1996

Adsorption of trichloroethylene onto mineral surfaces

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ADSORPTION OF TRICHLOROETHYLENE ONTO MINERAL SURFACES

A Thesis

Presented to

The Faculty of the Department of Geology

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Richard Charles Vorst

December, 1996

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ABSTRACT

ADSORPTION OF TRICHLOROETHYLENE ONTO MINERAL SURFACES

By Richard C. Vorst

Eight phyllosilicates and four oxides were examined to determine their affinity for trichloroethylene (TCE). Batch sorption experiments were conducted with 0.001 and 1.0 N solutions of NaCl and CaCl₂. Linear isotherm distribution coefficients (K_d s) varied from near zero for some minerals to 14 mL/g for montmorillonite.

The adsorption of TCE is strongly correlated with the hydrophobicity of the minerals, which for each phyllosilicate is strongly correlated to its contact angle with water, surface charge density, and Lewis base strength. The capacity of phyllosilicates for adsorbing TCE increased by 9% to 82% in the stronger electrolyte solutions whereas that of the oxides decreased by 14% to 122%. These trends can be explained by differences in the hydrophobic expulsion effect near the mineral surface compared with the bulk solution. A model based on the relationships observed can be used to predict K_d of a sediment sample.

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INTRODUCTION

Since the early 1980's, it has been recognized that extensive contamination of groundwater has occurred. Groundwater contamination has become a vital concern for the public and regulatory agencies because groundwater is a major source of drinking water in many parts of this country. A primary threat to groundwater integrity is the widespread use of nonionic organic compounds in a variety of industrial and agricultural applications, which increases the likelihood that they will eventually contaminate groundwater. Of the identified nonionic organic compounds in subsurface drinking water supplies, halogenated volatile organic compounds (VOCs) have been determined to be major constituents of concern. This concern stems from the fact that halogenated VOCs are detrimental to human health and the environment, even at very low concentrations (Environmental Protection Agency, 1985). Making matters worse, halogenated VOCs have been detected at the highest concentrations and with the greatest frequency in groundwater (Westrick et al., 1984). For instance, eighteen states that were surveyed in 1980 reported that a total of 2894 wells contained VOCs, of which trichloroethylene, a halogenated VOC, was the most often detected compound (Council on Environmental Quality, 1981).

The problem is further complicated by the fact that many of the halogenated VOCs contaminating groundwater are very resistant to biological and chemical transformation. Even when halogenated VOCs do break down, their decay products may become more toxic. Halogenated VOCs also pose problems when they are present in a discrete liquid phase which, because of its greater density, may sink deeply into the aquifer. This process can contaminate aquifers with higher concentrations of the constituent over a large area.

Such problematic attributes have prompted recent intensive studies of halogenated VOCs in aquifer systems. Many, in particular, have focused on determining the factors affecting the transport, distribution, and fate of these compounds in groundwater. Field studies and computerized contaminant groundwater transport models already have established that halogenated VOCs often migrate at slower rates than the average groundwater velocity due to sorption by the solid matrix. Thus, a key to predicting the environmental fate of these contaminants lies in first understanding halogenated VOCs' interaction with solid matrices. An improved understanding of these sorptive processes will lead to more accurate risk assessments and better remedial actions.

A large body of previous work has concentrated on correlating hydrophobic (low water solubility), nonionic, organic compound sorption with organic carbon or organic matter content in soil and aquatic systems. One conclusion drawn from this previous work is that the inorganic component of the matrix plays an insignificant role in sorption if the organic carbon content is $>0.1\%$ (Schwarzenbach and Westall, 1981). Models were developed to describe sorption of hydrophobic, nonionic, organic compounds (HNOs) when the organic carbon content is above the 0.1% in soil and aqueous systems (e.g., Karickhoff et al., 1979; Hassett et al., 1980; Kenaga, 1980; Schwarzenbach and Westall, 1981; Rao et al., 1982).

Prediction of HNO sorption by these models worked reasonably well, and estimates within a factor of two were possible in many cases. These predictive models usually work best if the organic carbon content is $>0.1\%$ or if the ratio of clay mineral to organic carbon content is <60 (Karickhoff, 1984). Under circumstances where these conditions are not met, the organic carbon-based models often underestimated the sorptive capacity of the sediment (Karickhoff, 1984). These underestimates may reflect the failure of the models to consider the contribution of the mineral components to

sorption. One might expect that these two conditions are not met in aquifers found in arid and semi-arid alluvial fan deposits. Such aquifers are prevalent in many parts of California. These types of depositional environments form organic-poor, coarse-textured sediments that are interstratified with layers of clay-size particles. Even the coarser sediments that normally characterize a water-bearing zone have interstitial spaces that may be significantly filled with clay-size particles.

Many studies have pointed out that clay-size particles may be an important factor in sorption of nonionic organic compounds (e.g., Khan et al., 1979; Hassett et al., 1981; Schwarzenbach and Westall, 1981; Karickhoff, 1984; Curtis and Roberts, 1985; Bishop et al., 1989; Olsen and Davis, 1990), although little consideration has been given to the individual minerals that could significantly contribute toward overall HNO sorption in natural sediments. Even less has been written on the interaction between potential mineral sorbents and small, volatile, HNOs such as halogenated VOCs. According to Karickhoff (1984), perhaps the most extensively studied interaction between mineral surfaces and organic contaminants has been with pesticides and clays. Many of these pesticides, however, because of their chemical makeup, behave differently at the solid/liquid interface and in solution than do halogenated VOCs.

Further research is needed on the interaction of halogenated VOCs with different minerals, especially with those minerals commonly found in aquifer systems. Consideration should be given not only to the minerals themselves in the sorption of halogenated VOCs, but also to the properties of the aqueous solution in which the halogenated VOCs are dissolved.

This study is part of an effort to advance the understanding of the interactions between minerals and halogenated VOCs in aqueous solutions. More specifically, this study explains whether a halogenated VOC trichloroethylene (TCE) has distinct affinities

for different mineral surfaces. It also gives insight into the reasons why TCE might have a higher affinity for one mineral surface over another. This study has concentrated on phyllosilicate minerals because they were most frequently implicated as a potentially important sorbing medium in natural systems (Sposito, 1984; Bolt and van Riemsdijk, 1987). Illite, kaolinite, vermiculite and minerals in the smectite group (e.g., montmorillonite) are regarded as especially important because they often occur as extremely small particles with high specific surface areas and they are widespread (Davis and Kent, 1990). Other phyllosilicates were selected for this study so that a full spectrum of surface characteristics could be assessed. These additional minerals are talc, pyrophyllite, muscovite, and margarite. This study also included sorption experiments with two oxides (hematite and pyrolusite), an oxyhydroxide (goethite), and a hydroxide (gibbsite), because these metallic “oxides” frequently are present in natural aquifer systems as well. The sorption studies were conducted with electrolyte solutions of CaCl_2 and NaCl at two concentrations (0.001 N and 1.0 N) to determine the influence of the solutions on the sorption of TCE by the selected minerals.

BACKGROUND AND THEORY

In order to fully appreciate the wide variety of sorption phenomena of HNOs on sediments in aqueous systems, it is important that one recognizes the heterogeneous nature of these systems. The heterogeneity of the system comes from the different attributes of the minerals and organic matter which are present and from their various proportions. In aqueous systems these attributes also are affected by the composition of the aqueous solution. The heterogeneity of the solid and the interaction with the bathing medium can significantly affect sorption of HNOs. An understanding, therefore, of the interrelationships among the minerals, organic matter, and the composition of the aqueous solution is necessary to an understanding of the sorption process.

The following sections will address the various processes that lead to sorption of HNOs by the solid matrix, especially to mineral surfaces. Emphasis will be placed on how the mineral fraction may contribute to adsorption of HNOs to help understand when this fraction becomes important when evaluating total sorption in a system. These sections also will address the interaction between HNOs and the solvent (water), and the influences that the type and concentration of electrolytes have on adsorption.

Before proceeding, several frequently used terms that are often referred to in the following sections need to be clarified:

- **Sorption** denotes the uptake of a solute by a solid (or by a component of the solid) without reference to a specific mechanism.
- **Adsorption** describes the process where constituents are concentrated at the interface of two phases (e.g., the solid-liquid boundary).

- **Distribution coefficient (K_d)** is defined as the ratio of the concentration of a compound sorbed by a solid matrix (C_s) to the concentration of the compound left remaining in solution (C_w). That is, $K_d = C_s/C_w$.
- The term **nonpolar compound** describes a solute that lacks overall polarity due to its symmetry of electron distribution, lack of functional groups, and nonionic (neutral) nature.
- A **polar compound** is a solute that shows a lack of symmetry in its electron distribution but still lacks functional groups and is nonionic.
- An **HNO** (hydrophobic nonionic organic compound) is a nonpolar or weakly polar solute that has little affinity for water. The hydrophobicity of the solute is indicated by its solubility and octanol-water partition coefficient (K_{ow}).
Concurring with the arbitrary definition given by Voice et al. (1983), a solute is classed as hydrophobic if its K_{ow} is > 100 . This K_{ow} equates to a calculated solubility of less than ≈ 33.3 mM. TCE has a solubility of ≈ 11.6 mM or $\approx 1,100$ mg/L; therefore, TCE is considered hydrophobic. Generally, a more polar solute has a greater solubility in water, making it less hydrophobic (or more hydrophilic).
- **Organic matter** and **organic carbon** refer to native organic compounds found in soil and sediment. Either organic matter or organic carbon content of sorbents have been reported. The ratio of organic matter to organic carbon varies by soil type, but a typical value is 1.724 (Olsen and Davis, 1990). These two terms will be used interchangeably.

Overview of Sorptive Forces

Sorption occurs in an aqueous system when the attractive forces between the solid surface and the sorbing species overcome the attractive forces between the sorbing species and the solvent (Zettlemoyer and Mical, 1971). The net accumulation of a solute at the sorbent surface ceases when the rates of two opposing processes are equal. The first is the rate at which molecules transfer from the aqueous phase into the sorbed state and the second is the rate at which molecules transfer from the sorbed state into the aqueous phase. When these two rates are equal, it is said that equilibrium is obtained.

In thermodynamic terms, sorption takes place when the free energy of the sorption reaction (ΔG_r) is negative, where $\Delta G_r = \Delta H_r - T \Delta S_r$ (Hassett and Banwart, 1989). The free energy of a sorption reaction may be negative because of the enthalpy term (ΔH), the entropy term (ΔS), or the contributions from both terms. The enthalpy term is primarily a function of the difference in the bond energy between the sorbing surface (sorbent) and the sorbate (solute), and the bond energy between the solvent (water) and the solute. The entropy term is related to the increases or decreases in the order of the system upon sorption.

Two general cases can describe when the net affinity of the sorbate for the sorbent is greater than the affinity of the sorbate for the solvent. In the first case, a specific interaction between the sorbate and the sorbent has occurred (Hassett et al., 1981). Among these enthalpy-related adsorption interactions are London-van der Waals, Coulombic-electrostatic, charge transfer, π -bonds, hydrogen bonding, ligand exchange, dipole-dipole or orientation energy, induction or dipole-induced dipole, and chemisorption (Hassett and Banwart, 1989). These specific attractive interactions at the sorbent surface can overcome even fairly strong solute-solvent interactions (Hassett et al., 1981).

Sorption that is characteristic of the second case occurs not because of a large specific sorbate-sorbent interaction but because of a weak solute-solvent interaction

(Hassett et al., 1981). In such a case, even a weak positive sorbate-sorbent interaction can overcome an extremely weak solute-solvent interaction. TCE, like other HNOs, has a tendency to be “driven out” of solution because of its aversion to the aqueous phase. HNOs may be driven out, for example, onto mineral surfaces or into a gaseous phase. The tendency for this to occur often is dependent on the composition of the solution. For instance, the greater the ionic strength of the solution, the greater the tendency for TCE to be driven out from the solution. Sorption occurring due to this process is best termed “hydrophobic expulsion” but is often termed “hydrophobic sorption”. Hydrophobic expulsion increases as compounds become less polar.

The primary energy associated with hydrophobic expulsion is not related to increases in enthalpies (Chiou et al., 1979), but appears to be related to the large entropy change resulting from the removal of the solvated HNO molecule from solution (Hassett and Banwart, 1989). This increase in entropy occurs when the highly structured water envelope that formerly surrounded the HNO molecule collapses. If this HNO molecule were transferred to a solid surface, then only a portion of it would be exposed to water. This partially exposed solute molecule would form a less structured hydration envelope with water than when the solute molecule was in the aqueous phase. Because there is less order in the system when the solute molecule is at the solid surface than when it is in solution, the entropy of the system increases. The increased entropy can result in increased adsorption.

A solid surface can be strongly hydrophobic to strongly hydrophilic, depending on its interaction with water. Because all surfaces of minerals attract water molecules to a considerable degree, the term hydrophobic is used to describe a mineral surface that is nearly apolar (essentially containing only van der Waals energies) or is low energy. A hydrophilic surface is more polar or is higher energy. Similar definitions were proposed

by van Oss and Giese (1995). If the interaction between a solid and water molecules or solvated ions is weak, the surface is hydrophobic, and HNO adsorption at the solid interface is favored. In other words, the more the solid, itself, is hydrophobic, the greater the sorption of HNOs by that solid.

The hydrophobicity of the solid is the result of complex interactions, often referred to as hydrophobic interactions, between its surface and the molecules of the liquid in which it is immersed (van Oss et al., 1987b). The individual components of these interactions that comprise the total energy of interaction and that determine the degree of hydrophobicity of a surface are apolar and polar energies. Electrostatic energies do not usually play an important part in hydrophobic interactions (van Oss et al., 1987b).

The apolar energy of a surface is associated with van der Waals energies. Van der Waals interactions result in attractive forces for both strongly polar molecules (water) and weakly polar molecules (TCE) and even nonpolar molecules such as tetrachloroethylene (PCE). A surface with only apolar energy is considered hydrophobic.

The polar energy of a surface is often associated with its ability to make hydrogen bonds with water and hydrated ions. An increase in the polar energy on a solid surface represents a decrease in the hydrophobicity of the surface. This decrease brings forth greater interactions between surface sites and water molecules and hydrated ions. An increase in electrostatic energy on a solid surface can also increase the interactions between the surface sites and the hydrated ions.

The strong interactions between surface sites and water molecules and hydrated ions limit or prevent many HNO molecules from accessing these reactive sites. HNOs may adsorb to any remaining apolar sites surrounding the reactive sites, barring steric hindrance effects. With an increase in the hydrophobicity of a surface, the interactions between the surface and HNO increase because the interaction between water and

hydrated ions have diminished. Thus, the amount of adsorption of HNOs at the solid surface is dependent on the balance between hydrophobic and hydrophilic attributes of the solid as well as the hydrophobicity of the HNO.

Sorbents Most Implicated in Sorption of HNOs

The solid matrix in a sediment/soil-water system can be viewed as a multi-component sorbent. It has a mineral component that functions as a conventional adsorbent where the sorbate concentrates at the solid-liquid interface, and it has an organic-matter component that functions as a partition medium in which the sorbate permeates throughout the solid. Both of these components are in contact with a highly polar phase, water. The clay fraction of the mineral component and the organic-matter component of a sediment/soil-water system have been implicated in recent research as predominantly influencing the sorption of HNOs (e.g., Mingelgrin and Gerstl, 1983; Karickhoff, 1984; Bishop et al., 1989).

The organic matter in most sediments and soils is intimately bound to the clay as a clay-metal (cation)-organic complex (Stevenson, 1976). This makes it difficult to separate out the individual effects of either organic matter or clay on sorption. Clay and organic matter function more as a unit than as separate entities, and their relative contributions to sorption will depend on the extent to which the clay is coated with organic substances and on the amount of clay present (Dragun, 1988c). It will also depend on the type of clay present.

Nature of Phyllosilicates

The minerals of the phyllosilicate class are effective adsorbents in many systems due to their structure and high surface areas. The phyllosilicate class includes clay minerals, vermiculite, and the micas. Kaolinite and minerals in the smectite (e.g., montmorillonite),

vermiculite, and illitic mica (illite) groups are especially important phyllosilicates because they are widespread and are found in many aquifer systems of interest. Understanding the chemical composition and the structure of phyllosilicates is one of the keys in discerning their interactions with the chemical species from solution. In the case of HNO₃, one of the most important sorptive traits of phyllosilicates to understand is their hydrophobic nature.

Physicochemical Properties of Phyllosilicates Phyllosilicates consist of continuous sheet structures and are best described chemically as hydrous aluminum silicates. Phyllosilicate minerals may contain other metals, however, in addition to

Table 1. Physicochemical characteristics of listed phyllosilicates (Newman and Brown, 1987).

Mineral Type Phyllosilicate	Idealized Structural Formula	Calculated Layer Charge ^a
Pyrophyllite	$\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$	≈ 0
Talc	$\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$	≈ 0
Kaolinite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	0 to 0.08
Montmorillonite	$\text{Na}_{0.66}(\text{Al}_{3.34}\text{Mg}_{0.66})\text{Si}_8\text{O}_{20}(\text{OH})_4$	-0.66
Vermiculite	$\text{Mg}_{1.0-1.4}(\text{Al}_{1.0-1.4}\text{Si}_{6.6-7.0})(\text{Mg}, \text{Fe})_6\text{O}_{20}(\text{OH})_4$	-1.0 to -1.4
Illite	$\text{K}_{2-x}(\text{Al}_{2-x}\text{Si}_{6+x})(\text{Al}, \text{Fe})_4(\text{Mg}_6)\text{O}_{20}(\text{OH})_4$	$-(2.0-x)$ ^b
Muscovite	$\text{K}_2(\text{Al}_2\text{Si}_6)(\text{Al}_4)\text{O}_{20}(\text{OH})_4$	-2.0
Margarite	$\text{Ca}_2(\text{Al}_4\text{Si}_4)(\text{Al}_4)\text{O}_{20}(\text{OH})_4$	-4.0

^a Values given in equivalents per formula unit of $\text{O}_{20}(\text{OH})_4$ and are based on the idealized structural formula.

^b $x \approx 0.3$

aluminum, in particular, magnesium and iron (Table 1). The phyllosilicates have a characteristic unit cell structure—the smallest structural unit from which phyllosilicate crystals are formed—that is composed of alternating sheets of two kinds. The two types of sheets are a tetrahedrally coordinated silica $[\text{Si}_4\text{O}_{10}]^{4-}$ sheet and an octahedrally coordinated aluminum, magnesium, or iron hydroxide $[\text{Al}_2(\text{OH})_6, \text{Mg}_3(\text{OH})_6, \text{Fe}_2(\text{OH})_6]$ sheet. If mostly Al^{3+} or Fe^{3+} is present, only two-thirds of the possible octahedrally coordinated positions are filled, and this type of mineral is defined as having dioctahedral character. If mostly Mg^{2+} or Fe^{2+} is present, all the octahedrally coordinated positions are filled, and this type of mineral is defined as having trioctahedral character. An example of a dioctahedral mineral is pyrophyllite, and an example of a trioctahedral mineral is talc.

The tetrahedral and octahedral sheets combine to form either a two-layer (1:1) or three-layer (2:1) type of phyllosilicate (Fig. 1). The two-layer type consists of one tetrahedral and one octahedral sheet, whereas the three-layer type consists of an octahedral sheet sandwiched between two tetrahedral sheets. These structures form the elementary layers, or building blocks, that comprise more complex particles. Because of their sheet-like structure, these elementary layers combine into stacks in a direction perpendicular to the plane of the layers. These stacks form crystals that vary in thickness.

Cations, hydrated cations, and water may be intercalated between the elementary layers that form a crystal. The nature of the intercalate determines the c-axis (basal) spacing of the mineral, i.e., the thickness of the 1:1 or 2:1 layer plus the interlayer space. Kaolinite, pyrophyllite, and talc have nothing intercalated between their interlayers, and these interlayers are held together by van der Waals forces only. Because the interlayer spacing between layers is zero, the c-axis spacing or basal spacing for pyrophyllite and talc is $\approx 9.5 \text{ \AA}$, and that for kaolinite is $7 \text{ \AA}$ (Fig. 1). For minerals such as illite and the micas,

Figure 1. (a) Two-layer type of phyllosilicate. (b) Three-layer type of phyllosilicate. Note that only two of the three possible sites in the octahedral sheet are occupied, making these dioctahedral sheets (upper figures reproduced by permission from Sposito, 1984; lower figures after Schulze, 1989).

cations occupy the interlayer positions. Their interlayer spacing and c-axis spacing are dependent on the size of these cations and on how well these cations fit between the two opposing basal surfaces. For the smectites and vermiculite, solvated cations and water usually can easily intercalate between their interlayer regions (see montmorillonite in Fig. 2). In an aqueous system, the distance between their layers can vary considerably

Figure 2. The structure of pyrophyllite and montmorillonite (after Schulze, 1989).

and depends on the interposed cation and the ionic strength of the solution. Unlike the smectites and vermiculite, the other phyllosilicates generally do not readily permit intercalation of water between their interlayers in aqueous systems.

Owing to their sheet-like structure, many phyllosilicates have large specific surface areas. These large specific surface areas give phyllosilicates numerous potential adsorption sites to interact with various chemical species. If one estimates the total specific surface area of a phyllosilicate having a and b dimensions for its unit cell of 5.20 and 8.96 Å, respectively, its value is $\approx 760 \text{ m}^2/\text{g}$ (Quirk, 1968). This value represents the total area when both basal planes of a 2:1 unit cell of the mineral are available to the adsorbate (surface area of the edge is neglected). If the layers of this clay combine to form crystals, the surface area that the adsorbate can access usually is reduced. Under normal conditions, the reduction in adsorption is because HNOs cannot access the

interlayer regions of the clay crystals. The interlayer region of montmorillonite and vermiculite may or may not intercalate HNO₃ depending on whether adsorption would be energetically favorable or not. If the interlayer region is inaccessible, the surface area that is left to interact with HNO₃ is the one that is directly exposed to the aqueous solution. The amount of this exterior surface area is dependent on the number of elemental layers per crystal. For example, a pyrophyllite crystal with seven layers and one with ten layers would have respective specific exterior surface areas of $\approx 110 \text{ m}^2/\text{g}$ and $\approx 76 \text{ m}^2/\text{g}$. The thickness of these crystals would be 66.5 Å for the former and 95 Å for the latter. These estimated values assume that the crystals have a fixed c-axis spacing of 9.5 Å and that the total theoretical specific surface area is 760 m²/g.

The reactivity of potential adsorption sites at the phyllosilicate surface is dependent to a large extent on the type and distribution of isomorphic cation substitutions within the sheets. These substitutions result in a permanent net negative charge on the basal surfaces of the 1:1 or 2:1 layer (Table 1). Isomorphic cation substitutions can occur in the octahedral sheet, in the tetrahedral sheet, or in both sheets. In the octahedral sheet, divalent cations generally replace trivalent cations and, in the tetrahedral sheet, trivalent cations replace Si⁴⁺ cations. The strength of the surface charge (Table 2) is governed by the location and degree of isomorphic substitution within these sheets.

The 2:1 layer phyllosilicates differ significantly from each other by the amount of their negative layer charge (Table 2). At one end of the spectrum, the dioctahedral mineral pyrophyllite and the trioctahedral mineral talc have very little ionic substitution, which gives them a negligible layer charge (≈ 0 equivalents per O₂₀(OH)₄). The brittle mica, margarite, is on the other end of the spectrum and has a theoretical layer charge close to ≈ 4 equivalents per O₂₀(OH)₄.

Table 2. Sheet layer charges and surface charge densities of representative phyllosilicates (source of data from Newman and Brown, 1987, unless otherwise noted).

Mineral Type	Tetrahedral charge ^a	Octahedral charge ^a	Total layer charge ^a	Surface charge density ^b
Talc	0	0	0	0
Pyrophyllite	- 0.06	+ 0.05	- 0.01	0
Kaolinite	- 0.092	0	- 0.092	- 0.11 to - 0.15 ^l
Montmorillonite	- 0.21	- 0.54	- 0.75	- 0.127
Vermiculite	- 2.19	+ 0.59	- 1.58	- 0.210
Illite	- 1.19	- 0.38	- 1.57	- 0.276
Muscovite	- 1.97	+ 0.03	- 1.94	- 0.332
Margarite	- 4.02	+ 0.32	- 3.70	- 0.663

^a Experimentally derived values given in equivalents per formula unit of $O_{20}(OH)_4$.

