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NITRATES *in* GROUNDWATER

Larry W. Canter
University of Oklahoma
Norman, Oklahoma

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Contract Editor: Joel Stein
Project Editor: Carole Swearmen
Marketing Manager: Greg Danielle
Direct Marketing Manager: Arlene Massey
Cover Design: Denise Craig
PrePress: Kevin Luong
Manufacturing: Sheri Schwartz

Library of Congress Cataloging-in-Publication Data

Canter, Larry W.
Nitrates in groundwater / Larry W. Canter.
p. cm.
Includes bibliographical references and index.
ISBN 0-87371-569-1 (alk. paper)
1. Nitrates--Environmental aspects. 2. Agricultural pollution.
3. Groundwater--Pollution. I. Title.
TD427.N5C36 1996
628.1'684--dc20 96-5855
CIP

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No claim to original U.S. Government works
International Standard Book Number 0-87371-569-1
Library of Congress Card Number 96-5855
Printed in the United States of America 1 2 3 4 5 6 7 8 9 0
Printed on acid-free paper

PREFACE

This book summarizes current information on nitrogen in the subsurface environment, with emphasis given to agricultural sources of nitrates and appropriate prevention and treatment measures. Efforts have been made to include both historical and current reference materials; however, it is realized that such efforts frequently miss major works. Accordingly, this book should be viewed as a "snapshot" in time, related to the subject of nitrates in groundwater. The importance of the subject is best reflected by the realization that nitrates are probably the most ubiquitous of all chemical contaminants in groundwater.

Nitrate contamination of groundwater is typically a result of nitrogen movement into the unsaturated (vadose) zone, the occurrence of transformation processes in either the unsaturated or saturated zones, and nitrate movement with groundwater. Following an introductory chapter (1) that highlights the nitrogen cycle, sources of nitrates, and health concerns related to nitrates in groundwater, Chapter 2 addresses subsurface processes. A number of hydrogeological factors and agricultural practices influence the concentration of nitrates in groundwater. Examples of such factors and practices include precipitation/runoff, irrigation, soil type, soil depth, geological features (e.g., karst areas, fertilizing intensity, and crop types), and land usage. Chapter 3 highlights these factors and practices through a series of case studies from the United States and Europe.

Vulnerability mapping of groundwater resources represents an emerging tool useful in management decisions. Numerous techniques for vulnerability mapping have been developed, with these techniques generally involving the composite consideration of selected factors descriptive of the hydrogeology in given geographical areas. Vulnerability mapping is the subject of Chapter 4. Chapter 5 presents a nitrate pollution index, which can be used in evaluating actual or potential nitrate pollution from agricultural areas. Included in Chapter 5 is information on the development and testing of the index. There are numerous mathematical models and submodels that address the transport and fate of nitrogen and nitrates in the subsurface environment; Chapter 6 provides a summary. Categories addressed include source characterization models, nitrate transport models, and management models for developing pollution prevention and control programs. Detailed information is included on several nitrate transport models, particularly those involving mass balances associated with the unsaturated and saturated zones.

There are several fertilizer and management measures potentially useful in minimizing nitrate pollution of groundwater that results from agricultural prac-

tices. Included in such measures is "Best Management Practice." This measure and other measures are the subject of Chapter 7. Examples include matching the timing of fertilizer application to meet crop needs; matching fertilizer application rate to crop needs, and limiting fertilizer application in well recharge areas that are vulnerable to pollution. These measures represent a compendium of approaches that could be used to control nitrate pollution of groundwater from agricultural practices. The approaches can be used either singly or in various combinations. Finally, there are several treatment measures that can be used to remove excessive concentrations of nitrate from groundwater systems. The measures are primarily for application to pumped groundwater, and they are addressed in Chapter 8. Cost-effective treatment processes include ion exchange involving anionic resins, and biological denitrification. *In situ* denitrification is also addressed in Chapter 8.

This book could be used as a specialized reading component of an upper division or graduate course addressing groundwater quality protection. The course could be offered through the auspices of an engineering, geology, environmental science, or geography department, or it could be offered as an interdisciplinary effort of several departments. The book could also be used by practicing hydrogeologists, agricultural, chemical, and environmental engineers; environment scientists; chemists and microbiologists; soil scientists; geographers; and agronomists working on groundwater quality issues. In addition, the book would be useful to policy specialists working in groundwater protection programs at all governmental levels.

The author wishes to express his appreciation to several persons associated indirectly with the development of this book. First, Luciano Mulazzani of C. Lotti and Associates in Rome, Italy and Eric Girault of the World Health Organization in Copenhagen, Denmark provided an opportunity for the author to work on a groundwater pollution study involving nitrates from agricultural sources. The study was conducted in Tunisia, Algeria, and Morocco in North Africa; it was sponsored by the United Nations Development Program.

The author wishes to express his gratitude to a number of individuals who have participated directly or indirectly in the assemblage of information related to this book. These include former students, such as Drs. Robert Knox, Mohammed Lahlou, and Nadim Farajalla, and also Kea Herrington, Satish Kamath, and Laetitia Ramolino. These students have conducted research or participated in various related projects as part of their graduate work. In particular, Chapter 5 herein is largely based on the thesis research of Ms. Ramolino. The support and assistance of current and former colleagues at the University of Oklahoma is also gratefully acknowledged. Included are Drs. Robert Knox, James Robertson, David Sabatini, and Leale Streebin, and Professor George Reid.

Of major importance to the author is the positive attitude and helpfulness of Ms. Mittie Durham and Ms. Ginger Geis of the Environmental and Groundwater Institute, University of Oklahoma, in conjunction with typing and retyping original parts of this manuscript. Their technical abilities and pleasant attitude have made this book possible. The excellent typing skills of Ms. Geis is particularly acknowledged for the final copy.

This author also expresses his gratitude to the College of Engineering, University of Oklahoma for its support during the preparation of this book. Included are Dr. Ronald Sack of the School of Civil Engineering and Environmental Science and Dean Billy Crynes of the College of Engineering. Finally, the author thanks his wife for her encouragement and continued support in the process of developing this manuscript.

Larry W. Canter

AUTHOR

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Dr. Canter's research interests include environmental impact assessment (EIA) methodologies, groundwater pollution source evaluation and groundwater protection, soil and groundwater remediation technologies and market-based approaches for air quality management and impact mitigation. Currently, he is conducting research on cumulative impact assessment and valuation methods for groundwater resources. In 1982 he received the Outstanding Faculty Achievement in Research Award from the College of Engineering at the University of Oklahoma and in 1983 the Regent's Award for Superior Accomplishment in Research.

Dr. Canter has co-authored five books related to groundwater; examples include *Groundwater Pollution Control* (Lewis, 1985), *Ground Water Quality Protection* (Lewis, 1987), and *Subsurface Transport and Fate Processes* (Lewis, 1993). He has written six books related to environmental impact assessment; one example is *Environmental Impact Assessment* (McGraw-Hill, 1996, second edition). He is also the author or co-author of numerous book chapters, refereed papers, and research reports related to groundwater quality management.

Dr. Canter served on the U.S. Army Corps of Engineers Environmental Advisory Board from 1983 to 1989. Since 1993, he has been a member of the

Consultative Expert Group on Environmental Impact Assessment of the United Nations Environment Program in Nairobi, Kenya. Finally, he currently is Chairman of the Committee on Assessing the Future Value of Groundwater; this Committee is part of the Water Science and Technology Board of the National Research Council.

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DEDICATED TO

Donna

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1 FUNDAMENTAL ASPECTS OF NITRATES IN GROUNDWATER

INTRODUCTION

Groundwater pollution is a growing concern everywhere in the world. The basic problems are twofold: (1) extensive usage of groundwater leading to overdrafts and declining groundwater levels, and (2) pollution of fresh groundwater leading to undesirable effects on users or curtailment of groundwater usage. Groundwater is the source of drinking water to about 50% of the overall population in the U.S., and to over 90% of the rural population (Office of Technology Assessment, 1990). Groundwater is also essential to agricultural operations in many regions of the country.

Nitrates are one of the most problematic and widespread of the vast number of potential groundwater contaminants (Keeney, 1986). Nitrate test results can be expressed as either nitrate–nitrogen (NO_3–N) or as nitrate (NO_3). The drinking water quality standard in the U.S. for NO_3–N is 10 mg/l, whereas, for NO_3 it is 45 mg/l (Chandler, 1989).

To systematically address fundamental aspects of nitrates in groundwater, it is necessary to: (1) understand the nitrogen cycle from a chemical/microbiological perspective; (2) recognize the nitrogen cycle as related to the soil and groundwater environment; (3) delineate natural and man-related sources of nitrate to groundwater; and (4) identify health-related and other effects of excessive concentrations of nitrate in groundwater. This chapter highlights these four topics in addition to the results of a recent nationwide study that addressed, among other topics, nitrates in groundwater.

THE NITROGEN CYCLE

Nitrogen can exist in many forms in the environment. The movement and transformation of these nitrogen compounds through the biosphere can be characterized by the nitrogen cycle; this cycle is depicted in Figure 1.1 (U.S. Environmental Protection Agency, 1994). The atmosphere serves as a reservoir of nitrogen in the form of nitrogen gas (the atmosphere is 79% nitrogen).

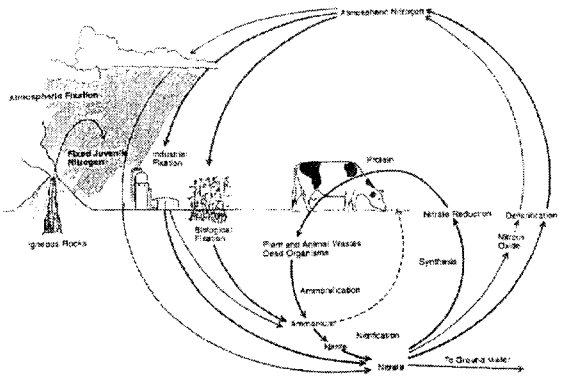

Figure 1.1 The nitrogen cycle. (From U.S. Environmental Protection Agency, in *Nitrogen Control*, Technomic Publishing, Lancaster, PA, 1994, pp. 1–22.)

Atmospheric nitrogen must be combined with hydrogen or oxygen before it can be assimilated by higher plants; the plants, in turn, are consumed by animals. Human intervention through industrial nitrogen fixation processes and the large-scale cultivation of nitrogen-fixing legumes has played a significant role in altering the historical nitrogen cycle. The amount of nitrogen fixed annually by these two mechanisms now exceeds by as much as 10% the amount of nitrogen fixed by terrestrial ecosystems before the advent of agriculture (U.S. Environmental Protection Agency, 1994).

