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Sorption of nonpolar organics on minerals and aquifer materials

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The College of William and Mary, 1987

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Sorption of Nonpolar Organics on Minerals and Aquifer Materials

A Dissertation

Presented to

Faculty of the School of Marine Science

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirement for the Degree of

Doctor of Philosophy

by

Thomas Bennett Stauffer

APPROVAL SHEET

This dissertation is submitted in partial fulfillment of

the requirement for the degree of

Doctor of Philosophy

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ABSTRACT

The sorption of nonpolar organic chemicals on hydrous oxides, clay minerals, and subsurface aquifer materials was studied using the batch isotherm technique. Radiolabeled (^{14}C) trichloroethylene, orthodichlorobenzene, naphthalene, and 1-methylnaphthalene were sorbed on mineral sorbents, subsurface aquifer materials, and a surface soil at six different equilibrium concentrations over a concentration range from 0.001 mg/L to 1.0 mg/L. A knowledge of the sorption coefficients of these fuel components and solvents is necessary to predict the transport of these chemicals through groundwater systems and ultimately to rivers, lakes, and estuaries.

Sorption on oxides and surface soils was found to be pH-dependent with decreased sorption at high pH. Increased ionic strength showed a slight increase in sorption on surface soils and some oxides. Sodium montmorillonite and Barasyn, a synthetic montmorillonite, sorbed more of the nonpolar sorbates than the oxides, but less than the surface soil. Aluminum-saturated montmorillonite took up more sorbate than calcium-or sodium-saturated montmorillonites, but the aluminum saturation process apparently involved changes in the clay structure.

Aquifer materials sorbed small amounts (<3ug/g) of the nonpolar organics. Sorption coefficients for two nonpolar sorbates were determined on seven different aquifer materials. K_{oc} varied by a factor of 10 over the aquifer material sorbents. Various sorbent chemical and physical properties, in addition to organic carbon, were

measured to discover any correlations between the properties and sorption coefficients. No predictive relationship was found between the sorption coefficient and selected chemical/physical properties of the sorbents.

Since the K_{oc} concept failed for the aquifer materials studied here and other predictive relations were not found, sorption coefficients must be determined for each aquifer material occurring at a contaminated site. These coefficients must be used in contaminant transport calculations.

SORPTION OF NONPOLAR ORGANICS ON MINERALS AND AQUIFER MATERIALS

GENERAL INTRODUCTION

1. Introduction

Groundwater is the primary water source for more than 40% of the U.S. population. Contamination of this vital resource which has been reported in at least 34 states is a growing national concern. Contamination sites are widespread and include wastes from industrial, military, and agricultural sources. Agricultural fertilizers and pesticides can percolate through soil systems and become mixed with groundwater. Leaking underground fuel storage tanks and transfer lines from facilities near lakes and estuaries can contribute fuel components to groundwater. Nitrogenous and phosphorus wastes can seep into groundwater from septic tanks located in urban areas. Since groundwater eventually feeds into surface streams, lakes, and estuaries, contaminants that are transported by groundwater become potential sources of surface water pollution. These nutrients and pollutants can contribute to the eutrofication (Sewell, 1982) and pollution of these receiving surface waters. This situation exists along the Atlantic Coastal Plain and thus in the rivers and estuaries of the Chesapeake Bay system. The contribution of groundwater-borne contaminants to the total contaminant load of such a system cannot be assessed until groundwater contaminant transport processes are well understood. The sorption work reported here is a contribution to the understanding of the transport process.

The importance of organic chemical transport in the environment has been recognized since the early 1960s, when concern was primarily limited to the movement of pesticides through treated soils. It was economically important to know how long these chemicals stayed in contact with the soil. Further study was needed to understand how the pesticides moved through the soil, and also through surface water and aquifers. In the late 1970s and early 1980s, it became apparent that the environment was contaminated not only by pesticides, but by a wide variety of organic chemical wastes in soil, water, and groundwater systems. A knowledge of the environmental transport, fate, and effect of the organic chemicals became necessary from a health standpoint due to the toxicity of many of these chemicals. An understanding of pollutant transport by groundwater is necessary to select cleanup strategy at sites of high contaminant concentration and to predict long-term distribution and fate of contaminants that cannot be recovered by cleanup procedures.

The sorption of organic chemicals to solid phases is a key element in determining environmental transport. The term "sorption" is used when it is not known whether the chemicals are absorbed into or adsorbed onto the sorbents in question. Equation (1) represents mass conservation for the movement of organic chemicals having linear sorption isotherms through groundwater systems under conditions of local sorption equilibrium (Freeze and Cherry, 1979).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D}{RD} \cdot \frac{\partial C}{\partial x}\right) - \frac{V}{RD}\frac{\partial C}{\partial x} \qquad (1)$$

where C is the solution concentration of the organic contaminant (mg/L), D is the dispersion coefficient (cm^2/hr), V is the groundwater velocity (cm/hr), and RD is the retardation factor. The retardation factor, V/V_c, is related to the sorption coefficient, K, as shown in equation (2),

$$RD = \frac{V}{V_c} = 1 + \frac{\rho}{n}\left(K\right) \qquad (2)$$

where, V is the average groundwater velocity (cm/hr), V_c is the velocity of the retarded contaminant (cm/hr), ρ is the mass bulk density (g/cm^3), n is the porosity (cm^3/cm^3), and K is the sorption coefficient (L/kg)(Freeze and Cherry, 1979). The sorption term in this equation expressed as a retardation factor, RD, forms the basis for this dissertation.

Physical sorption of a nonpolar organic chemical to a solid surface is driven by attractive forces between the solute and sorbent generally referred to as van der Waals' forces. These forces are composed of London dispersion forces which are dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and ion-dipole attractions induced between the sorbate electrons and the sorbent electrons.

Hydrophobic organic chemicals of limited water solubility may also be driven to the sorbent surface due to solvent entropy effects. Hamaker and Thompson (1972) referred to the overall process of sorption of nonpolar compounds on surfaces as "hydrophobic bonding."

Sorption of organic contaminants on aquifer material retards their transport in relation to the groundwater and leads to spatial separations of contaminants by chromatographic processes in the aquifer. A knowledge of the sorption coefficients for nonpolar contaminants on minerals and aquifer materials and how they relate to both sorbate and sorbent physical and chemical properties is a requirement for predicting contaminant movement. The ability to predict sorption of nonpolar organic chemicals on aquifer material based on some readily measured properties would be a significant aid in calculating contaminant transport by equation (1). Results from these calculations can be used to determine appropriate cleanup methods at sites of high contaminant concentration and to determine long-term distribution of dilute chemicals that cannot be recovered by cleanup procedures. Without the ability to predict sorption based on sorbent properties, complete sorption isotherms for each contaminant must be measured to provide the sorption coefficient used in transport equations. Isotherm measurement is laborious, time consuming, expensive, and beyond the capability of most small laboratories. A simple sorbent characterization that would allow sorption coefficient prediction would be a great aid in the field of groundwater contaminant transport.

There is a dearth of information on sorption of organic contaminants on materials from saturated zones below the surface soil horizons or on materials from subsurface confined aquifers. Freeze and Cherry (1979) define an aquifer as "a saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients." Aquifer material is not chemically specified by this definition. Existing predictive equations based on the organic carbon partitioning models generally do not provide satisfactory estimates for K values on these low carbon systems. Since aquifer material has low organic carbon content and relatively high mineral content, clay and mineral oxide surfaces are treated here in simple systems to assess their relative importance in sorption of nonpolar organics. Information gained from these single sorbent studies may provide insight on sorption by the more complicated aquifer materials.

The contribution of sorbent mineral components other than organic carbon has been noted, but little quantitative data exists in the literature. Sorption on aquifer materials must be measured to enlarge the data base and to assess the utility of predictive relations.

This dissertation examines the possibility of predicting sorption on aquifer materials based on a knowledge of aquifer material chemistry, sorption coefficient measurements on model mineral sorbents, and sorption coefficient measurements on aquifer materials. Several organic sorbates of differing polarities were used as surface probes to observe their sorption trends on the model mineral surfaces and aquifer materials. Experiments were conducted to determine the magnitude of sorption coefficients on inorganic oxides and clay minerals that are components of aquifer materials. Ionic strength and pH were varied over possible environmental ranges to observe effects on sorption. Montmorillonite clay saturated with different cations were used to determine if cation changes altered sorption coefficients as suggested by Rogers et al. (1980) and Rogers and McFarlane (1981). Sorption coefficients were measured for two nonpolar organic sorbates on seven representative aquifer materials to provide a comprehensive sorption data set. This represents the largest organic sorption data base on representative aquifer materials published to date. The aquifer materials were characterized for various physical and chemical properties to look for a relationship between these properties and sorption coefficients from this data set. Some related work has been done by Means et al. (1982), Hassett et al. (1980), and Karickhoff et al. (1979) using surface soils and sediments. They did not, however, include aquifer material sorbents and did not use the organic solvents and fuel components which are common groundwater contaminants. Their correlations included few chemical properties of the sorbent and sorbate, and their results may be of little utility in predicting sorption in groundwater systems.

REVIEW OF LITERATURE

a. Sorption and Sorbent Organic Carbon Content

Lambert et al. (1965) demonstrated the importance of sorbent organic carbon content (OC) in soil and sediment, and developed the relationship: $K_{oc} = K/f_{oc}$; where K is the sorption coefficient (L/kg), f_{oc} is the sorbent fraction organic carbon content, and K_{oc} is a carbon-normalized sorption coefficient (mL/g OC). It was found that the K_{oc} for a given organic compound remained constant for surface soils over a wide range of OC.

Extension of this preliminary work to include a wide variety of sorbents and sorbates has met with varying degrees of success in predicting organic chemical sorption. Karickhoff et al. (1979) studied the sorption of aromatic hydrocarbons and chlorinated hydrocarbons on pond and river sediments and found that on an OC basis, sand size fractions were considerably less effective in sorbing these chemicals than the finer fraction. Differences in sorption were attributed to the fact that the OC varied between the size fractions. Thus, to determine the sorption coefficient for the entire material, it was necessary to know OC distribution in the particle size fractions. Nkedi-Kizza et al. (1983) found similar results working with 2,4,5-T herbicides and diuron. Sorbents OC contents in these studies were generally high; greater than 1%. In an effort to predict sorption dependence on sorbate properties, the Karickhoff et al. (1979) regressed K_{oc} against sorbate octanol-water partition coefficients (K_{ow}) and water solubilities (S).

Octanol-water partition coefficients were found to be a good predictor of K_{oc} for the systems studied. These studies did not examine low OC sorbents or low molecular weight organic sorbates. The utility of K_{oc} in determining sorption on low organic carbon materials was not considered.

Hassett et al. (1980) measured sorption of polycyclic aromatic hydrocarbons (PAH) on a variety of surface soils and sediments and found that the sorption coefficient correlated well with OC. However, good correlations were also obtained with other sorbent properties, such as clay mineral content and cation exchange capacity. Sorbent OC were generally greater than 1% and the sorbates studied were a homologous series of PAHs. No attempt was made to characterize the naturally occurring organics or to examine low organic carbon content sediments.

Based on the above cited work, Karickhoff (1981) and Chiou et al. (1979, 1983, 1984) have published a number of studies where sorption has been viewed as partitioning or solution into the organic materials present, rather than sorption onto a sorbent surface. Karickhoff (1981) showed that, with the inclusion of certain molecular properties, K_{oc} values could be predicted that were within a factor of three of the measured K_{oc}. Chiou et al. (1979) studied the sorption of a number of short-chain chlorinated hydrocarbons and polychlorinated biphenyl isomers on a surface soil. They found no nonlinearity in the sorption isotherms and an inverse relation was observed when the srption coefficients were plotted against the corresponding solubilities. Based on this evidence, they postulated that the organics were partitioning into the organic matter. Only one surface soil, which contained 1.6% organic matter, was studied to support this. Chiou et al. (1983) studied sorption of similar compounds on Woodburn silt loam soil with 1.9% organic matter. Simultaneous sorption of binary mixtures produced linear isotherms with similar slopes to those for single solute isotherms, which was interpreted as further evidence for partitioning into the soil organic matter. They noted that any differences in the soil organic matter will affect the partition coefficients and the resulting correlation equations containing these coefficients. Chiou (1985) studied the sorption of parathion and lindane on two different soils from aqueous and hexane mixtures. Mineral surfaces controlled sorption from hexane solution in the absence of water. When water was present, the organic carbon content controlled the sorption and partitioning was assumed due to lack of competitive sorption, linearity of isotherms, OC-dependence, and low temperature dependence on equilibrium.

Mingelgrin and Gerstl (1983) have reevaluated partitioning as a mechanism for nonionic chemical adsorption in soil. They worked with several nonionic pesticides on Israeli soils of varying clay and organic content. Results showed linear isotherms on clays and some nonlinear isotherms on various soils. They pointed out that results presented by Chiou et al. (1979), who contended that linearity at concentrations near the solubility limit indicated partitioning, were with solutes of low solubility where surface coverage must be low. Under these conditions, linear isotherms would be expected, thereby casting doubt that linearity is a sufficient condition to prove partitioning. Alternate thermodynamic arguments were also presented, showing that a low ΔH of sorption did not prove partitioning. The authors conclude that the complexity of sorption on soil surfaces does not allow predictions based on correlations such as

K_{oc}, K_{ow}, and water solubility for a very diverse group of organic substances and that these correlations do not prove a partition process.

MacIntyre et al. (1982) demonstrated that a peroxide destruction of sediment organic carbon actually increased the sorption of nonionic organics. Garbarini and Lion (1986) fractionated soil organic matter and studied sorption of toluene and trichloroethylene on these fractions and commercially available soil organics. They found that these soil components had widely varying affinities for the sorbates studied which could not be entirely explained by their organic content. These two studies further demonstrate the difficulties in using soil organic matter as the sole criterion for explaining sorption of nonionic organics.

Several researchers have realized that the partitioning concept breaks down at low sorbent organic carbon concentrations and have proposed modifications to the partitioning concept (Karickhoff, 1984; Curtis et al., 1986; and McCarty et al., 1981). McCarty et al. (1981) and Karickhoff (1984) have presented two-phase models whereby sorption on mineral surfaces and partitioning into organic matter occur simultaneously. Differences between models of McCarty et al. (1981) and Karickhoff (1984) are primarily in the mode of action of mineral surface; that is, independent or in concert with the organic material. Curtis et al. (1986) indicate that these differences demonstrate the need for characterizing sorbed organic matter and the mineral matrix. Karickhoff (1984), using limited data sets, proposed that mineral contribution became important in sorption of nonpolar organics of less that 10 carbon atoms when the ratio of the mass of mineral matter to the mass of organic matter of the soil/sediment is >60. Schwarzenbach and Westall (1981) found that partitioning-related correlations understated the observed sorption when the organic carbon fraction was less than 0.001.

It is apparent that there is considerable controversy and varying opinion concerning adsorption versus partitioning and its role in predicting sorption. The concept of K_{oc} constancy is open to question. It is clear, however, that predictive relations based on K_{oc} seem to fail for nonionic organics when the sorbent OC is low (<0.1%) or when the ratios of mineral surfaces to OC is high (>60). Low OC are characteristic of aquifer materials, so the sorption work on aquifer materials presented here was necessarily directed to the determination of the utility of the K_{oc} concept in groundwater transport situations.

b. Clay and Mineral Oxide Surfaces

Clays and mineral oxides are weathering products of igneous and metamorphic rocks and are components of soils, sediments, and aquifer materials. Subsurface aquifer materials generally have low (<0.1%) OC and the organic matter present may not chemically resemble organic matter in surfacxe soils and sediments because of considerable diagenesis and oxidation. Hassett et al. (1981) and Karickhoff (1984) have noted that low OC and high mineral content in soils and sediments cause increased K values that may be attributed to sorption on inorganic sorbents. Research dealing with sorption of organic sorbates on aquifer materials requires the determination of the influence of these mineral sorbent surfaces, because of their large surface areas and low OC.

A review by Voudrias and Reinhard (1986) reported many possible organic reactions at clay and oxide surfaces, such as hydrolysis, elimination, substitution, redox reactions, and polymerization concurrent with chemical adsorption to surface Lewis and Bronsted sites. The most important environmental variables were temperature and water content. In completely saturated porous media, as in aquifers, hydration reduces the surface sorption and chemical reactions of organic compounds from their unhydrated sorbent surface values because most reactive sites are occupied by water. Thus, most of the reactions and mechanisms discussed by Voudrias and Reinhard (1986) do not apply due to the complete hydration of the surfaces in this study. Jurinak (1957) showed the importance of surface hydration by studying the sorption of ethylene dibromide (EDB) on homoionic montmorillonite. Differences in the amount of chemical adsorbed were attributed to the relative amount of water associated with the different exchangeable cations. The water present expanded the clay lattice providing more surface area for adsorption. Call (1957) studied the sorption of EDB on soils and montmorillonites, by varying the relative humidity (RH), and observing the changes in sorption. He found the usual competitive sorption between the organic chemical and water at the clay surface with a concomitant decrease in EDB sorption at high RH. He noted that at low RH, sorption of EDB actually increased with increasing water content, which was attributed to expansion of the clay lattice, but then followed the normal trend of decreased sorption at high RH. Call (1957) noted that on soils, water content also played a role in sorption by hydrating the soil organic colloids. These studies demonstrate the competitive nature of organic sorbate/water sorption on mineral surfaces and the resulting sorption attenuation for organic contaminants under saturated versus unsaturated conditions.

Several authors have investigated sorption of polar organic molecules from aqueous solution by clays and minerals in soils. Artiola-Fortuny and Fuller (1982) measured the adsorption of monohydroxybenzene derivatives by soils which were high in clay and low in OC and ranged in pH from 4.5 to 7.8. They found that percentage iron oxide and solution pH were the most important factors related to sorption, with the less soluble phenols being better sorbed. Hydrous iron oxide can react with both anions and cations and also hydrogen bond with sorbates. These characteristics may explain the observed sorption. Differences in sorbate uptake were attributed to the hydrophobic character of the sorbate and differences in sorbate chemical properties caused by changes in ring substituent groups. Juo and Oginni (1978) found that iron-oxide rich soils sorbed more paraquat than did the strongly acidic sedimentary soils. Multiple regression analyses of the Langmuir adsorption maxima for the paraquat cation against soil properties showed 96% of the sorption could be explained by the percentage Fe_2O_3 and cation exchange capacity. These two studies show the importance of mineral surfaces on sorption of ionizable compounds.

