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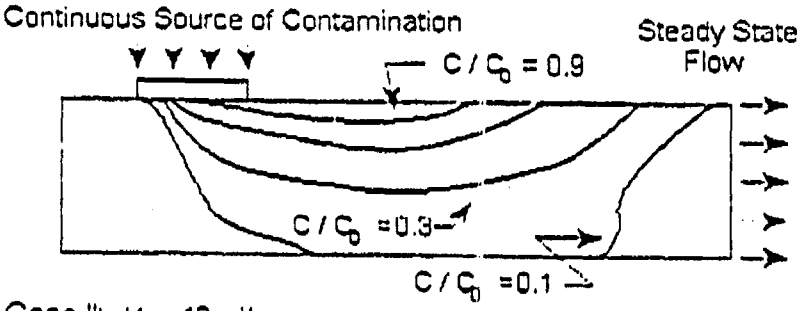
UNDERSTANDING VARIATION IN PARTITION COEFFICIENT, K_d, VALUES

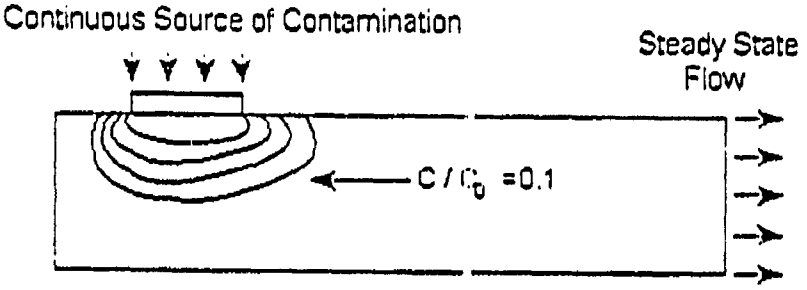
Volume II:

Review of Geochemistry and Available K_d Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (^3H), and Uranium

Case I: $K_d = 1$ ml/g



Case II: $K_d = 10$ ml/g



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1.0 Introduction

The objective of the report is to provide a reasoned and documented discussion on the technical issues associated with the measurement and selection of partition (or distribution) coefficient, K_d,[1,2] values and their use in formulating the retardation factor, R_f. The contaminant retardation factor (R_f) is the parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials (*i.e.*, soil, sediments, rocks, and geological formations, henceforth simply referred to as soils[3]). It includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. Specifically, it describes the rate of contaminant transport relative to that of groundwater. This report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions. The two-volume report describes the conceptualization, measurement, and use of the K_d parameter; and geochemical aqueous solution and sorbent properties that are most important in controlling the adsorption/retardation behavior of a selected set of contaminants.

This review is not meant to assess or judge the adequacy of the K_d approach used in modeling tools for estimating adsorption and transport of contaminants and radionuclides. Other approaches, such as surface complexation models, certainly provide more robust mechanistic approaches for predicting contaminant adsorption. However, as one reviewer of this volume noted, "K_d's are the coin of the realm in this business." For better or worse, the K_d model is integral part of current methodologies for modeling contaminant and radionuclide transport and risk analysis.

The K_d concept, its use in fate and transport computer codes, and the methods for the measurement of K_d values are discussed in detail in Volume I and briefly introduced in Chapters 2 and 3 in Volume II. Particular attention is directed at providing an understanding of: (1) the use of K_d values in formulating R_f, (2) the difference between the original thermodynamic K_d parameter derived from the ion-exchange literature and its "empiricized" use in contaminant

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[1] Throughout this report, the term "partition coefficient" will be used to refer to the K_d "linear isotherm" sorption model. It should be noted, however, that the terms "partition coefficient" and "distribution coefficient" are used interchangeably in the literature for the K_d model.

[2] A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

[3] The terms "sediment" and "soil" have particular meanings depending on one's technical discipline. For example, the term "sediment" is often reserved for transported and deposited particles derived from soil, rocks, or biological material. "Soil" is sometimes limited to referring to the top layer of the earth's surface, suitable for plant life. In this report, the term "soil" was selected with concurrence of the EPA Project Officer as a general term to refer to all unconsolidated geologic materials.

transport codes, and (3) the explicit and implicit assumptions underlying the use of the K_d parameter in contaminant transport codes.

The K_d parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. As typically used in fate and contaminant transport calculations, the K_d is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Soil chemists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default K_d values can result in significant errors when used to predict the impacts of contaminant migration or site-remediation options. To address some of this concern, modelers often incorporate a degree of conservatism into their calculations by selecting limiting or bounding conservative K_d values. For example, the most conservative (*i.e.*, maximum) estimate from the perspective of off-site risks due to contaminant migration through the subsurface natural soil and groundwater systems is to assume that the soil has little or no ability to slow (retard) contaminant movement (*i.e.*, a minimum bounding K_d value). Consequently, the contaminant would travel in the direction and at the rate of water. Such an assumption may in fact be appropriate for certain contaminants such as tritium, but may be too conservative for other contaminants, such as thorium or plutonium, which react strongly with soils and may migrate 10^2 to 10^6 times more slowly than the water. On the other hand, when estimating the risks and costs associated with on-site remediation options, a maximum bounding K_d value provides an estimate of the maximum concentration of a contaminant or radionuclide sorbed to the soil. Due to groundwater flow paths, site characteristics, or environmental uncertainties, the final results of risk and transport calculations for some contaminants may be insensitive to the K_d value even when selected within the range of technically-defensible, limiting minimum and maximum K_d values. For those situations that are sensitive to the selected K_d value, site-specific K_d values are essential.

The K_d is usually a measured parameter that is obtained from laboratory experiments. The 5 general methods used to measure K_d values are reviewed. These methods include the batch laboratory method, the column laboratory method, field-batch method, field modeling method, and K_{oc} method. The summary identifies what the ancillary information is needed regarding the adsorbent (soil), solution (contaminated ground-water or process waste water), contaminant (concentration, valence state, speciation distribution), and laboratory details (spike addition methodology, phase separation techniques, contact times). The advantages, disadvantages, and, perhaps more importantly, the underlying assumptions of each method are also presented.

A conceptual overview of geochemical modeling calculations and computer codes as they pertain to evaluating K_d values and modeling of adsorption processes is discussed in detail in Volume I and briefly described in Chapter 4 of Volume II. The use of geochemical codes in evaluating aqueous speciation, solubility, and adsorption processes associated with contaminant fate studies is reviewed. This approach is compared to the traditional calculations that rely on the constant K_d construct. The use of geochemical modeling to address quality assurance and technical defensibility issues concerning available K_d data and the measurement of K_d values is also

discussed. The geochemical modeling review includes a brief description of the EPA's MINTEQA2 geochemical code and a summary of the types of conceptual models it contains to quantify adsorption reactions. The status of radionuclide thermodynamic and contaminant adsorption model databases for the MINTEQA2 code is also reviewed.

The main focus of Volume II is to: (1) provide a "thumb-nail sketch" of the key geochemical processes affecting the sorption of a selected set of contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment; and (4) identify, when possible, minimum and maximum conservative K_d values for each contaminant as a function key geochemical processes affecting their sorption. The contaminants chosen for the first phase of this project include cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium (^3H), and uranium. The selection of these contaminants by EPA and PNNL project staff was based on 2 criteria. First, the contaminant had to be of high priority to the site remediation or risk assessment activities of EPA, DOE, and/or NRC. Second, because the available funding precluded a review of all contaminants that met the first criteria, a subset was selected to represent categories of contaminants based on their chemical behavior. The six nonexclusive categories are:

- Cations - cadmium, cesium, plutonium, strontium, thorium, and uranium(VI).
- Anions - chromium(VI) (as chromate) and uranium(VI).
- Radionuclides - cesium, plutonium, radon, strontium, thorium, tritium (^3H), and uranium.
- Conservatively transported contaminants - tritium (^3H) and radon.
- Nonconservatively transported contaminants - other than tritium (^3H) and radon.
- Redox sensitive elements - chromium, plutonium, and uranium.

The general geochemical behaviors discussed in this report can be used by analogy to estimate the geochemical interactions of similar elements for which data are not available. For example, contaminants present primarily in anionic form, such as Cr(VI), tend to adsorb to a limited extent to soils. Thus, one might generalize that other anions, such as nitrate, chloride, and U(VI)-anionic complexes, would also adsorb to a limited extent. Literature on the adsorption of these 3 solutes show no or very little adsorption.

The concentration of contaminants in groundwater is controlled primarily by the amount of contaminant present at the source; rate of release from the source; hydrologic factors such as dispersion, advection, and dilution; and a number of geochemical processes including aqueous geochemical processes, adsorption/desorption, precipitation, and diffusion. To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically and scientifically defensible manner. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibium exists, such as at a point source, an area where high contaminant concentrations

exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical steady state exist, such as in areas far from the point source. Diffusion flux spreads solute via a concentration gradient (*i.e.*, Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces.