Nitrogen can form a variety of compounds due to its different oxidation states. In the biosphere, most changes from one oxidation state to another are biologically induced. The following nitrogen forms are of interest in relation to the soil/water environment (U.S. Environmental Protection Agency, 1994).

Nitrogen compound	Formula	Oxidation state
Ammonia	NH_3	−3
Ammonium ion	NH_4^+	−3
Nitrogen gas	N_2	0
Nitrite ion	NO_2^-	+3
Nitrate ion	NO_3^-	+5

The un-ionized, molecular ammonia exists in equilibrium with the ammonium ion, the distribution of which depends upon the pH and temperature of the biospheric system; in fact, very little ammonia exists at pH levels less than neutral. Transformation of nitrogen compounds can occur through several mechanisms, including fixation, ammonification, synthesis, nitrification, and denitrification.

Each can be promulgated by particular microorganisms with either a net gain or loss of energy; energy considerations are basic to determining which reactions occur (U.S. Environmental Protection Agency, 1994).

Fixation of nitrogen refers to the incorporation of inert, gaseous nitrogen into a chemical compound such that it can be used by plants and animals. Fixation of nitrogen from N_2 gas to organic nitrogen is predominantly accomplished by specialized microorganisms and the associations between such microorganisms and plants (U.S. Environmental Protection Agency, 1994). Atmospheric fixation by lightning and industrial fixation processes (fertilizer and other chemicals) plays a smaller, but significant, role as a fixation method. The following processes and products are relevant.

Fixation process		Product
N_2 gas	→ Biological	→ Organic nitrogen compounds
	→ Lightning	→ Nitrate
	→ Industrial	→ Ammonium, nitrate

Ammonification refers to the change from organic nitrogen to the ammonium form. An important hydrolysis reaction involves urea, a nitrogen compound found in urine:

$$\underset{\text{Urea}}{H_2NCONH_2} + 2H_2O \xrightarrow{\text{urease}} \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3}$$

In general, ammonification occurs during decomposition of animal and plant tissue and animal fecal matter and can be expressed as follows:

$$\text{Organic nitrogen} + \text{Microorganisms} \rightarrow NH_3/NH_4^+$$

(Protein, amino acids, etc.)

Synthesis, or assimilation, refers to biochemical mechanisms that use ammonium or nitrate compounds to form plant protein and other nitrogen-containing compounds as follows:

$$NO_3^- + CO_2 + \text{Green plants} + \text{Sunlight} \rightarrow \text{Protein}$$

$$NH_3/NH_4^+ + CO_2 + \text{Green plants} + \text{Sunlight} \rightarrow \text{Protein}$$

Animals require protein from plants and other animals. With certain exceptions, they are not capable of transforming inorganic nitrogen into an organic nitrogen form.

Nitrification refers to the biological oxidation of ammonium ions (U.S. Environmental Protection Agency, 1994). This is accomplished in two steps: first

to the nitrite form, then to the nitrate form. Two specific chemoautotrophic bacterial genera are involved, using inorganic carbon as their source of cellular carbon as follows:

$$NH_4^+ + O_2 \xrightarrow[\text{bacteria}]{\text{Nitrosomonas}} NO_2^- + O_2 \xrightarrow[\text{bacteria}]{\text{Nitrobacter}} NO_3^-$$

The transformation reactions are generally coupled and proceed rapidly to the nitrate form; nitrite levels at any given time are relatively low. The nitrate formed may be used in synthesis to promote plant growth, or it may be subsequently reduced by denitrification, as suggested by Figure 1.1 (U.S. Environmental Protection Agency, 1994).

Denitrification refers to the biological reduction of nitrate to nitrogen gas. The reduction can proceed through several steps in a biochemical pathway. A fairly broad range of heterotrophic bacteria are involved in the process, requiring an organic carbon source for energy as follows (U.S. Environmental Protection Agency, 1994):

$$NO_3^- + \text{Organic carbon} \rightarrow NO_2^- + \text{Organic carbon} \rightarrow N_2 + CO_2 + H_2O$$

It should be noted that if both oxygen and nitrate are present the bacteria typically will preferentially use oxygen in the oxidation of the organic matter because it yields more energy. Thus, for denitrification to proceed, anoxic conditions must usually exist, although this is not strictly the case for all bacteria (U.S. Environmental Protection Agency, 1994).

The ammonification, synthesis, nitrification, and denitrification processes are the primary mechanisms employed in the treatment of contaminated groundwater for nitrogen control and/or removal. Additional information on transformation processes is found in Chapter 2; Chapter 8 highlights treatment technologies for contaminated groundwater.

The transport mechanisms primarily responsible for the movement of nitrogen through the environment include precipitation, dustfall, sedimentation in water systems, wind, groundwater movement, stream flow, overland runoff, and volatilization (U.S. Environmental Protection Agency, 1994). Although these are not mechanisms by which transformations take place, they can cause a change in the environment whereby conditions will force changes and transformations will occur. Environmental conditions that affect the above processes include temperature, pH, microbial flora, oxidation/reduction potential, and the availability of substrate, nutrients, and oxygen. Although transport and transformation mechanisms are typically considered as individual processes, it is important to recognize that these comprise a dynamic continuum and there may be no distinct boundary governing the transformation of specific forms of nitrogen (U.S. Environmental Protection Agency, 1994).

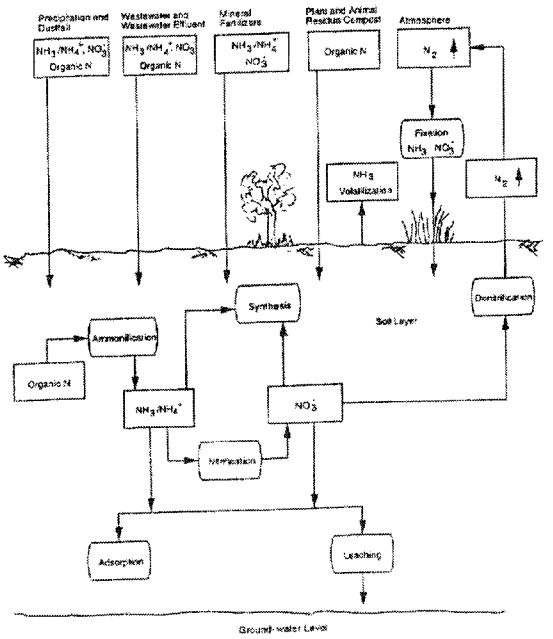

Figure 1.2 The nitrogen cycle in soil and groundwater. (From U.S. Environmental Protection Agency, in *Nitrogen Control*, Technomic Publishing, Lancaster, PA, 1994, pp. 1–22.)

THE NITROGEN CYCLE IN SOIL AND GROUNDWATER

Figure 1.2 delineates the major aspects of the nitrogen cycle associated with the soil-groundwater environment (U.S. Environmental Protection Agency, 1994). Nitrogen can enter the soil from the application of wastewater or sewage treatment plant effluent, commercial fertilizers, plant and animal matter, precipitation, and dustfall. In addition, nitrogen-fixing bacteria in the soil convert nitrogen gas into forms available to plant life. Humans have increased the amount of nitrogen fixed

biologically by cultivation of leguminous crops (e.g., peas and beans) (U.S. Environmental Protection Agency, 1994).

Usually, more than 90% of the nitrogen present in soil is organic, either in living plants and animals or in humus originating from decomposition of plant and animal residues. The nitrate content is generally low because it is (1) taken up in synthesis; (2) leached by water percolating through the soil; or (3) subjected to denitrification activity below the aerobic top layer of soil. However, synthesis and denitrification rarely remove all nitrates added to the soil from fertilizers and nitrified wastewater effluents. Accordingly, nitrates leached from soil are a major groundwater quality problem in many areas in the U.S. and elsewhere around the world (U.S. Environmental Protection Agency, 1994).

SOURCES OF NITRATE IN GROUNDWATER

Sources of nitrate in groundwater can be considered in four categories: (1) natural sources, (2) waste materials, (3) row crop agriculture, and (4) irrigated agriculture (Keeney, 1986, 1989). Table 1.1 lists examples for these four categories. The major sources include intensive animal operations, with nitrate from over-application of animal wastes, and irrigated and row crop agriculture, with nitrate from fertilizer-induced mineralization of soil organic nitrogen and from over-application (Keeney, 1989; Canter, 1987). Septic tank systems and other sources such as landfills can be of concern in localized areas. Additional information on nitrate sources is given in Chapter 3. Examples of prevention measures for nitrate contamination of groundwater are found in Chapter 7.

Agrichemicals include both commercial fertilizers and pesticides. In 1986, approximately 75% of all farms in the U.S. were subjected to fertilizer applications (Office of Technology Assessment, 1990). Farming operations that may not use commercial fertilizers include extensive livestock operations, organic farms, and small hobby farms. Nitrate–nitrogen (NO_3–N) concentrations in vadose-zone water below agricultural fields are in the range of 5 to 100 mg/l, with frequent detections in the range of 20 to 40 mg/l (Bouwer, 1990).

Table 1.2 summarizes 1986 data on the national averages of nitrogen fertilizer applications, in selected countries, to arable land and permanent crop land (Conway and Pretty, 1991). Countries where more than 200 kg N/ha was applied are listed in Table 1.2.

Septic tank systems also represent a significant fraction of the nitrogen load to groundwater in the U.S. (U.S. Environmental Protection Agency, 1994). Approximately 25% of the population is served by individual home sewage disposal systems. Effluent from a typical septic tank system has a total nitrogen content of 25 to 60 mg/l. Of this, 20 to 55 mg/l exists as ammonia and less than 1 mg/l exists as nitrate. One specific study characterized a typical system effluent as containing approximately 7 mg/l organic nitrogen, 25 mg/l ammonium-nitrogen, and 0.3 mg/l nitrate-nitrogen (U.S. Environmental Protection Agency, 1994). Septic tank leach fields exhibit rapid nitrification of ammonium-nitrogen under

Table 1.1 Examples of Sources of Nitrate in Groundwater

Natural sources
Geologic nitrogen which can be mobilized and leached to groundwater via irrigation practices
Unmanaged (natural) climax forests that are normally nitrogen conserving; however, nitrogen losses to groundwater can occur from man-initiated clearcutting and other forest disturbances
Waste materials
Animal manures which may be concentrated in large commercial poultry, dairy, hog, and beef operations
Land application of municipal or industrial sludge or liquid effluent on croplands, forests, parks, golf courses, etc
Disposal of household wastes or small business wastes into septic tank systems (septic tank plus soil absorption field);
Leachates from sanitary or industrial landfills or upland dredged material disposal sites
Row crop agriculture[a]
Nitrogen losses to the subsurface environment can occur as a result of excessive fertilizer application, inefficient uptake of nitrogen by crops, and mineralization of soil nitrogen
Nitrogen losses to the subsurface environment can occur as a function of fertilizer application rates, seasonal rainfall and temperature patterns, and tillage practices
Irrigated agriculture
Enhanced leaching of nitrogen from excessive fertilizer application rates and inefficient irrigation rates
Associated leaching of nitrogen from soils periodically subjected to leaching to remove salts so that the soils do not become saline and unproductive

[a] Refers to annual crops, tillage of the soil including plowing or some other form of seedbed preparation, and a long period when the soil may be bare, or weed control by herbicides or cultivation; also includes conservation tillage (Keeney, 1989).

aerobic conditions within the leach fields. Ammonium-nitrogen is easily exchanged in many soils below a leach field, whereas nitrate remains soluble and is easily transported to groundwater. If exchange sites become saturated, as in sandy soils, ammonium breaks through to groundwater before it nitrifies. When septic tank leach fields dry out in the summer, or are abandoned, previously adsorbed ammonium can be converted to nitrate, and eventually lost to leaching. Natural tertiary publicly owned treatment works (POTW) treatment systems utilizing soil infiltration or overland flow can typically produce a nitrogen loading to groundwater in a manner similar to septic tank leach fields. A typical final effluent of this type has a total nitrogen of 3 to 10 mg/l (U.S. Environmental Protection Agency, 1994).