^b Surface charge density based on structural formula: surface charge density = $e \cdot \Sigma(\text{interlayer cation charge})/2ab$, where e is the elementary charge, 1.6022×10^{-19} , and a and b are the unit cell parameters (Newman, 1987). Surface charge density values given in coulombs per unit area (C/m^2), where on a mass basis 1 meq/g is equal to 96.5 C/g.

^l Bolland et al., 1976.

The negative layer charge of the phyllosilicates is compensated by cations (frequently called counterions) at the mineral surface. The compensating cations on the exterior surfaces of phyllosilicate crystals can be readily replaced by other cations from solution, i.e., they are exchangeable. For smectites (e.g., montmorillonite) and vermiculite, their interlayer cations also are readily replaceable. The exchangeable cations on a phyllosilicate surface often are represented by the cation-exchange capacity (CEC) and are defined as milliequivalents of exchangeable cations per 100 grams of mineral.

When submerged in solution, the reactive surface sites created by the negative surface charge of a phyllosilicate attract polar and ionic substances, such as water molecules and cations, from solution. This in turn affects the amount of HNOs that will adsorb onto the basal surfaces of phyllosilicates. In general, the greater the layer charge of the phyllosilicate, the more its surface will adsorb water molecules and cations and the less the surface will adsorb HNOs. For example, pyrophyllite behaves differently from the smectites in its interaction with water and cations. Of the smectites, montmorillonite is closest to pyrophyllite in structure and chemical composition (Giese et al., 1991), but montmorillonite is a moderately hydrophilic clay whereas pyrophyllite is strongly hydrophobic (Steenberg and Harris, 1985; Kelebek, 1987; Kelebek et al., 1987). The major difference between these two minerals is that Mg^{2+} is substituted for some of the Al^{3+} in the octahedral layer of the montmorillonite (Fig. 2), creating a net negative charge imbalance on its basal surfaces. This surface charge imbalance leads to relatively strong polar bonds with water and solvated cations. For comparison, pyrophyllite forms, at best, only weak polar bonds because it does not have appreciable isomorphic substitution. Because montmorillonite is more polar than pyrophyllite, this mineral is more likely to adsorb water molecules and cations than nonpolar to weakly polar substances like HNOs.

The edges of phyllosilicates are not considered important sites for adsorption of HNO molecules. One reason is that the edges of the tetrahedral and octahedral sheets present broken primary bonds to the solute. These broken bonds are strongly hydrophilic, and they readily adsorb water molecules and ions. Because of the hydrophilic nature of the edges, they are less likely to adsorb HNOs. Another reason that edges are not considered important in HNO adsorption is that the surface area of the mineral edges is usually only a small proportion of the total surface area of a phyllosilicate. In the case of

the smectites, the edges are about 1% of the total surface area (Dyal and Hendricks, 1950). For these reasons, the adsorptive characteristics of the edges are of limited interest when considering HNOs.

Exchangeable Cations and the Diffuse Double Layer If immersed in an aqueous medium, phyllosilicates that have undergone isomorphic substitution develop an electrostatic or a double-layer potential that is dependent on the distribution of the counterions adjacent to the surface (van Oss et al., 1990). This potential is formed by the cloud of counterions that are neutralizing the negative layer charge at the mineral surface. It is the surface potential that produces the repulsive electrostatic interactions between particles and attractive electrostatic interactions between polar molecules, metal cations, and oppositely charged ionic or heteropolar solids. The potential decreases with increasing electrolyte concentrations and increasing valence of the exchangeable cation. The attractive van der Waals interaction, a major interparticle force, becomes relatively more influential as the double-layer surface potential decreases.

The potential that arises at the solid/liquid interface, in itself, does not necessarily play an important part directly in hydrophobic interactions because HNOs are nonionic. It does contribute, however, to the attraction of cations and water molecules at and immediately adjacent to the mineral surface. In turn, the distribution of cations and water molecules can alter the nature of the surface that then can affect the adsorption of the HNOs. Moreover, the type of surface cation can affect the adsorption of the HNOs (Norris et al., 1993).

Swelling Phyllosilicates Smectites and vermiculite share a unique property that other phyllosilicates do not ordinarily possess. These two minerals can readily swell (expand) in solution because they can intercalate hydrated cations and water. Upon swelling, the planar interlayers separate and form slit-shaped pores. The swelling characteristic of these minerals is important because solute molecules can adsorb not only onto the external surfaces but potentially into the interlayer region created by the slit-shaped pores. Before a solute molecule can physically fit within the pores of the expanding minerals, its minimum overall dimension would have to be less than the distance between the interlayers. If the layers become widely separated, the interlayer region can become especially important to adsorption.

Swelling of these minerals is caused by the layers of water associated with the exchangeable cations intercalated in the interlayers (see montmorillonite in Fig. 2). The number of intercalated water layers is dependent on the hydration properties of the intercalated exchange cations and on the properties of the elementary layer of the mineral. If a balance among the forces is reached, the interlayer spacing reaches equilibrium. These balancing forces are repulsive hydration forces, repulsive electrostatic forces (between negatively charged unit layers), attractive electrostatic forces between cations and unit layers, and attractive van der Waals forces.

The hydrated elementary layers of the swelling minerals can form quasicrystals (Fig. 3). The quasicrystal was originally proposed by Quirk and Aylmore (1971). Produced by attractive forces, a quasicrystal is the result of sequential stacking of layers that have interlayer spacings that are $\approx 10 \text{ \AA}$ or less. This definition is much like that given for a phyllosilicate crystal, except that the interlayers of a quasicrystal contain exchangeable hydrated cations. Quasicrystals have been called different names, such as

Figure 3. Conceptual illustration of quasicrystals, domains, and their stacking orders.

tactoids, domains, crystals, and packets, by different authors (see Banin and Lahav, 1968, for a list of these authors). The term domain will be used to describe stacked individual 2:1 layers or quasicrystals that have greater than $\approx 10 \text{ \AA}$ spacings between them. Figure 3 conceptually shows the arrangement of quasicrystals within a domain. The domain can be regarded as a structure or arrangement of crystals or quasicrystals that would have appreciable stability (units are not easily separated) and would behave as a single particle (Quirk, 1968).

The interlayer spacing of smectites is sensitive to the type of cation intercalating in the interlayers and to the concentration of the associated electrolyte solution. For example, if montmorillonite's intercalating cation is Na^+ and the associated electrolyte concentration is less than $\approx 0.3 \text{ N}$, progressive expansion between its interlayers occurs starting from $30 \text{ \AA}$ (Posner and Quirk, 1964). The more dilute this electrolyte solution is

than 0.3 N, the greater this expansion, until 0.1 N concentration is reached. If the electrolyte solution is <0.1 N, the opposing layers of the montmorillonite may become completely dissociated. If the electrolyte concentration is > 0.3 N, only limited expansion (≈ 9 Å) of the montmorillonite's interlayers occurs and quasicrystals are anticipated to form. An interesting occurrence takes place when the concentration is around 0.3 N; the interlayer spacing expands or contracts stepwise between ≈ 9 Å and 30 Å. This jump represents a transition from three water layers between the interlayers of montmorillonite to the development of a diffuse cation cloud (a Gouy layer) between its interlayers. Domains form if the interlayer spacing makes this jump to ≥ 30 Å. The layers, however, are still associated with each other, and these layers may be arranged parallel to one another over long distances (≥ 100 Å). This arrangement becomes more unstable as the separation between interlayers becomes greater, until the interlayers completely dissociate from each other (Quirk, 1968).

If the exchanging cation is divalent, montmorillonite usually exhibits only limited intraquasicrystalline swelling characteristics no matter how dilute the associated electrolyte concentration has become. In CaCl_2 solutions from essentially zero to about 2.0 N, the interlayer spacing of montmorillonite is around 10 Å (Posner and Quirk, 1964). This limited swelling is explained by the tendency of a divalent cation to bind opposing paired interlayers more strongly than do monovalent cations.

The interlayer spacing is not the only criterion that determines whether HNO adsorption will occur within the interlayer regions. Another potential steric hindrance effect is caused by the environment within the interlayer region. The interlayer fluid composition is often quite different from that near the exterior basal surfaces and in the bulk solution. The organization and concentration of solvated cations and water within the interlayer region create an environment that is similar to a concentrated aqueous

solution, although no anions exist (McBride, 1989). For montmorillonite and vermiculite, the cation concentrations within their interlayer region are twice those expected for the same volume of fluid that is immediately adjacent to their exterior surfaces. The increased concentration between the interlayers is because two charged surfaces are on opposite sides of the interlayer volume. Doubling the surface charge within the interlayer region of these minerals essentially requires twice the cation concentration to compensate for the increased charge.

Work by others gives some support to interlayer HNO adsorption. Estes et al. (1988) observed that, after the initial rapid uptake of TCE, a very gradual adsorption of TCE by montmorillonite continued over a period of 15 days. They postulated that the gradual uptake by montmorillonite was the result of very slow TCE mass transfer to adsorption sites and very slow adsorption reactions. They also postulated that the chemistry of the clay surface was slowly changing during contact with the solution and this change increased adsorption. They considered the chemical change of the clay surface to be more important than the mass transfer and adsorption kinetics in explaining the slow uptake of TCE. The slow mass transfer of TCE they observed, however, may have reflected the slow transfer of TCE into the interlayer regions of the quasicrystals. Ball and Roberts (1991a, 1991b) observed long-term sorption of PCE to sandy aquifer material that took on the order of tens to hundreds of days before equilibrium was reached. They interpreted their results to be due to slow intraparticle diffusion into the grains.

A cautionary note when reviewing long-term sorption experiments is that HNO molecules may be breaking down during the equilibration period either by chemical or biological degradation. This loss of molecular HNO gives rise to an overestimate of

adsorption. Without a careful mass balance measurement, it is difficult to detect if gradual adsorption through pore diffusion truly is occurring. Ball (1989) discussed this issue in greater depth.

Another characteristic of montmorillonite that can affect HNO adsorption is the number of layers per quasicrystal of this mineral. This number will vary with the cation type and, possibly, the electrolyte concentration. If a given mass of montmorillonite is exposed to a solution that lowers its number of layers per quasicrystal, the number of external surfaces exposed to the solute becomes greater. HNO adsorption to these exterior surfaces is expected to be significantly greater than within the interlayer region of the quasicrystal. In a dilute electrolyte solution (distilled water), a general consensus (presented in Sposito, 1984) is that dilute suspensions of Na-montmorillonite exist as essentially individual unit layers (averaging 1.2 ± 0.2 unit layers per quasicrystal). Under the same conditions for Ca-montmorillonite, four to eight layers make up each quasicrystal. More layers per quasicrystal may be possible for Ca-montmorillonite in dilute suspension. Shomer and Mingelgrin (1978) reported that they found an average of 16 layers per quasicrystal. They also reported that up to 20% of their bulk clay sample consisted of even thicker quasicrystals (≈ 50 layers per quasicrystal).

Posner and Quirk (1964) and Shomer and Mingelgrin (1978) indicated that the number of lamellae (2:1 layers) in each crystal (quasicrystal) of montmorillonite depends on the exchangeable cation and electrolyte concentration. Information regarding the number of layers per Na-montmorillonite quasicrystal with increased electrolyte concentrations is apparently not available. The same is true for Ca-montmorillonite in CaCl_2 systems. Apparently, the information is not available because of the great difficulties encountered in the methods used to analyze quasicrystal size when the particles begin to flocculate and settle out in stronger electrolyte solutions.

The domains and quasicrystals of montmorillonite are expected to be governed by the exchanging cation and the associated electrolyte concentration. Generally, in stronger electrolyte solutions, the domains are anticipated to be larger and more condensed than in weaker electrolyte solutions. This inference is based on how montmorillonite flocculates or coagulates in stronger electrolyte solutions (van Olphen, 1987). As ionic strength increases, the Gouy layer becomes compressed close to the particle. When this happens, the repulsive electrostatic interactions are not enough to counteract the attractive London-van der Waals interactions. Under this condition, the attractive interactions bring opposing layers closer together. If enough condensation between interlayers occurs, quasicrystals are formed.

The size of the domain can depend on the condensation power of the electrolyte. According to the Schulze-Hardy rule, the higher the valence of the ion in the added electrolyte that has a sign opposite to the sign of the charge of the particle, the more powerful the electrolyte is in its condensation action (van Olphen, 1987). The valency of the ion of the same sign has only a minor affect (Hardy, 1900). For montmorillonite, this means that Ca^{2+} is a more powerful condensation agent for a given concentration than Na^+ .

The domains of Ca-montmorillonite and Na-montmorillonite may have different stacking order of their individual 2:1 layers within a quasicrystal and quasicrystals within a domain along the c-axis. The Na-montmorillonite layers that form quasicrystals and quasicrystals that form domains in NaCl solutions are more likely to be haphazardly stacked than those of Ca-montmorillonite in CaCl_2 solutions (Fig. 3). Aylmore and Quirk (1967) found that Na-montmorillonite showed a less complete overlap of contiguous quasicrystals in domains than that of Ca-montmorillonite. With the less complete overlap, Na-montmorillonite had 20% greater available exterior surface area. Similar less

complete overlapping of individual 2:1 layers is expected within a quasicrystal. Less overlapping area of the quasicrystal and domain probably result in greater HNO interaction because more accessible surface area is available.

Vermiculite exhibits limited swelling between its interlayers if the exchanging cation is Na^+ or Ca^{2+} . This limited expansion also is unaffected by the electrolyte concentration. The number of elementary layers in a quasicrystal of vermiculite is much larger than that of montmorillonite. This means that most of the surface area of vermiculite is within its interlayers. The size of the quasicrystals of vermiculite is insensitive to whether Na^+ or Ca^{2+} is present and to the concentration of the associated electrolytes. A more in-depth discussion and references concerning swelling properties of this mineral and montmorillonite can be found in Grim (1968), Sposito (1984), and van Olphen (1987).

Surface Functional Groups Phyllosilicates have several types of surface functional groups that are products of the structure and chemical composition of the mineral. These functional groups have a profound effect on whether HNOs will adsorb to the surfaces of the phyllosilicates. This is not necessarily because the surface functional groups interact directly with HNOs, but because the surface functional groups can interact and form complexes with water molecules and hydrated cations. HNOs cannot compete with water and hydrated cations for these surface functional groups. Consequently, the larger the surface functional group interactions are with water molecules and cations, then the smaller the surface adsorption of HNOs.

Before proceeding, surface functional groups and the complexes that they form need to be defined. A surface functional group is defined by Sposito (1984) as a chemically reactive molecular unit bound into the structure of a solid at its periphery such

that the reactive components of the unit can be bathed by a fluid. When the solid is submerged in a fluid, the surface functional groups may react with dissolved chemical species from the surrounding fluid to form a stable unit called a surface complex. The process itself is termed surface complexation. Sposito (1984) presented two broad categories of surface complexes that were distinguished on structural grounds. If no water molecule is interposed between the surface functional group and the cation it binds, the complex formed is called an inner-sphere complex. If at least one water molecule is interposed between the functional group and the cation, the complex formed is called an outer-sphere complex. The general rule concerning these complexes is that outer-sphere surface complexes involve electrostatic bonding mechanisms and, therefore, are more unstable than inner-sphere surface complexes, which fundamentally involve either ionic or covalent bonding or some combination of the two. Surface functional groups exist on the basal plane and edge surfaces of phyllosilicates and have varying reactivity, and, thus, form complexes that vary in their stability.

The Siloxane Ditrigonal Cavity. Common to all phyllosilicates, a plane of oxygen atoms bounds the tetrahedral silica sheet and is called a siloxane surface. The functional group associated with this surface is termed the siloxane ditrigonal cavity and is formed by six corner-sharing silica tetrahedra linked to form a continuous sheet (Fig. 4). This cavity is bordered by six sets of lone-pair electron orbitals emanating from the surrounding ring of oxygen atoms (Sposito, 1984). This functional group is recognized as a Lewis base: a molecular unit that uses a doubly occupied electron orbital in initiating a chemical reaction (Sposito, 1981).

Figure 4. (a) The siloxane ditrigonal cavity (reproduced by permission from Sposito, 1984). (b) Plan view of a sheet of siloxane ditrigonal cavities (after Schulze, 1989).

The reactivity of the siloxane ditrigonal cavity depends on the nature of the electronic charge distribution in the phyllosilicate structure (Sposito, 1984). If no isomorphic cation substitutions occur to create deficits of positive charge in the underlying layer, the basal oxygen is electrostatically neutral and the ditrigonal cavity functions as a very soft Lewis base (electron donor) (Sposito, 1981). The very soft Lewis base would not be expected to form complexes with charged solutes but could complex neutral dipolar molecules, such as water molecules through weak hydrogen bonds. The complex with water, however, would be weak and not very stable, making this surface essentially hydrophobic. A surface with a weak Lewis base would likely significantly adsorb HNO₃. Examples of minerals that possess weak Lewis base strengths are talc and pyrophyllite. Both these minerals have little or no isomorphic substitutions; therefore, they have siloxane surfaces that are considered hydrophobic.

If isomorphic cation substitution does occur in the tetrahedral sheet, the octahedral sheet, or in both sheets, the resulting excess negative charge can be distributed over the siloxane surface and will enhance the Lewis base strength of the ditrigonal cavity. This leads to a substantial increase in the surface polarity of the mineral. Consequently, this makes it possible for the surface to form stronger complexes with cations or with water via hydrogen bonding. If isomorphic substitution occurs in the tetrahedral sheet, the excess negative charge can distribute itself primarily over just three surface (basal) oxygen atoms of one tetrahedron (Sposito, 1984). This makes the resulting charge on the siloxane surface less diffuse and this forms stronger complexes with cations and polar molecules because of localization of charge. This higher density of charge favors the formation of inner-sphere surface complexes when coupled with high permanent charge (Sposito, 1984). Exceptions to this general rule exist.

If the isomorphic substitution occurs within the octahedral sheet, the resulting excess negative charge can distribute itself principally over ten surface oxygen atoms of four tetrahedra linked to the substitution site (Sposito, 1984). The diffuse nature of the charge distribution that occurs from this substitution favors an outer-sphere surface complex between the exchangeable cation and the ditrigonal cavity. Again, exceptions to this general rule exist.

The relationship between location of isomorphic substitution and the strength of hydrogen bonding on the siloxane ditrigonal cavity was determined through infrared spectroscopic studies (Farmer and Russell, 1967; Donor and Mortland, 1971; Farmer, 1971). They concluded that the greater the localization of negative charge on an oxygen atom of the siloxane surface, the stronger the hydrogen bond. It was determined that the strongest hydrogen bonds occurred with oxygen atoms near sites of isomorphic substitution in the tetrahedral sheet and the weakest bonds involved the oxygen atoms that shared no excess negative charge from isomorphic substitution. Hydrogen bonds with surface oxygen atoms near sites of isomorphic substitution in the octahedral sheet had intermediate strength.

Edge Functional Groups. The other functional groups of phyllosilicates lie along the edge surfaces of the mineral where unsatisfied bonds are exposed. These functional groups consist of three main types of hydroxyl groups. In the dioctahedral minerals, the aluminol group ($=\text{AlOH}$) is found along the edge of the octahedral sheet; the silanol group ($=\text{SiOH}$) is found along the edge of the tetrahedral sheet. At the edge of the octahedral sheet, a Lewis acid site, which is any molecular unit that uses an empty electron orbital in initiating a reaction (Sposito, 1981), complexes with a water molecule

$[(\text{Al}^{3+})\cdot\text{H}_2\text{O}]$ to form the third group. These edge groups are very reactive and are primarily hydrophilic (Schrader and Yariv, 1990). In addition, they form stable complexes with polar and cationic solutes.

Additional Functional Group on 1:1 Phyllosilicates. For the 1:1 layer type of phyllosilicates, such as the dioctahedral mineral kaolinite, not only do these minerals have the siloxane ditrigonal cavity group on the faces of their tetrahedral sheets, they also have aluminol groups on the faces of their octahedral sheets. Unlike the aluminols located along the edges, the basal surface aluminols are non-reactive. This non-reactivity is because the oxygen ions of the face aluminols are coordinated with two Al atoms. This coordination balances the charge (Davis and Kent, 1990), and the surface aluminols do not form stable complexes with polar and cationic solutes. Because of the nonreactivity of the surface aluminols and the low ionic substitution within sheets of kaolinite, only weak interactions with water molecules will occur on kaolinite octahedral surfaces and even less will occur on its tetrahedral surfaces. Consequently, significant HNO adsorption is likely to occur on both basal surfaces of kaolinite.

Nature of Oxides, Oxyhydroxides, and Hydroxides

In recent years, oxide, oxyhydroxide, and hydroxide minerals have received increasing attention because of their contribution to the adsorption and desorption of various, mainly ionic and polar, compounds in aqueous media. These minerals may also have an affinity for HNOs under suitable geochemical conditions (i.e., favorable solution pH and ionic strength). Although these minerals may have a low overall abundance in soil and sediments, they generally exhibit significant specific surface area, which enhances their adsorption capacities (Taylor, 1987). Aluminum, iron, and manganese

form the most important oxide, oxyhydroxide, and hydroxide minerals in soils and sediments. Goethite [α -FeO(OH)] is one of the most prevalent crystalline iron oxide minerals found in soils. Fe(OH)₃ (amorphous) and ferrihydrate also commonly are found in soils. A less common iron oxide in soil, hematite [α -Fe₂O₃], frequently is formed in the soil through weathering of other iron-bearing minerals such as goethite. Gibbsite [γ -Al(OH)₃] is the most common pedogenic form of the aluminum oxide minerals and occurs in many different soil types (Taylor, 1987). Pyrolusite (β -MnO₂) is a common mineral that can form as direct deposits from cold groundwater in bogs and on the sea floor.

The term “oxides” has been used as a collective term by many to describe metal hydroxides, oxyhydroxides, and hydrous oxides (where non-stoichiometric water is included in the structure) (Taylor, 1987). This term is adapted here to describe these groups of minerals as a whole. The terms oxide, oxyhydroxide, and hydroxide will be used when the discussion is specific to these groups.

Physicochemical Properties of Oxides Certain general properties such as structure and surface adsorption apply to the groups of the oxides as a whole. Characteristic of most common oxides is either a hexagonal (α) or cubic (γ) close packed oxygen/hydroxyl octahedral sheet as their basic unit. Differences in these minerals arise from the proportion and ordering of metal cations occupying space within the mineral structure, which create changes within that structure. The site occupancy is determined by the valence of the cation and whether a hydroxyl group substitutes in part or totally for oxygen atoms. For instance, hematite and goethite both have trivalent Fe octahedrally coordinated in hexagonal close-packed oxygen layers. The Fe of goethite is surrounded by 3 (OH) and 3 O rather than 6 O as is the Fe in hematite (Busing and Levy, 1958).

These arrangements give goethite 12 Fe per 24 O and hematite 16 Fe per 24 O. In hematite each oxygen is coordinated to 4 Fe, whereas in goethite, replacement of an O by OH reduces its ability to be coordinated to a fourth neighboring Fe. This causes a reduction in, and resultant re-ordering of, the octahedral site occupancy, but bonding through the structure is maintained by hydrogen bonding to a non-hydroxyl oxygen neighbor (Taylor, 1987). These effects alter the charge density of the mineral surface and potentially the adsorption capacity of the minerals for HNO₃.

Surface Functional Groups on Oxides In marked contrast to the basal surfaces of phyllosilicates, the surface reactivity of oxides arises from unshared O and OH resulting from broken surface bonds. These broken bonds become hydroxylated by adsorption of H⁺ or OH⁻ to achieve full coordination of the surface atoms. The resultant charge that develops on these fully hydroxylated surfaces is not fixed, but is pH-dependent and has amphoteric characteristics (possessing both basic and acidic properties). Although isomorphic substitution of both higher and lower valent cations does occur in these oxides, their contribution to the net surface charge generally is negligible in relation to proton-bearing surface functional groups (Taylor, 1987).

Charges develop on these hydroxylated surfaces through a process that may be interpreted as either an amphoteric dissociation of the surface hydroxyls or adsorption of either H⁺ or OH⁻ ions (Taylor, 1987). In either case, the hydroxylated surfaces are said to function as Lewis acid sites. The model proposed by Parks and de Bruyn (1962) can be represented by Figure 5. As is shown in the figure, the removal or addition of the H⁺ or OH⁻ ions at the oxide surface controls the formation of surface charges. It also controls their magnitude and sign. The excess of positive or negative surface charge is balanced by an equivalent amount of anions or cations, respectively (Fig. 5).