2.0 The K_d Model

The simplest and most common method of estimating contaminant retardation is based on the partition (or distribution) coefficient, K_d. The K_d parameter is a factor related to the partitioning of a contaminant between the solid and aqueous phases. It is an empirical unit of measurement that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. The K_d metric is the most common measure used in transport codes to describe the extent to which contaminants are sorbed to soils. It is the simplest, yet least robust model available. A primary advantage of the K_d model is that it is easily inserted into hydrologic transport codes to quantify reduction in the rate of transport of the contaminant relative to groundwater, either by advection or diffusion. Technical issues, complexities, and shortcomings of the K_d approach to describing contaminant sorption to soils are summarized in detail in Chapter 2 of Volume I. Particular attention is directed at issues relevant to the selection of K_d values from the literature for use in transport codes.

The partition coefficient, K_d, is defined as the ratio of the quantity of the adsorbate adsorbed per mass of solid to the *amount of the adsorbate remaining in solution at equilibrium.* For the reaction

$$A + C_i = A_i, \tag{2.1}$$

the mass action expression for K_d is

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i} \tag{2.2}$$

where A = free or unoccupied surface adsorption sites
C_i = total dissolved adsorbate remaining in solution at equilibrium
A_i = amount of adsorbate on the solid at equilibrium.

The K_d is typically given in units of ml/g. Describing the K_d in terms of this simple reaction assumes that A is in great excess with respect to C_i and that the activity of A_i is equal to 1.

Chemical retardation, R_f, is defined as,

$$R_f = \frac{v_p}{v_c}, \tag{2.3}$$

where v_p = velocity of the water through a control volume
v_c = velocity of contaminant through a control volume.

The chemical retardation term does not equal unity when the solute interacts with the soil; almost always the retardation term is greater than 1 due to solute sorption to soils. In rare cases, the

retardation factor is actually less than 1, and such circumstances are thought to be caused by anion exclusion (See Volume I, Section 2.8). Knowledge of the K_d and of media bulk density and porosity for porous flow, or of media fracture surface area, fracture opening width, and matrix diffusion attributes for fracture flow, allows calculation of the retardation factor. For porous flow with saturated moisture conditions, the R_f is defined as

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \tag{2.4}$$

where ρ_b = porous media bulk density (mass/length^3)
n_e = effective porosity of the media at saturation.

The K_d parameter is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (*e.g.*, adsorbate concentration, solution/electrolyte matrix) in which it was measured. Site-specific K_d values should be used for site-specific contaminant and risk assessment calculations. Ideally, site-specific K_d values should be measured for the range of aqueous and geological conditions in the system to be modeled. However, literature-derived K_d values are commonly used for screening calculations. Suitable selection and use of literature-derived K_d values for use in screening calculations of contaminant transport is not a trivial matter. Among the assumptions implicit with the K_d construct is: (1) only trace amounts of contaminants exist in the aqueous and solid phases, (2) the relationship between the amount of contaminant in the solid and liquid phases is linear, (3) equilibrium conditions exist, (4) equally rapid adsorption and desorption kinetics exists, (5) it describes contaminant partitioning between 1 sorbate (contaminant) and 1 sorbent (soil), and (6) all adsorption sites are accessible and have equal strength. The last point is especially limiting for groundwater contaminant models because it requires that K_d values should be used only to predict transport in systems chemically identical to those used in the laboratory measurement of the K_d. Variation in either the soil or aqueous chemistry of a system can result in extremely large differences in K_d values.

A more robust approach than using a single K_d to describe the partitioning of contaminants between the aqueous and solid phases is the parametric-K_d model. This model varies the K_d value according to the chemistry and mineralogy of the system at the node being modeled. The parametric-K_d value, unlike the constant-K_d value, is not limited to a single set of environmental conditions. Instead, it describes the sorption of a contaminant in the range of environmental conditions used to create the parametric-K_d equations. These types of statistical relationships are devoid of causality and therefore provide no information on the mechanism by which the radionuclide partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. Understanding these mechanisms is extremely important relative to estimating the mobility of a contaminant.

When the parametric-K_d model is used in the transport equation, the code must also keep track of the current value of the independent variables at each point in space and time to continually update the concentration of the independent variables affecting the K_d value. Thus, the code must

track many more parameters and some numerical solving techniques (such as closed-form analytical solutions) can no longer be used to perform the integration necessary to solve for the K_d value and/or retardation factor, R_f. Generally, computer codes that can accommodate the parametric-K_d model use a chemical subroutine to update the K_d value used to determine the R_f, when called by the main transport code. The added complexity in solving the transport equation with the parametric-K_d sorption model and its empirical nature may be the reasons this approach has been used sparingly.

Mechanistic models explicitly accommodate for the dependency of K_d values on contaminant concentration, charge, competing ion concentration, variable surface charge on the soil, and solution species distribution. Incorporating mechanistic adsorption concepts into transport models is desirable because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, truly mechanistic adsorption models are rarely, if ever, applied to complex natural soils. The primary reason for this is because natural mineral surfaces are very irregular and difficult to characterize. These surfaces consist of many different microcrystalline structures that exhibit quite different chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface.

Less attention will be directed to mechanistic models because they are not extensively incorporated into the majority of EPA, DOE, and NRC modeling methodologies. The complexity of installing these mechanistic adsorption models into existing transport codes is formidable. Additionally, these models also require a more extensive database collection effort than will likely be available to the majority of EPA, DOE, and NRC contaminant transport modelers. A brief description of the state of the science is presented in Volume I primarily to provide a paradigm for sorption processes.

3.0 Methods, Issues, and Criteria for Measuring K_d Values

There are 5 general methods used to measure K_d values: the batch laboratory method, laboratory flow-through (or column) method, field-batch method, field modeling method, and K_{oc} method. These methods and the associated technical issues are described in detail in Chapter 3 of Volume I. Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating K_d values from experimental data. Consequently, it is not only common, but expected that K_d values measured by different methods will produce different values.

3.1 Laboratory Batch Method

Batch tests are commonly used to measure K_d values. The test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. The concentration of contaminant associated with the solid is determined by the difference between initial and final contaminant concentration. The primary advantage of the method is that such experiments can be completed quickly for a wide variety of elements and chemical environments. The primary disadvantage of the batch technique for measuring K_d is that it does not necessarily reproduce the chemical reaction conditions that take place in the real environment. For instance, in a soil column, water passes through at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a laboratory batch test. Consequently, K_d values from batch experiments can be high relative to the extent of sorption occurring in a real system, and thus result in an estimate of contaminant retardation that is too large. Another disadvantage of batch experiments is that they do not accurately simulate desorption of the radionuclides or contaminants from a contaminated soil or solid waste source. The K_d values are frequently used with the assumption that adsorption and desorption reactions are reversible. This assumption is contrary to most experimental observations that show that the desorption process is appreciably slower than the adsorption process, a phenomenon referred to as hysteresis. The rate of desorption may even go to zero, yet a significant mass of the contaminant remains sorbed on the soil. Thus, use of K_d values determined from batch adsorption tests in contaminant transport models is generally considered to provide estimates of contaminant remobilization (release) from soil that are too large (*i.e.*, estimates of contaminant retention that are too low).

3.2 Laboratory Flow-Through Method

Flow-through column experiments are intended to provide a more realistic simulation of dynamic field conditions and to quantify the movement of contaminants relative to groundwater flow. It is the second most common method of determining K_d values. The basic experiment is completed by passing a liquid spiked with the contaminant of interest through a soil column. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant

of interest. The retardation factor (a ratio of the velocity of the contaminant to that of water) is measured directly from the experimental data. A K_d value can be calculated from the retardation factor. It is frequently useful to compare the back-calculated K_d value from these experiments with those derived directly from the batch experiments to evaluate the influence of limited interaction between solid and solution imposed by the flow-through system.

One potential advantage of the flow-through column studies is that the retardation factor can be inserted directly into the transport code. However, if the study site contains different hydrological conditions (*e.g.*, porosity and bulk density) than the column experiment, than a K_d value needs to be calculated from the retardation factor. Another advantage is that the column experiment provides a much closer approximation of the physical conditions and chemical processes occurring in the field site than a batch sorption experiment. Column experiments permit the investigation of the influence of limited spatial and temporal (nonequilibium) contact between solute and solid have on contaminant retardation. Additionally, the influence of mobile colloid facilitated transport and partial saturation can be investigated. A third advantage is that both adsorption or desorption reactions can be studied. The predominance of 1 mechanism of adsorption or desorption over another cannot be predicted *a priori* and therefore generalizing the results from 1 set of laboratory experimental conditions to field conditions is never without some uncertainty. Ideally, flow-through column experiments would be used exclusively for determining K_d values, but equipment cost, time constraints, experimental complexity, and data reduction uncertainties discourage more extensive use.

3.3 Other Methods

Less commonly used methods include the K_{oc} method, *in-situ* batch method, and the field modeling method. The K_{oc} method is a very effective indirect method of calculating K_d values, however, it is only applicable to organic compounds. The *in-situ* batch method requires that paired soil and groundwater samples be collected directly from the aquifer system being modeled and then measuring directly the amount of contaminant on the solid and liquid phases. The advantage of this approach is that the precise solution chemistry and solid phase mineralogy existing in the study site is used to measure the K_d value. However, this method is not used often because of the analytical problems associated with measuring the exchangeable fraction of contaminant on the solid phase. Finally, the field modeling method of calculating K_d values uses groundwater monitoring data and source term data to calculate a K_d value. One key drawback to this technique is that it is very model dependent. Because the calculated K_d value are model dependent and highly site specific, the K_d values must be used for contaminant transport calculations at other sites.