Rogers and McFarlane (1981) measured sorption of nonpolar halogenated organic sorbates on soils and Al^{+3}- and Ca^{+2}-saturated montmorillonite clays. The Al-saturated clay sorbed more than the Ca-saturated clay. Rogers et al. (1980) reported that benzene sorption was minimal on two silty clay loam soils and Ca-saturated montmorillonite, but that Al-saturated clay sorbed three times more than the Ca-saturated clay. These studies show the importance of clay as a possible sorbent for nonpolar organics, and the differences caused by cation saturation. Unfortunately, the clays were assumed to have no associated organic material and were not characterized for OC, thereby casting some doubt on the interpretation of their sorption data. Without OC data, the importance of the saturating ion in the sorption studies is unclear.

MacIntyre et al. (1982) and MacIntyre and deFur (1985) observed hydrocarbon fuel component sorption on a Wyoming montmorillonite (Bentonite) from both multi-sorbate and single sorbate solutions. The clay had been washed with methanol prior to use, but OC values were not reported. Stauffer and MacIntyre (1986) reported significant sorption of low-polarity organics on iron oxide (goethite) and less sorption on aluminum oxides. Surface charge was implicated as a possible explanation for the sorption differences, but surface charge measurements were not made. Banerjee et al. (1985) studied the sorption of trichlorobenzene, o-chlorotoluene, and dimethylphthalate on a low OC subsurface materials and found that the sorption values correlated well with the clay size fraction for materials from lower depths. They reported mineral contribution to the observed sorption for orthochlorotoluene. Sorption of trichlorobenzene on shallow samples correlated with both OC and clay-sized particle content. It was concluded that sorbent OC is a good predictor for sorption down to about 0.2% OC and that, for "very hydrophobic" molecules, OC of the sorbent will control sorption down to levels that defy quantification. Mineral contribution to sorption was inferred from data falling within a zone of clay/OC ratio greater than 60 (see Karickhoff, 1984) when K_{oc} was plotted against clay/OC ratio. Little evidence was presented to support the speculation on sorption of "very hydrophobic" molecules.

Mineral surfaces play a role in sorption of organics on aquifer materials, especially where the organic carbon concentration is low. It is therefore necessary to study sorption onto these inorganic minerals, since they contribute to the overall sorption coefficient on aquifer materials. Organic chemical sorption measurements from aqueous solution onto clay surfaces involve pseudo-equilibrium systems, because it takes about 3 1/2 years for kaolinite to reach equilibrium water solubility (May et al., 1986) and further, smectites do not reach equilibrium.

c. Sorption Coefficients on Aquifer Materials

The literature on sorption by aquifer materials is complicated by the vague definition of an aquifer. Results of sorption studies on aquifer materials must be interpreted in terms of the chemical and physical properties of the aquifer material samples used.

Much of the literature is based on the Borden site in Canada, at which the aquifer material is a relatively homogeneous, bedded, unconsolidated glaciofluvial sand of fine to medium grain with small silt-clay content and low OC, about 0.05% (Sutton and Barker, 1984). Mackay et al. (1986) studied the sorption of halogenated solvents (carbon tetrachloride, bromoform, tetrachloroethylene, hexachloroethane, 1,2-dichlorobenzene) on Borden site aquifer material and found sorption coefficients ranging from 0.13 to 0.74 L/kg. Most sorption coefficients varied by a factor of two over the core depth, but tetrachloroethylene sorption coefficients varied by an order of magnitude. Sorption differences over the depth profile could not be explained by variations in OC or surface area, leading the authors to conclude that the observed sorption may be related to the amount and distribution of some unknown mineral phases.

Abdul and Gibson (1986) studied sorption of PAHs on aquifer materials from the Borden site and a site near Flint, MI. Measured sorption coefficients for Flint and Borden materials varied by factors of 3 and 4, respectively, compared to calculated values based on regressions proposed by Karickhoff (1979). The authors did not speculate why the predictive equations worked poorly on the high OC Flint sample (1.87%), and pointed out the necessity of further multivariate analysis to possibly predict PAH sorption in the saturated groundwater zone. They noted that parameters such as particle size and surface area may be important in controlling the amount of PAH sorbed, and should be considered in statistical analyses.

Schwarzenbach and Westall (1981) measured the sorption of methylbenzenes and chlorobenzenes on aquifer materials and on the minerals γ-Al_2O_3, SiO_2, and kaolinite. Strong correlation was found between the sorption coefficients and OC for sorbents with OC >0.1%. The authors stated that, in the absence of organic carbon, the specific surface area and nature of the mineral surface would have a considerable influence on sorption. Sorption coefficients (K)(L/kg) ranged from 1.2 for chlorobenzene to 37.9 for tetrachlorobenzene on an aquifer material with OC=0.73%, whereas K ranged from 0.6 for chlorobenzene to about 5.0 for tetrachlorobenzene on kaolinite and gamma Al_2O_3. The lower observed K values on the clay and oxide were presumeably due to lower OC or mineral sorption.

Uchrin and Katz (1985) studied sorption for hexachlorocyclohexane (Lindane) on two aquifer materials from New Jersey. They reported K values of 13 L/kg and 11 L/kg, respectively for materials with OC=4.4 and 2.2%. Their study focused on the issue of reversible desorption, but it is apparent from the results that organic partitioning could not account for the similarities in K reported. Wide variation in application of the term aquifer material is indicated by their interchangeable use of "soils" and "aquifer materials" and by failure to specify the depth and water-saturation state of the samples.

Johnson et al. (1985) investigated sorption of five chlorophenols and three chlorophenoxyphenols on material from a chemical disposal site in Oregon. Actual waste water solutions were used as sorbates, and they were added to the groundwater which had a pH of 10. K values (L/kg) for di- and tri-chlorophenols were near zero with tetrachlorophenol 1.8 ± 1.0 and pentachlorophenol 9.5 ± 1.8. The chlorophenoxyphenols had K between 14 and 28. Naphthalene served as a standard and produced a K of 16 ± 2 with the sorbents under these conditions. Soil organic content was 2.4 ± 0.3%. The authors indicated that calculation from a tabulated K_{oc} for naphthalene would produce organic carbon concentrations of about 1.8%, but could not explain this disparity. Significant sorption for some of the chlorophenols was found even though they were not protonated and existed as anions at the study pH, but no explanation was given. Zachara et al. (1986) measured the sorption of quinoline on several low-organic carbon subsurface materials and found poor correlation of the resulting Freundlich constants with subsoil properties, including organic carbon. Acidic subsoils sorbed more quinoline than neutral or basic subsoils, which was attributed to ion exchange reactions between protonated quinoline and the subsurface materials. Varying pH of the subsoil materials showed that the organic cation was retained more than the neutral molecule. These two papers show that pH can play a significant role in sorption of ionizable species.

Miller and Weber (1986) studied the sorption of lindane and nitrobenzene on four aquifer sands and found experimental K varied by a factor of 3 or 4 from the calculated values based on $\log K_{oc} = \log K_{ow} - 0.21$. Some deviations were as high as a factor of 10, and were explained *post facto* by a combination of the sorbate's high water solubility and the sorbent's low organic carbon content. Several of the other sorbent carbon contents were of the same level but did not exhibit similar deviations. Organic contents of the sands were generally low, 0.10 - 0.14%, except for one high-carbon content sand of 1.14%. No other explanations were given for the observed K variation.

d. Correlations to Sorbent Chemical/Physical Properties

Many researchers have noted organic carbon-sorption relations in soil and sediments, but only a few have studied sorption on a wide range of sediments/soils as a function of sorbent properties. Karickhoff et al. (1979) worked with PAH and noted a direct dependence of K on OC for five pond sediments. Karickhoff (1981) also found a high correlation between K and OC in 17 soil/sediments. Correlations to clay, silt, and cation exchange capacity (CEC) were much lower. Since the surface soil/sediments used were relatively high in OC (with only two samples less than 0.5%), no conclusions can be drawn for the use of OC-based sorption in low OC sorbent systems such as aquifer materials.

Means et al. (1980a, 1980b, 1982) and Hassett et al. (1980, 1981) did a series of experiments with different sorbates on fourteen sediment/soil samples collected along the Ohio, Wabash, Illinois, and Mississippi rivers. The statistical technique applied by Means et al. (1980a, 1980b, 1982) included an unspecified "matrix correlation" among variables, and separate linear regression of K against each of the various sorbent properties. In all cases, significant correlation (R^2 not specified) was found between the OC and the K values, with some correlation between percentage clay-CEC and percentage organic carbon-percentage N content. Again, the main hindrance to applying these results to aquifer materials is the relatively high OC of the soil/sediment samples which were a subset of those used by Karickhoff (1981), with only two soils less than 0.5% organic carbon. Two amino-substituted PAHs were found to interact with the clay portion of the soils/sediments, with pH dependent sorption. It was concluded that clay materials would influence the sorption of polar organics.

Hassett et al. (1980, 1981) continued studies of α-naphthol and dibenzothiophene on the 14 soils and sediments cited above. OC was again found to be significantly correlated to K. The α-naphthol showed widely divergent K_{OC} on the sediments where the percentage OC to percentage montmorillonite ratio was less than 0.1. This was attributed to the more polar compound interacting with the more accessible clay surfaces when the TOC was low.

Insufficient information is available to demostrate correlations between K values for intermediate molecular weight sorbates and aquifer material physical/chemical properties.

e. Sorbent Concentration Effects

O'Connor and Connally (1980) proposed a mathematical model showing an exponential dependence of K on the sorbent-to-liquid weight ratio. The model was applied to various published data to explain the apparent inverse relationship between K and sorbent concentration; i.e., K's determined at lower sorbent concentrations gave higher K values than similar isotherms run at higher sorbent concentrations. Although a good fit was demonstrated, no theoretical basis was suggested for the model.

Voice et al. (1983) noted a sorbent concentration dependence for polychlorobiphenyls (PCBs) on sediments and clays. They proposed a mathematical model to explain this effect which involved the transfer of sorbing or solute binding material from the sorbent to aqueous suspension. Several experiments were attempted to isolate and examine the nature of the transferred material. Residual turbidity, OC, and UV absorbance were used to examine the supernatant liquid from sorbent blanks. The presence of microparticles or any transferred materials was not proven.

Horzempa and DiToro (1983) studied the effect of sorbent concentration on PCB partitioning to sediments and clays. Variations in solution composition and kinetic effects were found to affect sorption, but neither of these factors appeared to adequately account for the magnitude of the observed sediment concentration effect. They speculated that the observed sediment concentration effect might be due to solid phase interactions between suspended particles.

Curl and Keoleian (1984) proposed a model to explain the concentration effect, but did no experimentation, relying on previously published kepone sorption data to show their model's utility. The model assumes competitive adsorption in which a naturally occurring sorbate already on the sorbent competes for sites with the introduced sorbate. While the model was only tested with a limited data set, it has the advantage of explaining observed K value variations with increased sorbent to liquid ratio based on a mechanistic argument.

Gschwend and Wu (1985) studied the sorption of PCBs on river and lake sediments to observe changes in K caused by varying sorbent concentrations. They observed a sorbent concentration effect, but they found that it was caused by sorption to nonsettling sorbent microparticles or macromolecules. If adequate care was taken to completely separate the solid phase from the liquid phase or account for the nonsettling particle sorption, the sorbent concentration effect disappeared and K values remained constant over sorbent concentration ranges encompassing four orders of magnitude. They concluded that previous experimental work suggesting "complex" sorptive behavior were subject to experimental artifacts caused by incomplete separation between liquid and solid phases.

The concentration effect was not detected in batch isotherm studies conducted by Karickhoff et al. (1979). This observed sorbent concentration effect may occur in nature or may be an artifact of the experimental procedure. The sorbent concentration effect may be important in environmental models where K values are used to predict transport over and through media with wide variations in sorbent concentration, such as suspended sediments and lake or river bottoms. If a sorbent concentration effect exists, it would make data comparisons between studies using different sorbent concentrations difficult.

f. Effects of Equilibration Time on Sorption Values

Karickhoff and Morris (1985) and Coates and Elzerman (1986) studied the desorption of PCBs from contaminated sediments. They found that the rate at which PCBs desorbed was related to the length of contact time prior to desorption, and that sorption continues to increase over days and weeks. Karickhoff and Morris (1985) proposed a two-step model of equilibration, a quick initial step followed by a slow step occurring over a period of days to months. Using kinetic relations based on experimental data, Karickhoff and Morris (1985) estimated equilibration times in excess of one year for organic sorbate/sediment systems with $K>10^5$ (L/kg). The slow step was attributed to intra-particle diffusion that was very slow for large molecules. Data of Coates and Elzerman (1986) also support the two-step model. They also found evidence for competitive effects during desorption in rate differences observed for the same compound in single- and multi-solute systems. Rates of desorption were retarded in the multi-solute system studied. Equilibration times in these studies ranged from 12 to 150 days.

Karickhoff and Morris (1985) noted that the greatest change in K value observed in long-term studies for pyrene above a 48-hour basis value was only a factor of two. Additionally, it was shown that the more highly sorbed chemicals sorbed more slowly. A slow step in approach to equilibrium would be less important for low molecular weight, less sterically hindered molecules. While the PCBs studied above biodegrade very slowly, other chemical compounds could be significantly degraded over long equilibration times.

EXPERIMENTAL METHODS

1. Rationale for Chosen Methodology and Conditions

The batch equilibration technique was used to measure nonpolar chemical sorption by low OC sorbents because it 1) allows for the determination of an entire sorption isotherm in a short amount of time, 2) is commonly used in similar studies of surface soil and sediments, and 3) involves fewer variables than dynamic (column) techniques (personal communication, Dr. W.G. MacIntyre, VIMS, Gloucester Pt., VA). Since small amounts of chemical were sorbed, liquid scintillation techniques were used to quantify uptake of ^{14}C-labeled sorbates. Use of the batch technique also provided better handling control of the radiolabeled chemicals.

In all sorption isotherm studies, 2.0 g of sorbent and 10 mL of aqueous sorbate were used. This ratio was selected to provide measurable changes in sorbate concentration without using too much sorbent. Sufficient solution was available for liquid scintillation counting and pH measurement. The fixed solution/sorbent ratio was maintained throughout and sorbate-solution separations by centrifugation were made as complete as possible to avoid possible sorbent concentration effects. Differences in sorbent density caused the solid-liquid ratio to vary somewhat because the same containers (constant total volume) were used in all isotherm experiments. These ratio differences are much smaller than those differences existing where a sorbent concentration effect was reported. All data acquired on the different sorbents within this work are comparable with regard to solid-liquid ratio. Any concentration effect would remain constant within this study and not affect comparisons between K values of a sorbate on different sorbents.

Milli-Q water was selected for all isotherm experiments to minimize organic and inorganic contaminants in the aqueous phase. No attempt was made to produce a "synthetic" groundwater by adding inorganic salts or buffers to the Milli-Q water, since each groundwater sample is a product of the particular geologic materials through which it passes and no standardized formulation can be made. The usual sorbate concentration range, 0.001 to 1 mg/L was chosen to cover the expected environmental groundwater contamination levels and to produce isotherms at concentrations less than half solute saturation. Resulting isotherm data were fit to a linear model because of its simplicity and widespread use. Other models were tested, but did not have any apparent advantage over the linear fit, and, as MacIntyre and deFur (1985) point out, the choice of model is usually arbitrary.

Ambient laboratory temperature ($22.5 \pm 1^{o}C$) was selected because a temperature significantly different from this would require all handling operations to be done in an environmental chamber. Near room temperature a $10^{o}C$ temperature change causes the K value to change by 25% (Chiou et al., 1977). Since there was only a $2^{o}C$ or less range in temperature, changes in K values due to temperature variation would be 5% or less. All isotherms were obtained by equilibration, centrifugation, dilution, and transfer at this temperature.

An equilibration time of 24 hrs was used because it has commonly been used in similar sorption experiments and was short enough to permit investigating a large number of sorbate/sorbent combinations. Preliminary experiments showed no observable sorption changes after 16 hrs. Periods longer than 24 hrs were not used due to possible biodegradation of sorbates over extended equilibration periods.

The batch isotherm technique used here measures macroscopic thermodynamic states, which are averages of an ensemble of microscopic states of the system considered to be at equilibrium. There is no way to deduce from this average state the condition of a particular molecule since this average is based on enormous numbers of molecules and energy states. However, it is possible to make inferences from the ensemble averages and our knowledge stemming from nonthermodynamic observation. Direct observations of single molecule/surface interactions are not possible by equilibrium methods.

2. Sorbent/Sorbate Materials

The sorbates chosen for study are low molecular weight, nonpolar organic compounds found in fuels and industrial solvents that have been identified at numerous groundwater contamination sites. The clay and oxide minerals selected as sorbents are decomposition products of igneous and metamorphic rocks and thus components of soils and aquifer material. A surface soil sample was included to establish a reference for comparison with sorption on the low carbon sorbents. The aquifer materials, selected as sorbents and collected from U.S. Government-owned sites, represent saturated zone material from different geologic regions.

Inorganic Oxides and Surface Soil

The four inorganic oxides were: goethite (Pfizer, New York, NY), Linde 0.3 micron alumina polishing powder (Union Carbide, Indianapolis, IN), gibbsite (Hydral 705; Alcoa, Alcoa Center, PA), and MIN-U-SIL[5]

(Pennsylvania Glass Sand Corporation, Pittsburgh, PA).

One surface soil sorbent was used: Appalachee Ap horizon (Soil Science Dept., University of Florida, Gainesville, FL).