Figure 5. The establishment of surface charge on a hydroxylated surface with the adsorption and desorption of potential determining ions (PDI) H^+ and OH^- (after Parks and de Bruyn, 1962).

At a certain solution pH, the net surface charge becomes zero. This value is often called the point of zero charge (PZC) or the zero point of charge (ZPC). The PZC represents the pH at which the quantities of adsorbed H^+ and OH^- ions at the surface are equal and the sum of the two quantities is at a minimum. It also represents the pH at which the anion and cation exchange capacities are equal to each other and at their smallest total value (Parks, 1967). Table 3 lists PZC values for several oxides. The PZC values given in Table 3 are only approximations because oxides from different origins and histories do vary in their PZC values (McBride, 1989).

Figure 6 represents a typical surface charge versus pH relationship for varying concentrations of an "indifferent" (nonspecific adsorbing) electrolyte. If the pH value of the solution is below the PZC shown in the figure, then the oxide surface is more positively charged than negatively charged. Mostly anions or the negative regions of a polarizable molecule are attracted to and electrostatically held adjacent to this surface (Taylor, 1987). Conversely, if the pH value is greater than the PZC shown in the figure, then the oxide surface is more negatively charged than positively charged. The same

Table 3. The pH values at point of zero charge (PZC) of various oxides.

Mineral	PZC
Pyrolusite [β -MnO ₂]	4.6–7.3 ¹
Goethite [α -FeO(OH)]	6.9 ²
Hematite [α -Fe ₂ O ₃]	7.5 ³
Gibbsite [α -Al(OH) ₃]	≈ 9 ⁴

¹ Davis and Kent, 1990.

² Gast, 1977.

³ Gu et al., 1995.

⁴ Hsu, 1989.

types of attractive forces now apply to cations or their equivalents. The further away the pH value is from the PZC, the greater the surface charge is on the oxide surface.

Furthermore, increasing the electrolyte concentration at a given pH causes an increase in the surface charge. It is near the PZC that the adsorption of HNO molecules would likely be at its greatest.

Adsorption of HNO solutes may occur at or near surface hydroxyl sites of the oxides. Various types of surface hydroxyl sites exist at the oxide surface (Sposito, 1984). These sites are distinguished based on stereochemical reasoning (i.e., on their spatial arrangement and how this affects their properties). Analyses of these different hydroxyl groups suggest that they have different reactivities (James and Parks, 1982; Sposito, 1984) that reflect the type and stability of the surface complexes formed. The reactivities determine how these hydroxyl sites will respond to water molecules and ions. If the reactivity of the hydroxyl site is small, interactions with water molecules and ions are weak and limited, and it is at or near these sites that adsorption of HNOs is most likely to occur.

Figure 6. The pH titration curves for synthetic goethite showing variations in surface charge with pH for various electrolyte concentrations (data manually digitized from Gast, 1977, pg. 38; curves fitted to digitized data). The symbol Γ refers to the adsorption density, which is frequently used to express the amount adsorbed.

Nature of Organic Carbon

Organic matter in soils and sediments encompasses a range of substances from easily degradable biological products to polymers that are extremely stable. As these compounds degrade, humus is formed. Humus is a complex and rather refractory mixture of amorphous and colloidal substances modified from original tissue or synthesized by

soil microorganisms. Humus comprises three classes based on the solubility in acids and alkalis (Dragun, 1988a):

- fulvic acid, which is soluble in both acids and alkalis and is lowest in molecular weight and lightest in color;
- humic acid, which is soluble in alkali but insoluble in acid and it possesses intermediate molecular weight and color;
- humin, which is insoluble in both acid and alkali and possesses high molecular weight and dark brown color.

These classes of organic matter may be present as a thin coating on mineral surfaces, may be dissolved in water, or may exist in larger aggregates.

A single or a few molecular layers of organic matter on a mineral surface may be considered to act as a modifier to the sorptive capacity of the surface. For example, organic matter adsorbed onto a hydrophilic mineral surface can reduce the Lewis base strength (Norris et al., 1992) and, thus, reduce the hydrophilicity of that surface by satisfying the polar interaction on the mineral surface. This will make the Lewis base sites more hydrophobic and make any already hydrophobic sites more readily available to HNOs. Consequently, this will increase the sorption of HNOs to that surface. Larger amounts of adsorbed organic matter will also provide its own sites for HNO sorption.

Karickhoff et al. (1979) reported a significant positive correlation between linear partition coefficients or K_p —analogous to K_d —and organic carbon content. When the measured partition coefficients were divided by the fraction of organic carbon of the respective sediments (f_{oc}), a constant called the organic-carbon-normalized distribution

coefficient (K_{oc}) was derived that was independent of sediment properties and dependent only upon the nature of the organic sorbate:

$$K_{oc} = \frac{K_p}{f_{oc}}.$$

The K_{oc} for a specific organic compound can be estimated from its water solubility or its octanol-water partition coefficient (K_{ow}) (Karickhoff et al., 1979; Karickhoff, 1984). The K_{ow} is the equilibrium ratio of an organic compound's concentration in octanol (an organic liquid) to its concentration in water. Once K_{oc} is estimated, the equation above allows K_p to be predicted for a given solute-sorbent system.

A few studies have addressed the topic of conditions under which the inorganic fraction contributes significantly to adsorption of HNOs, rendering the above relationship no longer valid to estimate sorption by itself. Usually the above relationship becomes invalid when f_{oc} is below a critical level of organic carbon (f_{oc}^{crit}). Schwarzenbach and Westall (1981) have determined that the above relationship was not valid for soils with a f_{oc} that was less than a f_{oc}^{crit} value of 0.001 (0.1% or 1,000 mg/kg). McCarty et al. (1981) developed an equation to calculate f_{oc}^{crit} using the surface area of the soil/sediment and the K_{ow} of an organic compound. The equation is written as

$$f_{oc}^{crit} = \frac{sa}{200(K_{ow})^{0.84}},$$

where sa is the specific surface area of the soil/sediment (m^2/g). As an example, let TCE be the organic compound, which has a calculated K_{ow} of 2.29 (Olsen and Davis, 1990), and let the sediment sample (clay content of 30% with a sa of 80 m^2/g and remaining fraction with a sa of 5 m^2/g) have a total surface area of 27.5 m^2/g . Entering these data

into the above equation, the f_{oc}^{crit} would be 0.002. This resultant f_{oc}^{crit} indicates that if the f_{oc} of the sediment sample is below 0.002, sorption is not expected to be adequately predicted by K_{oc} and f_{oc} alone.

Mineral surfaces and their coatings of organic matter can be viewed as a two-compartment system. Stevenson (1972) reported that the relative contributions from organic and inorganic surfaces to sorption depend on the extent to which the clay is coated with natural organic substances. Assuming monolayer coverage of the mineral surfaces by organic substances, Walker and Crawford (1968) estimated that 1% carbon would reduce the available mineral surfaces by 32 m²/g.

McCarty et al. (1981) proposed a two-component model for sorption at low f_{oc} . This model assumes that adsorption to the mineral surfaces occurs concurrently with the absorption to the organic matter and assumes that these two components are additive. The two-component model proposed by McCarty et al. (1981) was written as

$$K_d = K_{io}f_{io} + K_{oc}f_{oc}$$

where

- K_{io} = the distribution coefficient of the mineral component,
- K_{oc} = the distribution coefficient of the natural organic component,
- f_{io} = the fractional mass of the mineral in the whole sediment, and
- f_{oc} = the fractional mass of organic carbon in the whole sediment.

Karickhoff (1984) has developed semi-quantitative threshold values at which inorganic surfaces contribute significantly to sorption. The values are based on the ratio of clay fraction (*cm*) to organic carbon fraction (*oc*):

- neutral organic compounds with polar functional groups, 25–60 *cm/oc*,
- nonpolar organic compounds with less than 10 carbons, >60 *cm/oc*, and
- large nonpolar organic compounds with more than 10 carbons, >100 *cm/oc*.

If cm/oc is <25 , the inorganic mineral surface would not be expected to contribute significantly to adsorption. Using the ratio of 60 as an example, an aquifer sediment that contains 0.14% organic carbon would have to contain 8.4% clay before mineral surfaces began to play a role in HNO adsorption. This percentage or greater percentages of clay commonly are found in sedimentary aquifer systems.

Nature of HNOs

The extent of HNO adsorption onto a solid depends not only on the interaction of the compound with different surfaces, but also on the HNO's interaction, or lack thereof, with the solvent. Generally, the sorption of neutral organic compounds onto a surface is dependent largely upon the hydrophobicity of the solute (Karickhoff, 1984). The hydrophobicity of an organic compound is inversely related to its solubility in water and is directly related to its K_{ow} . The K_{ow} often is used to compare incompatibilities of different organic compounds with water. Usually, the greater the K_{ow} and, thus, the hydrophobicity of the organic compound, the greater the HNO's potential for sorption onto hydrophobic sites at the mineral surface. An explanation of this phenomenon is that hydrophobic molecules create a substantial thermodynamic gradient driving the molecules out of solution (Voice and Weber, 1983). The greater the hydrophobicity of the neutral organic compound, the larger the driving force becomes. This force coupled with the small van der Waals-type interactions of the HNO with water is responsible for its hydrophobic expulsion from solution.

Characteristics of HNOs

Neutral organic compounds are either polar or nonpolar. The polarity of the solute molecule affects its ability to interact with the solvent and the solid and is dependent upon the dipole moment of the molecule. One important factor in determining the polarity of a molecule is its symmetry. Tetrachloroethylene (PCE) with its symmetry (Fig. 7) has no dipole moment (0 debye; McClellan, 1974). The replacement of a chlorine atom with a hydrogen atom in the TCE molecule creates a charge asymmetry (Fig. 7) which gives TCE a small dipole moment (0.99 debye; McClellan, 1974). Through the dipole-dipole interaction, the slightly polar TCE can interact more freely with other polar molecules (e.g., water) than the nonpolar PCE can with those same polar molecules.

Trichloroethylene, even with its slight dipole moment, has been described by some to be nonpolar because it shares characteristics similar to those of other nonpolar halogenated VOCs (e.g., Voice et al., 1983). Some of these characteristics are that TCE is moderately hydrophobic and it lacks polar functional groups. Also, the dielectric constant of TCE (3.42; Gray, 1963) is close to that of other nonpolar halogenated VOCs such as PCE (2.30; Gray, 1963). In comparison, the dielectric constant of water is much higher, about 80. Even with its similarities to nonpolar halogenated VOCs, TCE is considered slightly polar relative to the strict definition of a nonpolar molecule. i.e., the dipole moment is equal to zero debye.

The shape of PCE and TCE molecules is an important consideration in determining whether they will fit within the pore spaces of minerals, for example, within the interlayer region of the swelling phyllosilicates. Shown in Figure 8 are the estimated molecular dimensions for PCE and TCE. These dimensions are based on the dimensional estimates derived by Ball (1989) for PCE. These two halogenated hydrocarbons are similar to each other, except that TCE has a hydrogen atom replacing one of the four chlorine atoms.

Figure 7. Dipole moments [debye (*D*)] of PCE and TCE molecules (values from McClellan, 1974). The schematic diagram shows the polarity of bonds and molecules. The icon $\rightarrow$ symbolizes a dipole where the arrow points from positive to negative.

Figure 8. Estimated molecular dimensions of TCE and PCE. Molecular dimensions for PCE are from Ball (1989). Overall molecular dimensions for TCE are assumed to be the same as for PCE. The third dimension orthogonal to the plane of the molecule is ≈ 3.6 Å.

This fact, however, should not significantly affect the overall dimensions of a TCE molecule compared with that of a PCE molecule. PCE and TCE are planar molecules with an estimated effective thickness of 3.6 Å. The thickness of the two halogenated hydrocarbons is assumed to be the van der Waals diameter of a chlorine atom.

HNOs in Water

The solubility characteristics of HNOs are determined chiefly by their polarity. but they also are determined by molecular size, pH of the aqueous system, nature of the intermolecular interaction and other factors (Horvath, 1982). Usually, nonpolar (PCE) or weakly polar (TCE) compounds dissolve in nonpolar or weakly polar solvents (octanol); highly polar compounds dissolve in highly polar solvents. Neither PCE nor TCE is readily soluble in water. This is because the highly polar water molecules are attracted to each other by very strong dipole-dipole interactions due to their high dipole moment of 1.85 D (McClellan, 1974) and are held together by hydrogen bonds. Therefore, only weak attractive forces exist between TCE molecules and water molecules and even less attractive forces between PCE and water molecules. The bond energy between halogenated VOCs and water are of two types: van der Waals interaction and hydrogen bonding (Horvath, 1982). These bonds between halogenated VOCs and water are weak, varying between 0.93 and 1.58 kcal/g-mol, compared with the bonds between water molecules, varying between 4.5 and 5.0 kcal/g-mol (Horvath, 1982). This weak interaction with water gives TCE and PCE moderately low solubilities and moderately high hydrophobicities. These two factors are indicated in TCE and PCE solubilities of 1.100 mg/L (Olsen and Davis, 1990) and 150 mg/L (Verschueren, 1983), respectively, and their respective log K_{ow} values of 2.29 (Olsen and Davis, 1990) and 2.6 (Leo et al., 1971).

It has been said that water resists the intrusion of HNO molecules. The same force that resists the intrusion of HNO also is responsible for the force driving the HNO molecules out of solution (Tanford, 1980). This force can be explained in light of the current level of understanding regarding the structure of water. It is thought that H_2O molecules in liquid water exist in one of two types of structural associations (Voice and Weber, 1983). The first type of association is one in which each H_2O molecule is

tetrahedrally coordinated to other H_2O molecules via hydrogen bonds, yielding a structure similar to that of crystalline ice. The second association is an agglomeration of more densely packed, but less ordered, H_2O molecules. When an HNO molecule is introduced into liquid water, it can be held in solution by the lattice created by the ice-like water structure. This lattice forms cavities where guest constituents can reside and are stabilized by weak enthalpy interactions (van der Waals forces). Thus, guest molecules filling the cavities are not directly bonded to the water molecules of the framework, but reside in the cavities so long as the lattice remains intact.

The crystalline character of the water structure is enhanced when the water lattice is filled with the guest HNO molecule (Berecz and Balla-Achs, 1983). This phenomenon is also known as “hydrophobic hydration” or “the iceberg effect”. Although the enthalpy for hydrophobic hydration is favorable, it is countered by unfavorable entropy resulting from increased ordering of water molecules (Hamaker and Thompson, 1972) that make up the lattice. When an HNO molecule is transferred from the bulk aqueous phase to the solid/liquid interface, a positive entropy change occurs upon the collapse of the lattice structure. This collapse creates a greater disorder in the system at the expense of increasing the enthalpy.

HNOs in Electrolyte Solutions

Adding electrolytes to water can reduce the solubility of uncharged compounds (i.e., HNOs) compared with their solubility in pure water. This effect on uncharged compounds is known as the “salting-out” effect (Gordon and Thorne, 1967). The decrease in solubility of an uncharged compound in an electrolyte solution occurs largely because more of the water molecules of the solution enter the hydration shells of the electrolyte ions and less water is available for solvating the uncharged solute. Usually, activity

coefficients of uncharged species are near unity in dilute solutions and increase above unity as the electrolyte concentration increases. If the activity coefficients of uncharged species are increased, their solubility in an aqueous solution diminishes (Garrels and Christ, 1965). This trend is the opposite to that of charged species.

The salting out not only reduces the solubility of an HNO in solution, but also enhances the hydrophobic expulsion of this type of compound from solution. The stronger the interaction of the electrolyte with water compared with the interaction between the HNO and water, the greater the effectiveness of this expulsion, i.e., the greater tendency to be “driven out” of solution (Garbarini and Lion, 1985; Gossett, 1987). Both of the halogenated VOCs, PCE and TCE, exhibit behavior typical of neutral molecules in electrolyte solutions, i.e., increased salting out with increased ionic strengths (Garbarini and Lion, 1985).

For a given HNO, not only is the electrolyte concentration of the solution important in affecting the solubility and hydrophobic expulsion of an HNO, but also the type of electrolyte. The effects that different electrolytes have on solubility and hydrophobic expulsion can be explained by the effects different ions have on the structure of water. The interaction of ions with water can be divided into two groups based on their effect on the structure of water: structure-makers and structure-breakers (Frank and Wen, 1957). Generally, ions with large Z/r^2 values (where Z is the charge number, and r is the ionic radius), e.g., Li^+ , Na^+ , Ca^{2+} , F^- , are structure-makers. Ions with low Z/r^2 values (mainly larger ions of low charge), e.g., K^+ , NH_4^+ , Cs^+ , Cl^- , Br^- , are structure-breakers (Berecz and Balla-Achs, 1983). If the net influence of the structure-maker ion on the solvent is greater than that of the structure-breaker ion, the electrolyte is said to be a net structure-maker (e.g., NaCl and CaCl_2). If the net influence of a structure-breaker ion on the solvent is greater than that of the structure-maker ion, the electrolyte is said to be a net

structure-breaker (e.g., KCl and CsBr). In the case of HNOs, more energy is required to create a cavity in the structure-maker solution for the organic molecule to occupy than in the structure-breaker solution. Therefore, the solubility of the HNO is lower and the hydrophobic expulsion of the HNO is higher in the net structure-maker solution than in the structure-breaker solution.

The effect of net structure-makers and net structure-breakers on solubility of a nonpolar organic compound was evaluated in a study conducted by Gordon and Thorne (1967). The solubility of naphthalene was determined in several inorganic electrolyte solutions over a range of concentrations. Figure 9 illustrates the effects CaCl_2 and NaCl (net structure-makers) solutions and KCl and CsBr (net structure-breakers) solutions have on the solubility of naphthalene. It can be seen that CsBr, a strong net structure-breaker salt, has little effect on decreasing the solubility of naphthalene over that of pure water. The weak net structure-breaker KCl shows slightly less of an effect than the weak net structure-maker solution NaCl, while the stronger net structure-maker solution CaCl_2 shows the most influence on decreasing the solubility of naphthalene. The trends shown in Figure 9 would also be expected to apply to hydrophobic expulsion of naphthalene from solution.

Thermodynamics of Solute and Mineral Surface Interactions

Recent developments in the theory of surface thermodynamics of polar systems (Chaudhury, 1984; van Oss et al., 1987a, 1988) have led to an increased understanding of the surface free energy components of mineral surfaces. Knowledge of the mineral-surface free energy components can be used to describe the interactions between facing mineral surfaces in an aqueous system. This understanding can also be used to evaluate if

Figure 9. Salting out of naphthalene by CaCl_2 , CsBr , KCl , and NaCl (constants and equations used to derive this graph are from Gordon and Thorne, 1967).

interactions between a mineral surface and a solute in an aqueous system will occur and to what degree. Several different interactions can occur simultaneously at a mineral surface. Spontaneous adsorption of a solute by a mineral may occur if the total free energy of interaction between the solute and the mineral surface is negative. This adsorption will take place if it can overcome two other interactions: (1) the interaction between the surface site and other species of the bulk solution (e.g., water and solvated ions); and (2) the interaction between the solute and the bulk solution.

Theory of Surface Free Energy

The current understanding of the total surface free energy (ΔG^{TOT}) of a solid and a liquid can be defined by and equated to the sum of three surface free energy components: (1) “apolar” (LW) surface free energy component (ΔG^{LW}); (2) “polar” (AB) surface free energy component (ΔG^{AB}); and (3) electrostatic (EL) surface free energy component (ΔG^{EL}). This relationship can be written as

$$\Delta G^{\text{TOT}} = \Delta G^{\text{LW}} + \Delta G^{\text{AB}} + \Delta G^{\text{EL}}.$$

The ΔG^{LW} is due to Lifshitz-van der Waals (LW) interactions and represents the electrodynamic contributions to the total surface free energy of a surface (van Oss et al., 1990). Three distinct electrodynamic interactions that make up the ΔG^{LW} are the London-van der Waals (dispersion) interaction, the Keesom dipole-dipole interaction, and the Debye dipole-induced dipole interaction (van Oss et al., 1987a). Of these three, Keesom and Debye interactions are found with molecules that have permanent dipole moments (van Oss et al., 1988). The London interaction is universal and is present in atom-atom interactions as well. Chaudhury (1984) pointed out that, on a macroscopic scale, all three electrodynamic interactions can be described by the ΔG^{LW} term. The ΔG^{LW} term, which reflects the total of these three interactions, is normally considered to represent attractive energies and is overwhelmingly dominated by the London-van der Waals interaction. Because of this dominating interaction, ΔG^{LW} is referred to as the “apolar” component of the surface free energy (see van Oss et al., 1987a, for the development of this rationale).

The ΔG^{AB} or polar interaction energy encompasses the electron-acceptor–electron-donor interactions, or Lewis acid-base (AB) interactions (van Oss et al., 1987a).

and it includes the hydrogen acceptor–donor interactions in aqueous systems. Unlike the apolar Lifshitz-van der Waals interactions, the electron-acceptor–electron-donor or polar interactions are essentially asymmetrical and can only be satisfactorily treated by taking this asymmetry into account (van Oss et al., 1988). In other words the two polar parameters must be known before the ΔG^{AB} component can be described.

The ΔG^{EL} or EL interaction energy is the electrostatic interaction energy. In aqueous systems, most minerals have electrostatic interaction energy because their surfaces have electrical charge. This interaction energy is responsible for the formation of the diffuse double layer of ions that surround the minerals in electrolyte solutions.

For the phyllosilicates, the distribution and magnitude of the three surface free energy components mainly depend on the chemical makeup and crystal structure of the mineral. The amount of isomorphic substitution in the phyllosilicates greatly affects the surface free energy components. Minerals like pyrophyllite and talc have negligible isomorphic substitution, so they are expected to have the lowest total surface interaction energy of the 2:1 phyllosilicates (Giese et al., 1991). As the isomorphic substitution increases, the total surface interaction energy of the phyllosilicate increases (Giese et al., 1991). How this energy is distributed on a surface depends on whether the substituting cations are located in the tetrahedral or octahedral sheet (Sposito, 1984).

Solutes also have varying magnitudes of the three surface free energy components. For HNOs, the EL interaction is negligible because these types of molecules do not possess charges. If the HNOs are nonpolar, they only have the LW interaction energy. Polar molecules have not only the LW interaction energy but also the AB interaction energy.

Surface Free Energy Relationships between Solutes and Minerals

If an HNO solute is nonpolar and if it interacts with a surface, adsorption can be described by

$$\Delta G^{\text{TOT}} = \Delta G^{\text{LW}}.$$

The attractive energy of the LW interactions can be large between the surface and an HNO molecule if they are only short distances apart from each other.

When a polar nonionic substance such as water interacts with a mineral surface, interactions are not only with LW sites, but also with AB sites. This AB interaction is of the hydrogen-bonding type (van Oss et al., 1988). These types of interactions are most conveniently described by the Lewis acid-base (AB) system (van Oss et al., 1987a). The total surface free energy at the solid surface involving polar substances can be written as

$$\Delta G^{\text{TOT}} = \Delta G^{\text{LW}} + \Delta G^{\text{AB}}.$$

The greater the G^{AB} energy component of the mineral, the less effectively an HNO can compete with more polar substances (e.g., water) for adsorption sites at the mineral surface.

The EL interaction is an important component in attracting ionic species adjacent to the solid surface. Besides the component ΔG^{EL} , the ΔG^{AB} component also is significant in attracting hydrated ions from an aqueous solution to a polar solid surface. The polar moment of the water molecule facing away from the ion is attracted to a surface that has an opposing polar moment. The strength of this attraction for the hydrated ion is dependent on the strength and type (either electron acceptor or electron donor) of AB interaction energy. The total surface free energy involving hydrated ionic species adsorbing onto a solid surface can be written as

$$\Delta G^{\text{TOT}} = \Delta G^{\text{LW}} + \Delta G^{\text{AB}} + \Delta G^{\text{EL}}.$$

The concentrated counterion swarm that may develop adjacent to a mineral surface could reduce the adsorption of certain nonionic solutes. Different counterions surrounding a surface may drive the nonionic solutes away from that surface in varying amounts. The mechanism driving the solute away from the surface may be much like that mechanism driving nonpolar molecules from solution, i.e., through hydrophobic expulsion. Hydrophobic expulsion of HNO solutes away from a surface, however, has not been substantiated yet.