3.4 Issues

A number of issues exist concerning the measurement of K_d values and the selection of K_d values from the literature. These issues include: using simple versus complex systems to measure K_d values, field variability, the "gravel issue," and the "colloid issue." Soils are a complex mixture

containing solid, gaseous, and liquid phases. Each phase contains several different constituents. The use of simplified systems containing single mineral phases and aqueous phases with 1 or 2 dissolved species has provided valuable paradigms for understanding sorption processes in more complex, natural systems. However, the K_d values generated from these simple systems are generally of little value for importing directly into transport models. Values for transport models should be generated from geologic materials from or similar to the study site. The "gravel issue" is the problem that transport modelers face when converting laboratory-derived K_d values based on experiments conducted with the <2-mm fraction into values that can be used in systems containing particles >2 mm in size. No standard methods exist to address this issue. There are many subsurface soils dominated by cobbles, gravel, or boulders. To base the K_d values on the <2-mm fraction, which may constitute only <1 percent of the soil volume but is the most chemically reactive fraction, would grossly overestimate the actual K_d of the aquifer. Two general approaches have been proposed to address this issue. The first is to assume that all particles >2-mm has a K_d = 0 ml/g. Although this assumption is incorrect (*i.e.*, cobbles, gravel, and boulders do in fact sorb contaminants), the extent to which sorption occurs on these larger particles may be small. The second approach is to normalize laboratory-derived K_d values by soil surface area. Theoretically, this latter approach is more satisfying because it permits some sorption to occur on the >2-mm fraction and the extent of the sorption is proportional to the surface area. The underlying assumptions in this approach are that the mineralogy is similar in the less than 2- and greater than 2-mm fractions and that the sorption processes occurring in the smaller fraction are similar to those that occur in the larger fraction.

Spatial variability provides additional complexity to understanding and modeling contaminant retention to subsurface soils. The extent to which contaminants partition to soils changes as field mineralogy and chemistry change. Thus, a single K_d value is almost never sufficient for an entire study site and should change as chemically important environmental conditions change. Three approaches used to vary K_d values in transport codes are the K_d look-up table approach, the parametric-K_d approach, and the mechanistic K_d approach. The extent to which these approaches are presently used and the ease of incorporating them into a flow model varies greatly. Parametric-K_d values typically have limited environmental ranges of application. Mechanistic K_d values are limited to uniform solid and aqueous systems with little application to heterogenous soils existing in nature. The easiest and the most common variable-K_d model interfaced with transport codes is the look-up table. In K_d look-up tables, separate K_d values are assigned to a matrix of discrete categories defined by chemically important ancillary parameters. No single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in K_d look-up tables. Instead, the ancillary parameters must vary in accordance to the geochemistry of the contaminant. It is essential to understand fully the criteria and process used for selecting the values incorporated in such a table. Differences in the criteria and process used to select K_d values can result in appreciable different K_d values. Examples are presented in this volume.

Contaminant transport models generally treat the subsurface environment as a 2-phase system in which contaminants are distributed between a mobile aqueous phase and an immobile solid phase

(*e.g.*, soil). An increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as colloids[1] that may be transported with the flowing water. Subsurface mobile colloids originate from (1) the dispersion of surface or subsurface soils, (2) decementation of secondary mineral phases, and (3) homogeneous precipitation of ground-water constituents. Association of contaminants with this additional mobile phase may enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or because the mathematical algorithms have not been developed, but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids. There are 2 primary problems associated with studying colloid-facilitated transport of contaminants under natural conditions. First, it is difficult to collect colloids from the subsurface in a manner which minimizes or eliminates sampling artifacts. Secondly, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases.

Often K_d values used in transport models are selected to provide a conservative estimate of contaminant migration or health effects. However, the same K_d value would not provide a conservative estimate for clean-up calculations. Conservatism for remediation calculations would tend to err on the side of underestimating the extent of contaminant desorption that would occur in the aquifer once pump-and-treat or soil flushing treatments commenced. Such an estimate would provide an upper limit to time, money, and work required to extract a contaminant from a soil. This would be accomplished by selecting a K_d from the upper range of literature values.

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different K_d methods, and perhaps more importantly, the underlying assumption of the methods in order to properly select K_d values from the literature. The K_d values reported in the literature for any given contaminant may vary by as much as 6 orders of magnitude. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate K_d value(s) for contaminant transport modeling.

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[1] A colloid is any fine-grained material, sometimes limited to the particle-size range of <0.00024 mm (*i.e.*, smaller than clay size), that can be easily suspended (Bates and Jackson, 1980). In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. The geochemistry of colloid systems is discussed in detail in sources such as Yariv and Cross (1979) and the references therein.

4.0 Application of Chemical Reaction Models

Computerized chemical reaction models based on thermodynamic principles may be used to calculate processes such as aqueous complexation, oxidation/reduction, adsorption/desorption, and mineral precipitation/dissolution for contaminants in soil-water systems. The capabilities of a chemical reaction model depend on the models incorporated into its computer code and the availability of thermodynamic and/or adsorption data for aqueous and mineral constituents of interest. Chemical reaction models, their utility to understanding the solution chemistry of contaminants, and the MINTEQA2 model in particular are described in detail in Chapter 5 of Volume I.

The MINTEQA2 computer code is an equilibrium chemical reaction model. It was developed with EPA funding by originally combining the mathematical structure of the MINEQL code with the thermodynamic database and geochemical attributes of the WATEQ3 code. The MINTEQA2 code includes submodels to calculate aqueous speciation/complexation, oxidation-reduction, gas-phase equilibria, solubility and saturation state (*i.e.*, saturation index), precipitation/dissolution of solid phases, and adsorption. The most current version of MINTEQA2 available from EPA is compiled to execute on a personal computer (PC) using the MS-DOS computer operating system. The MINTEQA2 software package includes PRODEFA2, a computer code used to create and modify input files for MINTEQA2.

The MINTEQA2 code contains an extensive thermodynamic database for modeling the speciation and solubility of contaminants and geologically significant constituents in low-temperature, soil-water systems. Of the contaminants selected for consideration in this project [chromium, cadmium, cesium, tritium (^3H), lead, plutonium, radon, strontium, thorium, and uranium], the MINTEQA2 thermodynamic database contains speciation and solubility reactions for chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI). Some of the thermodynamic data in the EPA version have been superseded in other users' databases by more recently published data.

The MINTEQA2 code includes 7 adsorption model options. The non-electrostatic adsorption models include the activity K_d^{act}, activity Langmuir, activity Freundlich, and ion exchange models. The electrostatic adsorption models include the diffuse layer, constant capacitance, and triple layer models. The MINTEQA2 code does not include an integrated database of adsorption constants and reactions for any of the 7 models. These data must be supplied by the user as part of the input file information.

Chemical reaction models, such as the MINTEQA2 code, cannot be used *a priori* to predict a partition coefficient, K_d, value. The MINTEQA2 code may be used to calculate the chemical changes that result in the aqueous phase from adsorption using the more data intensive, electrostatic adsorption models. The results of such calculations in turn can be used to back calculate a K_d value. The user however must make assumptions concerning the composition and mass of the dominant sorptive substrate, and supply the adsorption parameters for surface-

complexation constants for the contaminants of interest and the assumed sorptive phase. The EPA (EPA 1992; 1996) has used the MINTEQA2 model and this approach to estimate K_d values for several metals under a variety of geochemical conditions and metal concentrations to support several waste disposal issues. The EPA in its "Soil Screening Guidance" determined MINTEQA2-estimated K_d values for barium, beryllium, cadmium, Cr(III), Hg(II), nickel, silver, and zinc as a function of pH assuming adsorption on a fixed mass of iron oxide (EPA, 1996; RTI, 1994). The calculations assumed equilibrium conditions, and did not consider redox potential or metal competition for the adsorption sites. In addition to these constraints, EPA (1996) noted that this approach was limited by the potential sorbent surfaces that could be considered and availability of thermodynamic data. Their calculations were limited to metal adsorption on iron oxide, although sorption of these metals to other minerals, such as clays and carbonates, is well known.

Typically, the data required to derive the values of adsorption parameters that are needed as input for adsorption submodels in chemical reaction codes are more extensive than information reported in a typical laboratory batch K_d study. If the appropriate data are reported, it is likely that a user could hand calculate a composition-based K_d value from the data reported in the adsorption study without the need of a chemical reaction model.

Chemical reaction models can be used, however, to support evaluations of K_d values and related contaminant migration and risk assessment modeling predictions. Chemical reaction codes can be used to calculate aqueous complexation to determine the ionic state and composition of the dominant species for a dissolved contaminant present in a soil-water system. This information may in turn be used to substantiate the conceptual model being used for calculating the adsorption of a particular contaminant. Chemical reaction models can be used to predict bounding, technically defensible maximum concentration limits for contaminants as a function of key composition parameters (*e.g.*, pH) for any specific soil-water system. These values may provide more realistic bounding values for the maximum concentration attainable in a soil-water system when doing risk assessment calculations. Chemical reaction models can also be used to analyze initial and final geochemical conditions associated with laboratory K_d measurements to determine if the measurement had been affected by processes such as mineral precipitation which might have compromised the derived K_d values. Although chemical reaction models cannot be used to predict K_d values, they can provide aqueous speciation and solubility information that is exceedingly valuable in the evaluation of K_d values selected from the literature and/or measured in the laboratory.

