p-Xylene: 2456
- BENZENE (M.WT.=78) ORDER OF MOBILITY = 6 Solubility 1780 mg/l at 20°C; log P<sub>oct</sub> 2.13 Mobility Relative to p-Xylene: 10.5
- TOLUENE (M.WT.=92) ORDER OF MOBILITY = 5 Solubility 515 mg/l at 20°C; log P<sub>oct</sub> 2.69 Mobility Relative to p-Xylene: 2.8
- p-XYLENE (M.WT.=106) ORDER OF MOBILITY = 3-4 Solubility 198 mg/l at 25°C; log P<sub>oct</sub> 3.15 Mobility Relative to p-Xylene: 1
- ETHYLBENZENE (M.WT.=106) ORDER OF MOBILITY = 3-4 Solubility 152 mg/l at 20°C; log P<sub>oct</sub> 3.15 Mobility Relative to p-Xylene: 1
- p-CRESOL (M.WT.=108) ORDER OF MOBILITY = 7 Solubility 18,000 mg/l at 20°C; log P<sub>oct</sub> 1.92 Mobility Relative to p-Xylene: 16.9
- NITROBENZENE (M.WT.=123) ORDER OF MOBILITY = 8 Solubility 1,900 mg/l at 20°C; log P<sub>oct</sub> 1.85 Mobility Relative to p-Xylene: 20
- PARATHION (M.WT.=291) ORDER OF MOBILITY = 2 Solubility 24 mg/l at 20°C; log P<sub>oct</sub> 3.81 Mobility Relative to p-Xylene: 0.2
- DDT (M.WT.=354) ORDER OF MOBILITY = 1 Solubility 0.003 mg/l at 20°C;  $\log P_{oct}$  6.19 Mobility Relative to p-Xylene: 0.0009

USING THE INFORMATION GIVEN BELOW TO CALCULATE THE AMOUNT OF OXYGEN REQUIRED TO COMPLETELY OXIDIZE GASOLINE (ASSUME THE FORMULA FOR GASOLINE IS -CH<sub>2</sub>-) TO CARBON DIOXIDE AND WATER:

TOTAL AMOUNT OF GASOLINE: 1000 LBS. THE HALF REACTIONS ARE AS FOLLOWS:

 $2*(-CH_2 - + 2H_2O - CO_2 + 6e^- + 6H^+)$ 

 $3^{*}(O_{2} + 4e^{-} + 4H^{+} - 2H_{2}O)$ 

2-CH<sub>2</sub>- + 3O<sub>2</sub> -> 2CO<sub>2</sub> + 2H<sub>2</sub>O BALENCED REACTION REQUIRES 3 MOLES OF O<sub>2</sub> FOR EVERY 2 MOLES OF -CH<sub>2</sub>-

A. CALCULATE THE TOTAL POUNDS OF OXYGEN REQUIRED TO OXIDIZE THE 1000 LBS OF GASOLINE (ROUND OFF NUMBERS);

1000 LBS GAS\*450 G/LBS\*1 MOLE GAS/14 G GAS = 32143 MOLES GAS

SINCE 2 MOLES OF GAS REQUIRES 3 MOLES OF OXYGEN THEN ABOUT 45000 MOLES OF OXYGEN WOULB BE REQUIRED.

45000 MOLES  $O_2 * 32$  G/MOLE  $O_2 * 1$  LB/450 G = 3200 LBS  $O_2$ 

B. HOW MANY POUNDS OF WATER WOULD BE REQUIRED TO SUPPLY THE OXYGEN ASSUMING THAT THE WATER WAS IN EQUILIBRIUM WITH AIR (8 PPM  $O_2$ ).