Determination of Surface Free Energy Components

The change in surface free energy components ΔG^{LW} and ΔG^{AB} between a solid (S) and liquid (L) can be described as a function of their surface tension apolar component γ^{LW} and their surface tension polar parameters $\gamma^{\oplus}$ and $\gamma^{\ominus}$ (van Oss et al., 1990). The change in the surface free energy between a solid and liquid due to ΔG^{LW} can be expressed as

$$-\Delta G_{SL}^{LW} = 2 \left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} \right),$$

where the γ^{LW} component reflects the contributions from Lifshitz-van der Waals (LW) interaction energies. The change in the surface free energy between a solid and liquid due to ΔG^{AB} can be expressed as

$$-\Delta G_{SL}^{AB} = 2 \left(\sqrt{\gamma_S^{\oplus} \gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus} \gamma_L^{\oplus}} \right).$$

The terms $\gamma^{\oplus}$ and $\gamma^{\ominus}$ are two asymmetric surface tension parameters of the AB surface tension component γ^{AB} that reflects the contribution from the Lewis acid-base (AB)

interaction energy. For a single substance, van Oss et al. (1987a, 1988) defined the relationship between γ^{AB} and its asymmetric parameters as

$$\gamma^{AB} = 2\sqrt{\gamma^{\oplus}\gamma^{\ominus}}.$$

These parameters, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, reflect respectively the electron-acceptor and electron-donor surface tensions of the Lewis acid-base (AB) interactions. The relationship for surface tension component, γ^{LW} , and parameters, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, can be combined to reflect the total surface interaction energies of solid and liquid surfaces:

$$\Delta G^{TOT} = -\Delta G_{SL}^{LW} - \Delta G_{SL}^{AB} = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus}\gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus}\gamma_L^{\oplus}}\right).$$

The theory and derivation of ΔG^{LW} and ΔG^{AB} of a surface interacting with a liquid from surface tension measurements are given in van Oss et al. (1987a, 1987b, 1988, 1990).

Along with recent theoretical developments, experimental techniques have been refined that are necessary for deriving the surface interaction energies of minerals, particularly those of colloidal-sized minerals (van Oss et al., 1987a, 1987b, 1988, 1990; Giese et al., 1991; Costanzo et al., 1990). Using their technique to obtain the surface interaction energies of the minerals, the surface tension values given in mJ/m^2 are derived from measurements of the contact angles (θ) of polar and nonpolar liquids with the mineral surface. The relation between the contact angles and the surface tension components and parameters is given by the extended form of the Young equation (van Oss et al., 1987a, 1987b, 1988):

$$(1 + \cos \theta) \gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus}\gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus}\gamma_L^{\oplus}}\right)$$

where γ_L represents the total surface tension of the liquid. The unknown surface tensions of the solid are obtained by solving a set of simultaneous equations in which the surface tension values ($\gamma_L^\ominus, \gamma_L^\oplus, \gamma_L^{LW}$, and γ_L) for at least two polar liquids and one nonpolar liquid are known. Table 4 lists examples of surface tension values for selected nonpolar and polar liquids.

Several techniques for determining the contact angles of minerals exist. The physical characteristics (i.e., the size and the smoothness of the crystal face) of the mineral determine which procedure is most appropriate. Descriptions of several of these techniques can be found in Janczuk and Bialopiotrowicz (1988), Giese et al. (1991) and van Oss et al. (1992).

Table 4. The values of the surface tension components and parameters for selected liquids, given in mJ/m² (van Oss et al., 1992).

Liquid	γ_L	γ_L^{LW}	$\gamma^\oplus$	$\gamma^\ominus$
<u>Nonpolar Molecules</u>				
Heptane	20.1	20.1	0.0	0.0
Octane	21.6	21.6	0.0	0.0
Decane	23.8	23.8	0.0	0.0
<u>Polar Molecules</u>				
Water	72.8	21.8	25.5	25.5
Ethylene glycol	48.0	29.0	1.92	47.0
Formamide	58.0	39.0	2.28	39.6
Glycerol	64.0	34.0	3.92	57.4

When reviewing contact angle data, a few points should be kept in mind. If an essentially nonpolar liquid contacts a hydrophilic surface, the contact angle will be large. If the same nonpolar liquid contacts a hydrophobic surface, the contact angle will be much smaller and spreading of the liquid is likely to occur. A polar liquid will behave just the opposite of the nonpolar liquid.

The ΔG^{EL} of a surface with water can be calculated (in theory) from its zeta potential (ζ). This is the potential at the plane that separates the particle and its bound water molecules from the freely moving water molecules of the solution, and this plane is referred to as the slipping plane. A complete explanation of the steps necessary to determine ΔG^{EL} is given by Overbeek and Wiersema (1967), van Oss (1975), and van Oss et al. (1990).

Effects of LW and AB Interaction Energies

Surface thermodynamic theory allows a satisfactory means of correlating (nonionic) solute/solvent interactions on phyllosilicate surfaces (van Oss and Giese, 1993) with the surface free energy component ΔG_{SL}^{LW} and the parameters of the surface free energy component ΔG_{SL}^{AB} . As already mentioned, the ΔG_{SL}^{EL} does not play a direct role in adsorption of HNOs by a solid; however, this component may indirectly affect adsorption.

Phyllosilicates can interact with both polar and nonpolar molecules at their surfaces. The relative affinity these surfaces have for water molecules and HNO molecules depends on the degree to which the mineral is hydrophobic (or hydrophilic). The contact angles with water listed in Table 5 reflect the hydrophobicity of various phyllosilicates and one metal hydroxide.

Table 5. Values for the contact angle (θ) with water, the surface tension component, γ^{LW} , and the parameters, $\gamma^{\oplus}$ and $\gamma^{\ominus}$, derived from the Young equation for the selected minerals.

Mineral Type	θ (degree)	γ^{LW} (mJ/m ²)	$\gamma^{\oplus}$ (mJ/m ²)	$\gamma^{\ominus}$ (mJ/m ²)
Talc ¹	80.4	31.5	2.4	2.7
Pyrophyllite ¹	79.2	34.4	1.7	3.2
Illite ^{2, a, c}	70.7	35.1	0.0	16.9
Kaolinite ^{3, a}	55	35	<0.1	35
Montmorillonite ^{2, a}	39.0	41.5	0.7	36.2
Muscovite ^{2, a}	3.0	36.8	0.05	61.9
Vermiculite ^{4, b}	15.0	47.2	0.5	47.7
Gibbsite ^{5, a, d}	49.8	29.6	0.2	40.8

^a Contact angle was calculated using surface tension data from the reference and the extended form of the Young equation (van Oss et al., 1987a, 1987b, 1988).

^b Only $\gamma_L (1 + \cos \theta) = 144 \text{ mJ/m}^2$, γ^{LW} , and the contact angle with water were given in Schrader and Yariv (1990). As a first approximation it was assumed that $\gamma^{\oplus}$ value of vermiculite was 0.5 mJ/m^2 based on the recommendations of van Oss et al. (1990) and Norris (1993). The $\gamma^{\ominus}$ was calculated from the extended form of the Young equation.

^c The mineral was assumed not to have been treated to remove the natural organic matter that often is associated with it.

^d The mineral was reported as a commercial grade $\text{Al}(\text{OH})_3$. The commercial grade $\text{Al}(\text{OH})_3$ used in this thesis study was determined to be gibbsite. The sample used by Li et al. (1994) was assumed to be the same type of mineral.

¹ Giese et al., 1991.

² Li et al., 1991.

³ Murphy et al., 1991.

⁴ Schrader and Yariv, 1990.

⁵ Li et al., 1994.

In thermodynamic terms, the values of the $\gamma^{\ominus}$ parameter listed in Table 5 are the primary indicator of the relative hydrophobicity or hydrophilicity of the minerals. The reason for this is that the $\gamma^{\ominus}$ parameter represents the strength of the electron-donor or Lewis-base surface interaction energy that can form hydrogen bonds at the basal surface with water and hydrated cations. Because the basal surface represents most of the surface area of the phyllosilicates, this parameter reflects the majority of the polar interaction energy of the mineral, and therefore, this parameter best indicates the hydrophobicity or hydrophilicity of the phyllosilicates. In comparison, the $\gamma^{\oplus}$ parameter is much smaller (Table 5). These smaller values occur because the $\gamma^{\oplus}$ parameter represents the electron-acceptor or Lewis acid surface interaction energy of the limited surface area of the phyllosilicates' edges. The LW component vary only slightly among most of the phyllosilicates as reflected by their γ^{LW} values (Table 5). This slight variability does not permit using γ^{LW} values to help predict the relative hydrophobicity or hydrophilicity of the phyllosilicates.

The difference in the $\gamma^{\ominus}$ parameters among the phyllosilicates listed in Table 5 reflects the varying amount of surface charge created by isomorphous substitution. Pyrophyllite and talc have the smallest $\gamma^{\ominus}$ value because of their limited tetrahedral and octahedral substitutions (Schrader and Yariv, 1990). The small $\gamma^{\ominus}$ values suggest that the basal oxygen molecules are nearly neutral and are not favorable for forming hydrogen bonds. The basal oxygen molecules, therefore, should be weak Lewis bases with the basicity coming from the lone pair of electrons, which are directed away from the basal surfaces (Giese et al., 1991). This type of surface is highly hydrophobic and is expected to adsorb more of an HNO compared to the surfaces of other phyllosilicates. In comparison, montmorillonite has isomorphous substitutions in both of its tetrahedral sheets and in its octahedral sheet (Table 2). The increased isomorphous substitution within the 2:1

layers of montmorillonite substantially increases the electron-donating properties of this mineral. This increase is reflected in the larger $\gamma^{\ominus}$ value for montmorillonite compared to that of pyrophyllite and talc (Table 5). Montmorillonite would be expected to adsorb less HNO than the pyrophyllite and talc because of its stronger Lewis base strength. The increased Lewis base strength of montmorillonite produces enhanced hydrogen bonds with water molecules and hydrated cations, and these molecules occupy space at and near the surface of the mineral, limiting HNO access to the surface.

The van der Waals energies, represented by the γ^{LW} values (Table 5), may contribute to attracting HNO molecules onto the phyllosilicate surfaces. These energies also can attract water molecules to the surface, leading to a competition between HNOs and water molecules for sites on the surface. The γ^{LW} values for water and for most HNOs are essentially the same (21.8 mJ/m²; van Oss and Good, 1991). Because water and HNOs can have similar γ^{LW} values, they are expected to have similar abilities in competing for the LW sites.

Effects of EL Interaction Energy and Cation Exchange

According to Voice and Weber (1983), the EL component does not need to be examined when considering adsorption of hydrophobic solutes by soils and sediments. Presumably, this is because of the nonionic nature of an HNO molecule. This is correct when considering a direct relationship between EL forces and HNOs, but, when looking at indirect relationships, this statement is not necessarily true. Although the electrostatic interactions do not directly contribute to HNO adsorption, they do influence the adsorption of hydrophilic inorganic (and hydrophobic organic) cations. In turn, exchanging different cations at phyllosilicate mineral surfaces has shown, in limited

studies (Janczuk et al., 1990a, 1990b; Norris et al., 1993), that the surface free energies of LW interactions and AB interactions of phyllosilicate minerals can be altered depending on which cation is present.

Norris et al. (1993) found that when the surface of synthetic Laponite RD was exchanged with nine different cations, $\gamma^{\oplus}$ and γ^{LW} varied slightly (1.4 to 2.1 mJ/m², and 42 to 44 mJ/m², respectively) while $\gamma^{\ominus}$ varied to a greater degree (29 to 37 mJ/m²). The $\gamma^{\ominus}$ for the Na⁺, Ca²⁺, and Mg²⁺ (major groundwater cations) varied over a much smaller range (29.6 to 31.6 mJ/m²), indicating that, while these cations affect the surface characteristics of the mineral that influence adsorption of HNO₃, they do so approximately equally.

Effects of Organic Carbon

Organic coatings on minerals can modify certain surface interaction energies of the mineral. In a study by Norris et al. (1992), ten montmorillonite samples were coated with different primary *n*-alkylammonium cations, each having a different number of carbon atoms (C₆ to C₁₅) in the alkyl chain. An eleventh sample was coated with the inorganic cation ammonium (C = 0). They found that the $\gamma^{\ominus}$ of montmorillonite was much lower when the organic cations were adsorbed than when NH₄⁺ was adsorbed (Fig. 10). Except for the NH₄⁺, and the C₁₀ and C₁₅ alkylammonium treated montmorillonite, a linear relationship between Lewis basicity and the number of carbon atoms in the alkyl chain was observed. The Lewis base strength decreased as alkyl chain length of the compound covering the basal surface increased (Norris et al., 1992). The γ^{LW} and $\gamma^{\oplus}$ were not significantly affected by the adsorption of these organic cations. The results of this study indicates that organic coatings on phyllosilicate surfaces serve to reduce the Lewis base strength which in turn would increase adsorption of HNO₃.

Figure 10. The variation in electron-donor parameter (γ^0) with increasing the number of carbon atoms in the *n*-alkylammonium cations covering the surface of SWy-1 montmorillonite (data from Norris et al., 1992). The straight line was fitted without the data points for C₀, C₁₀, and C₁₅.

Determination of Sorption

The extent of sorption of a chemical by sediments or soils is measured by equilibrating aqueous solutions containing different concentrations of the test chemical with a known quantity of sediment or soil. The most common procedure used to measure sorption uptake of a solute onto a solid phase is the short-term batch sorption method. This method involves introducing a known quantity of solute to a known quantity of sediment or soil and aqueous solution in a closed system. The mixture is shaken for a predetermined time at a constant temperature. The period necessary to attain equilibrium usually is determined by preliminary rate experiments. Once equilibrium is reached, the

distribution of the chemical between the water phase (C_w) and the solid phase (C_s) is quantitatively measured by a suitable analytical method. Then, sorption constants for each particular concentration are calculated by using the appropriate empirical equation, such as the linear, Langmuir, or Freundlich isotherm (Drever, 1988). Finally the isotherm is fitted to the sorption data using linear or non-linear least squares methods. The term “isotherm” is applied to the relationships because the experiments are carried out at a constant temperature.

The widely used linear isotherm empirical equation is derived from the Freundlich isotherm equation (Dragun, 1988b):

$$X/m = C_s = KC_w^{1/n}$$

where

- X = the mass of chemical adsorbed from a given volume of solution (μg).
- m = the mass of solid adsorbent (g),
- C_s = the equilibrium concentration of the chemical in the solid phase ($\mu\text{g/g}$),
- C_w = the equilibrium concentration in the liquid phase ($\mu\text{g/mL}$),
- K = equilibrium constant (mL/g), and
- $1/n$ = an empirical constant (unitless).

The terms K and $1/n$ are empirical constants characteristic of the particular compound and solid adsorbent where K , the Freundlich sorption constant, is indicative of the strength of the adsorption, and $1/n$ describes non-linearity.

The linear portion of the isotherm is described by the Freundlich equation when the exponential term ($1/n$) is equal to unity and the reaction is reversible. This yields the linear isotherm equation:

$$X/m = C_s = K_d C_w$$

where K_d (the distribution coefficient) is the sorption constant. If the isotherm is linear and reversible, the isotherm is uniquely defined by the distribution coefficient, and K_d is equal to the slope of the isotherm. Schwarzenbach and Westall (1981) have reported that a linear isotherm method can be used to describe sorption of HNOs by natural sediments.

The sorption of many, if not most, neutral organic compounds on soils and sediments produces linear isotherms up to 60% to 80% of their solubility in aqueous solution (Chiou et al., 1979; Karickhoff et al., 1979; Hassett et al., 1980). At concentrations above 60% to 80% of the solubility, the amount apparently sorbed increases rapidly, whereas the equilibrium concentration in solution of the sorbing species does not increase or increases slowly (Hassett and Banwart, 1989). This causes the isotherms to turn upwards sharply and has been explained by either the formation of a discrete organic phase or the use of techniques that overestimate adsorption (Hassett and Banwart, 1989).

METHODS

Overview

The major emphasis in this study was to evaluate the TCE sorptive capacities of twelve minerals. Eight of these minerals were from the phyllosilicate class and the remaining four minerals were from the oxide class. To evaluate the sorptive capacities of these minerals, a modified short-term batch sorption method based on scintillation counting of ^{14}C -labeled TCE was used. Rate experiments were conducted first to establish the time required for TCE sorption to reach equilibrium between the solution and the mineral/solution interface. Sorption experiments were conducted in NaCl and CaCl_2 at 0.001 and 1.0 N concentrations to study the effects that differing electrolytes and concentrations have on sorption. For each mineral equilibrated in each of the electrolyte solutions, seven sorption experiments were conducted. Each experiment represented a different initial TCE concentration. Initial concentrations ranged between 50 $\mu\text{g/L}$ and 1000 $\mu\text{g/L}$. The data from these seven experiments were used to plot isotherms. From the plotted isotherms, distribution coefficients were calculated.

Minerals

Sample Acquisition

Table 6 lists the minerals used in this study, the locations from which they were collected, and the vendors who supplied them. The selected phyllosilicate minerals were chosen so that a full spectrum of hydrophobic to hydrophilic surfaces from this class of minerals could be assessed. Another objective of the mineral selection was to include minerals that commonly are found in sediment and soil. The common minerals from the phyllosilicate class are illite, kaolinite, montmorillonite and vermiculite. The four selected oxides also can be ubiquitous in many natural systems.

Table 6. List of minerals studied and their sources.

Mineral Type	Vendor	Mineral Location
Talc	WNSE ¹	Balmat, New York, U.S.A.
Pyrophyllite	WNSE	Robbins, North Carolina, U.S.A.
Kaolinite (well-ordered)	CMSSCMR ²	Washington County, Georgia, U.S.A.
Illite (Gray Shale)	WNSE	Fifthian, Illinois, U.S.A.
Montmorillonite	CMSSCMR	Crook County, Wyoming, U.S.A.
Vermiculite	MRC ³	Palabora Open Pit, Phalaborwa, Transvaal, Republic of South Africa
Muscovite	MRC	Louis Ranch, Custer, Pennington County, South Dakota, U.S.A.
Margarite	MRC	Chester, Massachusetts, U.S.A.
Hematite (Kidney Ore)	WNSE	Cleator Moor, Cumberland, England
Goethite	WNSE	Biwabik, Minnesota, U.S.A.
Pyrolusite	WNSE	Casa Grande, Arizona, U.S.A.
Gibbsite (synthetic)	J.T.B. ⁴	not applicable

¹ Ward's Natural Science Establishment, Inc., Rochester, New York, U.S.A.

² Clay Minerals Society Source Clay Minerals Repository, Department of Geology, University of Missouri, Columbia, Missouri, U.S.A.

³ Mineralogical Research Company, San Jose, California, U.S.A.

⁴ J.T. Baker, Inc., Phillipsburg, New Jersey, U.S.A.

The minerals were received in various forms. Talc, pyrophyllite, and illite were received in their natural aggregate state. Montmorillonite, kaolinite, and gibbsite came in powdered form. Margarite, muscovite, and vermiculite were obtained as monocrystalline sheets. Goethite, hematite, and pyrolusite were obtained in rock form. A synthetically generated gibbsite in powder form was used because of the large amount of inherent impurities associated with a natural specimen of this mineral.

Mineral Preparation

Processing the Clay Minerals Talc, pyrophyllite, kaolinite, montmorillonite, and illite were processed similarly to obtain the final size fraction and to remove associated organic substances. Talc, pyrophyllite, and illite, which were in aggregate form, were disaggregated using a hand mortar and pestle. All the clay minerals were then ground dry using an automatic mortar and pestle. During each grinding, approximately three grams of a sample were ground at a rate of 150 revolutions per minute (rpm) for 10 minutes. Pérez-Rodríguez et al. (1988) recommended not to grind samples for longer periods because of potential changes in the structure of the minerals.

Following grinding, the clay minerals were treated to remove, to the extent possible, the natural organic matter associated with these samples. The treatment method adopted for rapid routine destruction of organic matter was developed by Anderson (1963). This method involved using sodium hypochlorite (NaOCl, bleach) to destroy the organic matter through oxidation. Hydrogen peroxide (H_2O_2) has also been commonly used for destruction of organic matter associated with clays and oxides. Compared with the hydrogen peroxide method, the NaOCl method had been shown to be more effective in destroying organic matter and less destructive to oxides or crystalline clay components (Anderson, 1963; Lavkulich and Wiens, 1970).

The sodium hypochlorite treatment procedure involved placing 10 g of mineral sample in 250-mL centrifuge tubes and then adding 40 mL of a prepared NaOCl solution. Immediately before its use, the NaOCl solution was prepared using a stock bleach solution consisting of a minimum of 6% available chlorine adjusted to pH 9.5 with HCl. The tubes were placed in a boiling water bath for 15 minutes with occasional stirring of the mineral contents. The tubes were centrifuged until a clear supernatant was obtained, which was then decanted. This treatment was repeated three more times for the contents of each tube.

Following this treatment, the samples were fractionated to obtain the desired particle sizes. An upper particle size limit was selected that would give a reasonable yield of sample product during the separation process, while it would provide a reasonable amount of specific surface area and diminish the inorganic particle impurities commonly associated with these natural samples. For illite, kaolinite, and montmorillonite the selected range of particle sizes was finer than 2 μm . For pyrophyllite and talc, the particle size range selected for these minerals was finer than 10 μm . A particle-size range of < 2 μm for these two minerals was desired, but product yield below 2 μm was insignificant. Further grinding would have been required to obtain enough sample that was smaller than 2 μm . Further grinding of these minerals was not attempted because additional grinding could have significantly altered the original crystallinity of these samples.

Particle size-fractionization was accomplished by using the centrifugation method described by Jackson (1975). A 50-mL aliquot of 2% sodium carbonate solution with a pH of 9.5 was added to 10 g of sample in the 250-mL centrifuge tubes. To promote flocculation, the samples were stirred and heated in the boiling water bath. This was followed by centrifugation and then decantation of the clear supernatant. This process

was repeated for a total of three times. After the final decantation of the supernatant, the sedimented samples were shaken for 12 hours with double distilled Milli-Q water. Next the samples were ultrasonically dispersed and centrifuged to obtain the desired size fraction. The duration and centrifugal-G force necessary to obtain the <2- μ m and 10- μ m fraction at 20°C was calculated from equations found in Jackson (1975). After centrifugation, the suspension of the desired fractional size was decanted into another 250-mL centrifugation tube. The remaining sample was ultrasonically resuspended in double distilled Milli-Q water, recentrifuged, and the suspended minerals again decanted into a separate 250-mL centrifugation tube. This process was done two more times, after which the recovery of any suspended fraction was not enough to justify continuing the processing.

Processing of the Micas, Oxides, and Vermiculite The micas, oxides, and vermiculite were processed differently from the clay minerals. The oxides, which were received in rock-form, were crushed using a hydraulic press to a size of ≈ 2.5 cm in length. Using a sample crusher (Model 150, Progressive Exploration Products, Reno/Stead, Nevada), the samples were further crushed until they could pass through a sieve opening of 6.35 mm. For the micas and vermiculite, a razor blade was used to separate the sheets and to cut these sheets into pieces smaller than 2.5 cm. These pieces were placed in a Warn industrial-grade blender and were chopped until the samples could pass through a sieve opening of 6.35 mm. At this stage, the micas, oxides, and vermiculite were processed with a pulverizer unit (Model 100, Progressive Exploration Products, Reno/Stead, Nevada) with a sample product size controller. The controller was set to grind the samples to a final size that would pass through a sieve opening of 74 μ m. The final step in arriving at the fraction size required for experimentation was accomplished through using a standard dry-sieving technique (ASTM, 1985).

Samples were placed on a series of U.S. Standard Mesh (ASTM E-11 specification) brass sieves with the final sieve having a screen opening of 30 μm (custom-made). The samples were vibrated with Ro-Tap equipment for 15 minutes. After sieving, the coarser fractions were reground and then resieved. A smaller size was wanted for these samples, but ultimately it was decided after preliminary processing that it was not feasible. The micas, oxides, and vermiculite were not treated to remove organic matter because these minerals were not anticipated to have significant quantities of organic matter associated with them.

Cation Exchange Processing Following particle-size fractionation, all the samples were processed to exchange any unwanted cations on the mineral surface with either Na^+ or Ca^{2+} . Using 250-mL centrifuge tubes, ≈ 200 mL of either a 1.0 N NaCl or CaCl_2 solution was added to 10 g of each sample. The samples were ultrasonically dispersed in their solutions and then centrifuged to settle out the mineral phase. After centrifugation, the supernatant was decanted. This procedure of saturating the samples with the selected electrolyte was completed three times.