5.0 Contaminant Geochemistry and K_d Values

The important geochemical factors affecting the sorption[1] of cadmium (Cd), cesium (Cs), chromium (Cr), lead (Pb), plutonium (Pu), radon (Rn), strontium (Sr), thorium (Th), tritium (^3H), and uranium (U) are discussed in this chapter. The objectives of this chapter are to: (1) provide a "thumb-nail sketch" of the key geochemical processes affecting sorption of these contaminants, (2) provide references to key experimental and review articles for further reading, (3) identify the important aqueous- and solid-phase parameters controlling contaminant sorption in the subsurface environment, and (4) identify, when possible, minimum and maximum conservative K_d values for each contaminant as a function key geochemical processes affecting their sorption.

5.1 General

Important chemical speciation, (co)precipitation/dissolution, and adsorption/desorption processes of each contaminant are discussed. Emphasis of these discussions is directed at describing the general geochemistry that occurs in oxic environments containing low concentrations of organic carbon located far from a point source (*i.e.*, in the far field). These environmental conditions comprise a large portion of the contaminated sites of concern to the EPA, DOE, and/or NRC. We found it necessary to focus on the far-field, as opposed to near-field, geochemical processes for 2 main reasons. First, the near field frequently contains very high concentrations of salts, acids, bases, and/or contaminants which often require unusual chemical or geochemical considerations that are quite different from those in the far field. Secondly, the differences in chemistry among various near-field environments varies greatly, further compromising the value of a generalized discussion. Some qualitative discussion of the effect of high salt conditions and anoxic conditions are presented for contaminants whose sorption behavior is profoundly affected by these conditions.

The distribution of aqueous species for each contaminant was calculated for an oxidizing environment containing the water composition listed in Table 5.1 and the chemical equilibria code MINTEQA2 (Version 3.10, Allison *et al.*, 1991). The water composition in Table 5.1 is based on a "mean composition of river water of the world" estimated by Hem (1985). We use this chemical composition simply as a convenience as a proxy for the composition of a shallow groundwater. Obviously, there are significant differences between surface waters and groundwaters, and considerable variability in the concentrations of various constituents in surface and groundwaters. For example, the concentrations of dissolved gases and complexing ligands, such as carbonate, may be less in a groundwater as a result of infiltration of surface water through

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[1] When a contaminant is associated with a solid phase, it is commonly not known if the contaminant is adsorbed onto the surface of the solid, absorbed into the structure of the solid, precipitated as a 3-dimensional molecular coating on the surface of the solid, or absorbed into organic matter. "Sorption" will be used in this report as a generic term devoid of mechanism to describe the partitioning of aqueous phase constituents to a solid phase. Sorption is frequently quantified by the partition (or distribution) coefficient, K_d.

the soil column. Additionally, the redox potential of groundwaters, especially deep groundwaters, will likely be more reducing that surface water. As explained later in this chapter, the adsorption and solubility of certain contaminants and radionuclides may be significantly different under reducing groundwater conditions compared to oxidizing conditions. However, it was necessary to limit the scope of this review to oxidizing conditions. Use of the water composition in Table 5.1 does not invalidate the aqueous speciation calculations discussed later in this chapter relative to the behavior of the selected contaminants in oxidizing and transitional groundwater systems. The calculations demonstrate what complexes might exist for a given contaminant in any oxidizing water as a function of pH and the specified concentrations of each inorganic ligand. If the concentration of a complexing ligand, such as phosphate, is less for a site-specific groundwater compared to that used for our calculations, then aqueous complexes containing that contaminant and ligand may be less important for that water.

Importantly, water composition in Table 5.1 has a low ionic strength and contains no natural (*e.g.*, humic or fulvic acids[1]) or anthropogenic (*e.g.*, EDTA) organic materials. The species distributions of thorium and uranium were also modeled using pure water, free of any ligands other than hydroxyl ions, to show the effects of hydrolysis in the absence of other complexation reactions. The concentrations used for the dissolved contaminants in the species distribution calculations are presented in Table 5.2 and are further discussed in the following sections. The species distributions of cesium, radon, and tritium were not determined because only 1 aqueous species is likely to exist under the environmental conditions under consideration; namely, cesium would exist as Cs^+, radon as Rn^0(gas), and tritium as tritiated water, HTO (T = tritium, ^3H).

Throughout this chapter, particular attention will be directed at identifying the important aqueous- and solid-phase parameters controlling retardation[2] of contaminants by sorption in soil. This information was used to guide the review and discussion of published K_d values according to the important chemical, physical, and mineralogical characteristics or variables. Perhaps more importantly, the variables had include parameters that were readily available to modelers. For instance, particle size and pH are often available to modelers whereas such parameters as iron oxide or surface area are not as frequently available.

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[1] "Humic and fulvic acids are breakdown products of cellulose from vascular plants. Humic acids are defined as the alkaline-soluble portion of the organic material (humus) which precipitates from solution at low pH and are generally of high molecular weight. Fulvic acids are the alkaline-soluble portion which remains in solution at low pH and is of lower molecular weight" (Gascoyne, 1982).

[2] Retarded or attenuated (*i.e.*, nonconservative) transport means that the contaminant moves slower than water through geologic material. Nonretarded or nonattenuated (*i.e.*, conservative) transport means that the contaminant moves at the same rate as water.

Table 5.1. Estimated mean composition of river water of the world from Hem (1985).[1]

Dissolved Constituent	Total Concentration	
	mg/l	mol/l
Silica, as H_4SiO_4	20.8	2.16×10^{-4}
Ca	15	3.7×10^{-4}
Mg	4.1	1.7×10^{-4}
Na	6.3	2.7×10^{-4}
K	2.3	5.9×10^{-5}
Inorganic Carbon, as CO_3	57	9.5×10^{-4}
SO_4	11	1.1×10^{-4}
Cl	7.8	2.2×10^{-4}
F	1	5×10^{-5}
NO_3	1	2×10^{-5}
PO_4	0.0767	8.08×10^{-7}

[1] Most values from this table were taken from Hem (1985: Table 3, Column 3). Mean concentrations of total dissolved fluoride and phosphate are not listed in Hem (1985, Table 3). The concentration of dissolved fluoride was taken from Hem (1985, p. 120) who states that the concentration of total dissolved fluoride is generally less than 1.0 mg/l for most natural waters. Hem (1985, p. 128) lists 25 µg/l for average concentration of total dissolved phosphorous in river water estimated by Meybeck (1982). This concentration of total phosphorus was converted to total phosphate (PO_4) listed above.

Table 5.2. Concentrations of contaminants used in the aqueous species distribution calculations.

Element	Total Conc. (μg/l)	Reference for Concentration of Contaminant Used in Aqueous Speciation Calculations
Cd	1.0	Hem (1985, p. 142) lists this value as a median concentration of dissolved cadmium based on the reconnaissance study of Duram *et al.* (1971) of metal concentrations in surface waters in the United States.
Cs	--	Distribution of aqueous species was not modeled, because mobility of dissolved cesium is not significantly affected by complexation (see Section 5.3).
Cr	1.4	Hem (1985, p. 138) lists this value as an average concentration estimated by Kharkar *et al.* (1968) for chromium in river waters.
Pb	1.0	Hem (1985, p. 144) lists this value as an average concentration estimated by Duram *et al.* (1971) for lead in surface-water samples from north- and southeastern sections of the United States.
Pu	3.2×10^{-7}	This concentration is based on the maximum activity of $^{239,240}Pu$ measured by Simpson *et al.* (1984) in 33 water samples taken from the highly alkaline Mono Lake in California.
Rn	--	Aqueous speciation was not calculated, because radon migrates as a dissolved gas and is not affected by complexation (see Section 5.7).
Sr	110	Hem (1985, p. 135) lists this value as the median concentration of strontium for larger United States public water supplies based on analyses reported by Skougstad and Horr (1963).
Th	1.0	Hem (1985, p. 150) gives 0.01 to 1 μg/l as the range expected for thorium concentrations in fresh waters.
^{3}H	--	Aqueous speciation was not calculated, because tritium (^{3}H) migrates as tritiated water.
U	0.1 and 1,000	Because dissolved hexavalent uranium can exist as polynuclear hydroxyl complexes, the hydrolysis of uranium under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations (0.1 and 1,000 μg/l) of total dissolved uranium were used to model the species distributions. Hem (1985, p. 148) gives 0.1 to 10 μg/l as the range for dissolved uranium in most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 μg/l.

5.5 Lead Geochemistry and K_d Values

5.5.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Lead has 3 known oxidation states, 0, +2, and +4, and the most common redox state encountered in the environment is the divalent form. Total dissolved lead concentrations in natural waters are very low ($\sim 10^{-8}$ M). Dissolved lead in natural systems may exist in free ionic form and also as hydrolytic and complex species. Speciation calculations show that at pH values exceeding 7, aqueous lead exists mainly as carbonate complexes [$PbCO_3^0$(aq), and $Pb(CO_3)_2^{2-}$]. Important factors that control aqueous speciation of lead include pH, the types and concentrations of complexing ligands and major cationic constituents, and the magnitude of stability constants for lead-ligand aqueous complexes.