3200 LBS  $\Theta_2 * 1 \text{ LB H}_2\text{O}/0.000008 \text{ LBS } \Theta_2 = 400000000 \text{ LBS H}_2\text{O}$ 

GIVEN THAT Rd = 1 + pKd, where n **Rd** = **RETARDATION FACTOR**.  $p = DENSITY (g/cm^3),$ n = POROSITY, AND Kd = DISTRIBUTION COEFFICIENT (ml/g) CALCULATE Kd AND Rd FOR THE FOLLOWING: Kd p/n SPECIES KOC OC Rd 1.02 ACETONE 1.0 0.002 0.002 12 CHLORO-BENZENE 372 9.93 0.002 0.744 12 M-XYLENE 600 0.002 1.20 12 15.4 NOTE. Kd = KOC X OC **BELOW IS AN ISOCONCENTRATION MAP FOR A** HYPOTHETICAL WASTE SITE WITH GROUND WATER CONTAMINATION. LABEL ISOCONCEN-TRATION LINES WITH APPROPRIATE SPECIES **BASED ON Rd. M-XYLENE CHLOROBENZENE** ACETONE

· 1

GIVEN THAT Rd = 1 + <u>pKd</u> , where					
n Rd = RETARDATION FACTOR,					
$p = DENSITY (g/cm^3),$					
n = POROSITY, AND					
Kd = DISTRIBUTION COEFFICIENT (ml/g)					
CALCULATE Kd AND Rd FOR THE FOLLOWING:					
<b>SPECIES</b>	KOC		Kd	p/n	Rd
CTET	275	0.001	0.275	10	3.75
PCE	257	0.001	0.257	10	3.57
1,1,1-					
ТСА	186	0.001	0.186	10	2.86
TCE	166	0.001	0.166	10	2.66
NOTE. Kd = KOC X OC					
BELOW IS AN ISOCONCENTRATION MAP FOR A					
HYPOTHETICAL WASTE SITE WITH GROUND					
WATER CONTAMINATION. LABEL					
<b>ISOCONCENTRATION LINES WITH</b>					
APPROPRIATE SPECIES BASED ON Rd.					
CTET P	<b>ÇE 1,</b> 1	1,1 <b>-TCA</b>		Ε	

UP GRADIENT: MW-3 SOURCE: MW-2 DOWN GRADIENT: MW-1

DESCRIBE CHEMICAL EVOLUTION OF GROUND WATER FROM PRE- TO POST-CONTAMINANT CONDITIONS. CONSIDER REDOX, MINERAL-SOLUTION INTERACTIONS, AND CONTAMINANT MIGRATION.

Iron and manganese are mobile under reducing conditions in the absence of hydrogen sulfide. Elevated concentrations of iron and manganese within organic-contaminated ground water are the result of reduction and dissolution of ferric and manganese hydroxides. These elements are concentrated at the leading edge of the ground water plume. Benzene and MTBE are also mobile due to their high aqueous solubilities. Ethyl benzene, toluene, and xylene isomers are less soluble in aqueous solutions relative to benzene and MTBE. Section 19

# Aquifer Restoration

Lecture by: William Deutsch Woodward-Clyde Consultants

# SECTION CONTENTS

1

Additional References:

Deutsch, W.J. and J.W. Thackston, 1986. Aquifer Restoration Considerations at Inactive Uranium Mill Tailings Sites, *Proceedings of the Fourth Annual Hazardous Materials Management Conference.* 