Pursuant to Section 305(B) of the Clean Water Act of 1987 in the U.S., each state submits biennially a water quality report to the U.S. Environmental Protection Agency. In a review of 42 such reports in relation to public groundwater supplies, 19 states provided monitoring data on a total of 51 organic and 21 inorganic chemicals. Frequently detected contaminants included nitrates, trichloroethylene (TCE), volatile organic compounds (VOCs), arsenic, and fluorides. The most frequently identified contaminant sources were underground storage tanks (35 states), septic tank systems (31), surface impoundments (29), municipal landfills (27), agricultural activities (26), abandoned hazardous waste sites (24), regulated hazardous waste sites (19), land application/treatment (18), injection

Table 1.2 National Average Nitrogen Fertilizer Applications to Arable Land and Permanent Crops in Selected Countries, 1986

Countries over 500 kg N/ha	
The Netherlands	(557)
Singapore	(550)
Countries 400–500 kg N/ha	
Bahrain	(470)
Countries 300–400 kg N/ha	
Martinique	(315)
Countries 200–300 kg N/ha	
Egypt	(260)
Korean DPR	(253)
Belgium/Luxemburg	(247)
U.K.	(238)
Federal Republic of Germany	(212)
Countries 100–200 kg N/ha	
Korean Rep	(195)
Saudi Arabia	(154)
Japan	(145)
China	(138)
France	(135)
Surinam	(135)
Countries 50–100 kg N/ha	
Cuba	(99)
Mauritius	(92)
U.S.	(75)
Indonesia	(64)
Malaysia	(57)
Mexico	(54)
Sri Lanka	(53)
Fiji	(50)
Countries 0–50 kg N/ha	
Bangladesh	(46)
Colombia	(40)
India	(39)
Philippines	(31)
Zimbabwe	(30)
Kenya	(27)
Chile	(20)
Thailand	(13)
Nigeria	(6)

Note: All countries applying more than 200 kg N/ha are included in this list.

From Conway, G. R. and Pretty, J. N., *Unwelcome Harvest — Agriculture and Pollution*, Earthscan Publications, London, 1991, p. 159. With permission.

wells (18), and on-site industrial and other landfills (16). This composite analysis indicates widespread groundwater contamination problems of a diverse nature, with nitrates being of concern throughout the U.S. (Canter and Maness, 1995).

NATIONAL SURVEY OF NITRATES (AND PESTICIDES) IN DRINKING WATER WELLS

The U.S. Environmental Protection Agency (EPA) recently completed a 5-year National Survey of Pesticides and Nitrates in drinking water wells. The drinking water wells include both community water system (CWS) wells and domestic wells. The EPA designed the survey with two principal objectives corresponding to its two phases. In Phase I, the EPA developed national estimates of the frequency and concentration of pesticides and nitrates in drinking water wells in the U.S. (U.S. Environmental Protection Agency, 1990). In Phase II, the EPA conducted statistical analyses of the collected data as well as information from other databases to enhance understanding of influencing factors on the presence of pesticides and nitrates in drinking water wells (U.S. Environmental Protection Agency, 1992a).

The Phase I survey was designed to yield results that are statistically representative of the nation's CWS wells. The EPA used statistical methods to select a nationally representative subset of CWS wells. The results are not representative of any state or local area. In the first stage, about 51,000 community water systems (CWSs) were identified throughout the country from the EPA's Federal Reporting Data System (FRDS). Then, the EPA characterized all the counties in the U.S. according to pesticide use and relative groundwater vulnerability — the two critical factors affecting the presence of pesticides in drinking water. The counties were categorized into high, moderate, low, and uncommon pesticide use by concentrating on agricultural pesticide use. Groundwater vulnerability scores were determined using the DRASTIC scoring system for each of the counties. The DRASTIC score was used to categorize the counties into areas of relatively high, moderate, and low groundwater vulnerability. It should be noted that fertilizer application rates are related to pesticide usage; thus, the characterization approach also has relevance to nitrates from agricultural sources. The emphasis herein will be on the nitrates results. Additional information on DRASTIC and other aquifer vulnerability mapping or evaluation techniques is given in Chapters 4 and 5.

A sample of 7083 CWSs was selected randomly from the 51,000 CWSs; the sample was stratified by the pesticide usage and groundwater vulnerability of the county in which each CWS was located (see Table 1.3) (U.S. Environmental Protection Agency, 1990). To improve the reliability of estimates made for the subset (domain) of CWS wells in the high vulnerability strata, the survey was designed to collect samples from higher percentages of systems from these strata. In the second stage, after a screening process, the EPA estimated that in the U.S., there are approximately 38,300 CWSs with groundwater wells, which together operate 94,600 wells.

Telephone interviews using a "CWS Screening Questionnaire" were held with the first-stage sample of 7083 CWSs. The results of the screening produced a frame of 5660 eligible systems from which the wells for water sample collection were selected. A sample of 599 eligible systems was then selected, with probabilities proportional to their number of wells for collecting water samples (see

Table 1.3 CWS First-stage Stratification Results

Stratum	Pesticide usage	DRASTIC score	Universe size*	Sample rate	Sample size*
1	High	High	1,310	0.22	293
2	High	Medium	2,669	0.10	276
3	High	Low	1,432	0.10	146
4	Medium	High	2,183	0.25	555
5	Medium	Medium	3,352	0.10	355
6	Medium	Low	2,559	0.10	265
7	Low	High	3,578	0.24	866
8	Low	Medium	7,198	0.10	771
9	Low	Low	5,545	0.12	647
10	Uncommon	High	3,472	0.22	777
11	Uncommon	Medium	9,511	0.11	1,069
12	Uncommon	Low	7,961	0.13	1,061
			50,771		7,083

* Number of systems.

From U.S. Environmental Protection Agency, "National Survey of Pesticides in Drinking Water Wells — Phase I Report," EPA 570/9-90-015, November, 1990, Office of Water, Washington, D.C.

Table 1.4) (U.S. Environmental Protection Agency, 1990). This number was selected with allowances for inability to sample prior to treatment; the minimum desired sample size after dropout was 564. The National Pesticide Survey (NPS) then obtained water samples from 566 selected CWS wells. After technical review of individual well plumbing systems and sample collection procedures, samples from 540 CWS wells were included in the analysis of results. An effort to minimize the temporal effect of the use and occurrence of pesticides in the wells was also undertaken by randomly allocating sampling dates to the wells across the data collection period. The survey was designed so that the number of detections of analytes in the 540 CWS wells provided estimates representative of the 94,600 CWS wells in the U.S. (U.S. Environmental Protection Agency, 1990). In addition to the CWS wells, 827 rural domestic wells (RDWs) were also sampled (Cohen, 1992). It is estimated that there are approximately 10.5 million RDWs in the U.S. (Cohen, 1992).

The well water samples were tested for the presence of 101 pesticides, 25 pesticide degradates, and nitrate. Nitrate and two pesticides, DCPA (dimethyl tetrachloroterepithalate) acid metabolites and atrazine, were detected most frequently. A total of 52.1% (49,300) of all the CWS wells (94,600) was estimated to contain detectable nitrate, of which 45% was due only to nitrate, and 7.1% included both nitrate and pesticides. Based on the results from the RDWs, it was estimated that 57% had detectable nitrate (Cohen, 1992). A total of 1.2% (1130) of the CWS wells was projected to have nitrate–nitrogen concentrations above the MCL/HAL (Maximum Contaminant Level)/(Health Advisory Level), which is equal to 10 mg/l. The median concentration from the Phase I survey was 1.6 mg/l; the maximum concentration was 13 mg/l; and the minimum reporting limit was 0.15 mg/l. Nitrate–nitrogen was projected to exceed the 10 mg/l MCL in 2.4% of the RDWs (Cohen, 1992).

Table 1.4 CWS Second-Stage Stratification Results

Stratum	Pesticide usage	DRASTIC score	Design sample size*
1	High	High	27
2	High	Medium	26
3	High	Low	14
4	Medium	High	45
5	Medium	Medium	32
6	Medium	Low	25
7	Low	High	73
8	Low	Medium	68
9	Low	Low	53
10	Uncommon	High	71
11	Uncommon	Medium	90
12	Uncommon	Low	75
			599

* Number of systems selected including allowances for inability to sample prior to treatment. Minimum desired sample size after dropout was 564.

From U.S. Environmental Protection Agency, "National Survey of Pesticides in Drinking Water — Phase I Report," EPA 570/9-90-D15, November, 1990, Office of Water, Washington, D.C.

Phase II of the NPS dealt with statistical analyses to test the hypotheses about the relation between individual variables and pesticide and nitrate detections and the degree of association between them. The EPA used a criterion of significance that ensured that there was less than a 5% probability that any single test result occurred by chance alone. The Phase II analyses included tests of association that used chi square analysis, linear and logistic univariate regression, and multiple regression to better understand the association of pesticide and nitrate detections in drinking water wells with different variables. The variables included groundwater sensitivity, pesticide and nitrate use, transport mechanisms, pesticide chemistry, and well condition (U.S. Environmental Protection Agency, 1992a). Variables influencing subsurface movement of contaminants are addressed in Chapters 4 and 5, and specific models related to subsurface transport and fate are delineated in Chapter 6.