A number of studies and calculations show that under oxidizing conditions depending on pH and ligand concentrations, pure-phase lead solids, such as $PbCO_3$, $Pb_3(OH)_2(CO_3)_2$, $PbSO_4$, $Pb_5(PO_4)_3(Cl)$, and $Pb_4SO_4(CO_3)_2(OH)_2$, may control aqueous lead concentrations. Under reducing conditions, galena (PbS) may regulate the concentrations of dissolved lead. It is also possible that lead concentrations in some natural systems are being controlled by solid solution phases such as barite ($Ba_{(1-x)}Pb_xSO_4$), apatite [$Ca_{(1-x)}Pb_x(PO_4)_3OH$], calcite ($Ca_{(1-x)}Pb_xCO_3$), and iron sulfides ($Fe_{(1-x)}Pb_xS$).

Lead is known to adsorb onto soil constituent surfaces such as clay, oxides, hydroxides, oxyhydroxides, and organic matter. In the absence of a distinct lead solid phase, natural lead concentrations would be controlled by adsorption/desorption reactions. Adsorption data show that lead has very strong adsorption affinity for soils as compared to a number of first transition metals. Lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils. Properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have greater affect on lead adsorption than soil pH.

5.5.2 General Geochemistry

Lead is an ubiquitous heavy metal and its concentration in uncontaminated soil ranges from 2 to 200 mg/kg and averages 16 mg/kg (Bowen, 1979). Annual anthropogenic lead input into soils has been estimated to be from 0.04 to 4 μg/kg (Ter Haar *et al.*, 1967). In contaminated soils, lead concentrations may be as high as 18 percent by weight (Mattigod and Page, 1983; Ruby *et al.*, 1994). Lead in nature occurs in 4 stable isotopic forms (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb). The isotopes, ^{206}Pb, ^{207}Pb, and ^{208}Pb are the stable end products of the ^{238}U, ^{235}U, and ^{232}Th thorium decay series, respectively (Robbins, 1980). Additionally, heavier isotopes of lead (^{210}Pb, ^{211}Pb, ^{212}Pb, and ^{214}Pb) are known to occur in nature as intermediate products of uranium and thorium decay (Robbins, 1978). The

most common valence state of lead encountered in the environment is the divalent form (Baes and Mesmer, 1976). Extensive studies of lead biogeochemistry have been conducted due to its known adverse effects on organisms (Hammond, 1977). Comprehensive descriptions of environmental chemistry of lead have been published by Boggess and Wixson (1977) and Nriagu (1978).

5.5.3 Aqueous Speciation

Lead exhibits typical amphoteric[1] metal ion behavior by forming hydrolytic species (Baes and Mesmer, 1976). Formation of monomeric hydrolytic species, such as $PbOH^+$, $Pb(OH)_2^0(aq)$ and $Pb(OH)_3^-$, is well established. Although several polymeric hydrolytic species such as Pb_2OH^{3+}, $Pb_3(OH)_3^{3+}$, $Pb_4(OH)_4^{4+}$, and $Pb_6(OH)_8^{4+}$ are known to form at high lead concentrations, calculations show that these types of species are unlikely to form at concentrations of dissolved lead ($\sim 10^{-9}$ M) typically encountered even in contaminated environments (Rickard and Nriagu, 1978). These investigators also showed that computation models of speciation of dissolved lead in fresh- or seawater predicted that at pH values exceeding about 6.5, the dominant species are lead-carbonate complexes. Lead is known to form aqueous complexes with inorganic ligands such as carbonate, chloride, fluoride, nitrate, and sulfate.

To examine the distribution of dissolved lead species in natural waters, MINTEQA2 model calculations were completed using the water composition described in Table 5.1. The total lead concentration was assumed to be 1 µg/l based on the data for natural waters tabulated by Duram *et al.* (1971) and Hem (1985). A total of 21 aqueous species (uncomplexed Pb^{2+}, and 20 complex species, listed in Table 5.8) were used in the computation. Results of the computation are plotted as a species distribution diagram (Figure 5.2). The data show that, under low pH (<6) conditions, free ionic Pb^{2+} appears to be the dominant species, and the neutral species, $PbSO_4^0(aq)$, accounts for about 5 percent of the total dissolved lead. Within the pH range of 6.5 to 7.5, the main species of lead appear to be free ionic species, Pb^{2+}, and the neutral complex species, $PbCO_3^0(aq)$ with minor percentage of the species consisting of $PbHCO_3^+$ (about 15 percent), $PbSO_4^0(aq)$ (<5 percent), and $PbOH^+$ (<5 percent). Between the pH range 7 to 9, the neutral complex species $PbCO_3^0(aq)$ dominates dissolved lead speciation. At pH values exceeding 9, in addition to $PbCO_3^0(aq)$, a significant fraction of soluble lead is present as the anionic carbonate complex, $Pb(CO_3)_2^{2-}$. These calculations also confirm Rickard and Nriagu's (1978) observation that polymeric species are not significant in the chemistry of lead in natural waters. The species distribution illustrated in Figure 5.2 does not change if the concentration of total dissolved lead is increased from 1 to 1,000 µg/l.

This speciation calculation demonstrates that the important factors that control aqueous speciation of lead include pH and the types of complexing ligands. Aqueous speciation of lead has a direct bearing on dissolution/precipitation of lead-solid phases and the adsorption/desorption

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[1] Amphoteric behavior is the ability of an aqueous complex or solid material to have a negative, neutral, or positive charge.

reactions. Complexation enhances the solubility of lead-bearing solid phases. This enhancement in solubility is dependent on the strength of complexation [indicated by the magnitude of stability constant] and the total concentrations of complexing ligands. Also, as will be discussed shortly, adsorption of lead is affected by the type, charge, and the concentration of lead complexes present in solution. Cationic lead species, especially Pb^{2+} and its hydrolysis species, adsorb more commonly than anionic lead complexes.

5.5.4 Dissolution/Precipitation/Coprecipitation

Lead solids in the environment may occur in a number of mineral forms (Rickard and Nriagu 1978; Mattigod *et al.*, 1986; Zimdahl and Hassett, 1977). However, these authors have identified a limited number of secondary lead minerals that may control the concentrations of dissolved lead in soil/water environments. If the concentration of dissolved lead in a pore water or groundwater exceeds the solubility of any of these phases, the lead-containing solid phase will precipitate and thus control the maximum concentration of lead that could occur in the aqueous phase. According to Rickard and Nriagu (1978), under oxidizing conditions, depending on pH and ligand concentrations, cerussite ($PbCO_3$), hydrocerussite [$Pb_3(OH)_2(CO_3)_2$], anglesite ($PbSO_4$), or chloropyromorphite [$Pb_5(PO_4)_3Cl$] may control aqueous lead concentrations. A review paper by McLean and Bledsoe (1992) included data which showed that lead concentrations in a calcareous soil was controlled by lead-phosphate compounds at lower pH and by mixed mineral phases at pH values exceeding 7.5. A study conducted by Mattigod *et al.* (1986) indicated that the mineral leadhillite [$Pb_4SO_4(CO_3)_2(OH)_2$] may be the solubility controlling solid for lead in a mine-waste contaminated soil.

Table 5.8. Lead aqueous species included in the speciation calculations.

Aqueous Species
Pb^{2+}
$PbOH^{+}$, $Pb(OH)_2^{0}(aq)$, $Pb(OH)_3^{-}$, $Pb(OH)_4^{2-}$ $Pb_2(OH)_3^{+}$, $Pb_3(OH)_3^{3+}$
$PbCO_3^{0}(aq)$, $Pb(CO_3)_2^{2-}$, $PbHCO_3^{+}$
$PbSO_4^{0}(aq)$, $Pb(SO_4)_2^{2-}$
$PbNO_3^{+}$
$PbCl^{+}$, $PbCl_2^{0}(aq)$, $PbCl_3^{-}$, $PbCl_4^{2-}$
PbF^{+}, $PbF_2^{0}(aq)$, PbF_3^{-}, PbF_4^{2-}