# **Aquifer Restoration**

- General geochemical principles
- Methods of restoration
- Examples

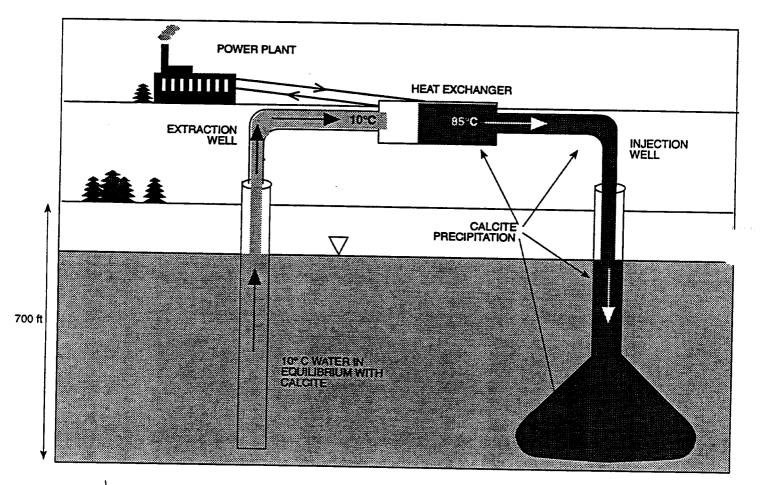
# **General Geochemical Principles**

- Develop a valid conceptual model of the hydrochemical system
  - Characterize water and rock chemistry
  - Establish dominant processes
  - Explain observed trends
- Work toward stable equilibria
  - Consider existing pH and EH of the environment
  - Use minerals present in the aquifer to your advantage
  - Consider reaction rates and the possible need for biological mediation

### **General Geochemical Principles (continued)**

- Evaluate potential detrimental side effects
  - Gas generation lower pH = generate CO2 gas
  - Mobilization of unwanted constituents
  - Clogging of pores

# **Aquifer Thermal Energy Storage**



heating up water that is at equilibrium, will cause calcite to be supersaturated + will precipitate calcite-Clogged up well within 15 min. Now they soften the water before reinjectives-Substitute Con for PUNa for Ca 19-4

# Hydrology Issues

- Rate at which aquifer can be pumped
- Diffusion of treatment chemicals into pores and contaminants out of pores
- Volume of water that must be treated

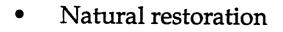
## **General Issues**

- Overall feasibility of the plan
- Time frame
- Applicability of institutional controls on water use
- Level of water quality improvement required
- Effect of restoration on nearby groundwater

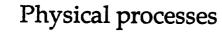
# **Aquifer Restoration Methods**

- Natural restoration
- Induced restoration
  - Groundwater speeping
  - Pump, treat, and reinject
  - In situ

# **Aquifer Restoration Methods**



will low or containing the containin



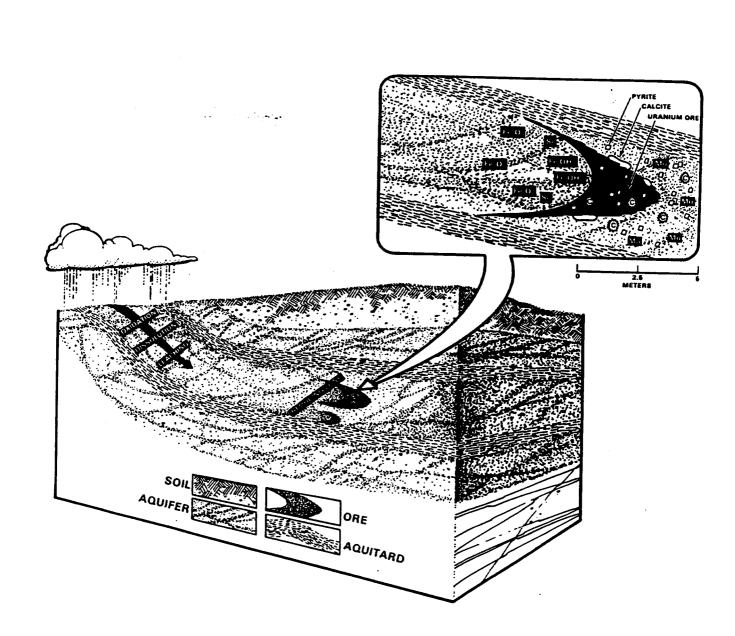
- -- dispersion
- -- diffusion
- **Chemical Processes**
- -- neutralization

precipitation

- -- mineral dissolution & ppt'n
- oxidation/reduction
- -- adsorption & ion exchange