Following electrolyte saturation, the minerals were rinsed with double distilled Milli-Q water to remove the excess Na^+ or Ca^{2+} and Cl^- . Most of the minerals were rinsed by adding double distilled Milli-Q water, ultrasonically resuspending the mineral, centrifuging, and decanting the supernatant. The cycles of rinsing continued until the specific conductance of the supernatant became stable, which suggested the removal of excess Na^+ or Ca^{2+} and Cl^- .

Removal of the excess electrolyte from the illite and montmorillonite samples required different processing than that for the other minerals. This is because these two minerals would not completely settle out during the centrifugation step. Without complete settling of these two minerals, sample losses would have been significant during

decantation. To remove the excess electrolyte, the two mineral samples were placed in dialysis tubes. The dialysis tubes were then submerged into containers filled with distilled water. Periodically, the solutions in the containers were replaced with new distilled water. The replacement with distilled water continued until the specific conductance of the solutions in the containers became stable.

To obtain the final powdered sample for the sorption experiments, all the samples were freeze-dried after the rinsing process. A container with a glass filter at its bottom was filled with activated carbon and was then attached to the mouth of the 250-mL centrifuge tubes that contained the samples. The activated carbon allowed water vapor to escape from the tubes but prevented potential organic contamination from the freeze-dryer vacuum pump from entering the 250-mL centrifuge tubes. Once dried, the samples were stored in a sealed container for future use.

Sample Characterization

After processing, various properties of the minerals were analyzed. The Particle Characterization Laboratory at Lawrence Livermore National Laboratory (LLNL), Livermore, California determined the specific surface areas of the minerals. To determine the specific surface area, LLNL used a BET approach with nitrogen gas as the adsorptive compound that was originally developed by Brunauer, Emmett, and Tell (1938). Fruit Growers Laboratory, Inc., Stockton, California evaluated the cation ion exchange capacities (CECs) and the organic carbon content (*oc*) of the minerals. They used the ammonium acetate procedure (Hesse, 1971) to evaluate the CECs of the minerals and the wet digestion procedure of Walkley-Black (Hesse, 1971) to evaluate the *oc* of the minerals. The sample identified in this study as gibbsite was received under the chemical name of $\text{Al}(\text{OH})_3$. To verify that this synthetically generated sample was gibbsite, a sample was analyzed by X-ray diffraction. X-ray diffraction analysis confirmed that the sample was gibbsite.

Sorption Studies

The intent of the sorption studies was to determine apparent equilibrium between the solid phase and the liquid phase over a range of concentrations. The term “apparent equilibrium” is used with a conditional understanding that true equilibrium is not presumed. The time at which apparent equilibrium was achieved was determined by conducting rate experiments. Rate experiments determined the sorption as a function of time. Distribution coefficients obtained for apparent equilibrium and as a function of time were determined through a short-term batch sorption method utilizing scintillation counting of ^{14}C -labeled TCE for the analytical method. The batch sorption method used in this study followed guidelines set forth by the EPA (1982) and ASTM (1984), but these methods were modified to suit the special requirements of this study. The batch sorption method was selected because it contains many desirable features. First, adsorption results are highly reproducible. The method provides excellent quantitative data readily amenable to statistical analyses. This method permitted several sets of multiple replicate samples to be run simultaneously for each particular mineral. Also, it has modest requirements for chemicals, mineral quantities, laboratory space, and equipment.

Sorption Experiment Protocol

Glassware Sorption experiments were conducted with 9-mL Pyrex centrifuge tubes with screw on solid caps and Teflon-silicon septa with foil liners. Each experiment required preparation of several “sets” of these tubes. Each set consisted of eight test tubes of which four were assigned to the “samples”, and the other four were assigned to the “controls”. Samples were tubes that contained the desired mineral and aqueous TCE solution. The controls were tubes that contained only the aqueous TCE solution. Except for the omission of the mineral, the controls were prepared and handled in the same manner as the samples.

The tubes, caps, aluminum foil liners, and septa were scrubbed with a laboratory detergent, rinsed thoroughly with distilled water and finally rinsed with methanol. The glassware was then oven dried at 100°C. The caps and septa were oven dried at 50°C: higher temperatures could result in potential warping. Once the caps and septa were dry, two laboratory-grade aluminum foil liners were placed on top of the Teflon liner of each septum so that the foil would be in contact with the aqueous solution. The test tube threads were wrapped with Teflon tape to prevent the caps from loosening during the mixing process. All other miscellaneous glassware was scrubbed with a laboratory detergent, rinsed thoroughly with distilled water, and oven dried at 100 °C. All syringes were rinsed with methanol and air dried between uses.

Electrolyte Solutions Solutions of 0.001 N CaCl_2 , 1.0 N CaCl_2 , 0.001 N NaCl, and 1.0 N NaCl were prepared for the sorption experiments. The salts were from J.T. Baker Chemical Co., Phillipsburg, New Jersey and of reagent grade. The water used to prepare the electrolyte solutions was relatively free of organic and inorganic constituents. It was double-distilled and then processed through a Milli-Q water purification system (Millipore Corporation, Bedford, MA). The purification system had an activated carbon filter plus a cation and anion resin exchanger. BC Analytical, Emeryville, California analyzed this processed water. They reported that the water contained 0.5 mg/L of total organic carbon and less than detection limits of inorganic constituents of interest. The electrolyte solutions were made just before their use. After the electrolyte solution was made, its pH was checked and, when needed, was adjusted to 7.0 with HCl or NaOH.

Addition and Preparation of the Minerals Depending on the mineral, approximately 0.25 g or 0.50 g of sample was added to the sample tubes. The 0.25 g quantity was used for talc, pyrophyllite, kaolinite, montmorillonite, and illite. This sample amount gave a ratio of mineral to aqueous solution of 2.78% (g/g). Increasing this percentage generally resulted in insufficient mineral dispersion (too viscous) during the mixing process and led to incomplete exposure of all the mineral particles to the TCE. The 0.50 g quantity was used for vermiculite, muscovite, and margarite, and the oxides. For this quantity of sample, a ratio of mineral to aqueous solution of 5.56% (g/g) was obtained. This increased ratio was necessary, because of the anticipated low adsorptive capacities of these minerals. Unlike the clay minerals, these minerals did not exhibit the same dispersion problems at the increased ratio.

The precise determination of mineral amounts added to the tubes was accomplished through mass differences. Masses were measured to within 0.001 g. On every day that these weighing measurements were done, the free water content of each mineral type used that day were determined. This step was done to reduce weighing errors introduced by variation in the moisture content of the sample resulting from fluctuations in humidity on different days. The determination of the free water content was accomplished by weighing samples placed in weighing boats and then placing them in an oven at 55°C for 24 hours. After 24 hours, the samples were placed in a desiccator and allowed to cool to an ambient temperature. This was followed by reweighing the samples and calculating the difference, if any, between the initial weighing and the final weighing. The difference was subtracted from the sorption experiment samples giving their dry weights. This step ensured that, when comparing results from experiments

prepared on different days, the weight difference due to fluctuating free water content was compensated for. Because the weight of the samples is used to calculate K_d , this compensation provided a more accurate comparison of K_d results for a particular mineral.

Before starting a sorption experiment, the samples in the centrifuge tubes were saturated and mixed with the desired experimental electrolyte solution. This step was done to assure that the samples would be fully dispersed during the sorption experiments. It was found in preliminary experiments that samples would remain agglomerated and not disperse properly during the sorption experiment without this step. This step also insured that the minerals were in equilibrium with the selected electrolyte solution. The procedure used in this step was to add ≈ 5 mL electrolyte solution to the sample tubes. The minerals were then ultrasonically dispersed and mixed with a vortex mixer. Once mixed, the test and control tubes were filled with the electrolyte solution to a level four millimeters from their tops and capped. Finally, the samples were agitated for at least 24 hours before the sorption experiments.

Preparation and Addition of the Solute To analyze the concentrations of TCE in the control and samples, a scintillation counting technique was used. ^{14}C -labeled TCE, which was necessary for scintillation counting, was acquired from Sigma Chemical Company, St. Louis, Missouri. The radiolabeled chemical was reported by the manufacturer to be more than 98% pure with a specific activity of 4.1 mCi/mmol. Unlabeled TCE was obtained as an analytical reagent grade solute from Aldrich Chemical Company, Milwaukee, Wisconsin.

Standards used for spiking TCE into samples and controls were prepared by adding an aliquot of ^{14}C -labeled TCE to a 100 mg/L solution of unlabeled TCE that was previously prepared. Enough of the ^{14}C -labeled TCE was added to provide scintillation

counts of at least 3200 counts per minute. This count rate was chosen to insure sufficient radiolabeled material for precise counting of 1-mL aliquot samples taken from the sample and control tubes after equilibration. The standard was stored in a 50-mL glass vial capped with an aluminum crimp cap containing a Teflon-silicone septum. When not in use the standard was stored in the dark at 4°C. After each use, the glass vial was recapped with a new septum. The radioactivity of the standard was checked prior to each experiment and compared to the initial reading. If losses were > 5%, a new standard was prepared.

An aliquot of the standard solution was added to each sample and control tube by means of an adjustable digital micrometer syringe (Hamilton Co., Reno, NV) designed to inject precise (increments of 0.00001 mL) quantities of solution, repetitively. To obtain a desired sample or control TCE concentration, a predetermined aliquot from the standard was extracted. These desired concentrations ranged from 50 to 1000 µg/L. The standard was injected below the surface of the sample or control solution to prevent TCE from volatilizing and escaping. Immediately after injection, additional electrolyte solution was added to eliminate the remaining head space, and then the test tube was capped. Preliminary blank experiments showed that less TCE was lost when no head space was present in the tubes. After spiking and sealing the test tubes, they were hand shaken until the minerals were fully dispersed. They were then weighed before proceeding on to the next step.

Equilibration Conditions and Solid Separation Equilibration conditions were designed to provide the maximum amount of contact between the mineral particles and the TCE solution. The sample and control tubes were placed horizontally into a temperature-controlled rotary shaking device. A concern was that insufficient mixing may occur during the equilibration period because of the lack of head space in the test tubes. Through visual inspections, it was determined that adequate mixing was occurring.

During mixing, the samples were kept in the dark at a constant temperature of $20\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. The mixing time ranged from minutes to days depending on whether rate of uptake or equilibrium experiments were being conducted. At the conclusion of the mixing period, the sample and control tubes were centrifuged at 2500 rpm (2800 G's) for one hour at a temperature of $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ to settle out the solid fraction and obtain a clear supernatant. When illite and montmorillonite were equilibrated in the 0.001 N solutions, a clear supernatant was not achievable due to dispersion effects. A minute fraction of illite and montmorillonite remained in suspension near the top of the test tube that gave the supernatant translucence (turbidity readings as high as 140 Nephelometric Turbidity Units [NTU]).

Aqueous-phase Sampling and Analysis After centrifugation, the aqueous phase of the sample and control tubes was sampled for scintillation analysis. This procedure consisted of extracting two 1-mL aliquots of supernatant solution from each test tube with a 2-mL glass syringe (B-D Yale, Becton-Dickerson and Co., Rutherford, NJ). The first 1-mL aliquot was used to rinse the interior surfaces of the syringe and the needle. The second 1-mL aliquot was injected into a preweighed ($\pm 0.001\text{ g}$) scintillation vial containing 15 mL of Insta-Gel scintillation cocktail. After injecting the samples into the scintillation vials, the vials were shaken and then reweighed. The quantity of the sample in the scintillation vial was determined by weight difference.

The samples in the vials were analyzed by ^{14}C counting with a Packard Tricarb Model 4530 scintillation counter (Packard Instrument Co.). Each sample was counted twice for 10 minutes. Measured counts per minute were recorded and were later converted to disintegrations per minute (dpm) by the external standard method. All counts were corrected for background radiation and quenching effects.

Data Reduction To achieve the final sorption data, several steps were taken to reduce the experimental measurements. The various experimental measurements were reduced to two values. One of these values was C_w ($\mu\text{g/mL}$), which represents the TCE concentration in the aqueous phase. The other value was C_s ($\mu\text{g/g}$), which represents the sorbed concentration of TCE. From these values, the distribution coefficient (K_d) was derived.

As part of the data reduction, the dpm values were normalized (dpm^n) to obtain expected dpm values if exactly 9 mL of aqueous solution was in the test tube and if exactly 1 mL of supernatant sample was extracted from the test tube for analysis. Converting dpm to dpm^n allowed more accurate comparisons among the samples and among the controls. It also allowed more accurate comparisons among K_d results. The equations used to convert dpm to dpm^n are

$$\text{dpm}_c^n = (\text{dpm}_c) \left(9 \text{ g} / \text{g}_c^w \right)^{-1} \left(\text{g}_c^s / 1 \text{ g} \right)^{-1}$$

and

$$\text{dpm}_s^n = (\text{dpm}_s) \left(9 \text{ g} / \text{g}_s^w \right)^{-1} \left(\text{g}_s^s / 1 \text{ g} \right)^{-1}$$

where

dpm_c^n = the normalized disintegration per minute of the supernatant from the control,

dpm_s^n = the normalized disintegration per minute of the supernatant from the sample,

dpm_c = the disintegration per minute of the supernatant from the control,

dpm_s = the disintegration per minute of the supernatant from the sample,

g_c^s = the mass of the control supernatant analyzed,

g_c^w = the mass of the aqueous solution in the control test tube,

(continued)

g_s^w = the mass of the aqueous solution in the sample test tube.

g_s^s = the mass of the sample supernatant analyzed,

9 g = the ideal mass of the aqueous solution in the sample or control tube, and

1 g = the ideal mass of the extractant analyzed.

The dpm_c^n and dpm_s^n values were then used with other variables to calculate C_s and C_w . The sorbed concentration, C_s , was calculated using

$$C_s = \left(\frac{dpm_c^n - dpm_s^n}{dpm_c^n} \right) \left(\frac{(\mu g / mL)(mL / g)(9 g)}{g_s} \right)$$

where

$\mu g / mL$ = the initial TCE concentration of the aqueous solution,

g_s = the mass of the mineral in the sample test tube,

9 g = the ideal mass of the aqueous solution in the sample test tube, and

mL / g = the inverse density of the aqueous solution.

The aqueous concentration, C_w , was calculated from

$$C_w = \left(1 - \frac{dpm_c^n - dpm_s^n}{dpm_c^n} \right) (\mu g / mL).$$

Quantification of System Losses and Mass Balance Sorption data derived from the technique described depend on measuring differences in TCE concentrations between the controls and the samples. The concentration of the control represents the total concentration in the system and theoretically accounts for any system losses. Losses may

include adsorption onto the glass or septum, leakage from the test tube, and volatilization losses during the injection and extraction steps. To find out if losses due to these factors were excessive, a blank loss experiment was run before the sorption experiment program began. One-milliliter aliquots from a 500 $\mu\text{g/L}$ TCE standard were injected directly into scintillation vials and immediately counted. Twenty test tubes containing 1.0 N NaCl solution were also injected with 1-mL aliquots from the TCE standard. These test tubes were treated in the same manner as those in the sorption experiments. The results of the blank loss experiment indicated that $94\% \pm 2\%$ of the TCE was recovered after 24 hours.

A concern that developed during experimentation with illite and montmorillonite equilibrated in 0.001 N electrolyte solutions was that minute amounts of suspended solid were still present after centrifugation. The suspended solid may lead to the K_d values for these minerals being underestimated, because of the minute withdrawal of suspended solid when the 1 mL was extracted from the sample tubes for scintillation counting. The counts would be higher in this situation than if no suspended solid were present in the 1-mL aliquot, and this could result in potentially lower K_d values.

To determine the approximate amount of suspended solid withdrawn in the 1-mL aliquot, test tubes containing illite and montmorillonite and the 0.001 N electrolyte solutions were treated in the same manner as those used in the sorption experiments. The only exception was that the test tubes were not injected with radiolabeled TCE solution. One-milliliter aliquots were removed from the test tubes, dispensed into a preweighed weighing boat, and then placed in an oven. After cooling in a dessicator, the residual mass of the mineral and salt was determined. The concentration of the mineral solid extracted in the 1-mL aliquot ranged from non-measurable (<0.001 g/mL) to 0.002 g/mL. This resulted in a maximum error of 1% in the K_d values for these two minerals if equilibrated in the 0.001 N NaCl or CaCl_2 solution. Attempts were initially made to use a filtration method

to remove the suspended clay particles from the 1-mL aliquot that was used for the scintillation counting. These attempts were unsuccessful due to the clay particles clogging the 0.45 μm silver filter membrane before the full 1-mL aliquot could be extracted.

Rate Experiments

Rate experiments were conducted with talc and montmorillonite to learn the time required for TCE to reach apparent equilibrium between these solids and the aqueous phase. Talc was selected because it was speculated that it would have a high adsorptive capacity resulting in potentially longer equilibration times than a mineral with lesser adsorptive capacity. Montmorillonite was chosen because of its swelling characteristic in certain aqueous solutions (e.g., in low molar concentrations of NaCl solution) which may result in substantial increases in interlayer surface area and in slow diffusion of TCE into these interlayer regions.

Rate experiments consisted of adding a 500- $\mu\text{g/L}$ -TCE spike to the sample and control test tubes containing 0.001 and 1.0 N NaCl and a 0.25-g sample of the mineral. Eight sets were prepared for each rate experiment. The total equilibration time of the experiments was 96 hours. During this period, at predetermined intervals of 0.5, 2, 4, 8, 24, 36, 48, and 96 hours, a set of tubes was removed from the batch and was processed to determine the distribution of TCE between the solid and aqueous phase. This method allowed monitoring the rate of TCE uptake and determination of TCE equilibration between the solid and aqueous phase. The rate experiments were not allowed to run beyond 96 hours. This is because preliminary blank experiment results suggested that beyond 96 hours, the system losses would introduce significant errors in the K_d results. The distribution coefficients where $K_d = C_s/C_w$ were plotted versus time, and from this graph, the time at which apparent equilibrium occurred was determined.

Short-term Equilibrium Experiments

The short-term equilibrium experiments involved running four batches of seven sets for each mineral. Individual sets from a batch represented a different initial TCE concentration and consisted of four samples and four controls. These initial concentrations ranged from 50 $\mu\text{g/L}$ to 1000 $\mu\text{g/L}$. Each batch represented one of the four electrolyte solutions (0.001 N NaCl, 1.0 N NaCl, 0.001 N CaCl_2 , and 1.0 N CaCl_2). Additional equilibrium experiments were conducted with illite and montmorillonite samples that were not treated to remove their natural organic coatings. These untreated minerals were equilibrated in 0.001 N CaCl_2 . All the minerals were allowed to equilibrate with TCE for at least 24 hours.

The data from the equilibrium experiments were reduced to the two isotherm parameters, C_s and C_w , and these parameters were used to construct linear isotherms. The isotherm parameters were plotted using linear scales for the axes. The four C_s and the four C_w measurements from each of the seven solute concentrations were averaged and plotted as a data point. The linear isotherm model was fitted to the data using a linear least squares method. The equilibrium K_d value was derived from the slope of the line ($K_d = \text{slope} = C_s/C_w$).

RESULTS

Mineral Characterization

Tables 7 and 8 present the results of the mineral characterization. Included in Table 7 are the specific surface area and cation exchange capacity of the study minerals. Table 8 contains the results of the organic carbon content analysis conducted on the study minerals.

Table 7. Specific surface area and cation exchange capacity of selected minerals.

Minerals	Specific Surface Area m ² /g	Cation Exchange Capacity meq/100 g
Talc	23.58 ± 0.20	16.80
Pyrophyllite	8.97 ± 0.05	19.70
Kaolinite	12.80 ± 0.01	17.00
Na-Montmorillonite	32.48 ± 0.36 ^a	-
Ca-Montmorillonite	29.90 ± 0.38 ^a	96.50
Illite	72.10 ± 0.22	23.30
Vermiculite	5.73 ± 0.01 ^a	7.60
Muscovite	16.34 ± 0.05	15.20
Margarite	39.61 ± 0.15	87.80
Hematite	3.60 ± 0.03	1.58
Goethite	1.64 ± 0.002	0.96
Pyrolusite	2.43 ± 0.01	14.00
Gibbsite	0.69 ± 0.003	0.79

^a Measurement does not include interlayer specific surface area. Assuming all interlayer surface is accessible, both montmorillonite and vermiculite would have theoretical specific surface areas approaching 760 m²/g.

- not analyzed

Table 8. Organic carbon content of minerals studied.

Minerals	Treated ^a		Untreated	
	wt% TOC ^b	f_{oc} ^c	wt% TOC	f_{oc}
Talc	0.085	0.00085	-	-
Pyrophyllite	0.030	0.00030	-	-
Kaolinite	0.012	0.00012	-	-
Na-Montmorillonite	-	-	-	-
Ca-Montmorillonite	0.16	0.0016	1.24	0.0124
Illite	0.13	0.0013	1.85	0.0185
Vermiculite	-	-	0.063	0.00063
Muscovite	-	-	0.11	0.0011
Margarite	-	-	0.15	0.0015
Hematite	-	-	0.020	0.00020
Goethite	-	-	0.035	0.00035
Pyrolusite	-	-	0.38	0.0038
Gibbsite	-	-	<0.0050	<0.000050

^a Treated with sodium hypochlorite to remove organic carbon.

^b Total organic carbon.

^c Fractional weight of organic carbon content present.

- not analyzed

Rate Experiments

Correlation of sorptive behavior with properties of system components (e.g., mineral surfaces and electrolyte solutions) mandated that equilibrium conditions be achieved. For this reason, it was important to establish when this condition was met. The results of the rate experiments with NaCl solutions and talc and montmorillonite suggested that this condition occurred within four hours, after which no additional sorption was evident (Figs. 11 and 12).

Figure 11. TCE distribution coefficients as a function of time with talc equilibrated in (a) 0.001 N and (b) 1.0 N NaCl.

Figure 12. TCE distribution coefficients as a function of time with montmorillonite equilibrated in (a) 0.001 N and (b) 1.0 N NaCl.

The results also showed that, for each mineral there was no significant difference in the rate of TCE uptake between the two NaCl solutions. Because equilibrium conditions were achieved after four hours, the term “apparent” will be dropped when discussing uptake results. Although after four hours no further uptake was observed, conservative judgment dictated an operational period of 24 hours for the short-term equilibrium studies. Also, EPA (1982) and ASTM (1984) recommend an equilibration time of 24 hours to 48 hours.

TCE Uptake by Phyllosilicate Minerals at Equilibrium

Sorption Isotherms

Linear isotherms that depict uptake of TCE by the eight phyllosilicates equilibrated in the four electrolyte solutions are presented in Figures 13 through 16. Uncertainties in the sample data for each of the seven solute concentrations were estimated as the standard deviation of the duplicates and are presented as error bars. Sorption of TCE onto the phyllosilicates followed a linear trend over the entire concentration range studied. Because of the linearity of the data, the linear isotherm model was considered the model that best represented the distribution of TCE between the aqueous phase and the solid phase. A summary of the distribution coefficients calculated from the slope of the isotherms and related statistical analyses is presented in Tables 9 and 10. The variance among the seven sets of data from which K_d s were derived was calculated as the standard deviation, and these standard deviations are presented next to the K_d values. Further justification for using the linear isotherm model was that the calculated coefficient of determination (r^2) values showed that the linear regression lines fit the data well (r^2 ranged from 0.938 to 0.999). Additionally, the isotherm intercepts were not significantly different from zero at the 95% confidence level.

Figure 13. Linear isotherms representing TCE sorption by selected phyllosilicates equilibrated in 0.001 N NaCl. Note the scale change of y-axis between the two graphs.

Figure 14. Linear isotherms representing TCE sorption by selected phyllosilicates equilibrated in 1.0 N NaCl. Note the scale change of y-axis between the two graphs.

Figure 15. Linear isotherms representing TCE sorption by selected phyllosilicates equilibrated in 0.001 N CaCl_2 . Note the scale change of y-axis between the two graphs.

Figure 16. Linear isotherms representing TCE sorption by selected phyllosilicates equilibrated in 1.0 N CaCl_2 . Note the scale change of y-axis between the two graphs.

Table 9. Distribution coefficients for TCE sorption by selected phyllosilicates equilibrated in 0.001 and 1.0 N NaCl solutions.