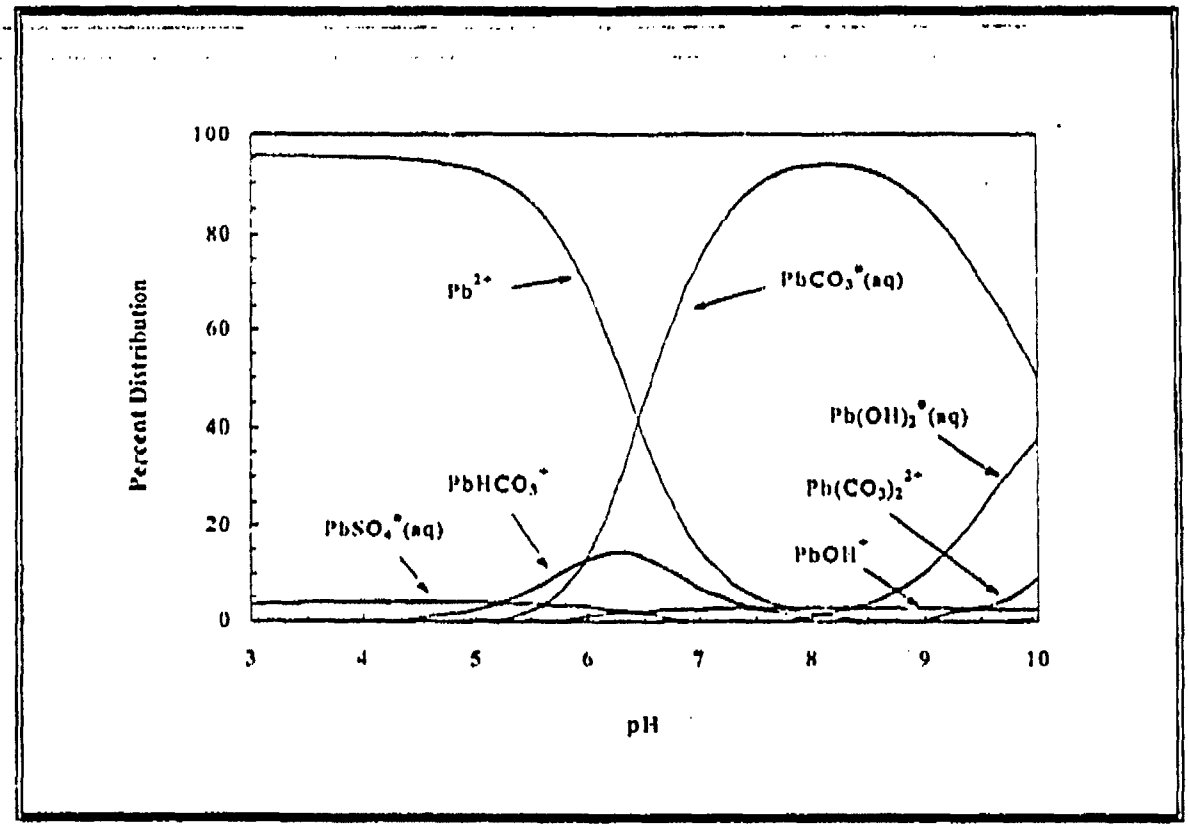

Figure 5.2. Calculated distribution of lead aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 μg/l total dissolved lead.]

Lead may also exist in soils as solid-solution phases. Solid solutions are defined as solid phases in which a minor element will substitute for a major element in the mineral structure. Depending on the degree of substitution and the overall solubility of the solid-solution phase, the equilibrium solubility of the minor element in the solid solution phase will be less than the solubility of the solid phase containing only the minor element (pure phase). For instance, lead may occur as a minor replacement in barite [$Ba_{(1-x)}Pb_xSO_4$], apatite [$Ca_{(1-x)}Pb_x(PO_4)_3OH$], calcite [$Ca_{(1-x)}Pb_xCO_3$], and iron sulfides, [$Fe_{(1-x)}Pb_xS$] (Driesens, 1986; Goldschmidt, 1954; Nriagu and Moore, 1984; Rickard and Nriagu, 1978). Consequently, the equilibrium solubility of lead controlled by these phases will be less than the concentrations controlled by corresponding pure phases, namely $PbSO_4$, $Pb_5(PO_4)_3OH$, $PbCO_3$, and PbS, respectively.

Under reducing conditions, galena (PbS) may control the lead concentrations in the environment. Rickard and Nriagu (1978) calculated that, within the pH range of 6-9, the equilibrium solubility of galena would control total lead concentrations at levels less than approximately 10^{-10} M (<21 ng/l). Therefore, if galena is present in a soil under reducing conditions, the aqueous concentrations of lead will be controlled at extremely low concentrations.

5.5.5 Sorption/Desorption

Lead is known to adsorb onto soil constituent surfaces such as clays, oxides, hydroxides, oxyhydroxides, and organic matter. Ion exchange reactions of lead on a number of clay minerals such as montmorillonite, kaolinite, illite, and vermiculite have been studied by a number of investigators. These studies showed that lead was preferentially adsorbed by exchange on clays, readily replacing calcium and potassium (Bittel and Miller, 1974; Overstreet and Krishnamurthy, 1950). Studies conducted by Lagerwerff and Brower (1973) on montmorillonitic, illitic, and kaolinitic soils confirmed that lead would preferentially exchange for calcium. Another clay mineral, vermiculite, is also known to exhibit very high ion exchange selectivity for lead (Rickard and Nriagu, 1978). Based on a number of studies Rickard and Nriagu (1978) also concluded that beyond neutral pH, precipitation reactions may control lead concentrations in solution rather than ion exchange and adsorption reactions involving clay mineral surfaces.

Experimental data show that only hydrogen ions and unhydrolyzed aluminum ions are capable of displacing lead from exchange sites on clay minerals (Lagerwerff and Brower, 1974; Zimdahl and Hassett, 1977). Clay minerals also differ in their exchange preference for lead. Bittel and Miller (1974) showed that the exchange preference for lead varies in the sequence,

kaolinite > illite > montmorillonite.

These studies also showed that, in neutral to high pH conditions, lead can preferentially exchange for calcium, potassium, and cadmium. Under low pH conditions, hydrogen ions and aluminum ions would displace lead from mineral exchange sites.

Studies of lead adsorption on oxide, hydroxide, and oxyhydroxide minerals show that the substrate properties, such as the specific surface and degree of crystallinity, control the degree of adsorption (Rickard and Nriagu, 1978). Experimental data by Forbes *et al.* (1976) showed that goethite (FeOOH) has higher adsorption affinity for lead than zinc, cobalt, and cadmium. Data show that manganese-oxide minerals also adsorb lead ions (Rickard and Nriagu, 1978). These investigators concluded that the high specificity of lead adsorption on oxide and hydroxide surfaces and the relative lack of desorbability (<10 percent) of adsorbed lead indicated that lead upon adsorption forms solid solutions with oxide or hydroxide surfaces. Therefore, this lack of reversibility indicated that the reaction is not a true adsorption phenomenon.

A number of studies have confirmed that many natural and synthetic organic materials adsorb lead. Data showing significant correlations between concentrations of organic matter and lead in

soils indicate that soil organic matter has a higher affinity for lead adsorption as compared soil minerals.

A number of lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils (Zimdahl and Hassett, 1977). A multiple regression analysis by Hassett (1974) of lead adsorption data indicated that properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have a greater effect on lead adsorption than soil pH. The results of a number of studies of lead adsorption on a variety of soil and mineral surfaces were summarized by McLean and Bledsoe (1992). These data show that lead has very strong adsorption affinity as compared to a number of first row transition metals (cobalt, nickel, copper, and zinc). According to a recent study (Peters and Shem, 1992), the presence of very strong chelating organic ligands dissolved in solution will reduce adsorption of lead onto soils. These data show that the adsorption of lead in the environment is influenced by a number of factors such as the type and properties of adsorbing substrate, pH, the concentrations of lead, and the type and concentrations of other competing cations and complex forming inorganic and organic ligands.

5.5.6 Partition Coefficient, K_d, Values

5.5.6.1 General Availability of K_d Data

The review of lead K_d data reported in the literature for a number of soils (Appendix F) led to the following important conclusions regarding the factors which influence lead adsorption on minerals and soils.[1] These principles were used to evaluate available quantitative data and generate a look-up table. These conclusions are:

- Lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

- Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation.

- A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases (as does precipitation) with increasing pH.

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[1] Since the completion of our review and analysis of K_d data for the selected contaminants and radionuclides, the studies by Azizian and Nelson (1998) and Yong and MacDonald (1998) were identified and may be of interest to the reader.

- Adsorption of lead increases with increasing organic matter content of soils.

- Increasing equilibrium solution concentrations correlates with decreasing lead adsorption (decrease in K_d).

The factors which influence lead adsorption were identified from the following sources of data. A description and assessment of these data are provided in Appendix F. Lead adsorption behavior on soils and soil constituents (clays, oxides, hydroxides, oxyhydroxides, and organic matter) has been studied extensively. However, calculations by Rickard and Nriagu (1978) show that the solution lead concentrations used in a number of adsorption studies may be high enough to induce precipitation. For instance, their calculations show that lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

Lead adsorption studies on manganese and iron oxides and oxyhydroxides indicate irreversible adsorption which was attributed to the formation of solid solution phases (*i.e.*, coprecipitation) (Forbes *et al.*, 1976; Grasselly and Hetenyi, 1971; Rickard and Nriagu, 1978). No correlations however have been established between the type and content of oxides in soil and the lead adsorption characteristics of soil.

Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation (Rickard and Nriagu, 1978). Presence of synthetic chelating ligands, such as EDTA, has been shown to reduce lead adsorption on soils (Peters and Shem, 1992). These investigators showed that the presence of strongly chelating EDTA in concentrations as low as 0.01 M reduced K_d for lead by about 3 orders of magnitude. By comparison quantitative data is lacking on the effects of more common inorganic ligands (phosphate, chloride, and carbonate) on lead adsorption on soils.