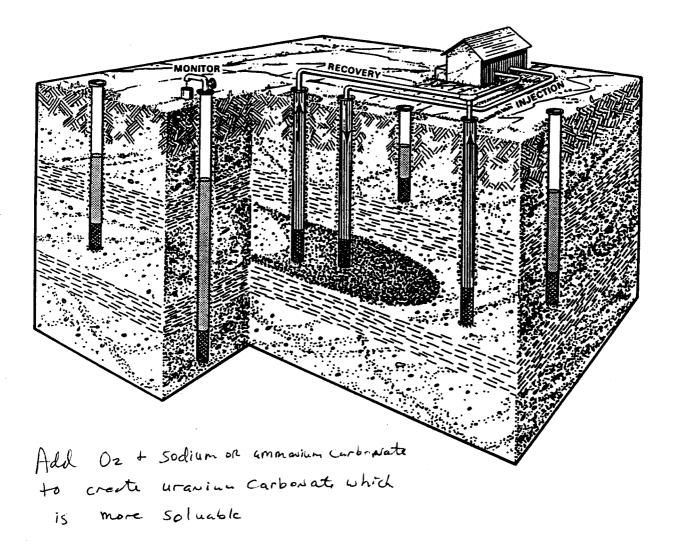
**Biochemical degradation** 

# **Uranium Roll-Front Schematic**

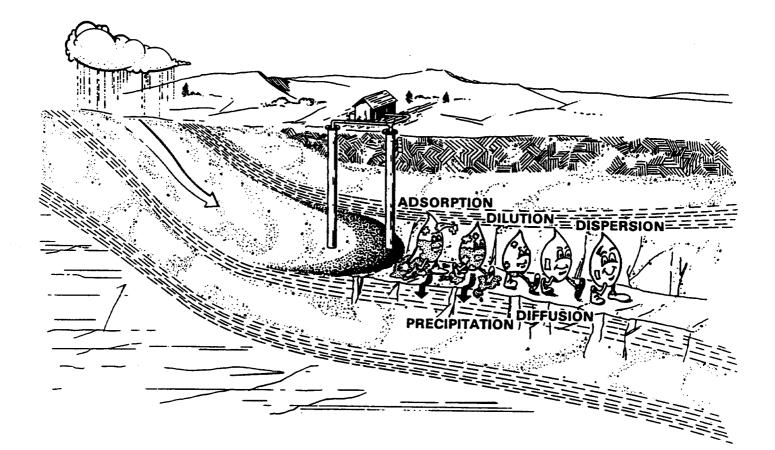


# **In-Situ Uranium Mine**

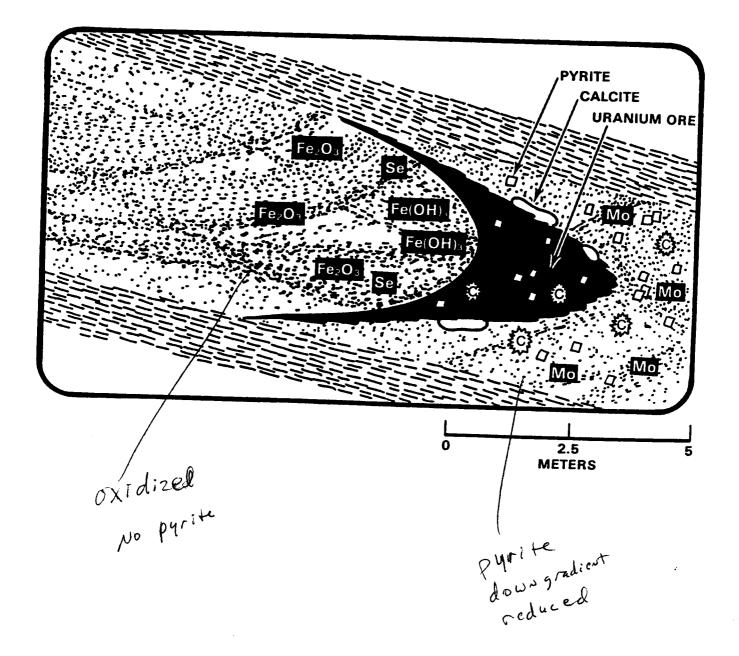
Injection, Recovery and Monitoring Well Pattern