Mineral Type	0.001 N NaCl		1.0 N NaCl	
	K_d (mL/g)	r^2	K_d (mL/g)	r^2
Talc	4.44 ± 0.22	0.997	7.59 ± 0.80	0.985
Pyrophyllite	1.08 ± 0.13	0.981	1.89 ± 0.23	0.980
Kaolinite	0.85 ± 0.11	0.964	1.55 ± 0.18	0.977
Montmorillonite	14.10 ± 2.41	0.938	7.66 ± 1.00	0.968
Vermiculite	0.53 ± 0.06	0.988	0.58 ± 0.04	0.998
Illite	1.85 ± 0.23	0.949	2.70 ± 0.35	0.969
Muscovite	0.51 ± 0.05	0.992	0.78 ± 0.07	0.980
Margarite	0.31 ± 0.03	0.984	0.37 ± 0.05	0.977

Table 10. Distribution coefficients for TCE sorption by selected phyllosilicates equilibrated in 0.001 and 1.0 N CaCl_2 solutions.

Mineral Type	0.001 N CaCl_2		1.0 N CaCl_2	
	K_d (mL/g)	r^2	K_d (mL/g)	r^2
Talc	4.23 ± 0.25	0.999	7.27 ± 0.62	0.994
Pyrophyllite	1.19 ± 0.14	0.968	1.85 ± 0.20	0.988
Kaolinite	0.99 ± 0.13	0.973	1.61 ± 0.19	0.970
Montmorillonite	3.69 ± 0.35	0.988	2.37 ± 0.25	0.983
Vermiculite	0.51 ± 0.03	0.997	0.60 ± 0.04	0.991
Illite	2.07 ± 0.18	0.989	2.51 ± 0.32	0.956
Muscovite	0.49 ± 0.03	0.994	0.74 ± 0.11	0.958
Margarite	0.33 ± 0.02	0.986	0.36 ± 0.04	0.977

Several notable sorption trends were observed among the phyllosilicate minerals. Talc, montmorillonite, and illite had the highest K_d values in all the electrolyte solutions. The next highest values in all solutions were pyrophyllite and kaolinite. Muscovite and vermiculite had lower K_d values than the rest of the phyllosilicates, and margarite had the lowest K_d values of the class. Except for montmorillonite, the K_d values for the phyllosilicates were greater in the 1.0 N electrolyte solutions than the 0.001 N electrolyte solutions. The K_d values for each mineral equilibrated in CaCl_2 solution were essentially the same as the K_d values for NaCl solutions of equal normality.

Montmorillonite was the exception to these last two trends. The K_d values were greater for montmorillonite equilibrated in the NaCl solutions than for montmorillonite equilibrated in the CaCl_2 solutions. For the NaCl solutions, the K_d value was notably greater for 0.001 NaCl than for the 1.0 N NaCl. The K_d value was higher for montmorillonite equilibrated in 0.001 N CaCl_2 than in 1.0 N CaCl_2 .

Normalized Sorption Isotherms

In order to compare sorptive properties of the surfaces of the different minerals, the comparison should be done on an equal surface area basis. K_d based on mL/g does not allow this direct comparison because the specific surface area (sa) varies significantly among the phyllosilicates. By correlating the K_d based on specific surface area (K_d^{sa}) with reported surface/chemical properties of the phyllosilicates, various relationships may be evaluated to learn the effects of these properties on adsorption. K_d^{sa} values were calculated from

$$K_d^{sa} = (C_s^{sa})/(C_w) = (\mu\text{g}/\text{m}^2)/(\mu\text{g}/\text{mL}) = \text{mL}/\text{m}^2$$

where

$$C_s^{sa} = C_s/sa = (\mu\text{g}/\text{g})/(\text{m}^2/\text{g}) = \mu\text{g}/\text{m}^2.$$

The K_d^{sa} values of the phyllosilicates (Fig. 17 through 20) were derived from isotherms created by normalizing the isotherm data from Figures 13 through 16 using the specific surface areas of the minerals given in Table 7. Figures 17 and 18 illustrate the normalized isotherms for phyllosilicates equilibrated in the NaCl solutions. The normalized linear isotherms for phyllosilicates equilibrated in the $CaCl_2$ solutions are shown in Figures 19 and 20. Tables 11 and 12 give the K_d^{sa} values for the phyllosilicates and the sa values used.

The sa values used to calculate K_d^{sa} were derived from the N_2 -BET analysis or were calculated from unit cell dimensions given in Newman (1987)(Table 7). For the non-swelling minerals that have only exterior surface areas exposed to the aqueous solution, the sa values were determined by BET analysis. These values are considered representative based on comparisons with other studies (Grim, 1968; Sposito, 1984; Newman, 1987).

For the expansive phyllosilicates montmorillonite and vermiculite, the N_2 -BET method underestimates the sa of these minerals, and this may result in misrepresentative K_d^{sa} values. This underestimation is because the nonpolar N_2 gas molecules cannot effectively access the interlayer region of these minerals. The reason for this is that during the N_2 -BET analysis, sorbed gases and most of the water are removed from the mineral surfaces by heating under vacuum. This process collapses the interlayer spaces of expansive minerals. Because of their size and nonpolar character, the N_2 gas molecules cannot effectively penetrate or expand the now partially or fully collapsed interlayer region. The specific surface area determined by N_2 -BET method, therefore, corresponds mainly to the external surface of montmorillonite and vermiculite. If fully hydrated, the surface areas of montmorillonite and vermiculite are an order of magnitude or more greater than the sa for any of the other layer silicates listed in Table 7.

Figure 17. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected phyllosilicates equilibrated in 0.001 N NaCl. Note the scale change of y-axis between the two graphs.

Figure 18. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected phyllosilicates in 1.0 N NaCl. Note the scale change of y-axis between the two graphs.

Figure 19. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected phyllosilicates equilibrated in 0.001 N CaCl_2 . Note the scale change of y-axis between the two graphs.

Figure 20. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected phyllosilicates equilibrated in 1.0 N CaCl_2 . Note the scale change of y-axis between the two graphs.

Table 11. Normalized K_d values (K_d^{sa}) with specific surface areas (sa) of phyllosilicates. K_d results are from equilibrium sorption experiments conducted with 0.001 and 1.0 N NaCl solutions.

Mineral Type	0.001 N NaCl K_d^{sa} (mL/m ²)	1.0 N NaCl K_d^{sa} (mL/m ²)	Surface Area sa (m ² /g)
Talc	0.19	0.32	23.58
Pyrophyllite	0.12	0.21	8.97
Kaolinite	0.067	0.12	12.80
Montmorillonite ^a	0.43	0.24	32.48
Montmorillonite ^b	0.019	0.010	760
Vermiculite ^a	0.093	0.10	5.73
Vermiculite ^b	0.00070	0.00076	760
Illite	0.026	0.038	72.10
Muscovite	0.031	0.048	16.34
Margarite	0.0079	0.0092	39.61

^a assumes only exterior surface area

^b assumes theoretical maximum surface area

The maximum theoretical sa value calculated from unit cell dimensions for montmorillonite and vermiculite is ≈ 760 m²/g. This theoretical value is in close approximation to sa measurements derived by using a combination of nonpolar and polar sorbates (Sposito, 1984). The surface available to TCE lies somewhere between that of the exterior surface area only and the theoretically maximum surface area; therefore, normalized isotherms for montmorillonite and vermiculite were plotted in Figures 17 through 20 using both the N₂-BET derived specific surface areas and the theoretically derived specific surface area.

Table 12. Normalized K_d values (K_d^{sa}) with specific surface areas (sa) of phyllosilicates. K_d results are from equilibrium sorption experiments conducted with 0.001 and 1.0 N CaCl_2 solutions.

Mineral Type	0.001 N CaCl_2 K_d^{sa} (mL/m ²)	1.0 N CaCl_2 K_d^{sa} (mL/m ²)	Surface Area sa (m ² /g)
Talc	0.18	0.31	23.58
Pyrophyllite	0.13	0.21	8.97
Kaolinite	0.078	0.13	12.80
Montmorillonite ^a	0.098	0.079	29.9
Montmorillonite ^b	0.0039	0.0031	760
Vermiculite ^a	0.089	0.11	5.73
Vermiculite ^b	0.00067	0.00079	760
Illite	0.029	0.035	72.10
Muscovite	0.030	0.046	16.34
Margarite	0.0085	0.0090	39.61

^a assumes only exterior surface area

^b assumes theoretical maximum surface area

Illite and montmorillonite have among the highest sorptive capacities for TCE based on K_d normalized to mass (Tables 9 and 10). In contrast, the surfaces with the highest sorptive affinities for TCE are talc, pyrophyllite, and kaolinite as suggested by their K_d^{sa} values based on surface area (Tables 11 and 12). The phyllosilicate surfaces that have moderate affinity for TCE are illite and muscovite. The K_d^{sa} values for margarite suggest that its surfaces have the least affinity for TCE.

Natural Organic Carbon Coatings

To assess the influence of natural organic coatings on TCE sorption, the sorption results for NaOCl-treated and untreated illite and montmorillonite were compared. The experiments were conducted in 0.001 N CaCl_2 . Except for not treating them to remove organic matter, the untreated minerals were processed in the same manner as their treated counterparts. That is, they were processed to exchange Ca^{2+} onto their surfaces and to obtain the $<2\text{-}\mu\text{m}$ fraction.

The distribution coefficients for the treated and untreated illite and montmorillonite are given in Table 13. The sorption results for untreated illite and montmorillonite show that they had considerably greater sorptive capacities for TCE before treatment than after treatment. Illite had more than four times the sorptive capacity before treatment than after treatment. The sorptive capacity of montmorillonite was nearly double.

Table 13. Comparison of sorptive capacities of Ca-montmorillonite and Ca-illite before and after treatment to remove organic carbon.

Sample Type	K_d (mL/g)	K_d^{sa} (mL/m ²)	TOC ^a (mg/kg)
Untreated montmorillonite	6.33 ± 0.31	0.21 ^b	12,400
Treated montmorillonite	3.69 ± 0.35	0.098 ^b	1,600
Untreated illite	8.51 ± 0.32	0.12	18,500
Treated illite	2.07 ± 0.18	0.029	1,300

^a Total Organic Carbon

^b assumes only exterior surface area

TCE Uptake by Oxide Minerals at Equilibrium

Sorption Isotherms

The minerals hematite, goethite, pyrolusite, and gibbsite were subjected to the same procedures outlined for the phyllosilicates. The linear isotherms for these oxides are presented in Figures 21 through 24. Each figure represents sorption results for these minerals equilibrated in one of the four different electrolyte solutions. The K_d values derived from these isotherms and related statistics are summarized in Tables 14 and 15. All the oxide isotherms showed a good fit with the linear isotherm model with r^2 values ≥ 0.889 . The data were randomly distributed about the regression line, and intercepts were not significantly different from zero at the 95% confidence level.

The isotherm data show that these oxides have low K_d values (similar to or less than those observed for vermiculite, muscovite, and margarite). K_d values for the oxides were somewhat lower in the 1.0 N NaCl than in the 0.001 N NaCl. The exception to this was pyrolusite, which showed increases in K_d for both electrolyte types with increased concentration. For the other minerals in CaCl_2 solutions, sorption was generally greater in the 0.001 N solution than in the 1.0 N solution. The trend for the oxides of increased adsorption with decreased electrolyte concentration is opposite of that observed for the phyllosilicate minerals. Another observation is that, except for pyrolusite, the K_d values for the oxides equilibrated in the NaCl solutions are greater than for the oxides equilibrated in the CaCl_2 solutions.

Figure 21. Linear isotherms for TCE sorption by selected oxides equilibrated in 0.001 N NaCl.

Figure 22. Linear isotherms for TCE sorption by selected oxides equilibrated in 1.0 N NaCl.

Figure 23. Linear isotherms for TCE sorption by selected oxides equilibrated in 0.001 N CaCl_2 .

Figure 24. Linear isotherms for TCE sorption by selected oxides equilibrated in 1.0 N CaCl_2 .

Table 14. Distribution Coefficients for TCE sorption by selected oxides equilibrated in 0.001 and 1.0 N NaCl solutions.

Mineral Type	0.001 N NaCl		1.0 N NaCl	
	K_d (mL/g)	r^2	K_d (mL/g)	r^2
Hematite	0.54 ± 0.071	0.968	0.34 ± 0.048	0.984
Goethite	0.30 ± 0.066	0.889	0.21 ± 0.064	0.914
Pyrolusite	0.37 ± 0.058	0.979	0.41 ± 0.069	0.962
Gibbsite	0.49 ± 0.075	0.961	0.43 ± 0.096	0.980

Table 15. Distribution Coefficients for TCE sorption by selected oxides equilibrated in 0.001 and 1.0 N CaCl_2 solutions.

Mineral Type	0.001 N CaCl_2		1.0 N CaCl_2	
	K_d (mL/g)	r^2	K_d (mL/g)	r^2
Hematite	0.32 ± 0.072	0.969	0.16 ± 0.047	0.938
Goethite	0.21 ± 0.054	0.925	0.10 ± 0.030	0.911
Pyrolusite	0.38 ± 0.071	0.947	0.49 ± 0.075	0.957
Gibbsite	0.40 ± 0.078	0.952	0.18 ± 0.044	0.938

Normalized Sorption Isotherms

As for the phyllosilicates, the K_d results for the oxides were also normalized to their specific surface areas (Table 7), and the results are plotted in Figures 25 through 28. Each figure depicts the sorption results of the oxides equilibrated in one of the four electrolytes.

Figure 25. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected oxides equilibrated in 0.001 N NaCl.

Figure 26. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected oxides equilibrated in 1.0 N NaCl.

Figure 27. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected oxides equilibrated in 0.001 N CaCl_2 .

Figure 28. Normalized linear isotherms (K_d^{sa}) for TCE sorption by selected oxides equilibrated in a 1.0 N CaCl_2 .

The K_d^{sa} values of the minerals are tabulated in Tables 16 and 17, which also include the determined specific surface area for each mineral. As seen in these tables, gibbsite had the greatest K_d^{sa} values of the four oxides in all four solutions.

Compared to the K_d values of the phyllosilicates, the oxides have smaller values. If their K_d^{sa} values are compared to the K_d^{sa} values of the phyllosilicates, the oxides have a similar range of values for all the electrolyte solutions. The K_d^{sa} values of gibbsite are the exception: its K_d^{sa} values are higher than those of the phyllosilicates.

Table 16. Normalized K_d values (K_d^{sa}) and specific surface areas (sa) of the oxides. K_d results are from equilibrium sorption experiments conducted with 0.001 and 1.0 N NaCl.

Mineral Type	0.001 N NaCl K_d^{sa} (mL/m ²)	1.0 N NaCl K_d^{sa} (mL/m ²)	Surface Area sa (m ² /g)
Hematite	0.15	0.096	3.60
Goethite	0.18	0.13	1.64
Pyrolusite	0.15	0.17	2.43
Gibbsite	0.72	0.63	0.69

Table 17. Normalized K_d values (K_d^{sa}) and specific surface areas (sa) of the oxides. K_d results are from equilibrium sorption experiments conducted with 0.001 and 1.0 N CaCl₂.

Mineral Type	0.001 N CaCl ₂ K_d^{sa} (mL/m ²)	1.0 N CaCl ₂ K_d^{sa} (mL/m ²)	Surface Area sa (m ² /g)
Hematite	0.088	0.045	3.60
Goethite	0.13	0.062	1.64
Pyrolusite	0.16	0.20	2.43
Gibbsite	0.58	0.26	0.69

DISCUSSION

The findings from this study indicate that certain phyllosilicates have a significant adsorptive capacity for TCE while other phyllosilicates and oxides show only limited adsorptive capacities. The type and strength of the electrolyte solution modified the adsorptive capacities of the phyllosilicates and oxides. The results from this study suggest that the mineral phase and the geochemistry of the aquifer system can be important factors affecting HNO contaminant transport.

Variations in TCE Uptake by Phyllosilicate Minerals

TCE uptake, as reflected in the K_d values, ranged over nearly 2 orders of magnitude between the different phyllosilicate minerals tested (Tables 9 and 10). Because adsorption is, in part, a surface phenomenon, two surface properties were examined to explain the variability in TCE adsorption: the hydrophobicity of the surface and the specific surface area of the minerals. In addition, the properties of the aqueous phase also are related to the variability in TCE adsorption. Four different electrolyte solutions were used to determine the influence that ion type and strength have on adsorption. As observed by others and in this study, natural organic carbon can greatly increase sorption to the solid phase if it occurs in amounts above a certain threshold value. Thus, organic carbon coatings on the mineral surfaces were examined as well.

The Effect of Mineral Surface Hydrophobicity

Because TCE is a moderately hydrophobic nonionic compound, it is likely to have a greater affinity for a hydrophobic surface than for a hydrophilic surface. As indicated in Table 5, mineral surface properties that reflect the extent of hydrophobicity, such as contact angle with water and electron-donor parameter, $\gamma^{\ominus}$, can vary by more than an

order of magnitude. The relationships between these hydrophobicity-related parameters and TCE adsorption can be evaluated using the experimental results obtained in this study. Because the surface charge density of the phyllosilicates (Table 2) is likely to control the contact angle and γ^θ , the relationship between surface charge density and adsorption also needs to be assessed. In an attempt to more clearly understand the phyllosilicate surface properties that affect hydrophobicity which in turn can affect adsorption, the relationships between these properties were first determined using data from the scientific literature and from this study.

Isomorphic substitution in the phyllosilicate structure is a fundamental property that distinguishes these minerals from each other. This substitution alters the negative surface charge density of the mineral, and this negative charge is a surface property that can affect other properties of the mineral surface, such as hydrophobicity. In an effort to determine how the negative surface charge affects the hydrophobicity of these minerals, a comparison between previously published values of the surface charge density and the contact angle of six phyllosilicates was made.

Figure 29 shows the relationship between contact angle with water (Table 5) and surface charge density (Table 2) for the selected phyllosilicate minerals. An increase in the contact angle indicates greater hydrophobicity. Neither measured nor derived contact angles were available for treated illite and margarite, so they were not included in the linear curve fitting.

If margarite were added, it would be expected to have a contact angle close to zero because it is a very hydrophilic mineral. The large, negative surface charge density of margarite (Table 2) puts it off the straight line plot. A curvilinear fit (dashed curve in Fig. 29) is needed to include margarite. It is possible that above a certain critical surface charge density (approximated by the x-intercept of the linear-fitted line), the contact angle is essentially zero and increasing the surface charge density has no discernible effect.

Figure 29. Linear and curvilinear relationships between contact angle (Table 5) and surface charge density (Table 2) for selected phyllosilicates. The linear curve was fitted to the data of talc through muscovite. The curvilinear fit included margarite (solid triangle) as well.

A surface property that may be directly responsible for the different hydrophobicities of the phyllosilicates is the Lewis base strength of the basal surface. An increase in Lewis base strength results in increasing interaction with water and hydrated cations through hydrogen bonds. This increased interaction correlates with a decrease in the hydrophobicity of the mineral. This relationship is seen in Figure 30 which shows a linear decrease in the contact angle with water with an increase in the electron-donor

Figure 30. Relationship between contact angle with water, θ , and electron-donor parameter, γ^θ , for selected phyllosilicates (Table 5).

parameter, γ^θ , where γ^θ reflects the Lewis base strength. Based on the limited range of γ^{LW} and the small values of γ^θ for the phyllosilicates (Table 5), it is unlikely that either of these parameters plays an important role in controlling TCE adsorption.

Surface charge density also should correlate with γ^θ , because the negative layer charge enhances the Lewis base strength of the basal oxygen atoms (Sposito, 1984). Similarly, Giese et al. (1991) have suggested that the total surface charge (Table 2) may control γ^θ . Six phyllosilicates were compared to verify that the relationship between the

electron-donor parameter, $\gamma^{\ominus}$ (Table 5), and surface charge density (Table 2) exists. As anticipated from the correlations shown in Figures 29 and 30, the electron-donor parameter for the six phyllosilicates are correlated with their corresponding surface charge densities (Fig. 31).

To evaluate the effect that hydrophobicity has on adsorption, contact angles with water (Table 5) were compared to the K_d^{sa} values for selected minerals. Four of these selected phyllosilicates included in the evaluation are talc, pyrophyllite, kaolinite, and muscovite. The K_d^{sa} values from the 0.001 N CaCl_2 experiments (Table 12) were chosen so that the K_d^{sa} value of a fifth phyllosilicate, untreated illite (Table 13), could be used. The remaining four minerals listed in Table 12 were not used because they have either unknown contact angles (margarite and treated illite) or uncertain K_d^{sa} values (montmorillonite and vermiculite) because of difficulty in measuring their specific surface areas.

The K_d^{sa} value for the untreated illite instead of treated illite was used because the large contact angle (70.7°) derived from the data of Li et al. (1991) suggests that they used a sample with high organic content. Significant amounts of natural organic carbon commonly appear to be associated with untreated illite, making it hydrophobic. For example, the untreated illite used in this study had a 1.85% organic carbon content.

The effect of the hydrophobicity of the five minerals on the adsorption of TCE can be seen in Figure 32. As indicated by the good fit of the line in Figure 32, hydrophobicity serves as a reasonable guide in determining the ability of the mineral to adsorb TCE. As one can see in Figure 32, plotting the published contact angle of 70.7° for illite (Li et al., 1991) against the K_d^{sa} value of the untreated illite shows a better fit with the trend than if this contact angle is plotted against the K_d^{sa} value for treated illite. The regression line does not pass through the origin. This may reflect the contribution to adsorption from a slightly polar interaction of TCE with the surface.

Figure 31. Relationship between electron-donor parameter, γ^e (Table 5), and surface charge density (Table 2) for selected phyllosilicates. Solid circles indicate data used to generate linear regression line. The solid triangle indicates a datum derived from the equation using the measured surface charge density value (Table 2).

Based on the relationship seen in Figure 32, the hydrophobicity of the mineral is considered one of the most important surface properties affecting the adsorption of TCE. A decrease in the hydrophobicity of a mineral reflects an increase in polar sites where hydrated cations and water adsorb. Evidently, TCE cannot compete effectively with the hydrated cations and water for these polar sites. The trend shown in Figure 32 should apply to other HNOs as well.

Figure 32. Relationship between K_d^{sa} results (Table 12) and surface contact angles with water (Table 5) for selected phyllosilicates equilibrated in 0.001 N CaCl_2 . The K_d^{sa} value of untreated illite is from Table 13. Solid circles indicate data used to generate linear regression line. Treated illite (solid triangle) was not included in generating the linear relationship.

If the strength of the Lewis base is the surface property that is controlling the hydrophobicity (Fig. 30), then it follows that it also is controlling the adsorptive capacities of the phyllosilicates for TCE. To test this, K_d^{sa} values from five phyllosilicates (talc, pyrophyllite, kaolinite, muscovite, and untreated illite) were compared with their $\gamma^\ominus$ values listed in Table 5. The K_d^{sa} values of the first four

phyllosilicates are from the 0.001 N CaCl_2 experiments (Table 12), and these values were used so that the data for untreated illite (Table 13) could again be included in the comparison. Figure 33 shows the correlation between the K_d^{sa} and the electron-donor parameter for the selected minerals. For montmorillonite and vermiculite, K_d^{sa} values were calculated and plotted using the reported $\gamma^\ominus$ values for the two minerals (Table 5). For treated illite, an $\gamma^\ominus$ value was calculated from the equation of the line, using its K_d^{sa} value from the 0.001 N CaCl_2 experiment (Table 12). This value also was plotted. A good correlation for the five minerals, which had both K_d^{sa} and $\gamma^\ominus$ values available, was observed between the electron-donor parameter and TCE adsorption (Fig. 33). The relationship reveals that, as the K_d^{sa} values decrease, the $\gamma^\ominus$ values increase. This relationship suggests that the Lewis base is not only controlling the hydrophobicity of the minerals but also their adsorptive capacities.

Because of the relationships developed in Figures 32 and 33, a correlation should exist as well between K_d^{sa} and surface charge density. To evaluate the possible relationship between K_d^{sa} and surface charge density, the K_d^{sa} values from five phyllosilicates, talc, pyrophyllite, kaolinite, muscovite, and treated illite, were compared with their surface charge density values listed in Table 2. The K_d^{sa} values used for these minerals are from the 0.001 N CaCl_2 experiments (Table 12). Figure 34 shows a good correlation between K_d^{sa} and surface charge density.

A linear fit was made to the data by excluding the datum for margarite. As was hypothesized in relationship to Figure 29, above a certain critical surface charge density, additional surface charge density will have an insignificant effect on the minimal amount of adsorption taking place. The main range of interest for surface charge density is from 0 to 0.40 C/m², since most common clay minerals found in soil/sediment fall within that range.