The groundwater sensitivity factor was defined as the intrinsic susceptibility of an aquifer to contamination. Sensitivity addresses the hydrogeologic characteristics of the aquifer and the overlying soil and geologic materials (U.S. Environmental Protection Agency, 1992a). The pesticide and fertilizer use factor represents the scope and amount of pesticides and nitrogen fertilizers applied near sampled drinking water wells, and activities, such as cattle raising, that could contribute to the presence of nitrate in places where they could be transported into drinking water wells (U.S. Environmental Protection Agency, 1992a). Transport mechanisms were related to the factors that contribute, either directly or indirectly, to the movements of pesticide and nitrate by water, including precipitation, irrigation, surface water, drainage ditches near wells, other bodies of water such as rivers and lakes, and nearby operating wells. However, transport does not include recharge or groundwater flow factors (U.S. Environmental Protection Agency, 1992a). The chemical characteristics include characteristics of pesticides,

such as organic partition coefficients (Koc) and half-life, and characteristics of groundwater, such as water temperature, pH, and conductivity, that could affect the behavior of pesticides or nitrates (U.S. Environmental Protection Agency, 1992a). Finally, the physical characteristics of wells included age, depth, state of repair, and protective devices, such as concrete pads, that could affect the presence of chemicals in the well water (U.S. Environmental Protection Agency, 1992a).

The data used for these variables were procured from both data generated by the NPS and data obtained from other sources such as the U.S. Geological Survey, National Oceanic and Atmospheric Administration (NOAA), census data, etc. Statistical tests were conducted to determine the association of each variable with pesticide or nitrate detection. Key results for tests of association came primarily from the analysis of nitrate detections in CWS wells. The relatively large number of associations involving nitrate detections is partly due to the fact that a significantly larger number of nitrate detections than pesticide detections was obtained. The Phase II analysis also carried out multivariate regression analyses to determine if particular combinations of variables would be strongly associated with the presence of nitrate and pesticides in groundwater.

Groundwater sensitivity at the county and subcounty level was determined using the EPA's agricultural DRASTIC system scores. The statistical analyses showed very little association of groundwater sensitivity with that of the presence of nitrate and pesticides in groundwater. Higher DRASTIC scores were not consistently associated with more frequent detections (the expected direction of association) or with less frequent detections. Different DRASTIC factors were more often associated with detections in CWS wells than with detections in RDWs. County level depth to water table was associated with pesticide detections, and county level hydraulic conductivity was associated with nitrate detections in CWS wells. Subcounty DRASTIC results showed similar inconclusive results. Again, stratification based on combined agricultural DRASTIC scores and county cropping patterns (the "cropped and vulnerable" strata) did not demonstrate a relationship between stratification variables and pesticide or nitrate detections (U.S. Environmental Protection Agency, 1992a).

Several factors related to pesticide use and agronomic activity were correlated with detections of nitrate and pesticides as well as concentrations of nitrate in groundwater. Significant correlations were found between sales of nitrogen fertilizer and nitrate concentrations in both CWS wells and RDWs. However, an analysis of the relationship between nitrogen fertilizer sales and detections of nitrate did not indicate an association between these variables. Crop value, acreage of cropland fertilized, and market value of livestock were all shown to be associated with nitrate concentrations above 0.15 mg/l in both CWS wells and RDWs. A correlation between the market value of livestock and nitrate detections was also observed. Multivariate analyses further supported that nitrate concentrations are affected by fertilizer use and agronomic activity. Two surrogate measures of agronomic activity that strongly related to pesticide and nitrate detections were the market value of crops and acres of fertilized rangeland (U.S. Environmental Protection Agency, 1992a).

Analyses of variables relating to transport of chemicals to groundwater, including several precipitation measures, indicated that increased precipitation was inversely related to detections and concentrations of nitrate. This result suggests that high levels of rainfall may cause the fertilizer to run off before entering groundwater, or to dilute the concentrations of nitrate to the point that they fall below the detection limits used in the survey. In contrast, flood irrigation was associated with a greater likelihood of detection in both CWS wells and RDWs. Nitrate detections were more likely in CWS wells drawing water from an unconfined aquifer. Some evidence was also obtained that nitrate detections in CWS wells were associated with moist conditions (U.S. Environmental Protection Agency, 1992a).

Some of the chemical characteristics factors were related with detections and concentrations of nitrates. The likelihood of detecting nitrate is greater in groundwater with low temperature or low pH. Also, the likelihood of detecting nitrate is greater in wells delivering water with low electrical conductivity. However, higher conductivity of well water was found to correspond to higher nitrate concentrations. In terms of well condition, shallower wells were found associated with nitrate detections in both CWS wells and RDWs, and with pesticide detections in CWS wells (U.S. Environmental Protection Agency, 1992a).

In addition to analyzing single factors, the EPA also studied whether combinations of variables are good predictors of the occurrence of nitrate. Table 1.5 shows that several factors, when analyzed together, are statistically related (U.S. Environmental Protection Agency, 1992b).

Table 1.5 Factors Associated with Contamination of CWS Wells

Nitrate Detections	Nitrate Concentrations
Fertilized pasture and rangeland	Monthly precipitation
Monthly precipitation	Well-water conductivity
Well-water pH	Total nitrogen fertilizer sales
Properly farmed	Well depth
	Palmer drought index score
	Market value of crops

From U.S. Environmental Protection Agency, "National Pesticide Survey — Update and Summary of Phase II Results," EPA 570/9-91-021, Winter, 1992, Office of Water, Washington, D.C.

Owing to the many limitations in the NPS and analysis process, it was suggested that the reported results should not be interpreted as conclusions drawn from controlled experiments or as evidence of causation. The results are statistical measures of association or correlation that were designed to test hypotheses developed from several scientific and policy questions. It was noted that the results should be used with caution as indicators of topics that may be suitable for further careful investigation. The factors that did not show statistical relationships should not be assumed to be unimportant.

The Phase II survey report included estimates of national population exposure and resultant health risks due to nitrate for RDWs and for CWSs (U.S.

Environmental Protection Agency, 1992a). Estimates were provided of the populations corresponding to quantiles of general interest (e.g., 95th and 99th percentiles), and of the number of individuals exposed above health-based levels. Summarized below is information related to CWSs. The results presented are based on the following nationwide data:

1. Approximately 136,000,000 people drink groundwater from CWS wells nationally.
2. There are approximately 94,600 wells in 35,800 CWSs that provide groundwater for drinking. On average, each system consists of approximately 2.6 wells.

Tables 1.6 and 1.7 present estimates of the number of people exposed to nitrate in CWS wells (U.S. Environmental Protection Agency, 1992a). The following comments are pertinent.

1. Approximately 3 million people drank water from CWS wells that contain nitrate at a concentration of at least 10 mg/l, the MCL for nitrate. Of the people exposed to nitrate above this level, approximately 45,500 are expected to be infants at possible risk of developing methemoglobinemia, particularly if the water is also contaminated with bacteria.
2. Approximately 85 million people drank water from CWS wells that contain nitrate.
3. The median nitrate concentration to which people in the United States are exposed is approximately 0.63 mg/l.

Table 1.6 Estimates of Population Exposed to Nitrate in Community Water System Wells by Distribution Percentile

Percentile	People exposed	Concentration (mg/l)	95% Confidence interval Lower bound (mg/l)	Upper bound (mg/l)
Median	68,000,000	0.63	0.45	0.95
95	6,800,000	6.52	5.34	7.60
99	1,360,000	14.2	10.6	17.7

From U.S. Environmental Protection Agency, "Another Look: National Survey of Pesticides in Drinking Water Wells — Phase II Report," EPA 579/09-91-020, January, 1992, Office of Water, Washington, D.C.

Table 1.7 Estimates of Population Exposed to Nitrate by Concentration in Community Water System Wells

Concentration (mg/l)	Population exposed	95% Confidence interval Lower bound	Upper bound
All concentrations >0	85,300,000	78,100,000	98,900,000
>10	2,980,000	1,600,000	4,260,000

From U.S. Environmental Protection Agency, "Another Look: National Survey of Pesticides in Drinking Water Wells — Phase II Report," EPA 579/09-91-020, January, 1992, Office of Water, Washington, D.C.

HEALTH CONCERNS RELATED TO NITRATES

The concentration of nitrates in groundwater is of primary concern due to potential human health impacts from groundwater usage. Depending on the use of the groundwater, animals, crops, or industrial processes could also be affected. The toxicity of nitrate to humans is due to the body's reduction of nitrate to nitrite. This reaction takes place in the saliva of humans of all ages and in the gastrointestinal tract of infants during their first 3 months of life. The toxicity of nitrite has been demonstrated by vasodilatory/cardiovascular effects at high dose levels and methemoglobinemia at lower dose levels (*Federal Register*, 1985).

Methemoglobinemia refers to an effect in which hemoglobin is oxidized to methemoglobin. When amounts of methemoglobin in blood increase, oxygen levels in blood dwindle. Cyanosis, the illness of oxygen starvation, results, and that particular cyanosis is referred to as methemoglobinemia (Winneberger, 1982). However, the effects of methemoglobinemia are rapidly reversible; and there are, therefore, no cumulative effects.

Infants up to 3 months of age are the most susceptible subpopulation with regard to nitrate. This is due to the fact that about 10% of ingested nitrate is transformed to nitrite in the infant (*Federal Register*, 1985). When nitrites combine with hemoglobin to form methemoglobin, the result is a diminished oxygen transport/transfer capability in the blood. The infant then suffers from cellular anoxia and clinical cyanosis (turns blue, hence the terms "blue baby" or "blue baby syndrome"). This phenomena can occur in infants when approximately 10% of the total hemoglobin has been converted to methemoglobin (World Health Organization, 1985). Additional reasons for concern include the low activity of the enzyme that reduces methemoglobin, higher susceptibility of infant methemoglobin to oxidation, and higher pH in the stomach and intestines that promotes bacterial reduction of nitrate to nitrite (Keeney, 1986).

In the U.S., the current maximum contaminant limit (MCL) for nitrate-nitrogen under the Primary Drinking Water Regulations is 10 mg/l (*Federal Register*, 1985). This level was based upon human case studies in which fatal poisonings in infants occurred following ingestion of groundwater containing nitrate concentrations greater than 10 mg/l nitrate–nitrogen. The World Health Organization (WHO) guidelines are 10 mg/l for nitrate–nitrogen and 1 mg/l for nitrite-nitrogen. The basis is that undesirable increases in methemoglobin levels in blood occur at levels from 10 to 20 mg/l nitrate; the ingestion of nitrite leads to a more rapid onset of clinical effects, thus the guideline value is correspondingly lower (1 mg/l). Additional information on water quality standards is summarized in Table 1.8 (World Health Organization, 1985).