A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH (Braids *et al.*, 1972; Bittel and Miller, 1974; Griffin and Shimp, 1976; Haji-Djafari *et al.*, 1981; Hildebrand and Blum, 1974; Overstreet and Krishamurthy, 1950; Scrudato and Estes, 1975; Zimdahl and Hassett, 1977). Griffin and Shimp (1976) also noted that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH values exceeded 5 or 6.

Solid organic matter such as humic material in soils is known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Correlative relationships between the organic matter content of soils and its

effect on lead adsorption have been established by Gerritse *et al.* (1982) and Soldatini *et al.* (1976).

Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that K_d values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l).

5.5.6.2 K_d Look-Up Tables

Among all available data, Gerritse et al (1982) obtained adsorption data at lead concentrations (0.0001 - 0.01 mg/l) which apparently precluded precipitation reactions. Also, these concentrations are within the range of lead concentrations most frequently encountered in ground waters (Chow, 1978). Additionally, data obtained by Rhoads *et al.* (1992) indicated that K_d values vary log-linearly as a function of equilibrium lead concentrations within the range of 0.00001 to 0.2 mg/l. The data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) were used to develop a look-up table (Table 5.9) of K_d as a function of soil pH and equilibrium lead concentrations.

5.5.6.2.1 Limits of K_d Values with Respect to pH

The pH ranges in the look-up table (Table 5.9) were selected from the rate of change that we noted in the K_d data as a function of pH. The K_d values within this pH range increase with increasing pH, and are greatest at the maximum pH limit (pH 11) of soils.

Table 5.9. Estimated range of K_d values for lead as a function of soil pH, and equilibrium lead concentrations.

Equilibrium Lead Concentration (µg/l)	K_d (ml/g)	Soil pH		
		4.0 - 6.3	6.4 - 8.7	8.8 - 11.0
0.1 - 0.9	Minimum	940	4,360	11,520
	Maximum	8,650	23,270	44,580
1.0 - 9.9	Minimum	420	1,950	5,160
	Maximum	4,000	10,760	20,620
10 - 99.9	Minimum	190	900	2,380
	Maximum	1,850	4,970	9,530
100 - 200	Minimum	150	710	1,880
	Maximum	860	2,300	4,410

5.5.6.2.2 Limits of K_d Values with Respect to Equilibrium Lead Concentrations

The limits of equilibrium lead concentrations (0.0001 mg/l to about 0.2 mg/l) were selected based on the experimental data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992). These investigators showed that within the range of initial lead concentrations used in their experiments the principal lead removal reaction from solution was adsorption and not precipitation. Four concentration ranges were selected to develop the K_d values.

5.6 Plutonium Geochemistry and K_d Values

5.6.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

In the ranges of pH and conditions typically encountered in the environment, plutonium can exist in all 4 oxidation states, namely +3, 4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist. Dissolved plutonium forms very strong hydroxy-carbonate mixed ligand complexes, therefore, its adsorption and mobility is strongly affected by these complex species. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes may be control adsorption and mobility of plutonium in the environment.

If plutonium is present as a distinct solid phase (amorphous or partly crystalline $PuO_2 \cdot xH_2O$) or as a solid solution, the upper limits of aqueous plutonium concentrations would be in the 10^{-12} to 10^{-9} M range. Dissolved plutonium in the environment is typically present at $\leq 10^{-15}$ M levels indicating that adsorption may be the principal phenomenon that regulates the mobility of this actinide.

Plutonium can adsorb on geologic material from low to extremely high affinities with K_d values ranging from 11 to 300,000 ml/g. Plutonium in the higher oxidation state adsorbed on iron oxide surfaces may be reduced to the tetravalent state by Fe(II) present in the iron oxides.

Two factors that influence the mobilization of adsorbed plutonium under environmental pH conditions (>7) are the concentrations of dissolved carbonate and hydroxyl ions. Both these ligands form very strong mixed ligand complexes with plutonium, resulting in desorption and increased mobility in the environment.

5.6.2 General Geochemistry

Plutonium is produced by fissioning uranium fuel and is used in the construction of nuclear weapons. Plutonium has entered the environment either through accidental releases or through disposal of wastes generated during fuel processing and the production and detonation of nuclear weapons. Plutonium has 15 isotopes, but only 4 of these isotopes namely, ^{238}Pu [$t_{1/2}$ (half life) =

Appendix F

Partition Coefficients For Lead

F.1.0 Background

The review of lead K_d data reported in the literature for a number of soils led to the following important conclusions regarding the factors which influence lead adsorption on minerals, soils, and sediments. These principles were used to evaluate available quantitative data and generate a look-up table. These conclusions are:

- Lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

- Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation.

- A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH.

- Adsorption of lead increases with increasing organic matter content of soils.

- Increasing equilibrium solution concentrations correlates with decreasing lead adsorption (decrease in K_d).

Lead adsorption behavior on soils and soil constituents (clays, oxides, hydroxides, oxyhydroxides, and organic matter) has been studied extensively. However, calculations by Rickard and Nriagu (1978) show that the solution lead concentrations used in a number of adsorption studies may be high enough to induce precipitation. For instance, their calculations show that lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

Based on lead adsorption behavior of 12 soils from Italy, Soldatini *et al.* (1976) concluded that soil organic matter and clay content were 2 major factors which influence lead adsorption. In these experiments, the maximum adsorption appeared to exceed the cation exchange capacity

(CEC) of the soils. Such an anomaly may have resulted from precipitation reactions brought about by high initial lead concentrations used in these experiments (20 to 830 mg/l).

Lead adsorption characteristics of 7 alkaline soils from India were determined by Singh and Sekhon (1977). The authors concluded that soil clay, organic matter, and the calcium carbonate influenced lead adsorption by these soils. However, the initial lead concentrations used in these experiments ranged from 5 to 100 mg/l, indicating that in these alkaline soils the dominant lead removal mechanism was quite possibly precipitation.

In another adsorption study, Abd-Elfattah and Wada (1981) measured the lead adsorption behavior of 7 Japanese soils. They concluded that soil mineral components which influenced lead adsorption ranged in the order: iron oxides>halloysite>imogolite, allophane>humus, kaolinite>montmorillonite. These data may not be reliable because high lead concentrations (up to 2,900 mg/l) used in these experiments may have resulted in precipitation reactions dominating the experimental system.

Anionic constituents, such as phosphate, chloride, and carbonate, are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation (Rickard and Nriagu, 1978). A recent study by Bargar *et al.* (1998) showed that chloride solutions could induce precipitation of lead as solid PbOHCl. Presence of synthetic chelating ligands such as ethylenediaminetetraacetic acid (EDTA) has been shown to reduce lead adsorption on soils (Peters and Shem, 1992). These investigators showed that the presence of strongly chelating EDTA in concentrations as low as 0.01 M reduced K_d for lead by about 3 orders of magnitude. By comparison quantitative data is lacking on the effects of more common inorganic ligands (phosphate, chloride, and carbonate) on lead adsorption on soils.

A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH (Bittel and Miller, 1974; Braids *et al.*, 1972; Griffin and Shimp, 1976; Haji-Djafari *et al.*, 1981; Hildebrand and Blum, 1974; Overstreet and Krishnamurthy, 1950; Serudato and Estes, 1975; Zimdahl and Hassett, 1977). Griffin and Shimp (1976) also noted that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH values exceeded 5 or 6.

Solid organic matter such as humic material in soils and sediments are known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Gerritse *et al.* (1982) examined the lead adsorption properties of soils as a function of organic matter content of soils. Initial lead concentrations used in these experiments ranged from 0.001 to 0.1 mg/l. Based on adsorption data, the investigators expressed K_d value for a soil as a function of organic matter content (as wt.%) and the distribution coefficient of the organic matter. The data also indicated that irrespective of soil organic matter content, lead adsorption increased with increasing soil pH (from 4 to 8). In certain soils, lead is

also known to form methyl- lead complexes (Rickard and Nriagu, 1978). However, quantitative relationship between the redox status of soils and its effect on overall lead adsorption due to methylation of lead species is not known.

Tso (1970), and Sheppard *et al.* (1989) studied the retention of ^{210}Pb in soils and its uptake by plants. These investigators found that lead in trace concentrations was strongly retained on soils (high K_d values). Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that K_d values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l). At a fixed pH of 8.35, the authors found that K_d values were log-linearly correlated with equilibrium concentrations of lead in solution. Calculations showed that if lead concentrations exceeded about 0.207 mg/l, lead-hydroxycarbonate (hydrocerussite) would probably precipitate in this soil.

The K_d data described above are listed in Table F.1.