Clay Minerals

The four clay minerals were obtained from the Clay Minerals Society, Source Clays Repository, University of Missouri, Columbia, MO 65211. They were: KGa-1, Kaolin, well crystallized, Washington County, GA; SAz-1, Ca-montmorillonite, Apache County, AZ; SWy-1, Na-montmorillonite, Crook County, WY; and Syn-1, Barasyn SSM-100, synthetic mica-montmorillonite.

Aquifer Materials

Seven aquifer materials were used. Canadian Borden site aquifer material was obtained from D.M. Mackay at Stanford University and is a subsample of the "bulk" sample described by Mackay et al. (1986). Lula aquifer material was collected at a depth of 5 m from the Johnson Ranch near Lula, OK and provided by Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, Ada, OK. Four aquifer materials were collected at different Air Force bases across the United States, representing a variety of geologic materials. Locations and drilling logs are given in Appendix I. An additional aquifer material was collected from the Coast Guard Station at Traverse City, MI. Petrographic descriptions of these aquifer materials are given in Appendix II.

Five ^{14}C-labeled chemical sorbates were used: o-dichlorobenzene (ODCB), naphthalene (NAPH), and pentachlorophenol (PCP) from Pathfinder Laboratories, Inc., 1,1,2-trichloroethylene (TCE) from New England Nuclear; and 1-methylnaphthalene (MNAP) from Amersham. Specific activities were 11.58 mCi/mmol for ODCB of 98% chemical purity, 6.12

mCi/mmol for NAPH of 98% chemical purity, 10.57 mCi/mmol for PCP of 98% chemical purity, 2.7 mCi/mmol for MNAP of 94% chemical purity, and 6.6 mCi/mmol for TCE of unspecified chemical purity.

3. Sorbent/Sorbate Characterizations

Specific surface areas were determined on all sorbents. Single point N_2 condensation surface area measurements were made with a Micrometrics Flowsorb 2300 instrument, using a thermal conductivity detector. All sorbents were pretreated by drying at $60^{o}C$ overnight in an evacuated drying oven. Samples were stored in a desiccator until analyzed. Samples were degassed immediately prior to N_2 uptake.

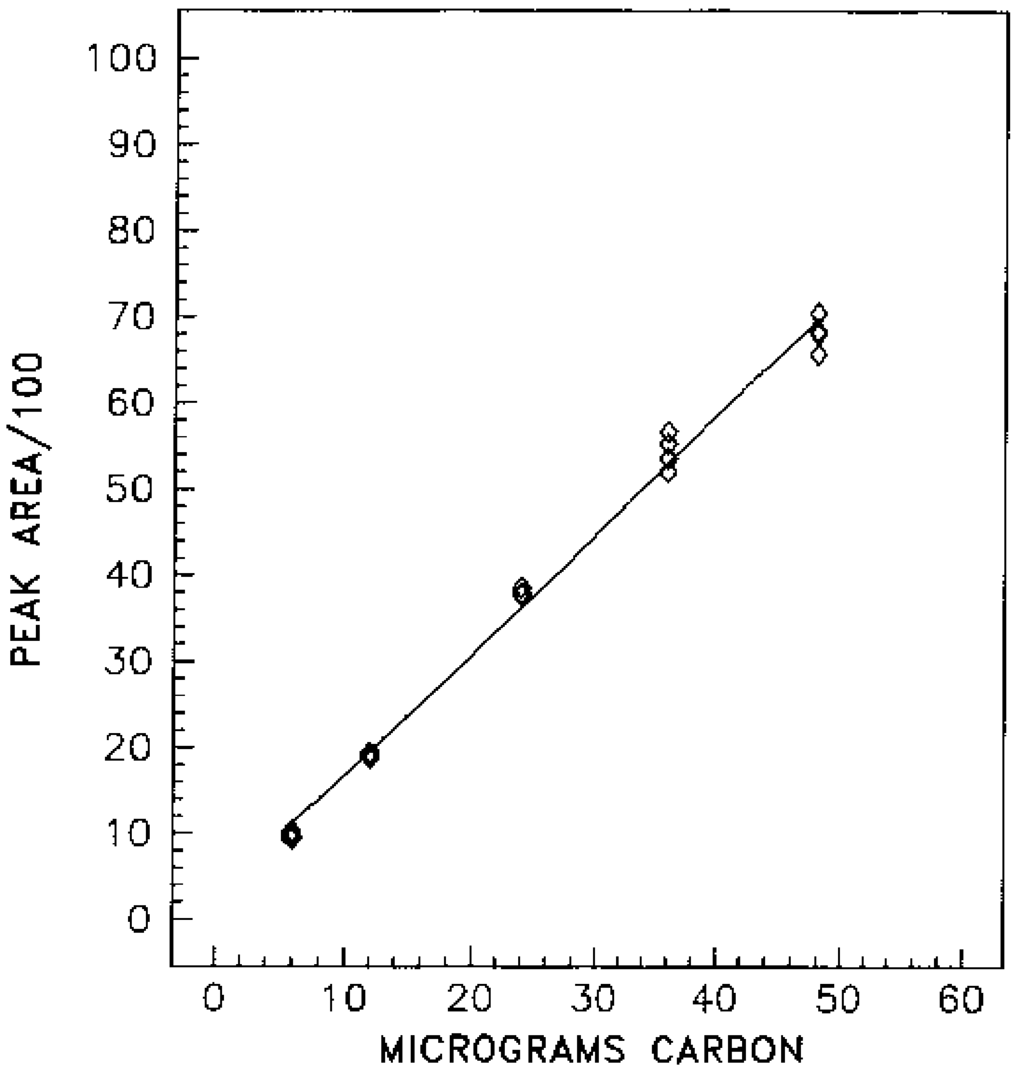
Sorbent OC was determined by several techniques. Dichromate oxidation of the sorbent followed by back titration with Fe_2SO_4 was done initially. This is called the Walkley-Black method (Nelson and Sommers, 1982). Titration results were questionable because most sorbents were very low in OC; therefore a modified method was tried. Dichromate oxidation was tested with the CO_2 liberated being trapped in ascarite and weighed. Small weight changes due to low sorbent OC again led to uncertain results.

A dry combustion method described below was finally selected for OC analysis. Initial trials used H_2SO_3 to remove inorganic CO_2 from dried sorbent samples placed in platinum crucibles. Some samples were high in carbonates and H_2SO_3 did not completely remove these carbonates, thereby producing errors in the OC determination. Treatment with H_2SO_3 was replaced by routine addition of 10 ml of 3N HCl to 10 g of sorbent, effectively removing all carbonates. The sorbent was then washed once with Milli-Q water to remove unreacted HCl and Cl^- and redried. Four subsamples of the dried sorbent weighing 100 mg or less were each combusted in a platinum boat at 900^{o}C in a Dohrmann model DC-80 TOC analyzer. The TOC analyzer was modified so that 200 cm^3/min of O_2 went directly through the combustion tube and into the Horiba IR photometer. A Perkin-Elmer LCI 100 integrator was connected to the IR output and used to determine peak areas from CO_2 produced during combustion. Prior to analyses, the calibration of IR photometer response was checked against manufacturers' data using a series of primary gas standards from Matheson Gas Company. The primary standard grade gas standards had a certified concentration accuracy of $\pm$0.02% absolute. A curve relating peak area to mass of CO_2 (Figure 1) was constructed by replicate injections of known aqueous concentrations of potassium acid phthalate. This combustion analysis proved the most sensitive and reproducible of the OC techniques. All sorbents were analyzed by the combustion method to provide a consistent data set.

Sorption system pH was measured with an Orion pH meter, Model 601A, using a combination glass electrode, number 13-639 90, from Fisher Scientific Company. The meter was calibrated using two standard buffer solutions spanning the pH range of the samples. Samples for pH analysis were taken from the supernatant liquid in the hypo-vials after centrifugation and represent equilibrium pH obtained after 24 hour contact of solution and sorbent.

Cation exchange capacity (CEC) for the surface soil material was determined by the ammonium saturation method (Chapman, 1965). The University of Florida Soil Characterization Laboratory determined the CEC for the aquifer materials as follows. Samples were extracted with ammonium acetate at pH 7.0 and filtered. The filtrate was analyzed for calcium, magnesium, sodium, and potassium by atomic absorption

Figure 1. Calibration curve for TOC analysis by combustion method.



100
90
80
70
60
50
40
30
20
10
0
PEAK AREA/100
0
10
20
30
40
50
60
MICROGRAMS CARBON

spectrophotometry. Exchange acidity was determined by leaching the aquifer material with 0.5N $BaCl_2$ and 0.055 N triethanolamine solution adjusted to pH 8 with HCl. The resulting solution was titrated with standard HCl. Exchange acidity was summed with the metal concentrations from the atomic absorption analysis to give the CEC. CEC data for the standard clays was given by Fripiat and van Olphen (1979).

Particle size distribution, percentage 2-layer clay (1:1), percentage 3-layer clay (2:1), iron content, and petrologic analyses on the aquifer materials were done by Twin Cities Research Center, Bureau of Mines, Minneapolis, MN 55417. Particle size distribution was done by standard sieve analysis and pipette analyses as outlined by Folk (1968). Elemental analyses were done by dissolving the samples with a mixture of concentrated perchloric, hydrochloric, and nitric acids. The resulting solution was analyzed on a graphite tube furnace using atomic absorption spectrophotometry. Iron determinations were performed by boiling 1.0 g aquifer material in 25 mL concentrated HCl and 10 drops HF until dissolved. The iron solution was titrated with standard $K_2Cr_2O_7$ solution (Westbrook et al., 1975).

Petrographic analyses were performed by examining the refractive index of oil immersion mounts of each aquifer material using a Zeiss petrographic microscope. Mineral phases were identified by their optical properties. Opaque heavy minerals and those heavy minerals which were very rare could not be definitely identified. Mineral abundances were determined by comparison to standard mineral abundance charts and by point counting mineral grains. Unidentified minerals generally composed 2% or less of the sample, except Tinker which contained approximately 4% unidentified minerals.

Clay size fractions ($\leq 2\ \mu m$) were separated from the bulk sample by sedimentation in a graduated cylinder (pipette analysis), mixed with deionized water to form a slurry and, spread across a glass slide, and evaporated. This method produced an oriented mount of clay films for x-ray diffraction analysis using a Philips Electronic Instruments APD 3600/01 automated powder diffractometer. X-ray reflections were gathered at the rate of 500 counts/sec. Samples were scanned from 2.5^0 to 60^0 two theta using CuK radiation at 40 Kv and 14 ma. Diffractograms were compared to current Joint Committee on Powder Diffraction Standards files and diffraction patterns in Brindley (1980).

Each sample was irradiated several times. All samples were irradiated dry and after treatment with ethylene glycol to swell smectites and aid in their identification. Slides were selectively heat treated to 110^0, 300^0, or 600^0 C depending on the suspected identity of the minerals. Changes in characteristic patterns caused by the heating procedure were used to confirm mineral presence in the sample.

Since all aquifer materials contained more than one clay mineral, the relative proportions for each clay were determined by x-ray diffraction using an external standard technique (Brindley, 1980). A standard mixture of kaolinite and smectite was prepared by mixing known portions of the clays. An illite standard was not available, so illite and mixed layer clay proportions were determined by difference between total clay and kaolinite plus smectite. Since illite and mixed layer clays were present at low levels (less than 1% for all aquifer materials except Carswell, which had about 4%), the impact of the unavailability of illite standard was minimal.

Clay mineral content was calculated by measuring reflected x-ray intensities of the sample and the external standard and substitution of these values into equation (4):

$$WP=(IP/I^{o}P)(u/uP) \qquad (4)$$

where WP is the weight proportion of component P, IP is the intensity of x-ray reflection of component P, $I^{o}P$ is the intensity of x-ray reflection of mineral standard, uP is the mass attenuation coefficient of the mineral standard, and u is the mass attenuation coefficient of the mixture. Mineral mass attenuation factors were given by Brindley (1980). Mass attenuation coefficients for each aquifer material were calculated by successive approximation. Areas under the strongest x-ray reflection for each mineral were used for the intensities of the component and mineral standard. The proportions of minerals in each sample were taken to be the same as the ratio of the intensity of the strongest x-ray reflection of each mineral. From this ratio, a weight-averaged attenuation coefficient was used to solve equation (4) for the abundance of each mineral. The calculated proportions were then used to calculate a new mass attenuation coefficient which was then substituted into the equation. This iterative process was repeated until results showed no significant change.

4. Sorbent Pretreatments

The oxides and the surface soil sorbents were pretreated by placing 40 g of material into 300-ml centrifuge tubes and adding 1 M NaOH, 1 M HCl or Milli-Q water, depending on whether the sorption experiments were to be run under basic, acidic, or "neutral" (unadjusted) conditions. The bottles were agitated for 24 hours and centrifuged at 1500 G for 10 min.

The supernatant liquid was decanted and replaced with Milli-Q water, and the process repeated three more times. The modified sorbent was then added as a slurry to the hypo-vials for sorption measurement. After equilibration and liquid scintillation analysis, the sorbents were dried overnight at 104^{o}C and weighed to provide the sorbent weights.

Na-montmorillonite swelled upon addition of Milli-Q water, and NaCl was added to degel the clay suspension so it could be centrifuged. A series of test tubes containing 2 g of clay and 10 mL of water was treated with increasing amounts of NaCl solution until the clay separated from the liquid after shaking. Separation occurred with an aqueous concentration of 0.6 M NaCl. All subsequent experiments with Na-montmorillonite were run in this salt solution. Since ionic strengths of this magnitude have been shown to slightly increase sorption in soils (Karickhoff et al., 1984, Stauffer and MacIntyre, 1986), the effect of NaCl addition on clay sorption was investigated by measuring sorption with and without salt solution added to isotherms of MNAP on kaolinite and barasyn.

Montmorillonites were Ca- or Al-saturated by weighing 40 g of clay into 300-mL centrifuge tubes and adding 200 mL of 0.1 M $CaCl_2$ or 0.1 M $AlCl_3$. The contents were agitated for several hours and then centrifuged at 1500 G for 10 minutes to separate phases. The exchanged salt solution was discarded and replaced with fresh salt solution. The clay was resuspended and agitated for several more hours before centrifugation. After discarding the supernatant liquid, Milli-Q water was added and the clay was resuspended and agitated for several hours to remove excess salt solution. After centrifugation, the supernatant liquid was tested for residual Cl^- by titration with $AgNO_3$ by the Mohr method. The washing procedure was repeated until residual Cl^- was not detected. The montmorillonites were then considered to be in the Ca- or Al-saturated form.

Barasyn, a synthetic montmorillonite, is NH_4^+ saturated when delivered. Attempts were made to saturate with Na^+, Al^{+3}, and Ca^{+2} ions to observe their influence on sorption, but without success. A slight ammoniacal odor remained on the barasyn after all substitution attempts, indicating residual ammonia. NaOH was added to try to exchange the NH_4^+, but this addition converted the barasyn to a thick gel that could not be broken or centrifuged. No further attempts were made to alter the barasyn, and it was used as received.

Aquifer materials were collected by a hollow-stem auger drilling rig from the saturated zone. Material from various depths in this zone was placed in polyethylene bags and transported to the laboratory. The materials were air dried and ground by mortar and pestle to pass a 1 mm screen. The dried materials were stored in appropriately labeled polyethylene bags until used. Equal weights of aquifer material from each identifiable region in the saturated zone at a drilling site were mixed to provide a composited sample of the aquifer material for the site. This sample is referred to in subsequent discussions of specific aquifers. Individual samples taken over specified depth intervals at each site were retained for studies of sorption variations with depth in the aquifer. Air dried aquifer materials were added directly to the hypovials for sorption measurement.

5. Sorption Experimental Details

Working solutions of the labeled compounds were prepared by breaking the sealed glass ampules of neat chemical and diluting with Milli-Q water. The aqueous solutions were stored in amber bottles at $5^{o}C$. Standard solutions of unlabeled chemicals were prepared by diluting known weights in acetonitrile and Milli-Q water, and subsequently stored at $5^{o}C$. Mineral oxides were used as received.

Radiopurity and chemical purity of the labeled compounds were tested using high performance liquid chromatography (HPLC). Chemical purity was determined by HPLC comparison between unlabeled reference standards and the radiochemicals. The chemical purities exceeded 99% for all sorbates used. The total activity of a known amount of the radiochemical was then injected on an HPLC column and the peak corresponding to that chemical was collected and counted. Radiochemical purity was taken as the ratio of the two activities. The radiopurities are as follows: MNAP, 91.7%; NAPH, 100.0%; TCE, 95.9%; ODCB, 101.7%; and PCP, 99.3%.

Solvent extraction experiments were done to test results by the concentration difference method for the surface soil. Samples were removed from vials for analysis and sorption calculated by the concentration difference method; the excess liquid in the vials was discarded and the vials refilled with an extracting solvent, the scintillation cocktail. The sample vials were resealed and agitated overnight. After centrifugation at 3,000 G, the vials were opened and the cocktail was removed for counting. Sorption coefficients obtained by this extraction were 98% of the value of those calculated by the solution concentration difference method.

Sorption isotherms for goethite by solvent extraction were performed using acetonitrile, because goethite formed intractable suspensions with scintillation cocktail. Acetonitrile was selected as the extractant because it mixed with goethite and scintillation cocktail. In these isotherm determinations, MNAP was sorbed on neutral goethite. The bottles were centrifuged after 24 hours of agitation, a supernatant liquid sample was removed for liquid scintillation counting and the results were used to calculate sorption by the solution concentration difference method. The remaining supernatant liquid was poured off and 5.0 mL of acetonitrile was added. The bottles were resealed and agitated for 24 hrs. After centrifugation, 3.0 mL of the acetonitrile were removed for analysis. Extractions were repeated twice with 3.0 mL aliquots of acetonitrile. An average of 90% of the sorbate was recovered in the three extractions based on the amount sorbed, as measured by the solution concentration difference method.