Figure 33. Relationship between K_d^{sa} values (Tables 12 and 13) and electron-donor parameter, γ^- (Table 5), for selected phyllosilicates in 0.001 N CaCl_2 . Solid circles indicate data used to generate linear regression line. Solid triangles indicate data derived from the equation of the line using the measured γ^- values for montmorillonite and vermiculite and the measured K_d^{sa} value for treated illite.

To include the margarite datum, an exponential curve needed to be fit to the data (Fig. 34). Additional determinations of K_d^{sa} for minerals with surface charge densities between those of muscovite and margarite would have to be made to better determine the nature of the relationship in that range.

Figure 34. Linear and curvilinear relationship between K_d^{sa} values (Table 12) and surface charge density (Table 2) for selected phyllosilicates in 0.001 N CaCl_2 . The data point for margarite (solid triangle) was not used in the exponential curve fit.

The Effects of Specific Surface Area

Although illite and montmorillonite are considered to be hydrophilic, they have larger K_d values than most of the other more hydrophobic phyllosilicates, talc being the only exception (Tables 9 and 10). These two hydrophilic minerals have much larger specific surface areas than their more hydrophobic counterparts, and it probably is this

factor that gives illite and montmorillonite their higher K_d values. The high and widely varying K_d values of montmorillonite are due, in part, to changes in the amount of surface area that was available for TCE adsorption in the different electrolyte solutions tested. The surface area available for TCE adsorption may change in response to variations in interlayer separation or quasicrystal size of this mineral, as discussed below.

Even when the specific surface area is high, if the mineral surface is not sufficiently hydrophobic, the adsorption of HNOs will be limited. Margarite falls into this category. This very hydrophilic mineral had a specific surface area that was more than three times greater than those of pyrophyllite and kaolinite (Table 7). It had K_d values, however, that were two to five times less than its more hydrophobic counterparts (Tables 9 and 10). The results of this study indicate that both the hydrophobicity and the specific surface area of a mineral must be taken into account in evaluating its adsorptive capacity for an HNO.

The Effects of Electrolyte Concentration and Type

Varying the concentration and type of the electrolyte solution produced significant variations in TCE adsorption (Tables 9 and 10). TCE adsorption increased significantly for most of the phyllosilicates in the 1.0 N electrolyte solutions compared to the 0.001 N electrolyte solutions, and the percentage that adsorption increased is shown in Table 18. The differences in adsorption between 0.001 N NaCl and CaCl_2 and between 1.0 N NaCl and CaCl_2 were minor, except in the case of montmorillonite. This indicates that CaCl_2 at half the molar concentration of NaCl had the same effect on adsorption. Two processes may account for the observations: (1) the different electrolytes may have expelled TCE from solution in varying degrees, and (2) the different exchangeable cations adjacent to the phyllosilicate surface may have altered the conditions at or near the surface and, consequently, affected TCE adsorption. Depending on the type and concentration of electrolyte present, it is likely that both mechanisms are operating concurrently, although varying in their intensity.

Table 18. Percent difference in adsorption with increase in concentration of equilibrating electrolyte.

Mineral Type	NaCl %	CaCl ₂ %
Talc	+71	+72
Pyrophyllite	+75	+55
Kaolinite	+82	+63
Montmorillonite	-84	-56
Vermiculite	+9	+18
Illite	+46	+21
Muscovite	+53	+51
Margarite	+19	+9

Hydrophobic Expulsion from Solution The dominant mechanism in the liquid phase affecting adsorption is most likely hydrophobic expulsion (salting-out effect) of TCE from the aqueous solution. Not only the strength of the electrolyte solution but also the type of electrolyte determines the hydrophobic expulsion effect. The stronger the interaction between the electrolyte and water compared with the interaction between the HNO and water, the greater the effectiveness of this expulsion, i.e., the greater tendency for TCE to be “driven out” of solution.

Electrolyte Concentration. The significant increase in adsorption at the higher normality (Table 18) is explained by the salting out of TCE from solution. The salting-out effect on TCE in this study is similar to the relationship shown in Figure 9. As the electrolyte concentration of a solution increases, the hydrophobic expulsion of TCE from that solution also increases. TCE may escape toward a gaseous phase or to a surface/solution interface.

In this study, the expulsion of TCE from solution was directed toward the surface/solution interface of the phyllosilicates. No head space was present in the closed system used in the adsorption experiments; therefore, TCE could have only been driven toward the solid phase.

Montmorillonite did not fit the trends that were seen for the other phyllosilicates (Table 18). This anomaly can be explained by its unique swelling characteristics in the different electrolyte solutions, which in turn altered the surface area available for TCE adsorption. The variations in the available surface area for this mineral were more than enough to counteract the gain in adsorption from the salting out of TCE in the stronger solutions.

Electrolyte Type. The adsorptive capacities of the phyllosilicates varied little between equal normal concentrations of NaCl and CaCl₂ (Tables 9 and 10). This lack of change can be explained by the different salting-out effects produced by different electrolytes as shown in Figure 9. Figure 9 shows that CaCl₂ would have approximately twice the salting-out effect of NaCl on an HNO for a given molarity; therefore, one would expect that the salting-out effect on TCE is essentially the same for the two electrolytes at the equal normalities used in this study. As indicated in Figure 9, the salting-out effect on an HNO by both the 0.001 N NaCl and CaCl₂ is negligible.

Effect of Exchange Cations Adjacent to the Surface Although salting out of TCE can account for part of the increased adsorption at greater electrolyte concentrations, it cannot explain it all, because the increase in adsorption is not uniform for the different minerals. In fact, increases in adsorption varied widely, from 9% to 82% (Table 18) between the two normalities tested. A plausible explanation for this observation is based on the varying degree to which the phyllosilicate surfaces adsorb hydrated cations. The greater the surface charge density, the greater the cation concentration is at the

phyllosilicate surface. The elevated concentration created by the accumulation of hydrated cations adjacent to the surface may reduce TCE adsorption by a hydrophobic expulsion effect away from the surface, driving TCE back into solution. This expulsion effect increases with increased surface charge density. Apparently the effect of hydrophobic expulsion of TCE away from the surface was the same whether Na^+ or Ca^{2+} were present. This is inferred from the adsorption results, which did not indicate appreciable differences in K_d between exchanging Na^+ for Ca^{2+} .

Evaluation of Swelling Phyllosilicates

The distribution of adsorbed TCE on the surfaces of montmorillonite and vermiculite is more difficult to assess than that of the other phyllosilicates. These swelling minerals may adsorb TCE into their interlayer regions as well as onto their exterior surfaces. Montmorillonite has additional complications in that its interlayer spacing and size of the quasicrystals and domains also are sensitive to the four different electrolyte solutions used in this study. In contrast, the interlayer spacing and quasicrystal size of vermiculite do not vary among the different electrolyte solutions used.

Adsorption within the Interlayer For a TCE molecule to fit within the interlayers of the two expanding minerals, its minimum overall molecular dimension must be smaller than the interlayer separation. The interlayer spacing of montmorillonite and vermiculite equilibrated in the four electrolyte solutions is given in Table 19. The minimum overall dimension for TCE is estimated to be its thickness ($\approx 3.6 \text{ \AA}$), which is assumed to be the van der Waals diameter of a chloride atom. Although TCE can fit between the $6 \text{ \AA}$ interlayer spacing of vermiculite, TCE molecules must orient their long and intermediate axes (Fig. 8) parallel to the two opposing layer surfaces in order to enter the interlayer region.

Table 19. Approximate interlayer separations of montmorillonite and vermiculite for electrolyte concentrations used in this study based on X-ray diffraction analysis (data from Norrish, 1954; Posner and Quirk, 1964; Walker, 1951). Values given in angstroms.

Mineral	0.001 N		1.0 N	
	Na ⁺	Ca ²⁺	Na ⁺	Ca ²⁺
Montmorillonite	≥100	10	9	10
Vermiculite	6	6	6	6

TCE that is free to orient and rotate within the interlayer region is more likely to be adsorbed onto a mineral with a larger separation such as montmorillonite, because of the greater freedom the TCE molecules will have to assume their most energetically favorable position.

In addition to restrictions from interlayer spacing, the solution environment within the interlayer region may also limit TCE access into this region. The cation concentration within the interlayer regions of montmorillonite and vermiculite is high because two charged surfaces are in close proximity to each other and these two charged surfaces have to be balanced by the counterions. These high concentrations could cause significant hydrophobic expulsion effects within the interlayer region driving TCE away.

Limited interlayer spacing and competition with highly concentrated, adsorbed cations, especially for an interlayer spacing of ≤ 9 Å, reduce the possibility of extensive interlayer adsorption of TCE. It must be kept in mind, though, that these minerals possess an extremely large potential surface area (*sa* approaching ≈ 760 m²/g). A significant portion of this surface area can exist within the interlayer region of these expanding minerals. For example, the interlayer *sa* for vermiculite is estimated to be 133 times greater than its measured external *sa* (5.73 m²/g). Only a very small fraction of the TCE

would need to be adsorbed within the interlayer regions to enhance adsorption significantly. For instance, the density of adsorbed TCE in vermiculite's interlayer region would only need to be 0.007 times as large as that on its external surface area to make a contribution equal to the external adsorptive capacity.

The K_d results and measured external surface area for vermiculite provide support for the adsorption of TCE into its interlayer region. If adsorption occurred only on the exterior surfaces of vermiculite ($5.73 \text{ m}^2/\text{g}$), only a limited amount of surface area would be available for TCE adsorption. If the K_d value from the 0.001 N CaCl_2 experiment (Table 10) is divided by the measured exterior sa , this would give vermiculite a K_d^{sa} value of $0.089 \text{ mL}/\text{m}^2$ (Table 12). This K_d^{sa} value is greater than that of kaolinite ($0.078 \text{ mL}/\text{m}^2$) equilibrated in the same solution, but vermiculite is less hydrophobic than kaolinite (Table 5). This leads to the inference that the calculated K_d^{sa} value for vermiculite based on its exterior surface area alone is too high. A plausible explanation for the greater adsorption on vermiculite is that TCE was able to access the substantial interlayer region of this mineral, in spite of its relatively small interlayer spacing.

The possibility that TCE adsorbs into the interlayer region of swelling minerals may be further demonstrated by the equation in Figure 33. This equation was used to predict a K_d^{sa} and then to estimate the surface area of vermiculite that adsorbed TCE (the effective sa). Using the $\gamma^\ominus$ value for vermiculite (Table 5), a K_d^{sa} value of $\approx 0.056 \text{ mL}/\text{m}^2$ was derived. As shown in Figure 33, the K_d^{sa} predicted for vermiculite falls midway between the K_d^{sa} for kaolinite and muscovite. This is consistent with its surface charge density (Table 2), which falls between these two minerals. The effective sa of vermiculite that adsorbed the TCE was calculated using its K_d value from the 0.001 N CaCl_2 experiment (Table 10) and the predicted K_d^{sa} value of $0.056 \text{ mL}/\text{m}^2$. Using the relationship $sa = K_d/K_d^{sa}$ derived from $K_d^{sa} = K_d/sa$, an effective sa of $9.11 \text{ m}^2/\text{g}$ was calculated for

vermiculite. This sa value is larger than the measured exterior sa of $5.73 \text{ m}^2/\text{g}$. Assuming that the difference between the two sa values ($9.11 \text{ m}^2/\text{g} - 5.73 \text{ m}^2/\text{g} = 3.38 \text{ m}^2/\text{g}$) is due to interlayer adsorption, 37% of the adsorption can be attributed to interlayer adsorption.

Although montmorillonite will likely adsorb more TCE into its interlayer region than vermiculite per given interlayer surface area, it will adsorb less per mass. This is because the montmorillonite sample has significantly fewer layers per quasicrystal than the vermiculite sample. Montmorillonite was shown not to have any quasicrystals in dilute NaCl systems and 4 to 8 layers per quasicrystals in dilute CaCl_2 systems (Sposito, 1984). On the other hand, vermiculite was calculated to have ≈ 133 layers per quasicrystal by dividing its measured exterior surface area of $5.73 \text{ m}^2/\text{g}$ (Table 7) into the theoretical total surface of $760 \text{ m}^2/\text{g}$. For a given mass, if a mineral has fewer layers per quasicrystal, the number of quasicrystals increases. An increase in the number of quasicrystals per given mass would increase the number of exterior basal surfaces exposed to solution and decrease the amount of interlayer surfaces. Adsorption to the exterior surfaces is significantly more energetically favorable than to surfaces of the interlayer region of a quasicrystal and greater adsorption occurs. The same analysis as used for vermiculite using Figure 33 cannot be done with montmorillonite to determine its interlayer adsorption of TCE. This is because the exterior surface area of montmorillonite changes significantly in electrolyte solutions relative to the dehydrated state under which its specific surface area was determined by the N_2 -BET method.

Adsorption on Quasicrystals and within Domains Different sizes of montmorillonite quasicrystals have already been shown to form in various types of electrolytes (Sposito, 1984). If the quasicrystal size of montmorillonite varies in NaCl and CaCl_2 solutions, this could significantly affect the adsorption results observed in this

study, but this phenomenon alone cannot fully explain the adsorption results for montmorillonite. It is proposed that the environment within domains inhibits TCE adsorption onto the quasicrystals contained within the domains (Fig. 3). The domains also appeared to be sensitive to the four different electrolyte solutions. Separating out the effect of the domains versus that of the quasicrystals on adsorption is difficult.

A higher adsorptive capacity was anticipated for Na-montmorillonite and Ca-montmorillonite in the 0.001 N electrolyte solutions based on the amount of potential surface area available for TCE adsorption. For example, the available surface area for Na-montmorillonite in 0.001 N NaCl should have approached a *sa* of 760 m²/g because montmorillonite exists as individual 2:1 layers in this solution. If this *sa* is freely available for TCE adsorption, it seems likely that montmorillonite, a moderately hydrophilic mineral, would have an adsorptive capacity several times larger than that reflected in the K_d value of 14 mL/g. The measured adsorptive capacity implies that TCE may be restricted from fully accessing all of the potential surface area. A possible factor restricting TCE from fully accessing the available exterior surfaces of the 2:1 layers is a solution environment within the domains that is less favorable to TCE than the bulk solution.

The importance of the size of a montmorillonite quasicrystal on TCE adsorption can be seen when comparing the adsorption results for this mineral equilibrated in 0.001 N NaCl and CaCl₂. The greater TCE adsorptive capacity of Na-montmorillonite in 0.001 N NaCl is due to its lack of quasicrystals. In dilute solutions of NaCl, quasicrystals are not expected to form (Sposito, 1984) and Na-montmorillonite exists in dilute suspension as essentially individual unit layers (averaging 1.2 ± 0.2 unit layers per quasicrystal). X-ray diffraction analysis of Na-montmorillonite after it was equilibrated in 0.001 N NaCl (Table 19) also indicates that quasicrystals do not form because the spacing between layers is 100 Å or greater, with no indication of the 10 Å spacing which defines

the quasicrystal. The lack of quasicrystals in 0.001 N NaCl causes Na-montmorillonite to have a relatively large external surface area and wide interlayer spacing (≥ 100 Å) of individual 2:1 layers within the domains, causing this mineral to have the highest K_d value of the four electrolyte solutions.

In dilute solutions of CaCl_2 , quasicrystals were shown to have four to eight layers per quasicrystal (Sposito, 1984). This should result in a significant reduction in adsorption compared to Na-montmorillonite in a weak electrolyte solution. If one compares the adsorptive results of the Ca-montmorillonite in the 0.001 N CaCl_2 solution to the Na-montmorillonite in the 0.001 N NaCl (Tables 9 and 10), the adsorptive capacity of Ca-montmorillonite was 26 to 31% of that of Na-montmorillonite. Adsorption was reduced by $\approx 72\%$ for the Ca-montmorillonite compared to Na-montmorillonite, probably because the exterior surface area also was reduced; an $\approx 72\%$ reduction in surface area equates to four or more layers per quasicrystal compared to that of individual layers in 0.001 N NaCl, assuming minimal contribution from interlayer adsorption. The difference in adsorption between Na- and Ca-montmorillonite shows strong evidence that quasicrystal size is significantly controlling the adsorptive capacity of montmorillonite. This would also indicate that electrolyte type in an aqueous solution is very important to the adsorptive characteristics of montmorillonite. The difference in quasicrystal size between weak solutions of NaCl and CaCl_2 can be related to the weak ability of Na^+ to bind silicate layers together compared with the ability of Ca^{2+} . Shomer and Mingelgrin (1978) showed the weak binding ability of Na^+ . Their study demonstrated that as Na^+ was added to a Ca^{2+} system, the number of layers per montmorillonite quasicrystal dropped significantly.

The sizes of the quasicrystals apparently are not known for montmorillonite equilibrated in stronger electrolyte solutions, but Posner and Quirk (1964) and Shomer and Mingelgrin (1978) suggested that quasicrystal size depends on the exchangeable

cation and electrolyte concentration. It seems reasonable that quasicrystalline size would be greater in the stronger 1.0 N electrolyte solutions because the flocculating particles found in this solution represent the condensation of montmorillonite particles. Some of these condensed particles may form quasicrystals. Quasicrystals are known to occur in 1.0 N NaCl based on X-ray diffraction measurements of the interlayer spacing after equilibrating the mineral in this electrolyte solution. Diffraction patterns indicate a 9 Å interlayer spacing for montmorillonite equilibrated in 1.0 NaCl (Table 19); consequently, quasicrystals should be present because a spacing ≤ 10 Å defines a quasicrystal. As seen in the K_d results for Na-montmorillonite (Table 9), its adsorptive capacity in 1.0 N NaCl was reduced to nearly half of that of 0.001 N NaCl. These results suggest that two or more layers per quasicrystal formed in 1.0 N NaCl. The domain size should have also changed in the 1.0 N NaCl and most likely it would have become condensed. Under this condition, the solution environment within the domains would probably become less favorable to TCE, than the solution environment within the domains in 0.001 N NaCl. The condensed domains in 1.0 NaCl may have significantly counteracted the effect of hydrophobic expulsion of TCE from solution as observed for the other phyllosilicates (Table 18). The reduction in adsorption observed for Ca-montmorillonite between 0.001 N CaCl_2 and 1.0 N CaCl_2 can be explained by the same possible processes of quasicrystal growth and domain effects described for Na-montmorillonite in the NaCl system.

Further study is necessary to quantify quasicrystal and domain size in different and stronger electrolyte solutions. Once this information is available, it could provide a more definitive explanation as to why the adsorption results obtained for montmorillonite were so variable. Also, the effects of the variability in quasicrystal and domain stacking order (Fig. 3) on adsorption cannot be discounted. Not much can be said, however, about their effects on adsorption until quasicrystal and domain size are better quantified for the different electrolyte systems.

Evaluation of Organic Coatings on Phyllosilicates

In an effort to quantify the contributions from the mineral fraction and the organic carbon fraction, analyses were conducted using the two-component model proposed by McCarty et al. (1981) (see page 38). This model is appropriate for predicting sorption to a solid matrix which has low organic carbon content. The K_d results for phyllosilicates equilibrated in 0.001 N CaCl_2 (Table 10) were used in this analysis.

The organic-carbon-normalized distribution coefficient (K_{oc}) value was derived from relationships based on the water solubility of TCE and the octanol-water partition coefficient (K_{ow}). One of the relationships using water solubility to predict K_{oc} is given by Kenaga, 1980:

$$\log K_{oc} = 3.64 - 0.55 \log W_l$$

where W_l is the water solubility of TCE (1,100 mg/L at 25°C). A relationship using K_{ow} to predict K_{oc} was derived by Karickhoff et al., (1979):

$$K_{oc} = 0.63 K_{ow}$$

where $\log K_{ow}$ is 2.29 for TCE (Olsen and Davis, 1990). The K_{oc} calculated using the formula from Kenaga (1980) is 93 mL/g, and the K_{oc} calculated from Karickhoff (1979) is 123 mL/g. These two values were averaged to give a value of 108 mL/g. Published equations to derive K_{oc} values can have some uncertainty associated with them which creates corresponding uncertainties in the partition coefficient (K_p) values calculated from them. As suggested by Olsen and Davis (1990), it is advisable when using these equations to select equations derived from a set of compounds similar to the chemical of interest. For this analysis, the equations from Karickhoff (1979) and Kenaga (1980)

seemed most appropriate. K_p was calculated from $K_p = K_{oc}f_{oc}$. The contribution to sorption from the mineral component (K_m) was calculated from the difference between the measured K_d values and the calculated K_p values. The mineral component is defined by the equation: $K_m = K_{io}f_{io}$. The term K_{io} is the distribution coefficient of the mineral component, and the term f_{io} is the fractional mass of that mineral found in the sample.

Table 20 presents the results of the two-component model analysis showing the calculated contributions of K_p and K_m to the total K_d of the samples. Table 21 shows the percentage of sorption attributable to the mineral fraction ($\%mf$) and the organic fraction ($\%of$). The $\%mf$ and $\%of$ are defined as

$$\%mf = \frac{K_m}{K_d} \times 100 \text{ and}$$

$$\%of = \frac{K_p}{K_d} \times 100.$$

The results given in Table 21 suggest that the inorganic fraction was by far the greater sorbent for all the phyllosilicates except margarite and untreated illite and montmorillonite. The percentage values for margarite suggest that the organic fraction contributed significantly to sorption of TCE. This contribution from the f_{oc} would explain why margarite had higher K_d^{sa} values than expected for a mineral whose surface is highly hydrophilic. The $\%mf$ values for the untreated illite and montmorillonite (Table 21) appear to be too high for samples with >1% organic carbon content. The model proposed by McCarty et al. (1981) was derived for predicting sorption by sediments with low f_{oc} , and consequently, this model may not be appropriate for the untreated illite or montmorillonite because of their considerable organic carbon content. The K_d results for the untreated illite and montmorillonite samples suggested that their natural organic

Table 20. Parameters used to calculate inorganic and organic contributions to sorption for phyllosilicate samples.

Mineral Type	K_{oc} (mL/g)	f_{oc}^a (-)	K_p^b (mL/g)	K_d^c (mL/g)	K_m^d (mL/g)
Talc	108	0.00085	0.09	4.23	4.14
Pyrophyllite	108	0.00030	0.03	1.19	1.16
Kaolinite	108	0.00012	0.01	0.99	0.98
Montmorillonite	108	0.0016	0.17	3.69	3.52
Illite	108	0.0013	0.14	2.07	1.93
Vermiculite	108	0.00063	0.07	0.51	0.44
Muscovite	108	0.0011	0.12	0.49	0.37
Margarite	108	0.0015	0.16	0.33	0.17
Untreated Mont. ^{e, f}	108	0.0124	1.34	6.33	4.99
Untreated Illite ^{e, f}	108	0.0185	2.00	8.51	6.51

^a f_{oc} = Mass fraction of organic carbon (Table 8).

^b $K_p = K_{oc}f_{oc}$.

^c K_d values of minerals equilibrated in the 0.001 N CaCl₂ solution (Tables 10 and 13).

^d $K_m = K_{io}f_{io}$.

^e Samples of illite and montmorillonite that were not treated to remove their organic coatings.

^f Organic carbon content of this mineral exceeded the maximum f_{oc} threshold of the model causing anomalous results.

(-) = dimensionless

component had two to four times the sorptive capacity of their inorganic component (Tables 10 and 13). For the minerals with low f_{oc} (Table 8), the organic coating on their surfaces in most cases does not appear to significantly increase their sorptive capacities (Table 21). Margarite was the exception.

Table 21. Percentage of inorganic (%*mf*) and organic (%*of*) contributions to TCE sorption for the phyllosilicate samples, and the fraction of organic carbon necessary to account for observed sorption results (f_{oc}^{abs}).

Mineral	% <i>mf</i>	% <i>of</i>	f_{oc}^{abs}
Talc	97.8	2.2	0.039
Pyrophyllite	97.3	2.7	0.011
Kaolinite	98.7	1.3	0.0092
Montmorillonite	95.3	4.7	0.034
Illite	93.2	6.8	0.019
Vermiculite	86.7	13.3	0.0047
Muscovite	75.9	24.1	0.0045
Margarite	51.1	48.9	0.0031
Untreated Mont.	78.9	21.1	0.034
Untreated Illite	76.6	23.4	0.019

Included in Table 21 is an analysis of the fraction of organic carbon (f_{oc}^{abs}) that would have to be present before all the sorption could be attributed solely to the organic carbon content. The f_{oc}^{abs} term was calculated from

$$f_{oc}^{abs} = \frac{K_d}{K_{oc}}.$$

The results in Table 21 suggest that the organic carbon content would have to have been much greater than the measured f_{oc} (Table 8) before it could have caused the sorption results observed for the studied phyllosilicates. For some untreated samples, illite, montmorillonite, and margarite, the measured f_{oc} values were a significant fraction of the predicted f_{oc}^{abs} .