# **Aquifer Groundwater/Sediment Interactions**

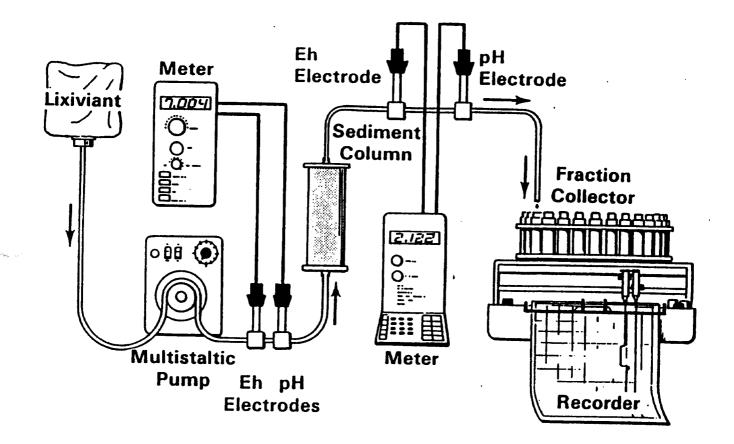


# **Roll-Front Mineralization In-Situ Uranium Mine**

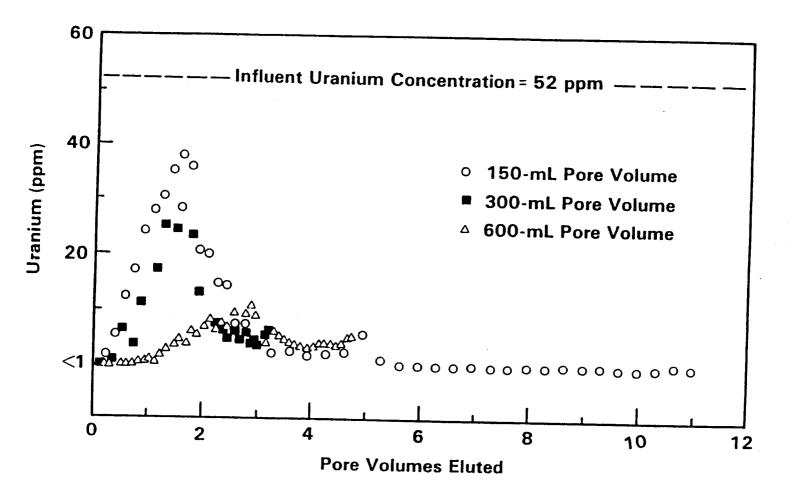


# Experimental Design of Flow-Through Column Experiments

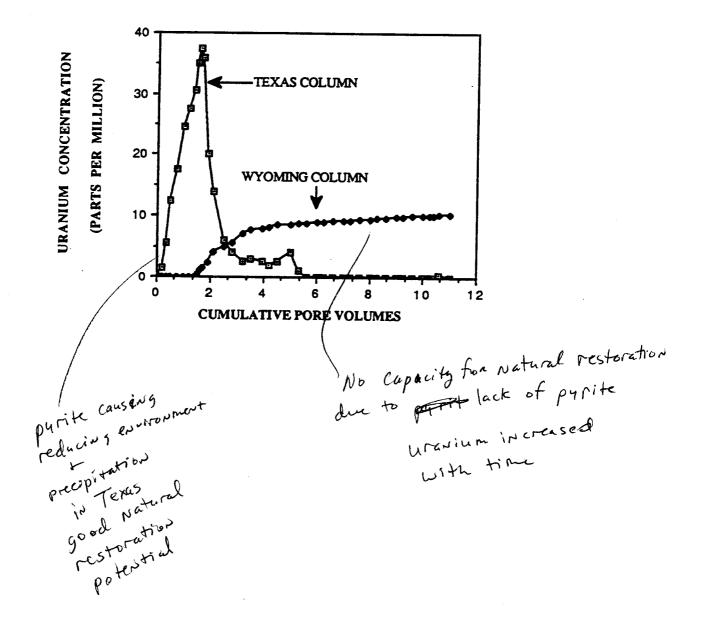
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# **Results of Column Experiments**