An additional public health issue of potential concern is that several studies have shown that simultaneous ingestion of nitrite (or nitrate with amines) results in cancers of many organ systems. The N-nitroso compounds are presumed to be the ultimate carcinogenic substances (Tannenbaum and Green, 1985). Several epidemiological studies have indicated significant positive correlations between exposure to nitrate and cancer risk; for example, nitrate in drinking water has been correlated with gastric cancer risk in Colombia and England; and exposure

Table 1.8 Limits for Nitrate in Drinking Water

Organization	Year	Limit specification	mg/l of NO_3–N
WHO European standards	1970	Recommended	11.3
		Acceptable	11.3–22.6[a]
		Not recommended	>22.6
WHO International standards	1971		10.2
WHO Working Group	1977	General population	
		Acceptable	11.3
		Borderline	11.3–22.6
		Unacceptable	>22.6
		Infants <6 months	
		Unacceptable	11.3
U.S. EPA	1977	Maximum contaminant level	10.2
Health and Welfare Canada	1978	Maximum acceptable concentration	10.2
EEC (Directive on quality of surface waters intended for abstraction of drinking water)	1977	Imperative limit	11.3
		Guide level	5.6
EEC (Directive on quality of water for human consumption)	1980	Maximum admissible concentration	11.3
		Guide level	5.6
WHO guidelines for drinking water quality	1984	Guideline value	10

[a] Within this range, although a problem may not be apparent, physicians should be notified of the possible occurrence of infantile methaemoglobinaemia.

Note: WHO, World Health Organization; EEC, European Economic Community; EPA, Environmental Protection Agency.

From World Health Organization, "Health Hazards from Nitrates in Drinking Water — Report on a WHO Meeting in Copenhagen, March 5–9, 1984," Regional Office for Europe, Copenhagen, 1985, pp. 3, 49–56. With permission.

to nitrate-containing fertilizer appeared to be linked to gastric cancer mortality in Chile. However, it should be noted that high risk for gastric cancer correlate not only with nitrate, but also with several other dietary or environmental factors, and whether any of these associations actually involve causation is far from clear (Tannenbaum and Green, 1985; Kleinjans, et al., 1991).

The question of whether nitrite itself is a carcinogen is currently unanswerable; however, research is ongoing on this issue (*Federal Register*, 1985). The role of nitrite as a precursor to carcinogenic nitrosamines and other N-nitroso compounds is firmly established. Nitrite reacts with amines or amides under a variety of conditions to yield the N-nitroso derivatives, the preponderance of which are carcinogenic to animals. The expectation that these N-nitroso compounds are also human carcinogens suggests a mechanism whereby exposure to nitrite might result in carcinogenesis (Tannenbaum and Green, 1985).

Detailed information on the toxicological effects of nitrate and nitrite is provided by Life Systems, Inc. (1987). Topics addressed include toxicokinetics and human exposure, health effects of nitrate and nitrite in humans and animals, and mechanisms and quantification of toxicological effects. Additional health-

related information is given by Dahab and Bogardi (1990) and the World Health Organization (1985).

Excessive nitrates in groundwater have also caused problems with ruminants (cud-chewing animals with divided stomachs). Sheep and cattle can be seriously affected by nitrates from birth through adulthood. Monogastric (single stomach) infants such as horses, pigs, and chickens are also candidates for health problems. As chickens and pigs mature, they are much less affected by the presence of nitrates. However, horses can be affected through adulthood (Chandler, 1989).

Symptoms of nitrate–nitrite poisoning in livestock include cyanosis in and about the non-pigmented areas (mouth and eyes), shortness of breath, rapid heartbeat, staggered gait, frequent urination, and collapse. In severe cases, convulsions, coma, and death may result within hours. A loss of milk production in cows and aborted calves are also signs of possible nitrate poisoning (Chandler, 1989).

SUMMARY

Nitrates in groundwater represent a widely distributed pollution concern: nitrates are perhaps the most ubiquitous of all groundwater contaminants. Natural and man-induced sources of nitrates in groundwater are a result of water usage for irrigation; excessive applications of commercial fertilizers or manure; and waste disposal practices associated with land application of sludges or wastewater effluents, municipal or industrial landfills, and septic tank systems. The key concern regarding usage of groundwater with excessive concentrations of nitrates is related to human health effects, particularly with regard to infants. The major effects are associated with losses in oxygen transport/transfer capabilities in the blood.

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2 INFLUENCE OF SUBSURFACE PROCESSES

INTRODUCTION

Nitrate contamination of groundwater is typically a result of nitrogen movement into the unsaturated (vadose) zone, the occurrence of transformation processes in either the unsaturated or saturated zones, and nitrate movement with groundwater. This chapter will summarize nitrogen transformation, and transport and fate processes in the subsurface environment; factors influencing nitrogen leaching from fertilizers; and the use of laboratory studies for examination of both the transformation processes and leaching.

NITROGEN TRANSFORMATIONS

Table 2.1 contains summary comments on 14 references dealing with nitrogen transformations in the subsurface environment. Only selected information from several of the 14 references will be included herein. The transport and fate of nitrogen in the subsurface environment depends upon the form of entering nitrogen and various biochemical and physicochemical processes involved in transforming one form of nitrogen to another form.

Nitrogen can enter the subsurface environment in either organic or inorganic forms, depending upon the source. Organic nitrogen consists of compounds from amino acids, amines, proteins, and humic compounds with low nitrogen content (Reddy and Patrick, 1981). Inorganic nitrogen consists of ammonium, nitrite, and nitrate forms. Nitrogen from untreated or partially treated wastewater discharges or human waste fertilizers may be in either organic or ammonium form, while nitrogen from chemical fertilizers will typically be in ammonium or nitrate form. Transformation processes in the subsurface include: (1) ammonification, (2) ammonia volatilization, (3) nitrification, and (4) denitrification. Transport processes that may be involved in subsurface movement of various forms include: (1) diffusion of ammonium forms, (2) diffusion of nitrate forms, and (3) movement of either form with the water phase. Abiotic processes such as adsorption and cation exchange may cause retention of some ammonium forms in the

Table 2.1 References Related to Nitrogen Transformations in the Subsurface Environment

Author(s) (year)	Comments
Allcldi (1983)	Discussion of transformation and transport processes in three main hydrogeological soil types
Behnke (1975)	Description of the biogeochemistry of nitrogen compounds in groundwater
Bradley, Aelion, and Vroblesky (1992)	Study of factors affecting denitrification in sediment contaminated with JP-4 jet fuel
Chopp, Clapp, and Schmidt (1982)	Effects of treated municipal wastewater effluents on ammonia-oxidizing bacteria in soil
Devitt, et al. (1976)	Effects of soil types and irrigation practices on nitrates in the subsurface environment
Howard (1985)	Influence of denitrification on nitrate concentrations in a major limestone aquifer
Keeney (1983)	Review of transformations and transport of nitrogen in the subsurface environment
Keeney (1986)	Review of the chemical properties of nitrate and nitrite, and the soil nitrogen cycle (including mineralization-immobilization, nitrification, denitrification, and plant uptake and recycling)
Lowrance and Pierke (1989)	Review of physical, biological, and chemical processes leading to changes in nitrate concentration in groundwater, and discussion of case studies illustrating the effects of these processes on different aquifers
Lowrance and Smittle (1988)	Measurement of denitrification losses of nitrogen, crop uptake of nitrogen, and resultant availability of nitrogen for leaching in intensive vegetable crop production systems in a sandy soil
Reddy and Patrick (1981)	Review of the agronomic and ecologic significance of nitrogen transformations and loss in flooded soils and sediments
Rolston and Broadbent (1977)	Field studies of denitrification in the subsurface environment
Rolston et al. (1980)	Field studies of the effects of irrigation frequency on denitrification in the subsurface environment
Schubauer-Berigan et al. (1990)	Examination of microbial degradation pathways and degradation rates, under both aerobic and anaerobic conditions, for nitrates in Long Island groundwaters

subsurface; in addition, biotic processes such as incorporation into microbial or plant biomass can occur. Figure 2.1 summarizes the nitrogen cycle in the subsurface environment (Reddy and Patrick, 1981). As suggested in Figure 2.1, the occurrence of certain transformation processes is a function of the presence of oxidizing or reducing conditions.

Ammonification is the first step in the mineralization of organic nitrogen. Ammonification is defined as the biological conversion of organic nitrogen to ammonium-nitrogen (Reddy and Patrick, 1981). Under anaerobic soil conditions, ammonium-nitrogen accumulation occurs because of the suppression of nitrification.

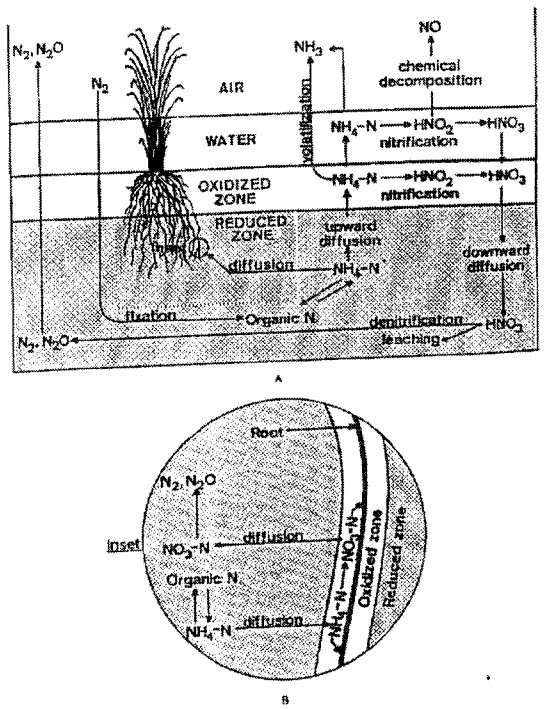

Figure 2.1 The nitrogen cycle in the subsurface environment. (From Reddy, K. R. and Patrick, W. H., in *CRC Critical Reviews in Environmental Control*, Vol. 13, No. 4, 1981, pp. 273–303.)

Ammonia volatilization is a physicochemical process where ammonium-nitrogen is known to be in equilibrium between the gaseous and hydroxyl forms as follows (Reddy and Patrick, 1981):

$$NH_3\,(aq) + H_2O \rightarrow NH_4^+ + OH \qquad (1)$$

Reaction (1) is pH dependent, with an alkaline pH favoring the presence of aqueous forms of NH_3 in solution, while at acidic or neutral pH, the ammonium-nitrogen is predominantly in the ionic form. Figure 2.2 shows the effect of pH and temperature on the distribution of ammonia and ammonium ions in water (Behrke, 1975).