6. Liquid Scintillation Details

Liquid scintillation analyses were performed on a Beckman 9800 liquid scintillation counter. The ^{14}C counting window was set to 670 nm and samples were counted to 2 sigma percent error; i.e., the 95% confidence level for the count. Background counts were obtained from the unspiked sorbent sample supernatant liquid and subtracted from sample counts. Backgrounds were usually very low, 40 dpm or less. Counts per minute (cpm) were converted to disintegrations per minute (dpm) by an internal program, which calculates a quench curve of seven radioactive standards containing similar radioactive carbon concentrations, but different quench. From this curve, a plot of efficiency versus quench is constructed. The amount of quench in each sample is determined and the cpm obtained is converted to dpm through the following relation:

$$\% \text{ Efficiency} = \frac{\text{cpm} \times 100}{\text{dpm}}.$$

Quench in the instrument is determined by analyzing the Compton edge produced by gamma rays from ^{137}Cs. Beckman Ready Solv^{TM} HP/b liquid scintillation cocktail was used for all aqueous samples without added NaCl. The flocculated clay solutions containing NaCl necessitated using Ready Solv^{TM} MP cocktail which could dissolve a greater volume of this solution. Slight differences in counting efficiency between the two cocktails were corrected through the quench curve so resulting dpm were the same.

7. Sorption Isotherm Determination

Sorption was measured by adding 2.0 g of sorbent to 10-mL hypo-vials. Diluted solutions of the labeled compounds were added, and the hypo-vials were level-filled with Milli-Q water (Millipore Corporation, Bedford, MA) and sealed with Teflon^{R}-lined septa. Two standards and three replicate samples were set up for each isotherm concentration point. Generally, six different initial sorbate concentrations were used to establish each isotherm.

The vials were tumbled for 24 hrs and centrifuged for 10 min at 3000 G. Aliquots of 1.40 mL of the supernatant liquid were removed for counting. Vials were refilled with water and weighed to calculate solution volumes.

The dpm from liquid scintillation analysis were used to calculate the amount adsorbed at each equilibrium concentration. The method of calculation is based on the difference in sorbate concentration between an equilibrated sample without sorbent and the equlibrated sample with sorbent, and is called the concentration difference method. The resulting data were fitted by linear least-squares to:

$$\frac{x}{m} = KC \qquad (3)$$

where x is the amount of material sorbed in ug; m is the mass of sorbent in g; C is the equilibrium concentration of sorbate in mg/L; and K is the sorption coefficient in L/kg. The amount of material sorbed is calculated as $x=(C_0-C)(V)$, where C_0 is the initial concentration in ug/mL; C is the equilibrium concentration in ug/mL; and V is the volume of solution in mL.

8. Statistical Methods

The data was fitted by linear least-squares because this linear fit is widely used in sorption from aqueous solution (Banerjee et al., 1985; Schwarzenbach and Westall, 1981; Karickhoff et al., 1979). The sorbate concentration range used here, 0.001 mg/L to 1.0 mg/L, is dilute and approximates ideal solution conditions where deviations from linear sorption behavior is not expected.

However, since the sorbate concentration range spanned nearly three orders of magnitude, several sorption isotherm data sets were log-transformed to a linearized Freundlich isotherm equation to see if this was a better model. The log-transformation procedure is sometimes used to ensure that the variance remains constant over the complete range of the isotherm (Bowman et al., 1984). Resulting coefficients of determination (R^2) were similar to those obtained from the linearized least-squares treatment. Since the Freundlich equation did not fit the sorption isotherm data any better than the simpler linear equation, the widely used linear equation was used here.

Although the major thrust of this study was to study sorption processes in relation to sorbate properties and on a variety of sorbent surfaces, a large body of data containing aquifer material characteristics was established during the work. Since this data was available, it seemed appropriate to statistically examine the data to see if it was possible to predict sorption based on sorbent properties.

Appropriate statistical technique for the sorption and aquifer material property data was not obvious. Multiple analysis of variance techniques were ruled out because establishing statistically valid variances for all characterizations performed would be cost prohibitive. Sample size, that is total number of aquifer materials, was limited by the high cost and difficulty of obtaining representative aquifers. Petrologic and mineralogic analyses were expensive and time consuming. Limited sampling also precludes knowing whether the observations conform to normal distributions. Also, many of the properties analyzed are not statistically independent variables and may therefore be correlated.

Since information on statistical treatment was absent in other publications dealing with sorption on surface soils and sediments as a function of sorbent properties, appropriate statistical techniques were investigated. Dr. J.D. Boon III (VIMS, Gloucester Pt., VA, personal communication) suggested using principal component analysis (PCA)(Davis, 1986). This analysis probes the data matrix of sorption coefficients and sorbent properties and establishes the number of linearly independent vectors that exist in the data matrix. This may then give a measure of the redundancy in the original data set.

However, interpretation of the principal component loadings is often difficult because there is no direct path back from these components to the original variables. That is, loading gives a measure of the relative importance of a variable within a principal component, but says nothing about the importance of the component itself. The component is a linear transformation of the original variables through the eigenvector of the original variance-covariance matrix; thus direct association of loading values with the original variables is impossible. A direct relationship describing sorbate property variable relation to sorption cannot be derived from these data analyses. Nonetheless, results from PCA, coupled with some general insights concerning the property variables, help interpret the results of this study.

To confirm PCA, Fortran programs and subroutines published in J.C. Davis' (1973) textbook were adapted to run on a computer using an MS-DOS operating system. To assure that the programs were operating correctly, data from a sample problem, published in a later edition of the textbook, were run through the PCA. Results were identical to those in the text. The data were also run on another computer system through PCA on STAT™80 (Graphic User Systems, Inc., Santa Clara, CA), a statistics package, again with identical results.

RESULTS

1. Sorption on Oxide Minerals

Alumina (Al_2O_3) and Gibbsite ($Al[OH]_3$) sorbed small quantities of all sorbates. Table I shows the equilibrium pH and sorption coefficient (K) for isotherms not adjusted in pH. Isotherms had linear regression coefficients (R^2) from 0.6 to 0.9 with K values ranging from 0.1 to 0.4 (L/kg). K values obtained for TCE on Al_2O_3, with $NaClO_4$ added prior to equilibration to adjust the solution ionic strength to 1.0 M, were not significantly larger than those in Table I. Table II shows the effects of varying pH on the K values for Al_2O_3, $Al(OH)_3$, and FeO(OH) (goethite). Little change in K with pH was noted for oxides except goethite.

Goethite sorbed considerably more of all sorbates at unadjusted pH than did the aluminum oxides. Varying the pH caused an order of magnitude change in sorption of NAPH and PCP by goethite (Table II). TCE was poorly sorbed relative to the other sorbates shown. There is an apparent trend that increasing pH lowers K values, especially on goethite.

Appalachee soil produced the highest K values of all sorbents studied, ranging from about 1.0 to 24.9 with very large R^2 values (Table III). The trend of decreased sorption with increasing pH noted with goethite was also noted for the Appalachee soil. TCE was sorbed the poorest, while PCP was sorbed the best. Varying the ionic strength from 0.01 to 1.0 M with $NaClO_4$ had little affect on the sorption of naphthalene on surface soil and goethite (Table IV). Figure 2 shows the

TABLE I. Sorption coefficients (L/kg) on oxides at unadjusted pH.

Sorbent	pH	MNAP K	R^2	pH	NAPH K	R^2
Al_2O_3		NA		8.5	0.15+0.07	0.68
$Al(OH)_3$	9.2	0.27+0.06	0.85	9.0	0.36+0.07	0.86
FeO(OH)	3.4	2.27+0.30	0.98	3.1	1.85+0.15	0.97
SiO_2	8.2	0.77+0.10	0.95		NA	

Sorbent	pH	ODCB K	R^2	pH	TCE K	R^2
Al_2O_3	6.8	0.13+0.05	0.63	8.6	0.32+0.18	0.63
$Al(OH)_3$	9.4	0.26+0.08	0.79	9.8	0.30+0.09	0.79
FeO(OH)	7.1	1.40+0.11	0.97	8.6	0.32+0.18	0.53
SiO_2		NA			NA	

Sorbent	pH	PCP K	R^2
Al_2O_3	7.9	0.20+0.05	0.89
$Al(OH)_3$	9.7	BD	
FeO(OH)	4.3	12.5+2.0	0.92
SiO_2	8.2	BD	

NA, Not Analyzed
BD, Below Detection

TABLE II. Sorption coefficients (L/kg) on Al_2O_3, $Al(OH_3)$, and FeO(OH) at different pH.

Sorbent	NAPH pH	NAPH K	NAPH R^2	TCE pH	TCE K	TCE R^2
Al_2O_3	1.8	0.15±0.12	0.32	2.0	0.31±0.10	0.77
	8.5	0.15±0.07	0.68	8.6	0.32±0.18	0.53
	12.4	0.15±0.15	0.55	11.5	0.29±0.12	0.72
$Al(OH)_3$	9.0	0.36±0.10	0.86	9.8	0.30±0.09	0.80
FeO(OH)	2.7	2.34±0.17	0.98	3.0	0.67±0.08	0.96
	3.1	1.84±0.15	0.97	3.7	0.40±0.07	0.92
	12.8	0.34±0.18	0.58	8.5	0.39±0.13	0.72

Sorbent	ODCB pH	ODCB K	ODCB R^2	MNAP pH	MNAP K	MNAP R^2
Al_2O_3	4.2	0.07±0.06	0.34		Not measured	
	6.8	0.13±0.05	0.63		Not measured	
	10.0	0.18±0.03	0.90		Not measured	
$Al(OH)_3$	9.4	0.26±0.08	0.79	9.2	0.27±0.06	0.85
FeO(OH)	3.5	1.31±0.08	0.99	3.2	2.27±0.25	0.96
	7.1	1.40±0.11	0.97		Not measured	
	11.5	0.34±0.07	0.88		Not measured	

Sorbent	PCP pH	PCP K	PCP R^2
Al_2O_3	4.2	4.16±0.30	0.97
	7.9	0.20±05	0.89
$Al(OH)_3$	9.7	0	
FeO(OH)	1.5	15.3±0.70	0.99
	4.2	13.8±0.50	0.99
	10.0	0	

TABLE III. Sorption coefficients (L/kg) for five sorbates on Appalachee surface soil at different pH.

Pretreatment	pH	MNAP K	R^2	pH	NAP K	R^2
Acid		NA		3.1	12.7±0.70	0.99
Unadjusted	5.5	16.2±1.0	0.99	5.4	8.18±0.23	0.99
Base		NA		11.0	2.74±1.10	0.64

Pretreatment	pH	ODCB K	R^2	pH	TCE K	R^2
Acid	4.1	6.13±0.40	0.99	3.2	1.17±0.10	0.80
Unadjusted	6.3	5.40±0.12	0.99	5.2	0.73±0.23	0.80
Base	10.8	2.32±0.51	0.92	10.3	0.58±0.18	0.76

Pretreatment	pH	PCP K	R^2
Acid		NA	
Unadjusted	5.9	24.9±1.0	0.99
Base		NA	

± one standard deviation of the mean

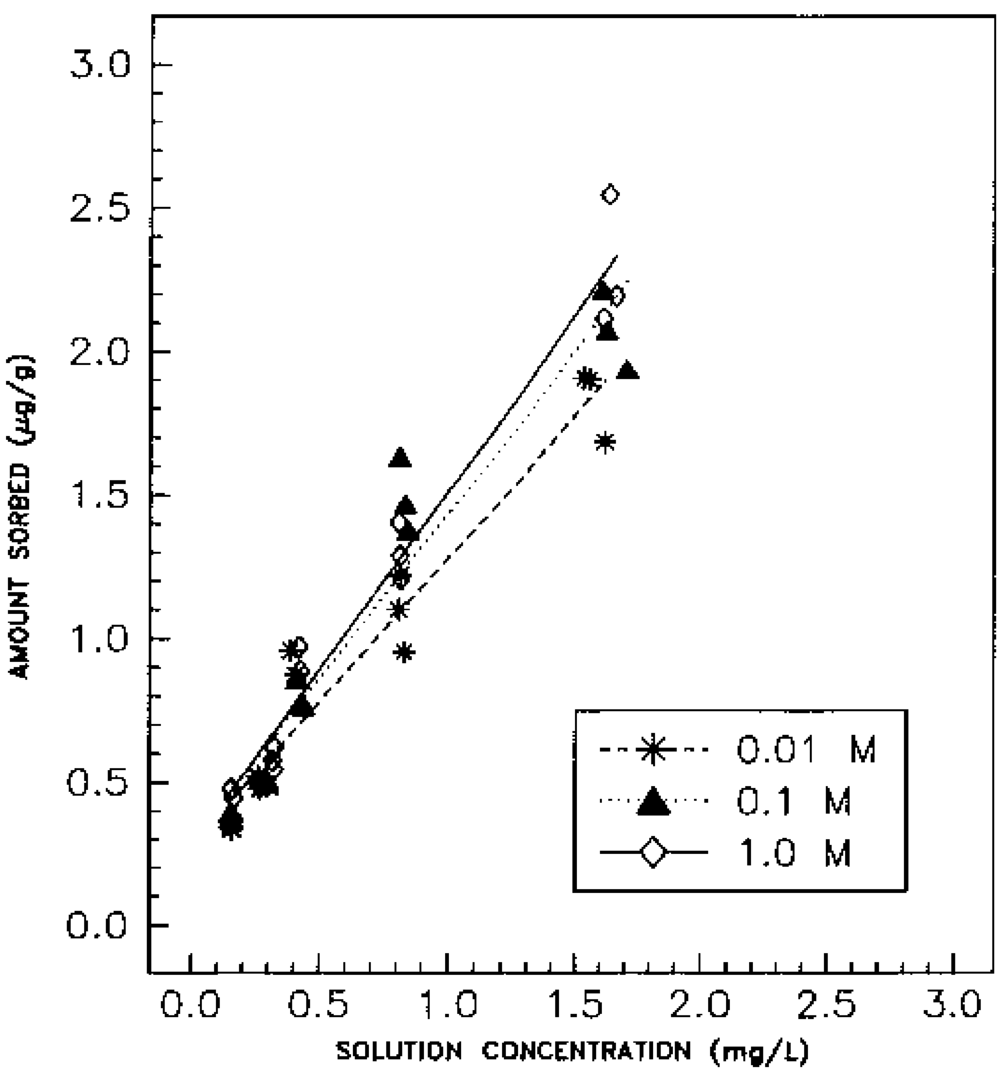
$\bar{K}$ values are average of three isotherm determinations

NA, Not Analyzed

TABLE IV. Sorption coefficients (L/kg) for NAPH at three ionic strengths.

IONIC STRENGTH	K	R^2
Appalachee soil		
1.0 M	7.67±0.44	0.99
0.1 M	6.73±0.67	0.97
0.01 M	6.31±0.32	0.99
Goethite		
1.0 M	1.16±0.13	0.97
0.1 M	1.15±0.19	0.93
0.01 M	0.99±0.16	0.93

Figure 2. Isotherm for NAPH on goethite at three ionic strengths.



3.0
2.5
2.0
1.5
1.0
0.5
0.0
AMOUNT SORBED (μg/g)
0.01 M
0.1 M
1.0 M
0.0
0.5
1.0
1.5
2.0
2.5
3.0
SOLUTION CONCENTRATION (mg/L)

isotherms of NAPH on goethite at the three ionic strengths studied.

Organic carbon concentrations for the oxides were very low (<0.05%)(Table V). The surface soil TOC was much higher at 1.40%. Specific surface areas ranged from 9.4 m^2/g to 19.6 m^2/g. Goethite, which had the highest K values of all oxides, had the lowest specific surface area. The soil sample had a surface area similar to the oxides, but took up much greater amounts of all sorbates.

Five replicate isotherms at unadjusted pH were measured for MNAP using goethite. Experiments were conducted over a one month period to demonstrate the replicability of K values. The arithmetic mean sorption coefficient was 2.31 (L/kg), with a standard deviation of 0.28, giving a coefficient of variation of 12%. Isotherms determined in this study were linear at the sorbate concentrations used, which generally ranged from 0.001 to 1.0 mg/L, thereby allowing comparison of sorption coefficients among the oxide minerals, clays, and aquifer materials.

Several replicate isotherms were measured on SiO_2 with the more strongly adsorbed sorbates. PCP was poorly sorbed on SiO_2 and MNAP was sorbed better on SiO_2 than on aluminum oxides, but not as well as on goethite (Table I). Since SiO_2 was a relatively inactive surface, it was not investigated further.

2. <u>Sorption on Clay Minerals</u>

Table VI shows the K values for five sorbates on kaolinite at neutral and acid pH and with ionic strength adjustment to 0.6 M NaCl. PCP gave the highest sorption coefficients. Since the standard deviations of the means overlap between adjusted and unadjusted experiments at the pH and ionic strength studied, effects of variation in pH or ionic strength could not be demonstrated for MNAP or PCP. Under unadjusted pH

TABLE V. Selected physical and chemical properties of soil and mineral sorbents.

Sorbent	TOC	CEC	Surface Area BET	Surface Area Glycol
	%	meq/100 g	m^2/g	m^2/g
Al_2O_3	0.0024±0.0015	NA	19.6	NA
$Al(OH)_3$	<0.01[a]	NA	11.9	NA
FeO(OH)	0.055±0.0028	NA	9.4	NA
Kaolin	0.017±0.002	2.0[b]	10.1[b]	NA
Na-Mont.	0.0239±0.0012	76.4[b]	31.8±0.2[b]	662[b]
Ca-Mont.	0.0230±0.001	120[b]	97.4±0.6[b]	820[b]
Barasyn	<0.01	140[b]	133.7±0.7[b]	NA
Appalachee	1.40	18.6	11.8	NA

NA, Not Analyzed; CEC, Cation Exchange Capacity; BET, Brunauer, Emmett, and Teller.
[a] Data supplied by Alcoa
[b] Data from van Olphen and Fripiat (1979)

TABLE VI. Sorption coefficients (L/kg) for five sorbates on kaolin at various pH and ionic strengths.