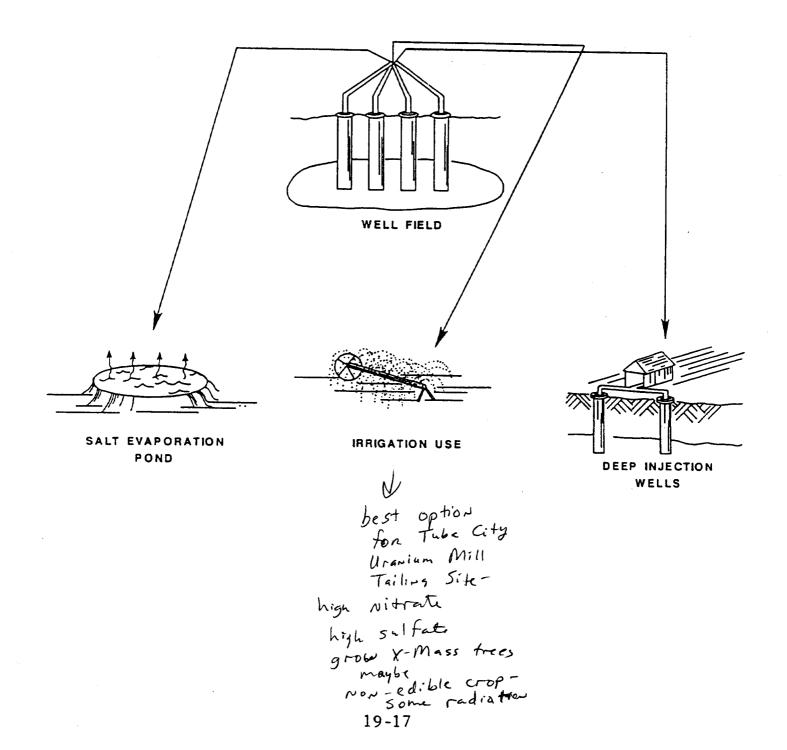
# Uranium Concentration in Effluent from Texas and Wyoming Natural Restoration Column Experiments