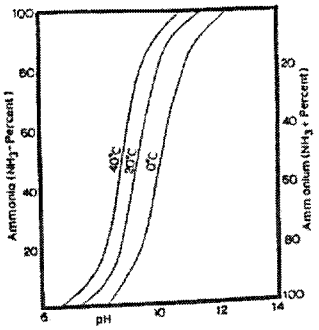

Figure 2.2 Effect of pH and temperature on the distribution of ammonia and ammonium ion in water. (From Behrke, J., *Journal of Hydrology*, Vol. 27, 1975, pp. 155–167 With permission of Elsevier Science, Amsterdam.)

Nitrification is defined as the biological oxidation of ammonium-nitrogen to nitrate-nitrogen (Reddy and Patrick, 1981). Nitrification is known to take place in two stages as a result of the activity of chemoautotrophic bacteria of the genera Nitrosomonas ($NH_4^+ \rightarrow NO_2$) and Nitrobacter ($NO_2 \rightarrow NO_3$). Both organisms are Gram negative, aerobic, chemoautotrophic rods. These nitrifiers derive energy from the oxidation of ammonium-nitrogen and/or nitrite-nitrogen. These organisms require O_2 during ammonium-nitrogen oxidation to nitrite-nitrogen and nitrite-nitrogen oxidation to nitrate-nitrogen. Ammonium oxidation of nitrite can be written as (Reddy and Patrick, 1981):

$$NH_4^+ + 1\frac{1}{2}O_2 \rightarrow NO_2^- + 2\,H^+ + H_2O \qquad (2)$$

Nitrite oxidation to nitrate can be written as (Reddy and Patrick, 1981):

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^- \qquad (3)$$

Combining reactions (2) and (3) yields:

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + 2\,H^+ + H_2O \qquad (4)$$

Therefore, it takes 2 moles oxygen to oxidize each mole of ammonium-nitrogen to nitrate. Stoichiometrically, the organisms require 4.57 g O_2 per gram of ammonium-nitrogen oxidized (Reddy and Patrick, 1981).

Several kinetic rate equations have been proposed for nitrification, including zero order, first order, and the Monod equation of population dynamics. Table 2.2 contains some first-order kinetic rate coefficients for nitrification in soils (Reddy and Patrick, 1981). Environmental factors influencing the nitrification rate include: (1) temperature, (2) pH, (3) alkalinity of water, (4) inorganic carbon source, (5) microbial population, and (6) ammonium-nitrogen concentration.

Table 2.2 First-Order Kinetic Rate Coefficients for Nitrification in Soils

Type of system and process	Temperature (°C)	First-order rate constant (k day^{-1})	Remarks
Salinas clay	24		Laboratory incubation
$NH_4 \rightarrow NO_2$		0.22	
$NO_2 \rightarrow NO_3$		9.0	
Milvill loam	22		Laboratory incubation
$NH_4 \rightarrow NO_2$		0.14	
$NO_2 \rightarrow NO_3$		9.00	
Tippera clay loam $NH_4 \rightarrow NO_3$	20	0.003	Laboratory incubation at varying temperatures
Columbia silt loam $NH_4 \rightarrow NO_3$		0.24–0.72	Steady-state flow through soil column maintained at −85 cm suction
Hanford sandy loam $NH_4 \rightarrow NO_3$		0.76–1.11	Steady-state flow through soil columns, using ^{15}N
Webster silt loam $NH_4 \rightarrow NO_3$	35	0.052	Laboratory incubation study with 35-day incubation
Marshall silt loam $NH_4 \rightarrow NO_3$	35	0.048	
Cole silty clay loam $NH_4 \rightarrow NO_3$	35	0.051	
Monona silty clay loam $NH_4 \rightarrow NO_3$	35	0.047	
Grundy silt loam $NH_4 \rightarrow NO_3$	35	0.072	
Lentic System Clinton River $NH_4 \rightarrow NO_3$		3.10	Field study conducted on the Clinton River between Pontiac, MI, and Rochester, MI. Nitrification rates calculated based on changes in NH_4-N and NO_3-N concentration

From Reddy, K. R. and Patrick, W. H., in *CRC Critical Reviews in Environmental Control*, Vol. 13, No. 4, 1981, pp. 273–303.

Denitrification is defined as the biological reduction of nitrate to gaseous end-products such as molecular N_2 or N_2O. A commonly accepted pathway for biological denitrification is (Keeney, 1986):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (5)$$

Under anaerobic or oxygen-free conditions and in the presence of available organic substrate, the denitrifying organisms can use nitrate as an electron acceptor during respiration. Genera involved in the denitrification process include *Pseudomonas*, *Acinetobacter*, *Bacillus*, *Micrococcus*, *Gluconobacter*, *Alcaligenes*, *Halobacterium*, *Thiobacillus*, *Xanthomonas*, *Moraxella*, *Paracoccus*, *Spirillum*, and *Rhodopseudomonas*. When oxygen is available, these organisms oxidize a carbohydrate substrate to CO_2 and H_2O as follows (Reddy and Patrick, 1981):

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \qquad (6)$$

Under oxygen-free conditions, some microorganisms oxidize a carbohydrate substrate to CO_2 and H_2O using nitrate instead of oxygen as an electron acceptor and converting the nitrate to N_2 gas, as shown by the following overall reaction (Reddy and Patrick, 1981):

$$5(CH_2O) + 4\ NO_3^- + 4\ H^+ \rightarrow 5\ CO_2 + 2\ N_2 + 7\ H_2O \qquad (7)$$

Several kinetic rate equations have also been proposed for denitrification, including zero-order and first-order relationships. Table 2.3 contains some first-order rate constants for denitrification in soils and sediments (Reddy and Patrick, 1981). Several factors are known to influence the rate of denitrification, either directly or indirectly. Among these are the absence of oxygen, presence of readily available carbon, temperature, soil moisture, pH, presence of denitrifiers, and soil texture.

As an example of the influence of denitrification in groundwater, Howard (1985) described the importance of this transformation process in a major limestone aquifer. The Chalk aquifer of eastern-central England is seriously affected by nitrates leached from agricultural land and, like many similar aquifers, its future as a potable resource depends on the nature and rates of denitrification. The regional distribution of nitrate supports a viewpoint based on thermodynamic criteria that denitrification is actively occurring and that the problem will be short-lived. More detailed considerations based on major-ion and environmental isotope data, however, indicate that denitrification is not significant and that the apparent lowering of the nitrate concentration (from >10 to <2 mg/l NO_3–N) in the apparent direction of flow is primarily due to mixing between waters of different origins. The presence of reduced nitrogen species is possible evidence of denitrification in some older waters. Howard (1985) concluded that denitrification cannot be relied upon to reduce elevated concentrations of nitrate in modern recharge waters.

Rolston et al. (1980) described a study focused on the influence of denitrification on the nitrate in irrigation return waters. Absolute amounts and rates of denitrification from a Yolo loam field profile at Davis, California, were studied in relation to the influence of irrigation frequency and soil incorporation of crop residue. Application frequencies of three irrigations per week, one irrigation per week, and one irrigation every 2 weeks were established on areas cropped with

Table 2.3 First-Order Rate Constants for Denitrification in Soils and Sediments

Soil/sediment	Temperature (°C)	First-order rate constant (k day⁻¹)	Remarks
Peat soil	5–36	0.1–0.5	Laboratory incubation study conducted at various temperatures; rates based on NO_3–N loss
Florida organic soils (8 soils)	30	0.1–1.5	Organic soils obtained from several locations in south and central Florida, soils incubated under anoxic conditions, and stirred continuously; rates based on NO_3–N loss
Huron soil (silty clay loam)	30 15 10	2.15 0.72 0.54	Soil obtained from cropped field
30 Soil types	35	0.03–0.90	Soils collected from several locations in the U.S.; rates are influenced by diffusion of NO_3–N from floodwater; rates based on NO_3–N loss
8 Soil types	30	0.03–0.76	Soils collected from several locations in the U.S.; soils incubated under anoxic conditions, and stirred continuously; rates based on NO_3–N loss
Crowley silt loam No floodwater 3-cm floodwater 6-cm floodwater	30	 0.37 0.18 0.13	Soil incubated to an O_2-free atmosphere, with NO_3–N present in both floodwater and underlying soil; rates based on NO_3–N disappearance
Hanford sandy loam Columbia silt loam Moreno clay loam	20–22	0.07 0.17 0.05 0.14	Rate constants measured under steady-state conditions
Yolo loam		0.004–0.03	Laboratory soil columns using ^{15}N
Norfolk sandy loam No waste added Beef waste added Poultry waste added Swine waste added	30	 0.07 1.06–2.57 0.10–1.34 0.18–0.68	Laboratory incubation study with no excess floodwater, soils treated with organic wastes that underwent various degrees of decomposition
Danish lake sediments (Copenhagen and Denmark)		0.04–0.76	Sediments obtained from various times during seasons; ^{15}N was used to determine denitrification; rates measured based on N_2 production

From Reddy, K. R. and Patrick, W. H., in *CRC Critical Reviews in Environmental Control*, Vol. 13, No. 4, 1981, pp. 273–303.

perennial rye grass. Fertilizer was applied at the rate of 300 kg N per hectare as KNO_3 enriched with 56 to 58% ^{15}N to 1-m² plots. The flux of volatile gases at the soil surface was measured from the accumulation of N_2O and ^{15}N, beneath air-tight covers placed over the soil surface for 1 to 4 hours at several times

immediately after irrigation and at less frequent intervals as denitrification fluxes decreased. Small rates of total denitrification were measured in this well-drained alluvial soil under normal cyclic applications of irrigation water. For plots without carbon addition, the largest denitrification of only 1.5% of the applied fertilizer was measured in the most frequently irrigated plot. For the least frequently irrigated plot of one irrigation every 2 weeks, only 0.7% of the applied fertilizer was denitrified. Denitrification rates decreased to near-zero values within 1 or 2 days after irrigation.

The application frequency of three irrigations per week gave higher NO_3^- concentrations as measured by both soil solution and soil samples within the root zone of the crop than those of the other two irrigation frequencies (Roiston et al., 1980). Thus, frequent, small irrigations tended to result in less leaching losses than frequent, large irrigations. Denitrification of nitrate fertilizer was simulated using a mathematical model that included transport and plant uptake of water and nitrogen in soil. The rate of denitrification was demonstrated to be a function of nitrate concentration, available carbon concentration, degree of soil-water saturation, and temperature.

In 1975, the loss of about 83,000 gallons JP-4 jet fuel resulted in contamination of a shallow aquifer near Charleston, South Carolina (Bradley, Aelion, and Vroblesky, 1992). A site-specific study was then conducted to examine influencing factors related to an *in situ* bioremediation program involving nitrate additions. The fate of the amended nitrate; the effect of pH, nitrate, and phosphate on denitrification; and the variability of denitrification in sediments collected at the site were examined. Denitrification (N_2O–N production) accounted for 98% of the depletion of nitrate-nitrogen under anaerobic conditions. Both carbon mineralization and denitrification rates increased asymptotically with increasing nitrate to a maximum at approximately 1 *mM* nitrate. Addition of up to 1 *mM* phosphate did not significantly increase the N_2O and CO_2 production. Denitrification rates were at least 38% lower at pH 4 than those observed at pH 7. Comparisons of samples with differing degrees of hydrocarbon contamination indicated that at least a tenfold variation in sediment denitrification occurred at the contaminated site (Bradley, Aelion, and Vroblesky, 1992).