	MNAP			NAP		
Condition	pH	K	R^2	pH	K	R^2
Unadjusted	4.9	0.53±0.11	0.88	5.2	Nil	
0.6 M NaCl	4.2	0.32±0.12	0.65		NA	
Acid	3.9	0.34±0.05	0.96		NA	

	ODCB			TCE		
Condition	pH	K	R^2	pH	K	R^2
Unadjusted	5.1	0.15±0.09	0.46	5.1	0.14±0.06	0.61
0.6 M NaCl		NA			NA	
Acid		NA		3.5	0.47±0.26	0.93

	PCP		
Condition	pH	K	R^2
Unadjusted	5.4	1.76±0.54	0.93
0.6 M NaCl	5.2	2.08±0.08	0.98
Acid	3.1	1.47±0.10	0.98

± one standard deviation of the mean
$\bar{K}$ values are averages of three isotherm determinations
NA, Not Analyzed

conditions, MNAP was sorbed better than NAPH, ODCB, and TCE. ODCB, TCE, and NAPH had K values ranging from near 0 to 0.15 with low R^2, indicating these compounds were poorly sorbed by kaolinite.

The K values for five sorbates on two standard montmorillonite clays and on the synthetic montmorillonite, barasyn, are shown in Table VII. Ca-montmorillonite sorbed much less than either Na-montmorillonite or barasyn. In general, sorption coefficients were five to ten times less for the Ca-substituted clay than the Na-substituted clay. Na-montmorillonite and barasyn behaved similarly, and differences in K values were not detectable, as indicated by overlap of their standard deviations with each sorbate. Addition of NaCl to barasyn to produce the 0.6 M NaCl solution used in the Na-montmorillonite measurements did not significantly change K values relative to unadjusted barasyn values.

All montmorillonites showed the following order of sorption; MNAP>ODCB>NAPH$\geq$TCE. PCP was poorly sorbed on the Na-montmorillonite. The montmorillonites sorbed relatively more when compared to kaolinite except for PCP which sorbed better on kaolinite. R^2 values were very large for both Na-montmorillonite and barasyn, averaging 0.98. Ca-montmorillonite R^2 values were somewhat smaller, near 0.7.

Al^{+3} and Ca^{+2} saturated montmorillonites were used to investigate the effect of cation substitution on sorption of NAPH and MNAP. Ca-substitution lowered the K value for MNAP from 1.72 $\pm$0.23 for Na-montmorillonite to 1.32$\pm$0.07. Al-substitution caused much greater change in sorption: K for MNAP increased from 1.72$\pm$0.23 to 3.56$\pm$0.18 and for NAPH from 0.85$\pm$0.07 to 1.45$\pm$0.11. The Al^{+3} substitution nearly doubled the sorption of the compounds used, with regression coefficients for MNAP and NAPH on Al-substituted montmorillonites of 0.99 and 0.98,

TABLE VII. Sorption coefficients of nonpolar sorbates on standard montmorillonite clays in Ca and Na forms and on the synthetic montmorillonite, Barasyn.

Sorbent	MNAP K	MNAP R^2	NAP K	NAP R^2
Ca-Mont.	0.41±0.12	0.86	0.07±0.08	0.69
Na-Mont.	1.72±0.23	0.97	0.85±0.07	0.95
Barasyn	1.82±0.19	0.98	0.78±0.09	0.92
Barasyn (0.6 M)	1.97±0.61	0.98		

Sorbent	ODCB K	ODCB R^2	TCE K	TCE R^2
Ca-Mont.	0.17±0.06	0.69	0.12±0.17	0.50
Na-Mont.	1.21±0.17	0.99	0.66±0.02	0.94
Barasyn	1.05±0.08	0.89	0.82±0.18	0.85

± one standard deviation of the mean
$\bar{K}$ values are averages of three isotherm determinations
All Na-Mont. isotherms run in 0.6 M NaCl

respectively, indicating reliable data.

MNAP was sorbed from 0.6 M NaCl solutions on selected mixtures of goethite, barasyn, and Na-montmorillonite (Table VIII). Data for the individual sorbates has been used to investigate the degree to which sorption on mixtures is related by additive linear combinations to sorption on individual sorbents.

Kaolinite, Ca-montmorillonite, and Na-montmorillonite had low organic carbon contents (Table V). Na-montmorillonite contained about the same amount of organic carbon as the Ca-montmorillonite. The synthetic montmorillonite, barasyn, contained no detectable organic carbon. Surface area and cation exchange capacity were small for the 2-layer clay and much greater for the expanding clays. Barasyn had the highest CEC and surface area of the montmorillonites used. Ca-montmorillonite exhibited intermediate CEC and surface area values.

3. Sorption on Aquifer Materials

K values for MNAP on the various aquifer materials range from 0.4 to 3.0, with R^2 values near unity; K values for ODCB were less than those of MNAP for all aquifer materials studied (Table IX). ODCB K values ranged from 0.1 to 1.3 with good regression coefficients, although somewhat lower than those for MNAP.

Based on the sorption isotherms for MNAP, ODCB, and NAPH on Borden site aquifer material, it is clear that ODCB and NAPH were taken up to nearly the same extent by the Borden aquifer material (Figure 3). From the lack of curvature shown by these representative isotherms, it is also apparent that the choice of a linear sorption model is appropriate. In contrast, sorption isotherms for TCE, ODCB, and MNAP on Tinker aquifer material differ in slope (Figure 4) which indicates that these three

TABLE VIII. MNAP K values (L/kg) for sorbent mixtures.

Sorbent Mixtures	pH	K	R^2
1.0 g Goethite+1.0 g Na-Mont.	7.4	2.75±0.25	0.99
1.5 g Goethite+0.5 g Barasyn	4.2	2.37±0.30	0.99
1.0 g Goethite+1.0 g Barasyn	4.5	2.15±0.07	0.99
0.5 g Goethite+1.5 g Barasyn	4.6	2.01±0.13	0.98
2.0 g Goethite	3.2	2.27±0.25	0.96
2.0 g Barasyn	5.1	1.82±0.19	0.98
2.0 g Na-Mont.	7.4	1.72±0.23	0.97

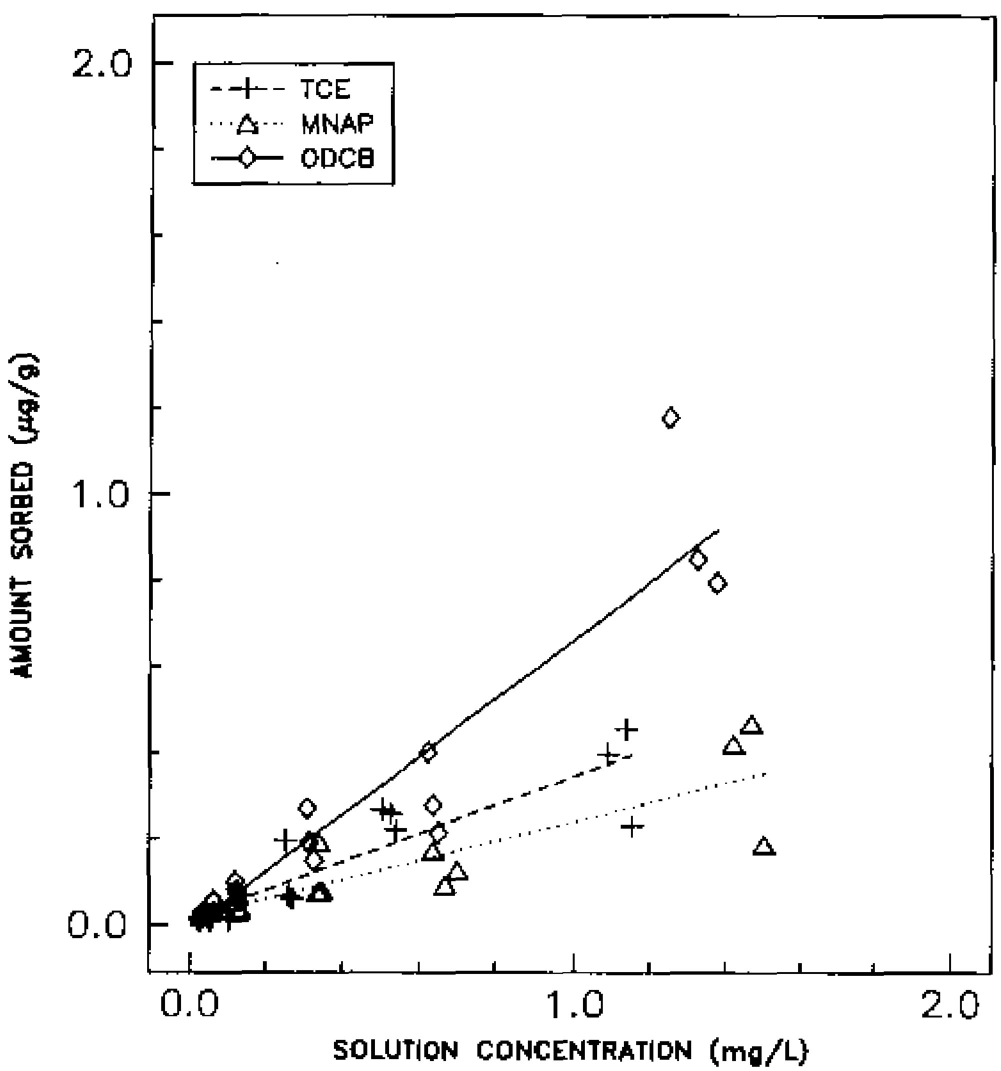
K values are averages of three isotherms ± one standard deviation of the mean

TABLE IX. Sorption coefficients (L/kg) for MNAP and ODCB on aquifer materials.

Aquifer Material	MNAP		ODCB	
	K	R^2	K	R^2
Tinker	0.44±0.03	0.88	0.10±0.05	0.73
Carswell	0.45±0.06	0.88	0.18±0.06	0.84
Barksdale	0.96±0.19	0.98	0.30±0.05	0.91
Blytheville	3.06±0.20	0.98	1.28±0.14	0.97
Traverse City	0.76±0.04	0.97	0.36±0.04	0.94
Borden	0.65±0.06	0.95	0.30±0.04	0.88
Lula	0.51±0.15	0.95	0.14±0.09	0.70

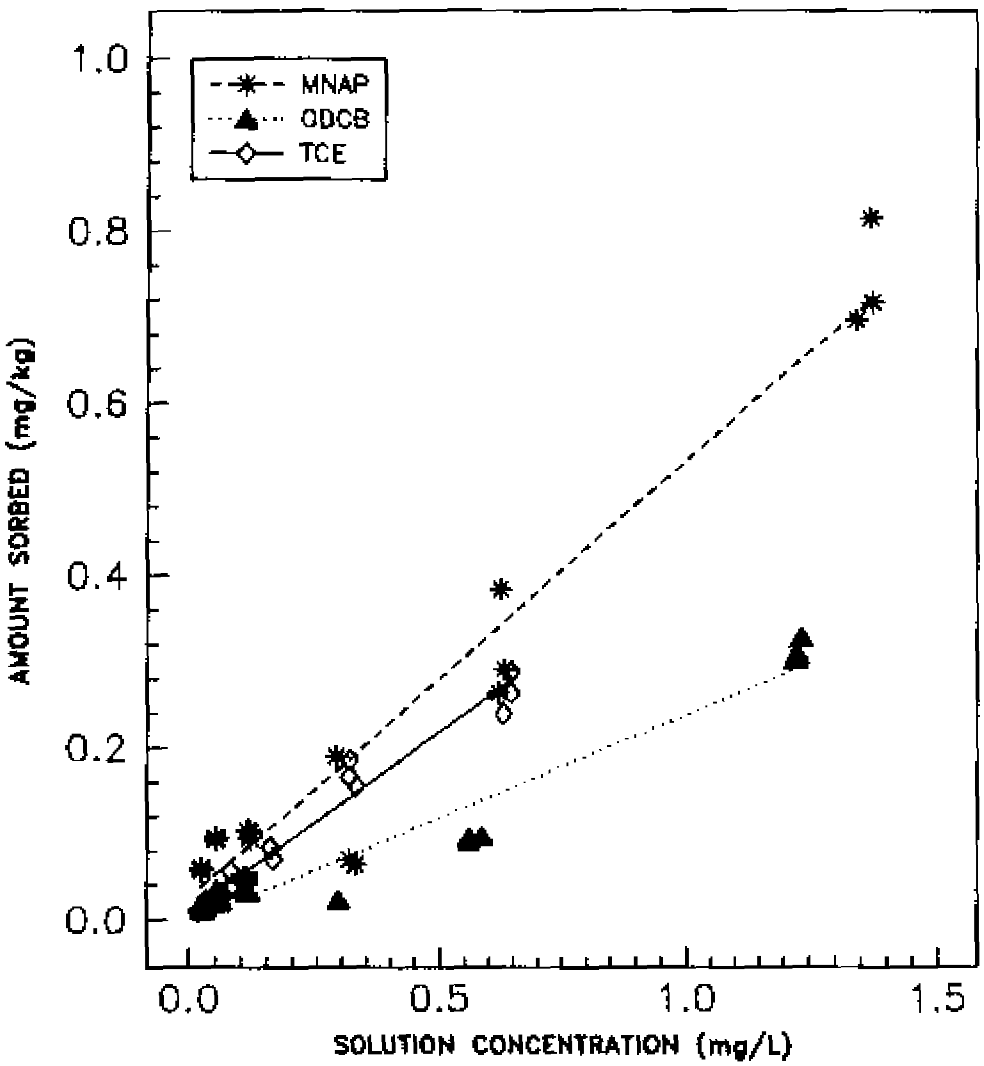
K values are averages of three isotherm determinations
± values are one standard deviation of the mean

Figure 3. Isotherms for selected sorbates on Borden Site aquifer material.



TCE
MNAP
ODCB
2.0
1.0
0.0
AMOUNT SORBED (μg/g)
0.0
1.0
2.0
SOLUTION CONCENTRATION (mg/L)

Figure 4. Isotherms for selected sorbates on Tinker aquifer material.



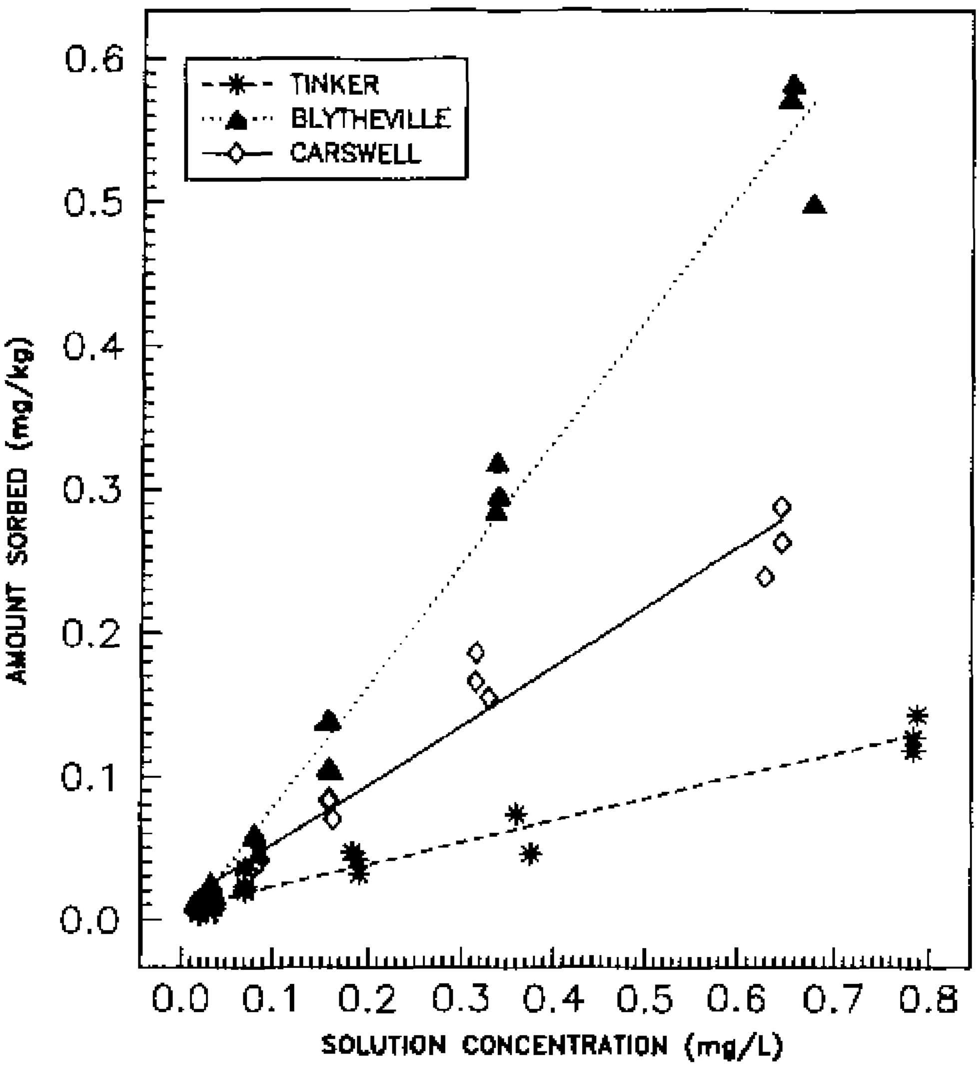
MNAP
ODCB
TCE
AMOUNT SORBED (mg/kg)
SOLUTION CONCENTRATION (mg/L)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5

sorbates are retained to quite different extents. The difference in retention properties of various aquifer materials is especially clear for TCE sorbed on three different aquifer materials which resulted in three distinct K values (Figure 5).

The aquifer materials differed considerably in percentage TOC, CEC, and specific surface areas (Table X). Organic carbon concentrations were generally quite low, 0.03% or less, except for the Barksdale and Blytheville aquifer materials, which had TOC greater than 0.1%. Cation exchange capacities ranged from 6 (Lula material) to 32 meq/100 g (Barksdale material). Samples with high sand contents usually had low CEC. Specific surface areas for the aquifer sorbents were low when compared to clays and surface soil, ranging from 0.2 to 11.8 m^2/g. Most of the aquifer materials had surface areas of 7-9.5 m^2/g, but the two glacial till samples from Borden and Traverse City were very low, near 0.2 m^2/g.