F.2.0 Approach

The initial step in developing a look-up table consisted of identifying the key parameters which were correlated with lead adsorption (K_d values) on soils and sediments. Data sets developed by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) containing both soil pH and equilibrium lead concentrations as independent variables were selected to develop regression relationships with K_d as the dependent variable. From these data it was found that a polynomial relationship existed between K_d values and soil pH measurements. This relationship (Figure F.1) with a correlation coefficient of 0.971 (r^2) could be expressed as:

$$K_d\ (ml/g) = 1639 - 902.4(pH) + 150.4(pH)^2 \qquad (F.1)$$

The relationship between equilibrium concentrations of lead and K_d values for a Hanford soil at a fixed pH was expressed by Rhoads *et al.* (1992) as:

$$K_d\ (ml/g) = 9{,}550\ C^{-0.335} \qquad (F.2)$$

where C is the equilibrium concentration of lead in µg/l. The look-up table (Table F.2) was developed from using the relationships F.1 and F.2. Four equilibrium concentration and 3 pH categories were used to estimate the maximum and minimum K_d values in each category. The relationship between the K_d values and the 2 independent variables (pH and the equilibrium concentration) is shown as a 3-dimensional surface (Figure F.2). This graph illustrates that the highest K_d values are encountered under conditions of high pH values and very low equilibrium lead concentrations and in contrast, the lowest K_d values are encountered under lower pH and higher lead concentrations. The K_d values listed in the look-up table encompasses the ranges of pH and lead concentrations normally encountered in surface and subsurface soils and sediments.

Table F.1. Summary of K_d values for lead adsorption on soils.

Soil Description	Clay Content (wt.%)	Organic Carbon (wt.%)	Iron Oxide content (wt.%)	pH	CEC (meq/100g)	K_d (ml/g)	Experimental Parameters	Reference
Sediment, Split Rock Formation, Wyoming	--	--	--	2.0	--	20	--	Haji-Djafari *et al.*, 1981
	--	--	--	4.5	--	100	--	
	--	--	--	5.75	--	1,500	--	
	--	--	--	7.0	--	4,000	--	
Sand (Soil C)	0	--	--	4.5	22	280	Batch Experiment	Gerritse *et al.* (1982)
Sand (Soil C)	0	--	--	5.0	22	1295	Batch Experiment	
Sandy Loam (Soil D)	2	--	--	7.5	16	3,000	Batch Experiment	
Sandy Loam (Soil D)	2	--	--	8.0	16	4,000	Batch Experiment	
Loam (Soil 2)	15	--	--	7.3	17	21,000	Batch Experiment	Sheppard *et al.* (1989)
Medium Sand (Soil 3)	2	--	--	4.9	5.8	19	Batch Experiment	
Organic soil (Soil 4)	<1	--	--	5.5	120	30,000	Batch Experiment	
Fine Sandy Loam (Soil 6)	11	--	--	7.4	8.7	59,000	Batch Experiment	
Sand (Hanford)	0.06	<0.01	0.41	8.35	5.27	13,000 - 79,600	Batch tracer studies (Initial activities 2.38 - 23.4 μCi/l	Rhoads *et al.* (1992)

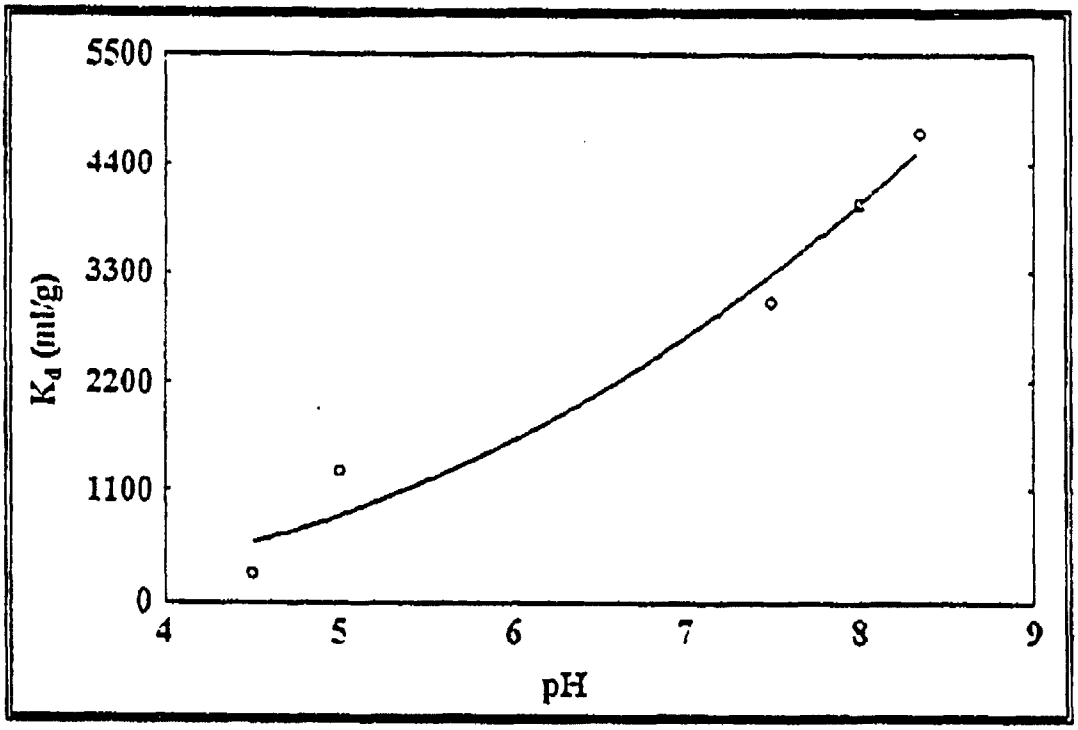

Figure F.1. Correlative relationship between K_d and pH.

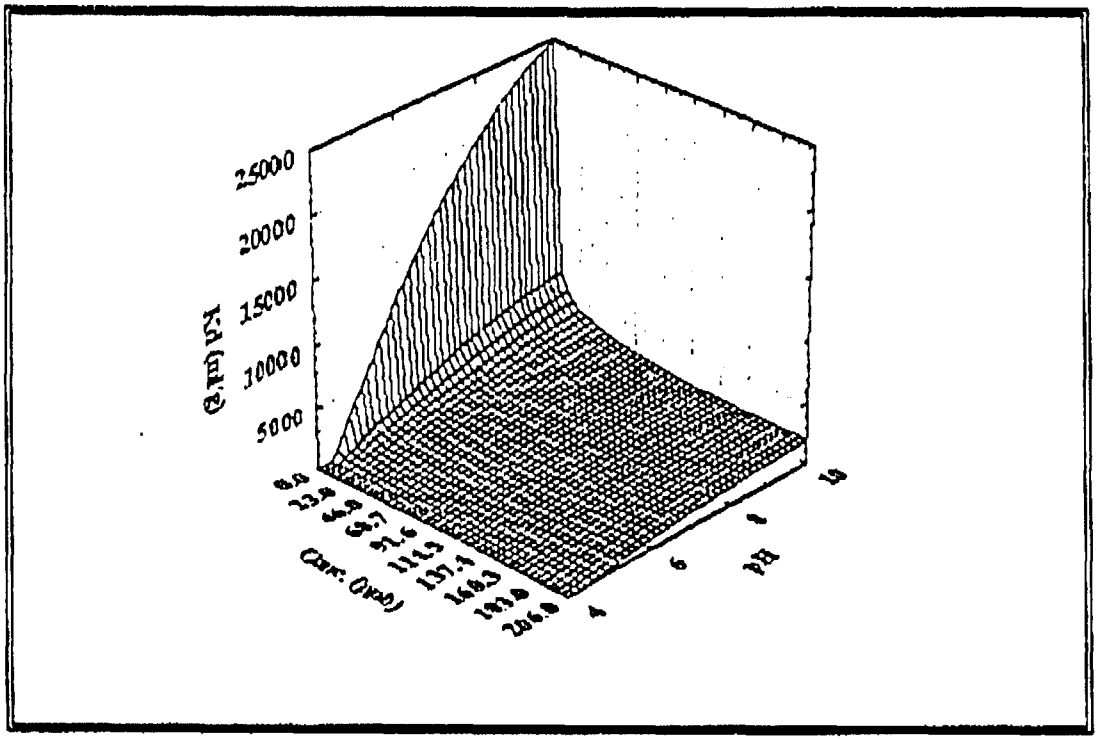

Figure F.2. Variation of K_d as a function of pH and the equilibrium lead concentrations.

F.3.0 Data Set for Soils

The data sets developed by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) were used to develop the look-up table (Table F.2). Gerritse *et al.* (1982) developed adsorption data for 2 well-characterized soils using a range of lead concentrations (0.001 to 0.1 mg/l) which precluded the possibility of precipitation reactions. Similarly, adsorption data developed by Rhoads *et al.* (1992) encompassed a range of lead concentrations from 0.0001 to 0.2 mg/l at a fixed pH value. Both these data sets were used for estimating the range of K_d values for the range of pH and lead concentration values found in soils.

Table F.2. Estimated range of K_d values for lead as a function of soil pH, and equilibrium lead concentrations.

Equilibrium Lead Concentration (µg/l)	K_d (ml/g)	Soil pH		
		4.0 - 6.3	6.4 - 8.7	8.8 - 11.0
0.1 - 0.9	Minimum	940	4,360	11,520
	Maximum	8,650	23,270	44,580
1.0 - 9.9	Minimum	420	1,950	5,160
	Maximum	4,000	10,760	20,620
10 - 99.9	Minimum	190	900	2,380
	Maximum	1,850	4,970	9,530
100 - 200	Minimum	150	710	1,880
	Maximum	860	2,300	4,410

F.4.0 References

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