NITROGEN TRANSPORT AND FATE

Diffusion of ammonium-nitrogen and nitrate in the subsurface environment plays a role in subsurface transport along with abiotic processes such as adsorption and ion exchange. The quantity of ammonium-nitrogen transferred by diffusion phenomena per unit area per unit time is proportional to the diffusion coefficient and the concentration gradient. At the soil/water interface, concentration gradients can be relatively large and, hence, diffusion of ammonium-nitrogen from the anaerobic layer can be rapid. Molecular diffusion is assumed to follow Fick's law and is expressed in terms of the whole soil or sediment diffusion coefficient, D, which includes the effects of tortuosity but not those of adsorption. Data in Table 2.4 show the D values for ammonium-nitrogen moving in several anaerobic

Table 2.4 Diffusion Coefficients for NH_4–N Movement in Soils and Sediments

Soil/sediment		Temperature (°C)	Diffusion coefficients (cm^2/day)	Remarks
Flooded soil				Experiment conducted with an initial ammonium-N concentration of 200 µg/g soil; incubation period of 2 days
Crowley silt loam		30	0.216	
Midland silt loam		30	0.172	
Mhoon silty clay loam		30	0.059	
Marine sediments (Long Island Sound)		20	0.850	Sediments with additional ammonium-N added; diffusion coefficients adjusted for adsorption; incubation period of 5.9 days
Volumetric water content (cm^3/cm^3)				Experiment conducted with soils treated with 14.3 meq/l. of $(NH_4)_2SO_4$ solution, and adjusted to various water contents; soils were sterilized using γ-radiation before use; incubation period of 5–17 days
Urbrae loam	0.10	21	0.005	
	0.15	21	0.009	
	0.20	21	0.013	
	0.25	21	0.019	
Wanbi sand	0.10	21	0.019	
	0.15	21	0.022	
	0.20	21	0.030	
Volumetric water content (cm^3/cm^3)				Experiment conducted with an initial ammonium-N concentration of 200 µg/g soil; nitrification inhibitor was used to prevent ammonium-N oxidation; incubation period of 7 to 15 days
Crowley silt loam	0.06	30	0.004	
	0.11	30	0.010	
	0.27	30	0.050	
Flood Maanas clay				Laboratory study conducted using undisturbed wetland soil cores; incubation period of 7 to 28 days
Prilled urea		25	0.019	
Super granule urea			0.022	
Sulfur-coated urea			0.016	

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soil or sediment systems (Reddy and Patrick, 1981). Nitrate diffusion coefficient data into underlying anaerobic soil is summarized in Table 2.5 (Reddy and Patrick, 1981). The D values for nitrate are typically greater than those for ammonium-nitrogen since nitrate is an anion and is not adsorbed onto the subsurface exchange complex.

Ammonium-nitrogen may not be transported through the unsaturated zone and into groundwater due to adsorption, cation exchange, incorporation into microbial biomass, or release to the atmosphere in the gaseous form. Adsorption is probably the major mechanism of removal in the subsurface environment. Under anaerobic conditions in the subsurface environment, positively charged ammonium ions (NH_4^+) are readily adsorbed onto negatively charged soil particles. Since anaerobic conditions in soils are usually associated with saturated soils, some movement of ammonia with groundwater can occur. However, this movement will be slow since adsorption will continue to occur on soil particles in the aquifer.

To serve as an example of the influence of adsorption, a study conducted by Sparks (1987) will be summarized. Nitrate retention as it affects groundwater

Table 2.5 Diffusion Coefficients for NO_3–N Movement in Soils

Type of system		Temperature (°C)	Diffusion coefficients (cm^2/day)	Remarks
Flooded soil				Experiment conducted with an initial nitrate-N concentration of 300 µg/ml, incubation period of 24 hr, saturated soil moisture content
Crowley silt loam		30	1.33	
Midland silt loam		30	1.94	
Mhoon silty clay loam		30	0.96	
Flooded organic soil		8	0.25	Experiment conducted with an initial nitrate-N concentration of 100 µg/ml, incubation period of 78 hr
		28	0.44	
Volumetric water content (cm^3/cm^3)				Experiment conducted with the soils amended with 28.6 meq/l of KNO_3 solution, and adjusted to various water contents; soils were sterilized using γ-radiation before use; incubation period of 1–5 days
Urbrae loam	0.10	21	0.04	
	0.20	21	0.17	
	0.25	21	0.32	
Wanbi sand	0.05	21	0.13	
	0.10	21	0.23	
	0.15	21	0.34	
	0.20	21	0.42	
Saturated water content (cm^3/cm^3)				Experiment conducted with silt, sand, or glass beads saturated with 0.1 *N* $NaNO_3$
Silt	0.43	30	1.15	
Sand	0.42	30	1.20	
Glassbeads	0.38	30	1.21	
Flooded soils		25		Nitrate diffusion from flood water into the underlying soil column was measured; diffusion coefficients for nitrate-N were measured, using the changes in chloride concentration of flood water
Everglades muck			0.51	
Floridana fine sand			0.33	
Astor sand			0.68	
Surrency sand			1.80	
Samsula muck			1.70	
Pickney fine sand			0.61	
Riviera fine sand			1.30	
Delray fine sand			1.20	
Chastain silt loam			0.35	
Brighton peat			0.42	
Iberia silty clay			0.45	
Chobee fine sandy loam			0.38	
Eureka fine sandy loam			0.72	
Valkaria fine sand			0.26	

From Reddy, K. R. and Patrick, W. H., in *CRC Critical Reviews in Environmental Control*, Vol. 13, No. 4, 1981, pp. 273–303.

pollution was investigated on nine major mid-Atlantic soil types. The soils had a wide range in organic matter, clay, and oxide content. Charge properties including anion exchange capacity (AEC) and point of zero salt effect (PZSE) were determined. The PZSE values were low, indicating little anion adsorption capacity; however, the AEC values were often significant and increased with profile depth as oxide and clay contents increased. The kinetics of nitrate retention and release and the effect of competitive anions on nitrate retention were investigated at pH 4.0, 5.5, and 7.0. Nitrate retention was highest at pH 4.0 and was strongly

correlated with clay and oxide contents. The adsorption kinetics were rapid and completely reversible, indicating that the nitrate adsorption mechanism was electrostatic. Whenever sulfate was present, nitrate retention significantly decreased and was even depressed when chloride was added (Sparks, 1987).

Cation exchange may be involved, along with adsorption in the retention of ammonium ions in soils. However, just as the adsorption capacity of a soil can be exceeded, the cation exchange capacity can also be exhausted. Under these conditions, the cation exchange sites in the soil beneath an ammonium input source would become equilibrated with the cations in the leachate. The leachate would then move to the groundwater with its cation composition essentially unchanged. Ammonia-nitrogen can be incorporated into microbial or plant biomass in the subsurface environment; however, this is probably not a major removal mechanism relative to nitrogen in the subsurface. Finally, as noted earlier, ammonia gas can be released to the atmosphere as a function of the soil/liquid pH conditions. When the pH is neutral or below, most of the nitrogen is in the ammonium ion form. As the pH becomes basic, the ammonium ion is transformed into ammonia and can be released from the soil as a gas.

Nitrate is typically more mobile in the subsurface environment than ammonium-nitrogen. When nitrogen in the form of nitrate reaches groundwater, it becomes very mobile because of its solubility and anionic form. Nitrates can move with groundwater with minimal transformation. They can migrate long distances from input areas if there are highly permeable subsurface materials that contain dissolved oxygen. The only condition that can affect this process is a decline in the redox potential of the groundwater. In this case, and as noted earlier, the denitrification process can occur.

FACTORS INFLUENCING NITROGEN LEACHING FROM FERTILIZERS

Nitrogen leaching from applied fertilizers is the precursor event to the transformation processes described in the previous section. Table 2.6 contains summary comments on 17 references dealing with factors influencing the leaching of nitrogen into the subsurface environment. To serve as examples, the amount of leaching and hence the amount of nitrates in groundwater have been found to be a function of the timing of fertilizer application, vegetative cover, and soil porosity (Borneff and Adabe, 1973); fertilizer application method and amount added (Gillings, 1973); fertilizer amount added and drainage volume from various water treatments (Letey et al., 1978); and fertilizer amount added and irrigation rate (Ludwick, Reuss, and Langin, 1976).

Borneff and Adabe (1973) described a 2-year sampling program, at 14-day intervals, for three wells in the Mainz, West Germany, area. The highest amount of nitrate in soil was found in the vicinity of two of the wells situated in a wine-growing area and corresponded with the fertilization period (June and July). A minimum amount was recorded in the winter. Groundwater abstracted from wells exhibited the highest concentrations of nitrates 6 months after fertilization. Nitrate fluctuation in the third well situated in a fruit- and vegetable-growing area was

Table 2.6 References Related to Leaching of Nitrogen into the Subsurface Environment

Author(s) (year)	Comments
Anonymous (1984)	Summaries of papers presented at a technical symposium: some deal with nitrogen leaching
Bergstrom (1987)	Study of effects of plowing and weather conditions on nitrate leaching from fertilizer applied to annual and perennial crops
Bergstrom and Brink (1986)	Influence of fertilizer application rate, season, and crop type on nitrogen leaching losses and distribution of inorganic nitrogen in soil in central Sweden
Berndt (1990)	Study of the contribution of land application of sewage plant effluent to nitrates in groundwater
Bornett and Adebe (1973)	Factors influencing nitrogen leaching in a fertilized agricultural area
Bouwer (1983)	Nitrate leaching through the vadose zone as a function of irrigation water application
Bumb et al. (1987)	Determination of first-order rate constant for the leaching of ammonia and nitrate from the storage area at a fertilizer plant
Desprez, Landreau, and Vogt (1982)	Unconfined aquifer zones vulnerable to nitrogen leaching
Gillings (1973)	Field experiment on nitrogen leaching as a function of normal agricultural practices
Letey et al. (1978)	Field experiments on nitrate leaching at commercial farming sites in California
Ludwick, Reuss, and Langin (1976)	Soil nitrate concentrations as a function of fertilizer applications
Martin et al. (1982)	Computer model for studying the interaction of nitrogen and water management on corn production
Morton, Gold, and Sullivan (1988)	Study of the influence of overwatering and fertilization rate on nitrogen losses from lawns in urban areas
Pal and Broadbent (1981)	Use of soil columns to study leaching of nitrogen from applied sewage
Spalding and Kitchen (1988)	Determination of influence of fertilization rate on vadose-zone nitrate content beneath irrigated cropland
Stone (1982)	Field study of water and nitrogen balances at a site in Kansas
Tolman (1985)	Survey of seasonal fluctuations of nitrate in groundwater at an Idaho site subjected to irrigation and precipitation influences

less evident; but concentrations were somewhat higher, even though the fertilization was not as intense as that in the wine-growing area. The extent of vegetative cover and the porosity of the soil were also found to be decisive factors for the fertilization-dependent nitrate concentration in groundwater. The leaching of naturally formed nitrate in the soil was also of considerable importance.