Aquifer materials texture, percentage iron, and percentage 2- and 3-layer clays varied considerably (Table XI). Most of the samples are quite high in sand content, and the clay size fraction is generally 5% or less of the sample. The percentage 3-layer clay ranged from below detection limits to 9.0. Two-layer clay contents were about one-half those for 3-layer clays. Total iron percentages were from 0.3 for Traverse City to 2.9 for Lula. Even though iron oxides and clays are not abundant, they tend to be widely distributed as coatings on the aquifer materials as noted in microscopic examination. In the Tinker material, for example, the quartz grains are variably coated with iron oxide; 25% of the grains are greater than 2/3 coated, and 50% have 1/3 to 2/3 of their surface coated. Iron oxide coatings were found to some extent on

Figure 5. TCE isotherms on three different aquifer materials.



TINKER
BLYTHEVILLE
CARSWELL
AMOUNT SORBED (mg/kg)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
SOLUTION CONCENTRATION (mg/L)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

TABLE X. Percentage TOC, CEC, and specific surface area of aquifer materials.

Aquifer Material	TOC	CEC	Surface Area
	%	meq/100g	m^2/g
Tinker	0.0096±0.0003	20.9	9.2±0.1
Carswell	0.0266±0.0010	8.0	9.5±0.1
Barksdale	0.1054±0.006	32.4	7.5±0.1
Blytheville	0.156±0.004	18.1	8.0±0.1
Trav. City	0.0113±0.003	14.4	0.2±0.0
Borden	0.0155±0.0021	NA	0.3±0.0
Lula	0.0201±0.0004	6.3	11.8±0.1

TOC, average of four determinations, ± one std. dev.
Surface area, average of three determinations, ± one std. dev.
NA, Not Analyzed

TABLE XI. Aquifer material texture analysis, clay mineralogy, and iron content.

Aquifer Material	Sand	Clay	Silt
		%	
Tinker	40.8	4.7	53.1
Carswell	74.8	NR	18.2
Barksdale	52.3	NR	41.5
Blytheville	67.8	3.5	27.3
Traverse City	98.2	NR	1.1
Borden	96.0	2.0	2.0
Lula	91.0	3.4	5.6

Aquifer Material	2-layer Clay	3-layer Clay	Iron
		%	
Tinker	9.0	0.8	1.4
Carswell	1.5	4.5	0.9
Barksdale	2.1	4.9	1.0
Blytheville	1.2	5.0	0.7
Traverse City	<0.1	<0.1	0.3
Borden	<0.1	<0.1	1.5
Lula	0.6	1.7	2.9

NR, None Retained

all aquifer materials. Clays were also found as particle coatings sometimes in conjunction with the iron oxides. The relatively small amounts of both the clays and iron oxides must be considered in relation to their presence on surfaces of other minerals, since this coating is encountered by the sorbate.

K values for MNAP vary by a factor of three over a depth profile on Carswell material (Table XII). Although there appears to be a general decrease of K with depth, especially from Zone #3 to Zone #6, the upper two zones do not follow the trend. Zone #2 appears to have the highest K value in the entire profile. Organic carbon content varied by a factor of four over the depth profile with the lowest carbon content occurring in the deepest zone. Zone #2 also appeared to have the highest organic content, with a general decrease apparent from Zone #3 to Zone #6.

Inspection of the results obtained by increasing the sorbate concentration range from the 0.001-1 mg/L range to the 0.4-10 mg/L range for MNAP on Carswell aquifer material, show the K value is invariant within experimental error over this range (Table XIII). The experiments were repeated on Tinker aquifer material, extending the MNAP concentration from 0.7-16 mg/L, near half MNAP saturation in water, without significant decrease in K value.

MNAP isotherms were measured on Carswell aquifer material with ODCB used as a competitive sorbate at a constant concentration of 1.5 mg/L. Resulting average K values were similar to those from single sorbate isotherms. In another set of experiments, isotherms of ODCB on Carswell aquifer material were measured in the presence of 25 mg/L MNAP. The resulting K for ODCB was similar to single sorbate K, indicating an absence of competitive interactions under these conditions.

TABLE XII. MNAP K value, OC, and surface area variation with depth for Carswell aquifer material.

Depth	K Value	OC	Surface Area
m	L/kg	%	m^2/g
1.3-1.7	0.53±0.14	0.0503±0.008	5.0±0.03
1.7-2.7	0.73±0.06	0.0512±0.002	12.7±0.10
2.7-3.1	0.57±0.05	0.0533±0.003	16.4±0.10
3.1-3.7	0.29±0.04	0.0318±0.004	11.7±0.07
3.7-4.4	0.25±0.01	0.0297±0.002	10.8±0.06
4.4-6.4	0.25±0.08	0.0131±0.002	3.5±0.03

K values are averages of three determinations, ± std. dev.
OC values are averages of four determinations, ± std. dev.

TABLE XIII. Comparison of aquifer K values at different concentration ranges for MNAP.

Aquifer Material	Concentration range mg/L	K L/kg
Carswell	0.001-2.0	0.45±0.06
Carswell	0.4-10.0	0.40±0.05
Tinker	0.001-2.0	0.44±0.03
Tinker	0.70-15.0	0.47±0.03

DISCUSSION

Division of the K values by the fraction of organic carbon in the surface soil sample gives a K_{oc} for NAPH of 585 and for ODCB of 385. The K_{oc} for NAPH found here is lower than the value of 1300 reported by Karickhoff et al. (1979). In contrast, the K_{oc} for ODCB is higher than the value of 186 reported by Chiou et al. (1983). These different values may reflect differences in soil organic matter. K_{oc} depends on the method of organic carbon determination; therefore the differences from reported values may also be explained by differences in this measurement.

Variation in the observed K for the surface soil with pH may be attributed to a number of factors. The reduction of K at high pH was probably caused, in part, by removal of humic acid materials. During NaOH washing, the aqueous phase turned dark brown and the resulting soil material was lighter in color. Increased sorption at acid pH was also noted. Possible causes for this increase may be changes in oxide surface charge, clay surface charge or cation saturation, and changes in functional groups of the organic substances (humics) present.

The small increase in sorption coefficient found here with the addition of $NaClO_4$ to isotherms for NAPH on Appalachee soil is attributed to the "salting out" process. The simplest explanation is that increased ionic strength decreases NAPH solubility and drives the displaced NAPH to the sorbent surface causing the small increase in K. Karickhoff et al. (1979) noted a similar increase when adding NaCl to equilibrium mixtures of sediment sorbents and pyrene.

Alumina and gibbsite took up small amounts of all sorbates. Gibbsite was included to observe possible sorption changes that could be attributed to different crystalline form. No significant difference in K values were apparent at unadjusted pH. The effect of pH on sorption could not be demonstrated for Al_2O_3. K values obtained for TCE on Al_2O_3 with $NaClO_4$ added prior to equilibration to adjust the solution ionic strength to 1.0 M were not significantly changed from those obtained in Milli-Q water. The low and similar K values and the relatively low R^2 values measured for Al_2O_3 indicate sorption at the lowest observable limit without changing the liquid to solid ratio. Although the specific surface areas for the two aluminum oxides differed by a factor of two, there was little difference in the amount of sorbate taken up by the two forms. Schwarzenbach and Westall (1981) reported a K value of 0.9 for p-dichlorobenzene on γ-Al_2O_3 having a BET surface area of 120 m^2/g. The material used here was a mix of 90% α-Al_2O_3 and 10% γ-Al_2O_3 with surface area of 19.6 m^2/g. The difference from the values reported here for ODCB, 0.13 ± 0.05, may be due to surface area, crystal form, or sorbate isomer dissimilarities.

Goethite took up more of each sorbate than did Al_2O_3, although goethite's specific surface area is smaller. K values for TCE on goethite were near the detection limit, whereas all other sorbates had higher K values. Variation of the solution acidity, with concomitant alteration of surface charge, caused little change in K values at acid and near-neutral pH, but the K value decreased at alkaline pH. Surface charge was not measured and the solution pH should not be used to estimate surface charge. The surface charge is dependent on both the solution pH and the sum of the contributions from positive and negative surface groups and potential determining ions (Yariv and Cross, 1979). Because the surface charge is dependent on these groups and ions, solution pH measurements are not sufficient to describe the surface charge. Since the zero point of charge for goethite is between pH 3.2 and 6.7, basic solutions may have produced a negative surface that inhibited sorption.

Both the Al_2O_3 and FeO(OH) had some organic material associated with the oxides as received. The carbon content of Al_2O_3 was considerably less than that of FeO(OH). This may contribute to the Al_2O_3 having a lower affinity for the sorbates. K_{oc} for NAPH sorption on both Al_2O_3 and FeO(OH) are calculated as 6250 and 3350, respectively, values which are much higher than those reported by Karickhoff et al. (1979) and those reported herein for surface soil. The aluminum oxide K_{oc} is questionable since it resulted from dividing a small K value near the detection limit by a small organic carbon content number which was also near the detection limit. The resulting error in K_{oc}, and the tacit assumption that all organic carbon materials sorb similarly, are major problems involved in the K_{oc} concept. The K_{oc} calculated from data for goethite gives a more believable result because resulting errors are relatively smaller. The NAPH K_{oc} is high and may indicate that it is a combination of both mineral and organic carbon contributions to sorption. This combined effect would also occur in the environment, since naturally occurring oxides could be expected to have some associated organic carbon.

Oxide minerals were selected because they occur in soils, sediments, and aquifer material and are structural subunits in clays. Abraded clay minerals can produce oxide surfaces at edge sites and broken plates which somewhat resemble the oxides studied here. Environmental weathering and diagenesis would alter the edge sites and broken plates so they would not necessarily be the same composition as the pure metal oxides studied here. These sites provide surfaces on which chemical pollutants may sorb.

Sorption on the smectites and kaolinite showed the anticipated general trend of increasing K value with increasing molecular size of the sorbate. Water solubility (Table XIV for selected physical and chemical properties of sorbates) does not explain this sorption order because MNAP and NAPH have nearly similar solubilities, but were sorbed quite differently. TCE, which is very soluble (approximately 1100 mg/L), sorbed to the same extent on the expanding clays as did NAPH, which is 30 times less soluble. ODCB, four times more soluble than NAPH, produced similar K's.

Molecular polarizabilities decrease in the following order; MNAP> NAPH>ODCB>TCE. Since sorbates are taken up in a similar order, it appears that there is a trend of higher K with higher polarizability. In contrast sorbate permanent dipole moments show no relation to K value. Dipole moments of the sorbates differed by a factor of 10, with MNAP, the best sorbed, having the lowest dipole moment excepting NAPH, with zero dipole moment. ODCB had intermediate K values and the highest dipole moment.

Molecular surface areas of the sorbates calculated in gas phase were reported by Yalkowsky and Valvanni (1979) and Yalkowsky et al. (1979). MNAP, with the highest surface area (172.5$Å^2$), was sorbed best, and TCE, with the smallest surface area (77.8$Å^2$), was taken up least. ODCB and NAPH have surface areas of 144.7$Å^2$ and 155.8$Å^2$ respectively, and give intermediate sorption values on the mineral surfaces. Sorbate molar

TABLE XIV. Properties of sorbates.

Sorbate	Molar Volume	Molecular‡‡ Polarizability	Molecular Surface Area	Dipole¶ Moment	Water Solubility
	cm^3/g-mol	cm^3	A^2	Debye	mg/L
MNAP	139.4	1.935×10^{-23}	172.5#	0.2296	28.5‡
ODCB	112.7	1.426×10^{-23}	144.7††	2.54	134§
NAPH	133.2†	1.752×10^{-23}	155.8#	0	31.3‡
TCE	90.2	1.004×10^{-23}	77.8††	0.99	1100¶

† at 100°C
‡ Burris, 1985
§ Beilstein Index (Debye = 10^{-18} esu)
¶ Callahan et al., 1979
# Yalkowsky and Valvanni, 1979
†† Yalkowsky et al., 1979
‡‡ calculated from the Clausius-Mossotti equation using density and refractive index values found in Beilstein Index

volumes, an indirect measure of molecular size, also decrease in the order MNAP>ODCB>TCE, which follows the sorption trend reported here on the mineral surfaces.

It is apparent that sorbate properties associated with molecular size and molecular polarizability are directly correlated to K values on the mineral surfaces studied here. Since van der Waal's forces increase with molecular size and are related to induced polarization, they probably account, at least in part, for the trends. However, a complete explanation cannot be given for the relation between K and sorbate molecular polarizability observed here. The polarizability referred to was measured in the liquid phase and thus is a time and space average over all molecular orientations and configurations for a large number of molecules. When a molecule is subjected to an external electric field, the molecule itself is deformed. This deformation is a function of the molecular orientation in the field and the field strength.

The polarizability of a molecule can be expressed in terms of components along the principal axes of the molecule. Single molecule polarizability components might better correlate with sorption that do the average polarizabilities, but literature data for the polarizability components of the molecules used were not found. It is possible, in principle, to obtain the polarizability components from molecular orbital calculations or from spectroscopic measurements. The presumed advantage of correlation of molecular polarizability components with sorption is based on the assumption that there is a preferred orientation for sorbate approach to and sorption on the sorbent surface.

We are presently unable to observe sorbed molecules in the presence of water by spectroscopic means or direct observation. Detailed correlations of molecular structure and properties with sorption assume a near complete knowledge of the surface, of solvent water, of the sorbate, and of their participation in the sorption mechanism. This is unlikely to be attained soon, but it would be interesting to obtain polarizability component data for further semi-empirical correlation with sorption. It is speculated that the observed sorption to the mineral surface was affected by ion-induced dipole or dipole-induced-dipole interactions between sorbate and sorbent based on the observed relation between sorbate molecular polarizability and K.

External specific surface areas varied considerably for the clay sorbents (Table V). Kaolinite had the lowest specific surface area and sorbed the least. Ca-montmorillonite had three times more surface area than Na-montmorillonite, but sorbed less of all sorbates. Barasyn had the largest surface area, but it had similar K values to Na-Montmorillonite of lower specific surface area. The montmorillonites all had much larger surface areas than the oxides, but sorbed approximately the same amount as goethite. Surface area may be casually associated with sorption, but is not the primary factor in determining K values. Cation exchange capacities followed similar trends to the surface areas and therefore provide little information on the sorption behavior of the clays.

The ethylene glycol (EG) surface areas for Ca- and Na-montmorillonite are a measure of the total clay surface area when interlayer surfaces are included (Table V). The Na-montmorillonite, which sorbed at least four times more of all sorbates than the Ca-montmorillonite, has a somewhat smaller EG surface area. In aqueous solutions these EG surface areas are irrelevant and do not represent the extent of clay expansion. A possible explanation for the greater sorption by Na-montmorillonite is due to basal expansion caused by cation hydration as discussed below.

The effect of cation substitution on sorption by a smectite clay was examined using Ca^{+2}-, Al^{+3}-, and Na^{+}- saturated montmorillonites described above. Ca-saturated montmorillonite adsorbed less MNAP than the Na-saturated clay, and Al-saturated montmorillonite sorbed more MNAP than either the Ca- or the Na-saturated montmorillonite. These results agree with Rogers and McFarlane (1981), who noted a similar trend for nonpolar halogenated organics on soils and Al- and Ca-saturated clays. Additional support for this observation comes from Rogers et al. (1980), who found benzene sorbed three times better on Al-saturated montmorillonite than on Ca-montmorillonite. No explanation was given for these differences in sorption results on the substituted clays, nor was TOC determined.

Sorption differences between the Na- and Ca-substituted montmorillonites measured here may be due to the changes in basal spacing caused by the cation substitution. The basal spacing for the Ca-montmorillonite is 19.1 Å (MacEwan and Wilson, 1980). Since Na-montmorillonite swelled, its basal spacing would be indefinite (MacEwan and Wilson, 1980), thereby presenting a greater surface area for sorption than the Ca-montmorillonite. This may explain the greater sorption exhibited by Na-montmorillonite reported here.

Explanations for the observed sorption increase caused by Al^{+3}-substitution are much more difficult. Addition of the $Al(Cl)_3$ to the montmorillonite not only causes cation exchange, but also changes the chemistry of the system (Dr. J.E. Mackin, SUNY at Stony Brook, NY, personal communication). The $Al(Cl)_3$ solution is quite acidic and probably modifies the clay lattice and surface. Aluminum hydroxide species are probably precipitated in the interlayers. New gibbsite layers might also be formed. Rogers et al. (1980) and Rogers and McFarlane (1981) failed to note or address these difficulties with the Al-saturated clay systems used in their sorption studies. Other researchers, such as Loeppert et al. (1986), have used Al-saturated montmorillonites in research studies without indicating the problems associated with the $Al(Cl)_3$-montmorillonite-water system.

Since the $AlCl_3$-Na-montmorillonite-water system is poorly characterized, interpretation of sorption results on the Al-montmorillonite is speculative. Al-saturated montmorillonite is strongly acidic (Loeppert et al., 1986), which could affect the sorption properties, especially for polar organics. Nonpolar organics would be affected primarily through dipole and ion-dipole attractions that may explain the increased sorption. The smaller, more highly charged Al^{+3} cation may change the local surface charge, thereby increasing interactions between sorbate and sorbent surface. The higher charge could also change the structured water distribution on the clay surface, allowing the sorbate to compete more favorably with water for available sorption sites. The highly hydrated Al^{+3} cation may also cause changes in interlayer spacing, which could contribute to the higher sorbate sorption observed here. Although results on gibbsite reported here show little sorption, amorphous aluminum species may sorb greater amounts.

Small quantities of organic carbon were found in all natural clay samples studied. Barasyn was extremely low in organic carbon, below the detection limit of <0.002%, but sorbed nearly the same amounts of all sorbates as Na-montmorillonite, which had at least 10 times more organic carbon. Ca-montmorillonite, contained similar quantities of organic carbon as Na-montmorillonite, but sorbed much less. It does not appear that organic carbon controls sorption on the clay surfaces.