# **Aquifer Restoration Methods (continued)**

- Induced restoration
  - Groundwater sweeping
     removal and disposal

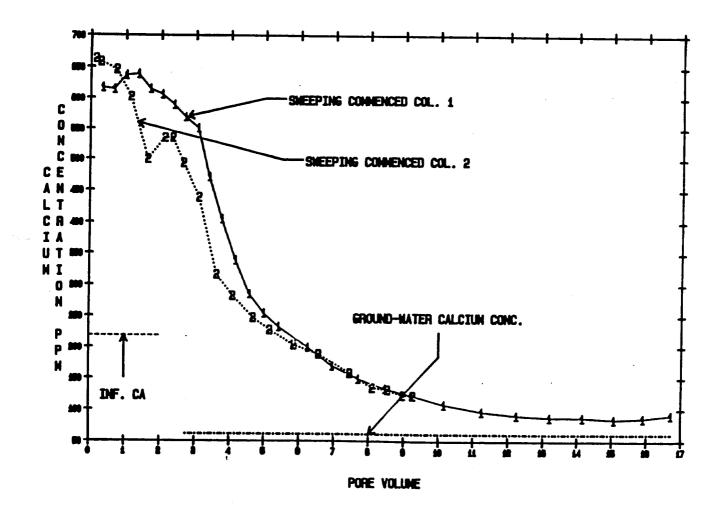
# **Removal and Disposal Alternatives**



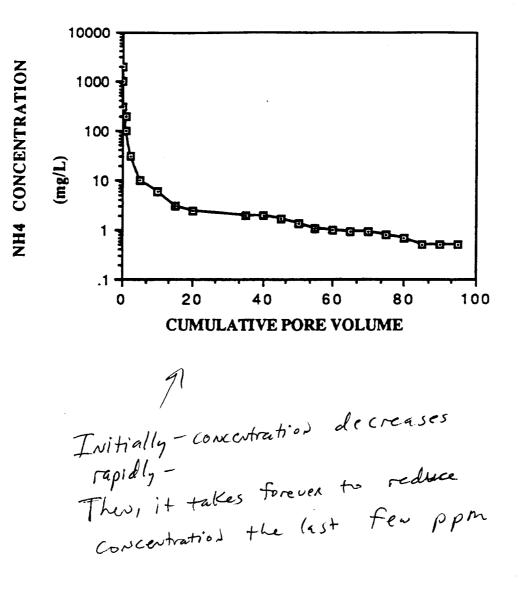
# Geochemical Factors Affecting Groundwater Seeping

- Water flowing into zone of contamination may increase contaminant level
- Slow desorption of strongly held contaminants may require long periods of sweeping

# Calcium Effluent Concentrations from Groundwater Sweeping Laboratory Test



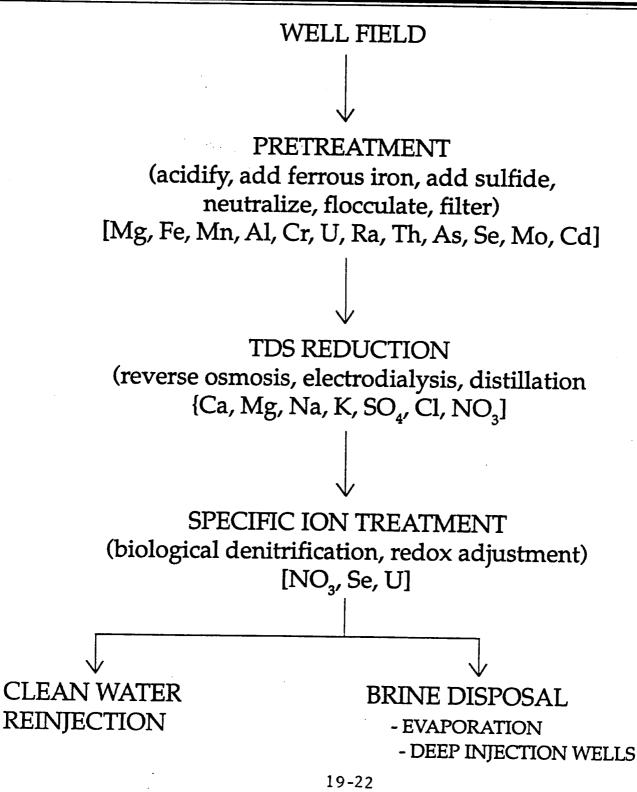
#### **Concentration of Ammonium Ions** in Effluent



## Induced Restoration Methods (continued)

- Pumping, surface treatment, and recirculation
  - Reduces volume of water that must be disposed
  - Direct chemical and physical treatment of contaminants