Prediction of Adsorption by Correlating Mineral Properties

The K_d of a phyllosilicate or sediment sample may be estimated more directly than the batch sorption experiments described above. This direct estimate may be accomplished by utilizing a modified version of the equation of McCarty et al. (1981) and the relationships developed in this discussion (Figs. 29 through 34). The values needed to solve the equations in Figure 29 through 34 can be obtained in several ways. The other information needed to make the direct estimate is fraction of the organic carbon (f_{oc}) and phyllosilicate (f_{io}) present in the sample, the specific surface area (sa) of the phyllosilicate fraction, and perhaps the type of dominant clay(s) present in the sample.

The adsorptive behavior of the phyllosilicate or sediment sample can be estimated by first estimating the K_d^{sa} value(s) for the phyllosilicate(s). A K_d^{sa} value can be predicted for a phyllosilicate if either its contact angle with water, electron-donor parameter, or surface charge density is known or can be determined. These values can be used with their corresponding equations found in either Figures 32, 33, or 34. Using the obtained f_{oc} , f_{io} , and sa values of the sample, a K_d value for the phyllosilicate or sediment sample can be derived. The equations in Figures 32 through 34 have a range in which they can be used to predict K_d^{sa} . For the equation in Figure 32, the range of contact angles for the minerals is between $\approx 0^\circ$ and $\approx 80^\circ$. In Figure 33, the range of $\gamma^\ominus$ values to estimate K_d^{sa} is between ≈ 0 and ≈ 60 mJ/m². Minerals that have contact angles approaching zero and $\gamma^\ominus$ values > 74 mJ/m² are not expected to adsorb TCE appreciably. For the equation in Figure 34, the range is less clear, but it appears to be between ≈ 0 and ≈ 0.40 C/m².

The modification suggested for the two-component model of McCarty et al. (1981) would be to replace K_{io} with the term $(K_d^{sa})(sa)$:

$$K_d = \sum (K_d^{sa})(sa)(f_{io}) + K_{oc}f_{oc}$$

where the summation function is for samples that have more than one discernible phyllosilicate present. The use of this model should be limited to systems that have low natural organic-carbon content. The definition of what constitutes high or low natural organic-carbon content varies with the amount of specific surface area of the sample. The equation of McCarty et al. (1981) to determine f_{oc}^{crit} can be used to assist in deciding if the two-component model for low organic-carbon systems would apply (see page 37).

Prediction of K_d for Monomineralic Samples To test the predictive ability of the equations in Figures 29 through 34, K_d^{sa} values were calculated for treated illite. From the K_d^{sa} values, the two component model was used to predict K_d values for the illite. As previously mentioned, neither the surface contact angle with water nor the electron-donor parameter for this mineral was available, and consequently, no data for this mineral was used to derive the linear equations in Figures 29 through 33. This being the case, illite was a good candidate for testing the linear equations ability to predict K_d^{sa} and K_d values.

The surface charge density of illite (Table 2) was used with the equations in Figures 29 and 31 to estimate a surface contact angle with water and an γ^θ value for this mineral. This step was added because a measured contact angle or an γ^θ value for this mineral was not available. The two derived values were used to calculate K_d^{sa} values from the equations in Figures 32 and 33. Predicted K_d^{sa} and K_d values for treated illite also were computed from the equation in Figure 34 using its surface charge density.

To calculate the predicted K_d values, only the inorganic contribution of the modified two-component model was used to determine the predicted K_d values. The contribution from the organic component (K_p) was not included in this analysis because the equations in Figures 29 through 34 already reflect a small K_p contribution (<8%; Tables 20 and 21) of a mineral towards the predicted K_d . This small K_p contribution is

considered adequately representative of the contribution from the limited organic fraction often associated with the treated natural minerals such as illite. To derive predicted K_d , the derived K_d^{sa} values were multiplied by the measured specific surface area of illite (Table 7) and the f_{io} was set to one.

The predicted K_d^{sa} and K_d values along with the derived contact angle and electron-donor parameter are presented in Table 22. As seen in Table 22, the predicted K_d^{sa} and K_d values for treated illite are reasonably close to its measured K_d^{sa} and K_d values. The K_d^{sa} and K_d values derived from predicting contact angle deviated the least from the measured K_d^{sa} and K_d values having a difference of 13% from those measured. A difference of 26% was observed between predicted values based on $\gamma^\ominus$ and the measured values. The results derived from the equation in Figure 34 deviated the most from the measured values where the difference between predicted and measured is 32%.

Prediction of K_d for Aquifer Sediment Samples The two-component model can incorporate the results of this study to estimate the distribution coefficients for sediment samples from aquifers if the natural organic carbon content is low. As suggested in this study, the model of McCarty et al. (1981) can be modified to replace K_{io} with $(K_d^{sa})(sa)$ term for the clay(s). In this model, the f_{io} term refers only to the clay-size fraction ($\leq 2\mu m$) of the sediment sample.

K_d^{sa} values for the model may be derived from the equation in either Figure 32, 33, or 34. To use the model in its simplest form, one clay type is preferred to dominate the clay-size fraction of the sediment under investigation. The dominant clay mineral(s) in the aquifer sediment sample can be identified by X-ray diffraction employing, for example, the technique of Hay et al. (1991) which may be used to estimate the relative percentages of the clay mineral(s) in the clay-size fraction. Perhaps this information is

Table 22. Predicted K_d^{sa} and K_d values for the treated illite sample.

Measured and Predicted Values	Treated Illite
<u>Results from Equations in Figures 29 and 32</u>	
Surface Charge Density (C/m^2)	0.276
Specific Surface Area (m^2/g)	72.10
Predicted Contact Angle (θ)	10.1
Predicted K_d^{sa} (mL/m^2)	0.032
Predicted K_d (mL/g)	2.33
Measured K_d^{sa} (mL/m^2)	0.029
Measured K_d (mL/g)	2.07
<u>Results from Equations in Figures 31 and 33</u>	
Surface Charge Density (C/m^2)	0.276
Specific Surface Area (m^2/g)	72.10
Predicted $\gamma^\ominus$ (mJ/m^2)	57.3
Predicted K_d^{sa} (mL/m^2)	0.036
Predicted K_d (mL/g)	2.60
Measured K_d^{sa} (mL/m^2)	0.029
Measured K_d (mL/g)	2.07
<u>Results from Equation in Figure 34</u>	
Surface Charge Density (C/m^2)	0.276
Specific Surface Area (m^2/g)	72.10
Predicted K_d^{sa} (mL/m^2)	0.038
Predicted K_d (mL/g)	2.73
Measured K_d^{sa} (mL/m^2)	0.029
Measured K_d (mL/g)	2.07

already available from previous studies. Once the dominant clay(s) are known, this information could be used with either the cited contact angle with water or electron-donor parameter (Table 5), or with the measured CEC of the mineral(s) and the corresponding equation in either Figure 32, 33, or 34 to determine an estimated K_d^{sa} value.

An alternative approach to identifying and determining the percent of clay(s) in the clay-size fraction might possibly be to measure the contact angle with water, electron-donor parameter, CEC, or combination of all three for a representative sample of the clay-size fraction. Each of the measured values of the representative sample might be used to represent a bulk average of that measured property for all the mineral types found in the clay-size fraction. Measurement of contact angle with water and determination of $\gamma^\ominus$ can be achieved using the methods described by van Oss et al. (1987a, 1987b, 1988, 1990), Giese et al. (1991), and Costanzo et al. (1990). Cation exchange capacity of the clay-sized fraction can be analyzed using the ammonium acetate procedure (Hesse, 1971). The gross surface charge density of the clay-size fraction can be derived from the CEC. The relationship between surface charge density (σ) and CEC is $\sigma = \text{CEC}/s_a$ (Newman, 1987). The surface charge density derived from this equation should be converted to proper SI units, coulombs per unit area (C/m^2) (Note: $1 \text{ meq/g} = 96.5 \text{ C/g}$). The value for specific surface area needed to determine surface charge densities from the CECs as well as the K_d s can be measured by the N_2 -BET method or might be obtained from the literature.

As a preliminary test of the validity of the modified two-component model in estimating K_d , predicted K_d^{sa} values using the equations in Figures 32, 33, and 34 and K_p values were derived for three sediment types found within an aquifer. Information on these sediment types are available from Bishop et al. (1991) and Smith et al. (1992). The sediments were collected from the upper aquifers at Lawrence Livermore National Laboratory (LLNL), California and are representative of alluvial and fluvial deposits that have low natural organic-carbon content. The selected sediment types characterize a range of lithology found in the saturated zone at LLNL, i.e., sandy gravel, clayey sand, and sandy clays. Table 23 lists selected properties of the three sediment types.

Table 23. Selected properties of three sediment types found within an aquifer at Lawrence Livermore National Laboratory (LLNL), California (Bishop et al., 1991). The values listed for each sediment type represent averaged values of measured properties for several samples. The number of sample values used to obtain the averaged value is also listed with the sediment types.

Sediment Type	f_{oc} (-)	Clay (%)	Silt (%)	Sand (%)	Gravel (%)	K_d (mL/g)
Sandy Gravel Average Number = 10	0.0004	5	6	33	56	0.22
Clayey Sand Average Number = 2	0.0006	21	19	48	12	0.76
Sandy Clay Average Number = 3	0.0007	39	29	30	2	1.11

The values listed for each sediment type represent averaged values of measured properties of aquifer samples that had similar lithologic characteristics. The number of sample values used for determining the averaged values are included in Table 23. Bishop et al. (1991) measured the K_d values of the sediment samples using the batch sorption method after removing the gravel content. The measured K_d values were normalized with the percentage of gravel yielding a distribution coefficient that represented the whole sediment. Smith et al. (1992) analyzed the clay content at the depth interval where the sediments were collected. The analyses revealed that the clay fraction was predominantly montmorillonite averaging 86% of the total clay content. On average, another 7.4% of the clay content consisted of illite. The remaining clay content consisted of various amounts of kaolinite and chlorite.

Only predicted K_d^{sa} values for montmorillonite and illite were used to predict K_d s for the sediment types because both these minerals had an ubiquitous presents in the depth interval of interest. For montmorillonite, K_d^{sa} values were derived from its contact angle with water and its $\gamma^\ominus$ value (Table 5) using the equations in Figures 32 and 33, respectively. For illite, the predicted K_d^{sa} values derived from the equations in Figure 32 and 33 were obtained from Table 22. A third predicted K_d^{sa} value for each of these two minerals was derived by converting their measured CEC given in Table 7 to surface charge density. The calculated surface charge density values for the minerals were used with the equation in Figure 34 to derive the K_d^{sa} values. Because of the uncertainty in the amount of kaolinite and chlorite present in the three sediment types, their contributions to the predicted K_d were not included. This exclusion was not considered important because the contribution of kaolinite and chlorite to the predicted K_d values was considered insignificant ($\leq 2.0\%$).

Since the sediments came from an aquifer system that had as its predominant cation Ca^{2+} , a predicted effective specific surface area of $45.5 \text{ m}^2/\text{g}$ was derived for montmorillonite. To derive this value, the equation in Figure 33 and the relationship $sa = K_d/K_d^{sa}$ were used. The $\gamma^\ominus$ value of montmorillonite (Table 5) was used with the equation in Figure 33 to solve for K_d^{sa} , and the K_d value of montmorillonite from the 0.001 CaCl_2 experiment (Table 10) was used in combination with K_d^{sa} to solve for the predicted effective surface area. The effective surface area of illite was set equal to its measured specific surface area (Table 7).

Using the modified two-component model given above, predicted K_d values were calculated and are shown in Table 24. The predicted K_{io} values for illite and montmorillonite were derived by solving for $(K_d^{sa})(sa)$. The K_{oc} of 108 mL/g was used with the f_{oc} of the sediments to derive K_p values. The K_{io} for each mineral was used with

Table 24. Predicted K_d s for three sediment types based on properties of the dominant clays, montmorillonite and illite, and the modified two-component model.

Measured and Predicted Values	Sandy Gravel		Clayey Sand		Sandy Clay	
	Mont.	Illite	Mont.	Illite	Mont.	Illite
<u>Results from using the Equation in Figure 32</u>						
Specific Surface Area (m^2/g)	45.5	72.10	45.5	72.10	45.5	72.10
Contact Angle with water (θ)	39.0	10.1	39.0	10.1	39.0	10.1
Predicted K_d^{sa} (mL/m^2)	0.079	0.032	0.079	0.032	0.079	0.032
Predicted K_{io} (mL/g)	3.59	2.33	3.59	2.33	3.59	2.33
Predicted K_m (mL/g)	0.15	0.009	0.65	0.04	1.20	0.07
Predicted K_p (mL/g)	0.04		0.07		0.08	
Predicted K_d (mL/g)	0.20		0.76		1.35	
Measured K_d (mL/g)	0.22		0.76		1.11	
<u>Results from using the Equation in Figure 33</u>						
Specific Surface Area (m^2/g)	45.5	72.10	45.5	72.10	45.5	72.10
Electron-donor parameter, $\gamma^\ominus$, (mJ/m^2)	36.2	57.3	36.2	57.3	36.2	57.3
Predicted K_d^{sa} (mL/m^2)	0.081	0.032	0.081	0.032	0.081	0.032
Predicted K_{io} (mL/g)	3.69	2.60	3.69	2.60	3.69	2.60
Predicted K_m (mL/g)	0.16	0.01	0.67	0.04	1.24	0.08
Predicted K_p (mL/g)	0.04		0.07		0.08	
Predicted K_d (mL/g)	0.21		0.78		1.40	
Measured K_d (mL/g)	0.22		0.76		1.11	
<u>Results from using the Equation in Figure 34</u>						
CEC ($\text{meq}/100\text{g}$)	96.50	23.30	96.50	23.30	96.50	23.30
Surface Charge Density (C/m^2)	0.12	0.31	0.12	0.31	0.12	0.31
Specific Surface Area (m^2/g)	45.5	72.10	45.5	72.10	45.5	72.10
Predicted K_d^{sa} (mL/m^2)	0.10	0.024	0.10	0.02	0.10	0.02
Predicted K_{io} (mL/g)	4.55	1.73	4.55	1.73	4.55	1.73
Predicted K_m (mL/g)	0.20	0.006	0.82	0.03	1.53	0.05
Predicted K_p (mL/g)	0.04		0.07		0.08	
Predicted K_d (mL/g)	0.25		0.92		1.66	
Measured K_d (mL/g)	0.22		0.76		1.11	

its percent of the clay fraction to derive their K_m value (Table 24). To obtain the predicted K_d value, the predicted K_m values of the two minerals and the K_p value were added (Table 24).

The predicted K_d values based on the contact angle and on the electron-donor parameter $\gamma^\ominus$ are in good agreement with the measured K_d values (Table 24). That based on CEC are in moderate agreement with the measured K_d values. This good to moderate agreement suggests that this modified model may be an alternative means to derive K_d values in lieu of elaborate, time-consuming, batch sorption studies. If one uses this approach to predict K_d , a note of caution is that the percent of true clay(s) needs to be the dominant mineral of the clay-size fraction. If other minerals, such as quartz and feldspar, make up the bulk of the clay-size fraction (f_{io}) of the sediments, the predicted K_d values based on assuming that f_{io} equals the clay content may be an over-estimate of the sorptive behavior of that sediment. To address this problem, perhaps the better approach might be to measure, as suggested above, one or all three properties (contact angle, electron-donor parameter, or CEC) for a representative sample of the clay-size fraction. Once the value(s) are measured, one might follow the steps shown in Table 24 to derive a predictive K_d using the modified two-component model. For either approach, further comparisons against several measured K_d values derived by traditional methods are suggested such as laboratory methods (batch sorption or column) or field-based methods. These comparisons should include aquifer samples that contain a variety of compositions to further determine if the modified model is applicable to a wide range of aquifer sediments.

Variations in TCE Uptake by Oxide Minerals

The results of this study show that the oxides can potentially adsorb HNOs in natural aquifer systems, especially under favorable aqueous geochemical conditions. Compared to the phyllosilicates studied, the oxides had smaller K_d values, while some of the oxides had larger K_d^{sa} values. Among the different oxides, their K_d values only varied slightly from each other whereas their K_d^{sa} values varied over an order of magnitude. Two possible explanations for the high K_d^{sa} values are: (1) the environment of the oxide surfaces is amenable to adsorbing TCE, and (2) organic coatings on the oxides was responsible for adsorbing the TCE.

The Effects of Electrolyte Concentration and Type

Electrolyte Concentration Of the two electrolyte concentrations used, the adsorption of TCE was greatest when the minerals were equilibrated in the 0.001 N electrolyte solutions (Tables 14 and 15). This greater adsorption can be attributed to a lower net surface charge on the oxide in the 0.001 N electrolyte solutions than in 1.0 N solutions (Fig. 6). With less surface charge density, hydrophobic expulsion of TCE from the surface of the mineral is likely to be less. The adsorption trends observed for the oxides with different electrolyte concentrations are in direct contrast to those observed for the non-swelling phyllosilicates. Apparently, the change in the surface conditions that reduced adsorption to the oxides was significant enough to offset those gains from hydrophobic expulsion of TCE from the 1.0 N electrolyte solution. Pyrolusite was the exception to the trend observed for the other oxides. A possible explanation is that the surface of pyrolusite was sufficiently covered with organic material (Table 8) to mask its inorganic character.

Electrolyte Type TCE adsorption onto most of the oxides was lower in the CaCl_2 solutions than in the NaCl solutions (Tables 14 through 17). Moreover, a greater difference in adsorption was observed between the 0.001 and 1.0 N CaCl_2 solutions than between the two NaCl solutions. One possible explanation for this greater difference could be that Ca^{2+} has a higher affinity for the surface of the oxide than does Na^+ (McBride, 1989). The Na^+ interacts with the oxide surface through nonspecific bonding and is electrostatically held loosely next to the surface (outer-sphere complexing). The Ca^{2+} can interact with the surface oxygen atoms through specific bonding (inner-sphere complexing) especially at higher pH levels (Hsu, 1989). The higher affinity of calcium for the surface oxygen atoms creates shifts in the PZC of the oxides (Table 3) toward lower values (McBride, 1989). This means that cation adsorption onto the oxides in a CaCl_2 system can begin at a lower solution pH than in a NaCl system.

The shift of the PZC to a lower value probably increased the equivalents ratio of Ca^{2+} next to the surface to Ca^{2+} in the bulk solution. This ratio was likely greater than that of the NaCl system. The greater concentration of Ca^{2+} next to the oxide surfaces in the CaCl_2 system compared to that of Na^+ in the NaCl system presumably produced greater hydrophobic expulsion of TCE from the oxide surface; consequently, the oxides adsorbed less TCE in the CaCl_2 system than in the NaCl system.

The greater decline in adsorption from 0.001 N to 1.0 N in the CaCl_2 system compared with the NaCl system could be due to a greater difference between the experimental solution pH and the oxides' PZC for the calcium system. In Figure 6, the farther away the pH is from the PZC, the greater the difference in surface charges of the oxide among various concentrations of the electrolyte. The greater difference in the surface charge causes a greater change in the ion exchange capacity of the oxide. In this

study, the greater difference in cation adsorption of Ca^{2+} compared with Na^+ between the 0.001 N and 1.0 N electrolyte concentrations presumably resulted in the oxides having a greater change in their adsorptive capacities for TCE in the CaCl_2 system than in the NaCl system.

Effects of Mineral Surface Area

Compared to the phyllosilicates studied, the oxides had smaller K_d values resulting from their limited surface areas (Table 7), but the K_d^{sa} values for the oxides were high. Much higher K_d values would be anticipated if these minerals were processed to obtain a size fraction that was $<2\ \mu\text{m}$, rather than the $<30\text{-}\mu\text{m}$ size used in this study. In natural settings, this smaller size fraction often is present in soils and sediments (Allen and Hajek, 1989).

Evaluation of Organic Coatings on Oxides

Another explanation for the comparably high K_d^{sa} values of the oxides may be that sorption is enhanced by organic coatings on their surfaces. An analysis of contributions from the mineral fraction and the organic fraction—similar to that performed for the phyllosilicates—was also performed for the oxides. The results of the analysis are presented in Tables 25 and 26. As indicated by the two-component model, most of the TCE adsorption is attributed to the mineral surfaces and not to the organic material. Pyrolusite was the exception in that all of the sorption observed was attributable to its f_{oc} ; the limits of the two-component model were exceeded, and calculated K_m and $\%mf$ are negative. The high contribution of organic carbon content to sorption would explain why pyrolusite did not follow the sorptive trend of the other oxides, whose K_d decreased as the electrolyte concentration increased.

Table 25. Parameters used to calculate inorganic and organic contributions to sorption for oxide samples.

Mineral Type	K_{oc} (mL/g)	f_{oc}^a (-)	K_p^b (mL/g)	K_d^c (mL/g)	K_m^d (mL/g)
Hematite	108	0.00020	0.02	0.32	0.30
Goethite	108	0.00035	0.04	0.21	0.17
Pyrolusite	108	0.0038	0.41	0.38	-0.03
Gibbsite	108	<0.00005	0.01	0.40	0.39

^a f_{oc} = Mass fraction of organic carbon (Table 8).

^b $K_p = K_{oc}f_{oc}$

^c K_d values from minerals equilibrated in the 0.001 N $CaCl_2$ solution (Table 15)

^d $K_m = K_{io}f_{io}$.

(-) = dimensionless

Table 26. Percentage of inorganic and organic contributions to TCE sorption for the oxide samples and fraction of organic carbon that would be necessary to account for observed sorption results.

Mineral	% <i>mf</i>	% <i>of</i>	f_{oc}^{abs}
Hematite	93.3	6.7	0.0030
Goethite	82.0	18.0	0.0019
Pyrolusite	-8.0	108	0.0035
Gibbsite	98.7	1.3	0.0037

CONCLUSIONS

Phyllosilicates and oxides are potentially important adsorbents of TCE. Of the eight phyllosilicates and four oxides examined, K_d values varied from near zero to 14 mL/g.

The adsorptive capacities of phyllosilicates are highly dependent on their hydrophobicity. As the hydrophobicity of a mineral decreases so did its affinity for TCE. The hydrophobicity of the phyllosilicates correlated with the surface charge density and with the electron-donor parameter, $\gamma^\ominus$, which reflects the Lewis base strength. As these parameters decreased, the hydrophobicity of the mineral increased. A third measure of hydrophobicity, the contact angle with water, increased as the hydrophobicity increased.

The specific surface area also was important in determining the TCE adsorptive capacities of the phyllosilicates. The minerals with large specific surface area, such as montmorillonite, talc, and illite, had some of the highest adsorptive capacities.

The composition of the electrolyte solution had a significant effect on TCE adsorption by the phyllosilicates. Increasing the CaCl_2 and NaCl concentrations from 0.001 to 1.0 N resulted in increases of up to 82% in adsorption by the non-swelling phyllosilicates. This increase in adsorption was due to hydrophobic expulsion (salting out) of TCE from solution.

The surface area of montmorillonite available to TCE adsorption varied widely in the different types and concentrations of the electrolyte solutions due to swelling. The variability in K_d was explained by expansion of the layers and the development of quasicrystals in the different electrolyte solutions. These factors control the accessibility of TCE to the mineral surface.

The adsorptive behavior of a phyllosilicate (K_d^{sa}) can be predicted if the contact angle with water, surface charge density, or Lewis base strength of a mineral is known or

can be determined. If the specific surface area of the mineral and organic carbon content of the sample also are known, a K_d value for the mineral can be derived. A similar predictive model can be used for an aquifer sediment sample.

Based on mass, the adsorptive capacities of the oxides studied were less than those of most of the phyllosilicates. The adsorptive capacities of some of the oxides based on surface area, however, were greater than those of most of the phyllosilicates.

The effect of cation type and electrolyte concentration on the adsorptive trend of the oxides was opposite to that of the phyllosilicates. The results showed that, by increasing the ionic strength of the solution, the adsorptive capacities of the oxides diminished. This effect was more evident for the CaCl_2 systems than the NaCl systems. This reduction in adsorption was most likely due to the increase in surface charge and the ion exchange capacity of the oxides, which in turn increase the hydrophilicity of the surface and hydrophobic expulsion of TCE from the surface.

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