It is apparent that clays and oxide minerals took up appreciable amounts of the sorbates studied and must be considered as contributors to sorption coefficients measured on aquifer materials whose organic carbon content may not be the prime predictor for nonpolar organic sorption.

As an antecedent to the aquifer material sorption and correlation studies, several mixtures of clays and oxides were studied to determine whether sorption on individual minerals could be used to predict the amount of sorbate taken up by a mineral mixture. Both mixtures of goethite and Na-montmorillonite and goethite and barasyn were used as sorbents for MNAP. Initial experiments with goethite and barasyn mixed in various ratios were frustrated by their similarity in sorbent affinity. For example, K for MNAP on barasyn was 1.82 ± 0.19 and the K for MNAP on goethite was $2.27 + 0.25$ (Table VIII). MNAP K value for the mixed sorbents was 2.15 ± 0.07. Confidence interval overlap prevented a test of the proposed additive effect and occurred for all sorbent combinations attempted (Table VIII). Another mixed sorbent system was selected where the sorbate affinities for the sorbent were considerably different. This system consisted of 1.0 g each of kaolinite and goethite as sorbent with PCP sorbate. Results from runs on this mixed sorbent showed that the amounts sorbed were additive. From single sorbent studies, the K for PCP on kaolin was 1.76 ± 0.54 and the K for PCP on goethite was 12.5 ± 2.0. The predicted PCP K for a mixed system (1.0 g of each sorbent) was 7.13 and the measured K for PCP was 7.56 ± 0.61.

Single sorbate/sorbent K values for each sorbent component of the binary mixture permitted calculation of K for the mixed sorbent.

Karickhoff (1984) alluded to this sorption independence, but did not experimentally demonstrate it. Results from the simple system studied here support sorption independence.

Sorption on aquifer materials from various geologic formations within the U.S. will be discussed in relation to the sorption on clays and mineral oxides. The objective is to determine if aquifer material mineral composition and other selected properties including organic carbon can be related to the observed sorption coefficients.

K_{oc} values were calculated for the aquifer materials by taking the average K value of three separate isotherm runs and dividing this by the average organic carbon content for each aquifer material (Table XV). Among the aquifer sorbents, the K_{oc} for MNAP varied by a factor of 5 and the K_{oc} for ODCB varied by an order of magnitude. To demonstrate the significance of these large variations in K_{oc}, equation (2) was used to calculate the retardation of ODCB movement relative to water over 50 years. The calculation is based on a average calculated aquifer material K value and on the actual ODCB K value measured on each aquifer material. The average K was calculated by averaging the K_{oc} over all aquifer materials. The calculated retardation results show that use of values based on K_{oc} leads to large errors in contaminant location even after this geologically short time (Table XVI).

There is considerable variation in available K_{oc} values. For naphthalene, Karickhoff (1979, 1981) reported K_{oc} of 1300 and 870 on surface soils and sediments, respectively. A K_{oc} of 1220 was measured here for naphthalene sorption on Borden aquifer material which is similar to Karickhoff's results on surface soils. Abdul and Gibson (1986) reported the K_{oc} for naphthalene on Borden aquifer material is 650,

TABLE XV. K_{oc} for MNAP and ODCB on aquifer materials.

Aquifer Material	K_{oc} MNAP	K_{oc} ODCB
Tinker	4580	1040
Carswell	1690	680
Barksdale	910	280
Blytheville	1960	820
Traverse City	6750	3200
Borden	3230	1935
Lula	2540	700

TABLE XVI. Comparison of calculated distances (m) of ODCB movement after 50 years based on K from average Koc and on actual K data.

Aquifer Material	Use of Average K_{OC}	Use of Actual K
	m	
Tinker	1006	1143
Carswell	514	785
Barksdale	155	552
Blytheville	107	159
Traverse City	930	475
Borden	759	552
Lula	594	945

Calculation Basis:
Average K_{OC} for ODCB on all quifer materials = 1236
Bulk mass density = 2.1 g/cm^3
Porosity = 0.20
Groundwater velocity = 45.7 m/yr
Time = 50 yr

about half the value found here. Johnson et al. (1985) measured a naphthalene K_{oc} of 660 on soils taken from a waste disposal site. Stauffer and MacIntyre (1986) found a NAPH K_{oc} of 470 on Lula aquifer material.

For ODCB, K_{oc} varied over an order of magnitude on the aquifer materials studied here. Chiou et al. (1983) reported a K_{oc} of 186 for ODCB on a surface soil which is generally much lower than obtained on the aquifer materials studied here. Mackay et al. (1986) reported K for ODCB on Borden aquifer material of 0.76 ± 0.03 from isotherm slopes and 0.69 ± 0.04 from a single point method. These values are somewhat comparable to 0.30 ± 0.04 reported here. Conversion of Mackay et al. (1986) K values to K_{oc} with their stated TOC, 0.018%, gives a K_{oc} of ODCB on Borden aquifer of 4200. The K_{oc} of 1940 for ODCB on Borden aquifer material found here is in fair agreement with Mackay et al. (1986), but both are much higher than on surface soil reported by Stauffer and MacIntyre, (1986) and Chiou et al. (1983).

Variation of the K_{oc} data found here is greater than that observed for surface soils. Differences may be caused by the geological variation of the samples or by varying degrees of organic diagenesis within the samples. Variation caused by difficulties with the definition and measurement of total organic carbon concentration has been largely ignored in previous work. Many authors do not describe the analytical method used. Differences between methods become more pronounced at low organic carbon concentrations. TOC data obtained from the University of Florida Soils Laboratory using Walkley-Black chromate oxidation differed from results obtained here using the combustion method (Table XVII). Differences between methods of determining organic carbon content

TABLE XVII. Interlaboratory analytical result comparison for selected aquifer material properties.

Aquifer Material	TOC		CLAY		2-LAYER		3-LAYER	
	%							
Tinker	0.07	0.01	14.1	11.3	3.8	9.0	4.2	0.75
Carswell	0.08	0.03	9.8	5.6	1.5	1.5	5.5	4.5
Barksdale	0.13	0.11	9.2	6.2	0.7	2.1	7.0	4.9
Blytheville	0.22	0.16	10.5	5.6	0.3	1.2	9.2	5.0
Traverse	0.08	0.01	1.0	0.1	0.05	0.001	0.25	0.001
Borden	N/A	0.02	N/A		N/A		N/A	
Lula	0.12	0.02	3.4		0.06		1.7	

NA, Not Analyzed
TOC Column 1, Univ. of FL. Soils Laboratory; Column 2, Author
%Clay, %2-Layer, and %3-layer Column 1, Univ. of FL; Column 2
Twin Cities Research Center.

(Table XVII) can account for variations of near one order of magnitude in K_{oc}, based on a given K value. TOC measured in this study for Borden material, 0.016%, compares well with results for Borden material published by Mackay et al. (1986), 0.018% and Abdul and Gibson (1986), 0.02%. The Walkley-Black method appears to give higher TOC values relative to the combustion method. Since K_{oc} is a function of both K value and TOC, it is necessary to consider effects of measurement difficulties from both analytical measurements when evaluating K_{oc} data.

It is questionable whether the K_{oc} concept, developed and generally applied to surface soils with organic content of >0.1%, can be used with aquifer material. The problem is made apparent from consideration of the TOC data (Table XVII). Most of the aquifer material samples have TOC <0.1%, a commonly used lower limit for organic carbon referenced sorption. Aquifer material samples with TOC above 0.1%, Barksdale and Blytheville, both included material from perched aquifers over the main water table. Even if the two high organic aquifer materials are excluded, the remaining K_{oc} range is still a factor of four (Table XV). These variations in K_{oc} are much larger than those normally encountered in surface soils and sediments, indicating the K_{oc} concept may not be useful in aquifers.

Exclusion of the Barksdale and Blytheville material from the data set gives K_{oc} values that are generally high (Table XIV). These high values may be attributed to mineral contributions to the sorption coefficient for low carbon materials, a contention that is supported by a threshold for mineral sorption observed by Hassett et al. (1980) and discussed by Karickhoff (1984). This threshold occurred when the ratio of swelling clay content to organic carbon content (cm/oc) is approximately 30. At (cm/oc) <30, mineral surfaces are generally covered by organic carbon and sorption contributions are reduced. Above this threshold, mineral surfaces may not be completely coated and add to the amount of sorbate adsorbed. The aquifer materials fall into the mineral sorption region where organic carbon control of sorption should not hold (Table XVIII). Mineral sorption may be much more sorbate specific due to selectivity of mineral surfaces. Karickhoff (1984) showed that biquinoline sorption exhibited a substantial mineral contribution, whereas pyrene was only slightly influenced. Since the aquifer materials fall in this mineral sorption region, K_{oc} can not completely describe sorption, and mineral composition must play a significant role in sorbate uptake on aquifer materials.

The other consideration regarding the utility of K_{oc} concerns the variability of the composition of the organic carbon material. Garbarini and Lion (1986) have shown that various components of soil organic matter sorb differently. Thus, a variation in composition of the organic matter will affect its sorptive properties. The question of sorbate partitioning versus sorption is not raised here. As Mingelgrin and Gerstl (1983) pointed out, it cannot be answered by equilibrium thermodynamic measurements. Differences in organic matter composition will influence sorption irrespective of the mechanism. Insufficient chemical data exist to adequately describe sediment and surface soil organic matter, let alone aquifer organic matter, so any differences remain unknown. Since the K_{oc} concept is not supported on aquifer materials, it is hereby abandoned.

Carswell aquifer material K varied with depth within the saturated zone (Table XII) with both MNAP sorption and organic carbon content

TABLE XVIII. Ratio of mineral content (cm) to organic carbon content (oc).

Aquifer Material	cm/oc*
Tinker	78
Carswell	169
Barksdale	46
Blytheville	32
Traverse City	22
Borden	N.D.
Lula	85

N.D. = No Data
* g clay mineral/g organic carbon

changing by a factor of three over the depth profile. Mackay et al. (1986) reported tetrachloroethylene (PCE) sorption as a function of depth in 10 cm increments at the Borden site. The K value for PCE varied by an order of magnitude, but specific surface area and organic carbon content varied little. PCE variation could not be explained by variation in specific surface area and/or organic carbon content.

One core study of halogenated sorbates on the Borden site as a function of depth was flawed due to oven drying of the sorbent at 130^{o} C, with a concomitant increase in sorption coefficient by approximately two. Using this flawed data, Mackay et al. (1986) noted that in most cases normalized K values for all the halogenated sorbates were approximately the same for a given strata, possibly indicating that spatial sorption variation for a given chemical class of compounds could be estimated by a single member. This preliminary work was published without sufficient data to confirm the speculation concerning spatial variation, but Mackay is continuing work to confirm it. The knowledge of sorption spatial variation is critical to the determination of contaminant transport and requires further field research. A fully documented publication presenting the finalized data set describing sorption spatial variability at the Borden site is awaited.

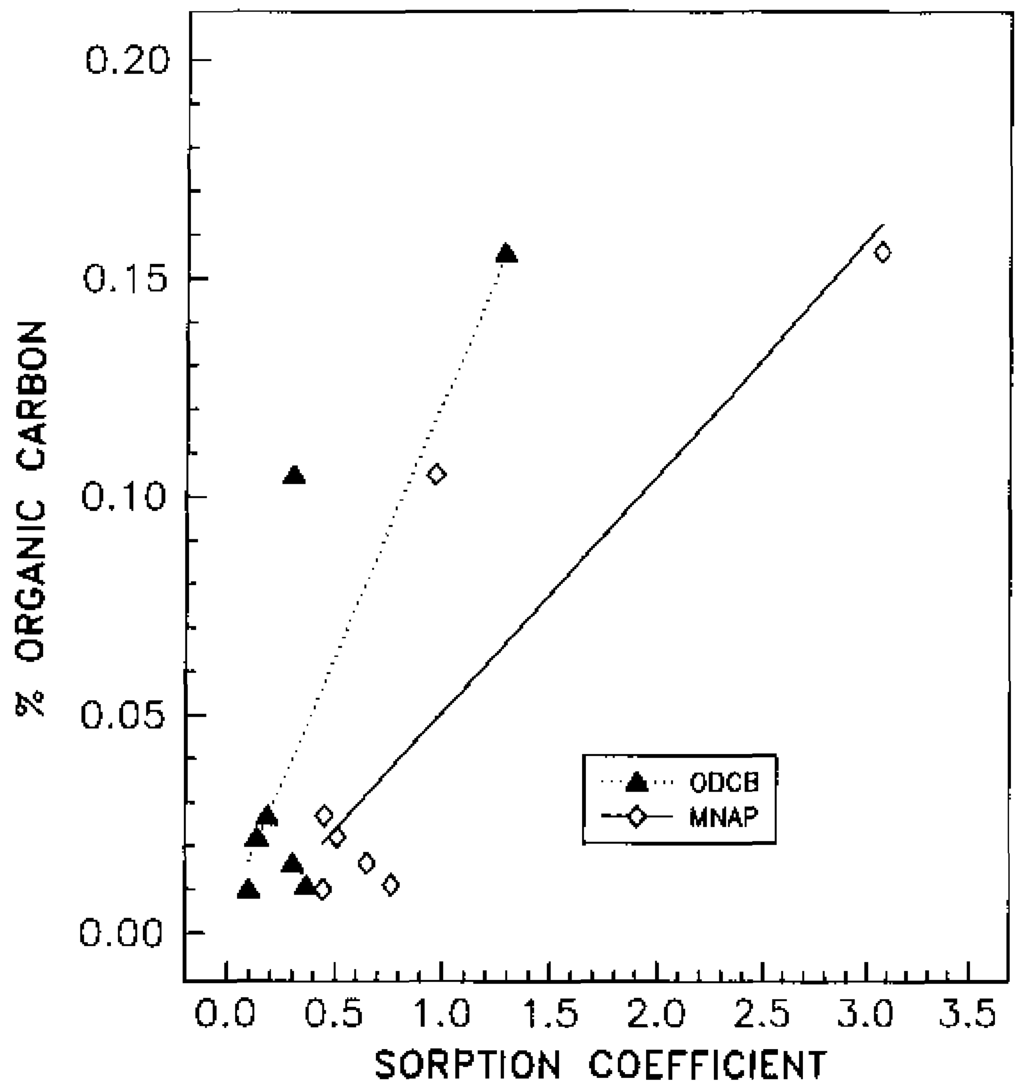
Banerjee et al. (1986) determined sorption on sections of a core of Lula aquifer material using several aromatic sorbates. The entire core length was analyzed, but results were not given separately for saturated and unsaturated zones. K value variation for orthochlorotoluene was generally within a factor of 3 to 4 over the length of the core, whereas other properties varied more, with organic carbon differing over an order of magnitude. Variations were less evident in deeper strata where K values became significantly correlated to mineral content. Variation results presented here for sorption on Carswell aquifer material as a function of depth are comparable to published results. Variation may have been greater if the core had been split into finer subdivisions. Averaging the K values from the depth profile gives an average K of 0.44, which is near the average K of 0.45 for the Carswell composite sample.

It is apparent that sorption on aquifer materials must include mineral sorption effects. A plot of MNAP and ODC8 sorption coefficients versus organic carbon concentration for all aquifer materials shows little relation between sorption coefficient and TOC (Figure 6). Inclusion of Barksdale and Blytheville materials force the least-squares fit and thus overemphasize the two points with higher carbon concentrations (Montgomery and Peck, 1982). Deletion of the Blytheville and Barksdale samples leave those samples with organic carbon less than 0.1% and greatly reduces correlation between organic carbon and K values.

Selected sorbent physical/chemical properties were measured for possible use in discovering a relationship between sorbent properties and nonpolar organic sorption on aquifer materials (Table X and XI). Choice of properties was based on sorption results on clays and oxides obtained here, on commonly used tests to characterize soil and sediment samples, and on properties used by other researchers for sorption investigations on surface soils and sediments (Means et al. [1980 a,b, 1982], Hassett et al. [1980, 1981], and Karickhoff et al. [1979]).

Means et al. (1980a) did an unspecified matrix correlation on a number of sorbent characterizations and demonstrated some interactions between percentage organic carbon and percentage nitrogen and between percentage clay and CEC. Their matrix correlation was followed by a

Figure 6. Percent organic carbon concentration versus sorption coefficient (L/kg) for MNAP and ODCB on aquifer materials.



0.20
0.15
0.10
0.05
0.00
% ORGANIC CARBON
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
SORPTION COEFFICIENT
ODCB
MNAP

separate linear regression of the K values from their study against each of the individual substrate properties. The procedure does not consider the interactions or contributions from more than one variable. The only "significant" (regression coefficient value unspecified) relationship found was K to percentage organic carbon. Means et al. (1980 b, 1982) did a similar sorbent property linear regression study versus K for PAHs and amino- and carboxy-substituted PAHs and found organic carbon dependence. Hassett et al. (1980) used dibenzothiophene on the same sorbents as Means et al. (1980 a,b, 1982), and found a significant correlation between K and percentage organic carbon at the 1% level. Other factors were not significant, but the statistical method used was not clearly stated. It is impossible to tell whether single independent regressions or multiple linear regressions were used.

PCA was run on a data matrix composed of MNAP K values, percentage organic carbon, percentage sand, percentage clay, percentage silt, specific surface area, CEC, percentage 2-layer clay, percentage 3-layer clay, and percentage iron content in all seven aquifer materials. Significant correlations (R^2>0.50) were found between many of the variables (Table XIX). Many of the interactions are expected because the associated sorbent parameters are phenomenologically related. The K values for MNAP were highly correlated with percentage organic carbon and percentage 3-layer clay. However, both percentage organic carbon and percentage 3-layer clays were also correlated with other variables and must then interact to some extent with K MNAP. Existence of all these interactions would frustrate the use of simple linear regression for this data.

TABLE XIX. Correlations found with PCA of aquifer properties and MNAP sorption.