Gillings (1973) described an experiment in which nitrate and ammonium fertilizers were applied to field plots containing sorghum and beets. Suction lysimeters were used to sample soil at the 1-, 4-, and 9-ft depths, and surface

runoff was also sampled. Nitrate, nitrite, and ammonium were determined in these samples. More nitrogen was lost to both surface runoff and deep leaching from broadcast fertilizers than from drilled fertilizers. Little difference in the levels of nitrogen (nitrate plus ammonium) in soil water was found between nitrate and ammonium fertilizers. The largest deep leaching of nitrates occurred in the fall and in the spring. The amount leached was proportional to the amount of nitrogen applied. When 175 kg N/ha was applied, the average (of three replications) amount of nitrate found in soil water at the 9-ft depth was 6 to 9 mg/l as nitrate-nitrogen. At the 4-ft depth, nitrate-nitrogen varied from 1 to 9 mg/l when treatment ranged from no nitrogen to 175 kg N/ha.

The amounts of leached nitrates for a given time period were determined by Letey et al. (1978) at various commercial farming sites in California, and in a carefully controlled experimental plot receiving various water and fertilizer application treatments. Some of the agricultural sites had tile drainage systems and others had "free drainage" to the groundwater. Linear regression analyses were conducted on the data. Similar results were observed for the tile and free drainage systems. The highest correlation coefficient was of the drainage volume and fertilizer nitrogen application. The next highest correlation coefficient was for amount leached versus drainage volume, followed by amount leached versus fertilizer nitrogen application. A significant linear relationship between amount of leached nitrate and drainage volume was also obtained at the experimental plot.

The purpose of the study by Ludwick, Reuss, and Langin (1976) was to evaluate soil nitrate accumulations following 4 years of continuous corn grown with different nitrogen and irrigation regimes, and to compare these results to present nitrate concentrations found in irrigated farm fields of central and eastern Colorado. Soil nitrate content in the 300-cm sampled profile was significantly influenced by both fertilizer nitrogen and irrigation treatments; the greater accumulations were associated with the two higher fertilizer nitrogen application rates and the two lower irrigation rates. Nitrate content increased linearly in relation to fertilizer nitrogen between 67 and 269 kg N/ha, and could be described by two simple regression equations separating the irrigation treatments into low rates and high rates.

USAGE OF LABORATORY STUDIES

Laboratory studies can aid in the development of information on transformation and transport and fate processes, and on factors influencing nitrogen leaching from fertilizers. Table 2.7 contains summary comments on ten references describing potentially relevant laboratory studies. General nitrogen transformations were the focus of two studies (Lindley, Dale, and Mannering, 1974; Williford et al., 1969), and denitrification was emphasized in four studies (Biswas and Warnock, 1985; Davenport, Lembke, and Jones, 1975; Schwan, Kramer, and Gericke, 1984; Willardson and Meek, 1969).

Lindley, Dale, and Mannering (1974) described a laboratory study of nitrogen transformation in wastewater percolating through soil columns. The study

Table 2.7 References Related to Laboratory Studies of Nitrogen Transformations in the Subsurface Environment

Author(s) (year)	Comments
Bachelor, et al. (1991)	User guide for a mathematical model (LT3VSI) developed to describe transport and fate processes, including denitrification, in nonhomogeneous laboratory scale-model aquifers
Biswas and Warnock (1985)	Use of laboratory soil columns as denitrifying reactors subjected to varying carbon-to-nitrogen ratios
Davenport, Lembke, and Jones (1975)	Study of denitrification in laboratory sandy columns with methanol added as a carbon source
El Ellreby and Laudelout (1988)	Use of columns of undisturbed loess soil to study the movement of tritiated water, chloride, and nitrate as related to the transfer of nitrate toward an aquifer
Lindley, Dale, and Mannering (1974)	Laboratory study of nitrogen transformations in wastewater percolating through soil columns
Lindstrom and Boersma (1990)	Development of a two-dimensional mathematical model for simulating denitrification in a nonhomogeneous laboratory scale, single-layer aquifer
Lindstrom et al. (1991)	Study of the influence of hydraulics, nitrogen chemistry, and microbiology in a nonhomogeneous laboratory-scale, single-layer aquifer, and use of model by Lindstrom and Boersma (1990)
Schwan, Kramer, and Gericke (1984)	Development of mathematical model of denitrification based on laboratory reaction vessels
Willardson and Meek (1969)	Use of large soil columns to study anaerobic reduction of nitrate
Willford et al. (1969)	Use of soil lysimeters to study the movement of nitrates in soil systems

addressed varying applied wastes, soil moisture contents, and soil types. Willford et al. (1969) reported on a study of the movement of nitrates in soil systems by using 14 lysimeters made of techite (fiber glass) pipe 15 in. in diameter and 6.7 ft in length. The lysimeters were filled with four major soil types from the west side of the San Joaquin Valley in California. The volumes extracted from the probes and collected in the leachates were recorded. The samples were analyzed for chlorides, ammonia, total nitrogen, and atom percent excess nitrogen. The nitrate levels in leachates collected during initial leaching and before fertilization ranged from 20,000 mg/l in oxalis clay to 2500 mg/l in panoche fine sandy loam. These high nitrate levels indicate how relatively low levels of native nitrates can be concentrated in the groundwater by leaching. The highest percentage of fertilizer nitrogen was leached from soils to which KNO_3 was applied. In panoche fine sandy loam and lenthent sandy clay loam, respectively, 82 and 65% of the total nitrogen collected in the soil extract was fertilizer nitrogen. By comparison, only 14 to 24% of the nitrogen in the extract was fertilizer nitrogen when ammonium sulfate and sulfur-coated urea were the nitrogen sources. Much of

the added ammonium-nitrogen was tied up by the clay complex of the soil near the soil surface.

As noted in Chapter 1, septic tank systems may be a source of nitrates in groundwater systems. Biswas and Warnock (1985) conducted a laboratory study related to denitrification of septic tank system effluents in the subsurface environment. The study was conducted using kitchen waste as the source of organic carbon for denitrification in an attached growth system. Soil columns were used as denitrifying reactors, with the feed solutions composed of a nitrified solution and kitchen waste. Five different carbon (expressed as methanol) to nitrogen ratios ranging from 2.2 to 6:1 were applied to 20 soil columns. A high degree of denitrification was obtained from C:N ratios of 4:1 or higher.

Davenport, Lembke, and Jones (1975) found that nitrate was effectively reduced when methanol was added as a substrate material to a slowly moving solution in porous columns. Applied nitrate exhibited 87% removal during 24 days at 24°C, and 62% removal following 27 days at 13°C. The passage of nitrate and chloride through the columns was accompanied by an increase in redox potential and, in some cases, discoloration of the effluent. The removal of a high percentage of nitrate at relatively large pore velocities was encouraging for the prospect of removing excess nitrate from soil water in the vicinity of tile drains. While a technique was not described, it could involve a system for water table control with additions of substrate material introduced by surface application or deep plowing.

Schwan, Kramer, and Gericke (1984) also studied denitrification using ten reaction vessels 1 m^3 in size. The vessels were filled with coarse sand or fine gravel. The pore volume (water saturation) was 227 to 260 liters. Anaerobic conditions were established by the addition of 6 g glucose. The reactors were fed tap water with 50 and 200 mg/l nitrate from KNO_3 in such a way that a volumetric rate of flow of 0.2, 0.4, and 0.8 l/d was created. The volumetric rates of flow approximated the natural recharge of groundwater, the recharge of groundwater under conditions of irrigation, and the recharge conditions of an intensive wastewater land treatment system. The effluent from the reaction vessels were monitored for nitrate concentration on a monthly basis. The concentration was stationary from the 7th to the 55th month after the beginning of the experiment.

Willardson and Meek (1969) described some laboratory studies on large soil columns with a controlled water table and submerged drains. These studies demonstrated that very low nitrate content water can be delivered from agricultural drains. A field experiment on drain submergence that intercepts groundwater high in native nitrate indicated that denitrified water from irrigated agriculture can reduce nitrate concentrations in drainage water by dilution. Where proper conditions can be established (including oxygen shortage, adequate organic carbon as an energy source, and a bacterial population), anaerobic conditions develop and result in denitrification. Based on the results obtained in the columns, a nitrate-nitrogen content of 500 mg/l in the groundwater would require a surface application of 1000 pounds per acre nitrogen as a nitrate fertilizer in a single application.

Finally, Lindstrom and Boersma (1990) described a two-dimensional mathematical model for simulating the transport and fate of organic chemicals in a laboratory-scale, single-layer aquifer. Two large (4 ft wide, 4 ft high, and 16 ft long) physical aquifers were used, with each aquifer containing three horizontal layers of material. Each layer was assumed to be homogenous and isotropic with respect to water flow. The systems were used for the study of transport and fate of chemicals, and for evaluation of growth characteristics of indigenous microbial populations. The physical aquifers can also be used for the study of proposed physical and biological remediation schemes. The developed mathematical model accounts for the major physical processes of storage, dispersion, and advection, and can also account for linear equilibrium sorption, three first-order loss processes (including microbial degradation, irreversible sorption and/or dissolution into the organic phase, metabolism in the sorbed state), and first-order loss in the sorbed state. A broad range of remediation scenarios may be considered by the use of the model, including placement of injection/extraction wells to induce plume spreading or plume shaping and the effects of regions of varying hydraulic conductivity on the shape of the plumes.

SUMMARY

Chemical and microbiological processes can influence the movement of various forms of nitrogen in the subsurface environment. Nitrification and denitrification processes, along with other microbial, abiotic, and hydrodynamic phenomena, influence nitrate concentrations in groundwater, such influences can be exacerbated spatially, vertically, and temporally. An understanding of subsurface processes is fundamental to identifying natural and man-made sources of nitrate contamination, evaluating influencing factors, modeling transport and fate, delineating appropriate protection measures, and selecting nitrate *in situ* remediation and/or pump and treatment cleanup schemes.

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