### Surface Treatment Methodologies



# Geochemical Considerations in Surface Treatment and Reinjection

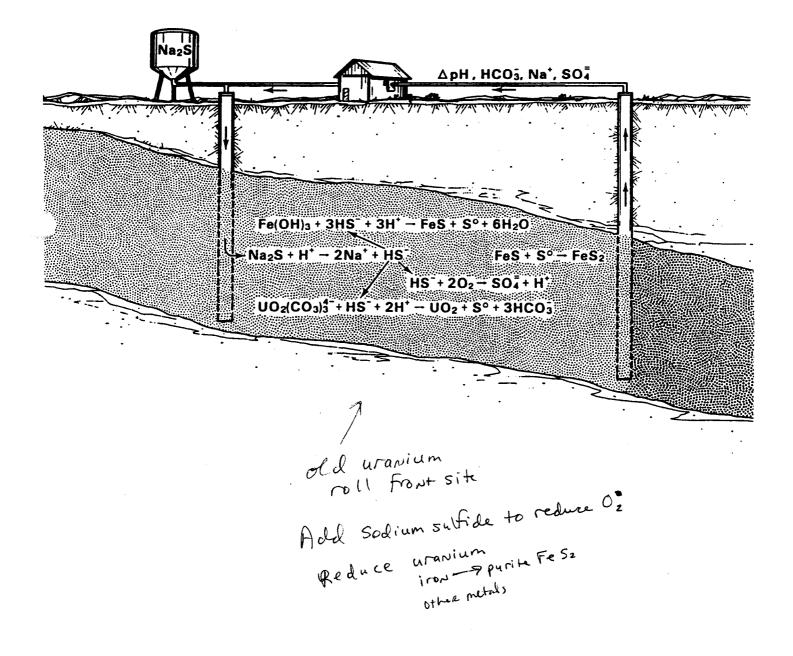
- Compatibility of treated water with aquifer
  - Expansion of clays adding No can expand clays
  - Precipitation of minerals and blockage of pores
  - Dissolution of contaminants

# Induced Restoration Methods (continued)

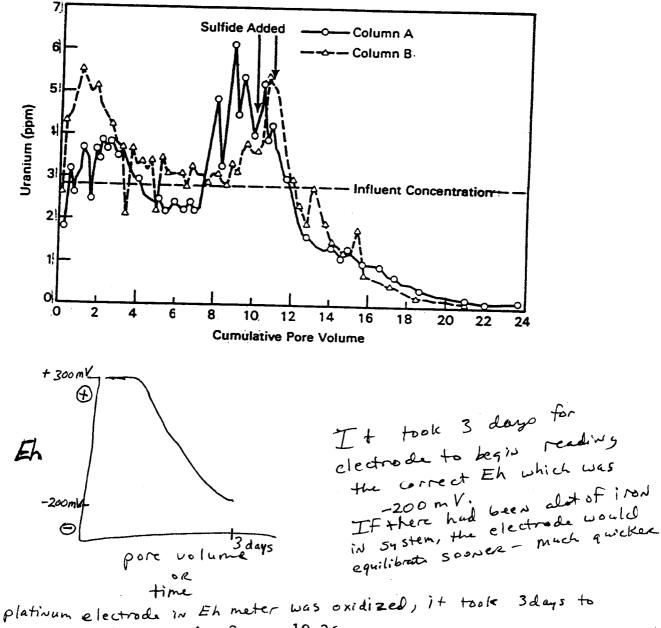
Good option modest chemical alteration + reinjection

- Chemical addition and recirculation (in situ)
  - Minimizes surface exposure of contaminants
  - Modest chemical alteration of natural groundwater followed by reinjection
  - Aquifer system reaches chemical equilibrium

# Aquifer Restoration Aided by Chemical Reduction



# Results of In Situ Treatment Column Experiments



remove platinum oxides from 19-26.

# Geochemical Considerations in Chemical Addition and Recirculation

- Effects of in situ treatment must be established
  - Lab tests
  - Field demonstration
- Associated reactions must be determined

# In Situ Treatment

#### <u>Advantages</u>

- Cost effectiveness
- Minimal disturbance to existing site
- On-site destruction of contaminants
- Continued treatment after shutdown of the project
- Permanent solution

# In Situ Treatment

#### **Disadvantages**

- Relatively new technology
- Requires proper hydrologic conditions
- May not lower concentrations of contaminants to required level
- May introduce unwanted chemicals or byproducts
- Not applicable for all contaminants

## **Aquifer Restoration Summary**

- Both chemical and physical natural restoration can be effective in certain circumstances
- Groundwater sweeping alone removes some contaminants but may not be effective for some redox-sensitive elements.
- Injection of chemical reductants can be useful for immobilizing metals, however, the reducing environment must be permanent
- For complex contamination involving metals, high TDS, and organics a combination of methods may be necessary for restoration