VARIABLES	R^2
K MNAP - % Organic Carbon	0.83
K MNAP - % 3-layer Clay	0.54
% Organic Carbon - CEC	0.53
% Organic Carbon - % 3-layer clay	0.76
% Clay - % 2-Layer Clay	0.54
% Clay - % Iron	0.50
% Silt - CEC	0.77
% Silt - % 2-Layer Clay	0.84
CEC - % 3-Layer Clay	0.51
CEC - Organic Carbon	0.53
% 2-Layer Clay - % Silt	0.84
% 3-Layer Clay - % Silt	0.50
Surface Area - % 3-Layer Clay	0.50
Surface Area - % Iron	0.50

Ninety-five percent of the variance for the entire data matrix can be combined in the first four eigenvectors (Table XX). However, inspection of the eigenvector matrix gives little loading information that may be attributed to the original variables (Table XXI). The first eigenvector, which accounts for 42% of the variation, weights sand quite heavily. The second eigenvector weights K MNAP, organic carbon content, and percentage 3-layer clay. The third eigenvector weights percentage clay, surface area, and iron content and may be important in describing surface area related properties. The total information gained from the PCA shows that four principal components can explain 95% of the variation and these involve percentage organic carbon, K MNAP, percentage 3-layer clay, and surface area related properties.

Since Barksdale and Blytheville aquifers were high in organic carbon, and both had perched aquifers, PCA was rerun, eliminating them from consideration. Several changes were apparent in the similarity matrix. The TOC-K MNAP correlation disappeared and more mineral-related correlations became apparent (Table XXII). The eigenvalues changed little, requiring only three components to explain 94% of the variation, instead of four components in the previous run. Inspection of the loadings for the eigenvectors showed intermediate loading values for K MNAP and sand in the primary vector, which accounted for 47% of the variance, but the higher loadings in the second vector (which accounted for 30% of the variation), seemed related to organic carbon, surface area, percentage 3-layer clay, and iron. Loadings in eigenvector three stressed clay and iron content. The eigenvector loadings, coupled with the results from the correlation matrix, lead to a stronger mineral influence on sorption. Petrologic examination also supports the

TABLE XX. PCA results for K MNAP and sorbent physical/chemical data matrix.

Eigenvector	Eigenvalue	% of Trace	Cum. % of Trace
1	5.670	56.703	56.703
2	2.406	24.058	80.761
3	0.980	9.804	90.565
4	0.48810	4.881	95.445
5	0.312	3.124	98.569
6	0.106	1.060	99.629
7	0.037	0.367	99.997
8	0.003	0.003	99.998
9	0.000	0.000	100.000
10	0.000	0.000	100.000

TABLE XXI. PCA results for K MNAP and aquifer material physical and chemical property data matrix.

	EIGENVECTOR			
Variable	I	II	III	IV
1	-0.2219	0.3663	0.3065	-0.5140
2	-0.3218	0.3734	0.2678	-0.1440
3	0.4495	0.2042	0.1342	-0.0579
4	-0.1195	-0.3986	0.3514	-0.5568
5	-0.4469	-0.2093	-0.1568	0.0144
6	-0.2201	-0.1560	0.5240	0.4681
7	-0.4038	0.0768	-0.2519	0.1217
8	-0.2916	-0.4349	-0.2536	-0.1578
9	-0.3450	0.3256	0.1618	0.3253
10	0.1246	-0.3957	0.4902	0.1918

Variable 1, K MNAP; Variable 2, % organic carbon; Variable 3, % sand; Variable 4, % clay; Variable 5, % silt; Variable 6, surface area; Variable 7, cation exchange capacity; Variable 8, % 2-layer clay; Variable 9, %3-layer clay; Variable 10, % iron.

TABLE XXII. Correlations from PCA correlation matrix of MNAP-aquifer data with Blytheville and Barksdale aquifer data deleted.

VARIABLES	R^2
K MNAP-% Sand	0.65
% Organic Carbon-Surface Area	0.58
% Organic Carbon-% 3-layer Clay	0.76
% Clay-% Silt	0.64
% Clay-% 2-layer Clay	0.68
% Clay-% Iron	0.66
% Silt-CEC	0.73
% Silt-% 2-layer Clay	0.99
% Silt-% Iron	0.92
CEC-% 2-layer Clay	0.77
CEC-% Iron	0.79
% Iron-% 2-layer Clay	0.88
% Iron-Surface Area	0.63
% 3-layer Clay-Surface Area	0.52

correlations between oxide and clay minerals and iron, since iron was present as coatings on many of the other minerals.

Although single linear regression analysis is not appropriate, it was done here for comparison purposes since single regression was performed in all relevant literature. The K values for MNAP were regressed against each of the individual variables in the data matrix (Table X and XI). The only significant regression coefficient (R^2 = 0.69) that was obtained was between K MNAP and percentage organic carbon. When Barksdale and Blytheville were deleted from the data matrix, this regression coefficient decreased to 0.14. The deletion of Blytheville and Barksdale also produced an R^2 of 0.54 to be observed between K MNAP and surface area. Single linear regression of ODCB Ks against each sorbent property showed an R^2 of 0.58 with surface area when Blytheville and Barksdale data were eliminated. No R^2 values >0.50 were found when the entire data set containing all aquifer materials were regressed.

PCA was rerun on the data matrix, with ODCB K values replacing MNAP K values. Results were quite similar, requiring the same number of vectors to explain data varations. Percentage of variation explained by each vector was within 1% of the value obtained from the MNAP sorption data, with the first four vectors accounting for 94% of the variation. The correlation matrix for ODCB was the same as for MNAP except that K ODCB had a 0.83 correlation to organic carbon content and 0.54 correlation to percentage 3-layer clay. When Blytheville and Barksdale data were removed and PCA rerun, results were comparable to those obtained for K MNAP without Blytheville and Barksdale data.

In all cited correlation studies of surface soils and sediments containing 0.1% or more organic carbon, a large R^2 was found between the K value for nonpolar compounds and the organic carbon content. The correlation was sufficient to permit use of organic content as a predictor of sorption.

Results from this study show that for low carbon content (<0.1%) aquifer materials sorption predictions based on sorbent carbon content fail to explain nonpolar chemical uptake. Minerals can sorb amounts of nonpolar chemicals similar to the amounts sorbed on the aquifer materials and must contribute to aquifer material sorption. The statistical methods applied to the data did not show a simple relation between sorbate uptake and sorbent properties. Although organic carbon content did not control sorption on the low carbon aquifer materials, it is a component of the overall sorption coefficient. There is no single surface or mineral phase that controls sorption on the aquifer material. Measured K values on aquifer material are a combination of contributing mineral components and organic matter which probably do not have similar sorptive properties to surface organic matter.

The distribution of the organic carbon on aquifer material particles may also be a critical factor in sorption on aquifer materials. At the extremely low concentrations of TOC in these aquifer materials, the organic carbon coverage may not be complete, allowing mineral surfaces to participate in sorption. There is no obvious way to directly observe the organic carbon distribution.

The true amount of organic carbon present on the aquifer materials is also open to question because measurements at low levels are difficult (Reijnders et al., 1977), and the measured TOC is a function of the analytical technique used. There is no guarantee that the combustion method used here to analyze the bulk TOC property was sensitive to the organic matter component which affects sorption. The sorptive properties of the organic carbon could be associated with functional groups and their orientation within the polymeric humic materials. In this case, TOC measurements would relate to sorption, but not be the best descriptor because of the lack of a known relation between carbon content and functional group composition and orientation.

Many of the sorbent characterizations used here are bulk property measurements not necessarily directed toward organic chemical sorption. The measurements involve several conventional definitions, and even though done correctly, cannot adequately describe the complex sorptive surface of aquifer materials. Some of these problems are described below for the properties used in this research.

Even though the clay minerals within the aquifer materials were characterized as to 2-layer or 3-layer clays, large differences exist within the smectites themselves. All 3-layer clays do not sorb similarly as indicated by Ca^{+2}, Al^{+3} and Na^{+} results reported here. Evidence presented shows that substituting exchangeable ions can affect sorptive properties and thus considerable sorptive difference may exist between the various members of this group. Sorption may also be a function of isomorphic substitution. Analyses performed here do not account for these differences.

Nitrogen gas was used to measure the surface area of the dry aquifer materials. Organic sorbates would probably not be able to sorb on this entire surface due to molecular size differences between N_2 and the organic sorbates. Agglomerated clay particles in aqueous suspension would also present less sorbing area than that measured by N_2 gas adsorption. The sorbent surface area actually exposed and available to the organic sorbate would be a function of the sampling and grinding of the aquifer material samples and of their hydration.

The particle size distribution data also contain many vagaries that may influence sorption correlations to this property. Agglomerated clay particles would show up in larger sieve fractions and could be characterized as silt or sand. Clay and oxide mineral particles were shown to adhere to quartz particles, thereby modifying the quartz particle apparent surface area and sorptive properties, and altering the particle size distribution. Particle size distribution would also be a function of how the sample was ground. Correlations between particle size distribution and K values would be compromised by any of these particle size changes.

Even if all the characterization methods used above were "perfect", there would be no guarantee that this set of measurements encompassed the necessary data to describe the reactive surface. Other measurements such as spectroscopic techniques can provide more detailed information about the reactive surface, but are generally applicable only to clean, dry surfaces. In addition to the inability to adequately know the physical and chemical nature of the hydrated sorbent surface, the changes caused by excess water are also largely unknown. When water is sorbed on the sorbent, it not only modifies the surface chemistry of the solid but its own configuration changes from that in the bulk liquid phase. Since the adsorbed water configuration is different from bulk phase water, its solvent properties will be different and consequently may affect sorption. Considerable spectroscopic evidence is available to support the existence of structured water on clays (Sposito, 1984), but the effect of water on sorption of nonpolar organics is unknown.

If new theory and analytical techniques are developed to better describe the sorptive surface, improved predictive correlations between sorption and surface properties might be possible. With the surface characterization techniques available, it was not possible to predict sorption on the fluvial and glacial till aquifer surfaces studied here in terms of the properties measured. A larger sampling of aquifer materials including materials from fractured carbonate, metamorphic and igneous rocks would be necessary to insure that the results found here are general for all types of aquifer material. Since quantitative predictors based on available sorbent properties were not found, experimental K values must be measured on each aquifer material occurring in a groundwater contamination situation. Experimental K value spatial distribution must then be used in all groundwater contaminant transport models based on linear sorption isotherm processes at local equilibrium.

However, results also showed that for the sorbates studied here sorption trends followed general hydrophobic sorption theory with the less polar sorbates being better sorbed. If this observation is generally true, relative contaminant transport can be predicted based on chemical polarity.

This study shows that nonpolar chemical sorption cannot now be adequately correlated to the properties of aquifer materials. Until better, reliable surface characterization techniques become available, universally applied, and cost effective, it is necessary to measure actual sorption coefficients on aquifer materials.

Thoughts For Future Research

1. A wider sampling of aquifer materials should be conducted to determine sorption properties and chemical and physical characteristics and their spatial variabilities. This should be done in conjunction with field research at several sites.

2. Higher molecular weight and more polar sorbates should be studied to describe their sorptive behavior on aquifer materials. A sorbate that exhibits non-linear sorption should also be studied to determine its sorption characteristics on aquifer materials.

3. Aquifer organic carbon materials should be chemically characterized to determine similarity to surface organic carbon materials.

4. The $Al(Cl)_3$-water-montmorillonite system should be studied in detail to provide a basis for sorption interpretations. A knowledge of this system chemistry would also be beneficial in assessing the effects of acid rain and understanding soil chemical reactions.

Appendix I. Core Data

Carswell AFB, Ft. Worth, TX

Capillary fringe was encountered at 58 in. Six zones within the saturated zone were apparent and sampled.

Zone 1	1.3- 1.7 m	Fine saddle-brown, uniform clayey sand
Zone 2	1.7- 2.8 m	Orange sand with clay and black stains
Zone 3	2.8- 3.2 m	Orange uniform sand
Zone 4	3.2- 4.1 m	Saddle-brown uniform sand
Zone 5	4.1- 4.4 m	Buff-brown uniform coarse sand
Zone 6	4.4- 6.4 m	Light-yellow coarse sand

Barksdale AFB, LA

Capillary fringe was encountered at 156 in. Samples from five apparent saturated zones were sampled.

Zone 1	4.3 - 4.5 m	Sandy silt with reddish brown clay
Zone 2	4.5 - 6.7 m	Very fine saturated silt
Zone 3	12.5 - 12.9 m	Buff-brown coarse sand
Zone 4	12.9 - 13.2 m	Gray sand with clay
Zone 5	13.2 - 13.9 m	Buff-brown coarse sand

Blytheville AFB, AR

Perched water table was found at 253 in. One surface zone and three zones within the saturated zone were recognizable.

Zone 1	0.1 - 0.4 m	Near surface silty loam (not included)
Zone 2	8.8 - 9.1 m	Confined sand lens above main formation
Zone 3	9.1 - 10.0 m	Blue-gray coarse sand

Coast Guard Station, Traverse City MI

Moist sand was encountered at 22 in. Saturated sand was sampled from two lower depths called zone 1 and 2.

Zone 1	3.4 - 4.1 m	Coarse sand
Zone 2	4.1 - 5.5 m	Coarser sand

Tinker AFB OK

Saturated material was encountered at 192 in. Near surface geologic strata caused drilling problems and frustrated zone descriptions.

Zone T3A	4.9 m	Thin saturated layer
Zone T2A	5.5 m	Saturated zone material
Zone T2B	7.2 - 8.0 m	Fluid material above sandstone
Zone T3B	8.0 - 8.6 m	Semi consolidated sandstone core material
Zone T1B	8.7 m	Deep saturated zone material

Appendix II. Aquifer Material Petrographic Descriptions

Carswell

The sample is yellowish-grey (5 Y 7/2) and characterized by subrounded to rounded quartz grains, and clay, accessory feldspar, and opaque minerals. Half of the quartz grains are partially (<1/3) coated with iron oxides. There are particles of dark green clay, probably chlorite, adhering to the surface of approximately one quarter of the sand grains. The average mineral composition of the sample is:

Mineral:	Quartz	Clay	Feldspar	Opaque	Miscellaneous
Percentage:	85-90	5-7	3-5	1-2	<1

Notes: Miscellaneous minerals include tourmaline, fragments of chert, and garnet. Opaque minerals are nonmagnetic and are either hematite or spinel.

Barksdale

This sample consists of grayish-orange (10 YR 7/4) subrounded to subangular quartz with accessory feldspar, calcite, rock fragments, and well-rounded opaque minerals. There is an iron oxide coating over 1/4 of the surface area of about half of the quartz grains. The approximate overall mineral composition of the sample is:

Mineral:	Quartz	Clay	Feldspar	Calcite	Miscellaneous.
Percentage:	88-90	6-8	1-2	0.5-1	<1

Notes: Miscellaneous minerals include nonmagnetic opaque minerals and rock fragments.

Blytheville

This sample is light olive-gray (5 Y 6/1) consisting of quartz, clay and feldspar with accessory hematite, calcite, amphibole, rock fragments, apatite, zircon and opaque minerals. The quartz and feldspar grains are lightly coated (<1/4) with iron oxides and clays. The calcite is stained with iron oxide. The degree of rounding varies according to mineral type. The quartz grains, rock fragments, and opaque minerals subrounded with the feldspar and amphibole grains are angular to subangular. The average mineral composition of the sample is:

Mineral:	Quartz	Clay	Feldspar	FeOx	Calcite	Misc.
Percentage:	83-90	5-7	3-5	1-3	0.5-1	<1

Notes: Miscellaneous minerals include amphibole, magnetite, non-magnetic opaque minerals, apatite, and zircon.

Traverse City

This sample is a pale yellowish-brown (10 YR 6/2) subrounded to subangular quartz with accessory dolomite, magnetite, clay, garnet, amphibole and tourmaline. There is an irregular coating of iron oxide and clay covering <1/3 of the surface area of the quartz grains.

The calcite sand is actually composed of fragments of very fine grained (micritic) limestone. There is relatively more magnetite in the coarser fraction of the sample than the finer. The average mineral composition is as follows:

Mineral:	Quartz	Dolomite	Magnetite	Clay	Miscellaneous
Percentage:	>95	2-3	1-2	<1	<1

Notes: Miscellaneous minerals include tourmaline (a chemically complex aluminosilicate, the variety in this sample is probably dravite), garnet, amphibole, apatite, zircon and unidentified opaque minerals.

Tinker

The Tinker sample consists of light brown (5 YR 5/6) subrounded quartz sand with kaolinite and accessory feldspar, calcite, heamatite, illite, zircon, mica, chlorite and pyroxene. The quartz grains are variably coated with iron oxide; 25% of the grains are greater than 2/3 coated with iron oxide, 50% have 1/3 to 2/3 of their surface areas coated with iron oxides, and the remainder have no iron oxide coating. The relative amounts of feldspar and calcite are greater in the finer (+400 mesh) than the coarser fraction (+200 mesh) of the sample. The overall mineral composition of the sample is tabulated below.

Mineral:	Quartz	Kaolinite	Feldspar	Calcite	Illite	Misc.
Percentage:	80-85	8-10	2-4	0.5-1	0.5-1	1-4

Notes: Miscellaneous includes hematite, chlorite, zircon, pyroxene and unidentified heavy minerals.

Borden

The sample is composed of quartz and feldspar (arkosic) sand with significant amounts of calcite and hornblende (amphibole). The sand and silt sized particles in the sample are well rounded to subrounded. Some of the grains are frosted indicating transport by wind at some time in the past. The grains are clean, only a few have partial coating of iron oxide or clay. The calcite in the sample is mostly well rounded sand-sized grains of very fine grained limestone however, there are significant quantities of single crystal calcite grains in the silt sized fraction of the sample. The amphibole is subangular to angular with very poor sphericity. Other accessory minerals in the sample include magnetite, pyroxene and garnet. The relative proportions of the minerals in this sample are:

Mineral:	Quartz	Feldspar	Calcite	Amphibole	Magnetite	Misc.
Percentage:	70-75	10-15	5-10	5-10	1-3	<2

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