COLLOIDS IN GROUNDWATER:
LABORATORY AND FIELD STUDIES OF THEIR INFLUENCE ON
HYDROPHOBIC ORGANIC CONTAMINANTS

by

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ABSTRACT

It has recently become apparent that colloids may enhance the transport of hazardous organic contaminants in the subsurface. For this process to be important, colloids must be present in groundwater as mobile species capable of sorbing significant quantities of the contaminants. The sorption potential of groundwater colloids for hydrophobic organic contaminants was examined in this thesis. Additionally, the importance of colloid-associated transport of these pollutants at a coal tar contaminated site was assessed.

The sorption potential of organic colloids (OC) was examined using a fluorescence quenching method. This method allows direct assessment of the importance of OC-enhanced pollutant transport for groundwater samples under in situ conditions without requiring isolation of OC or separation of equilibrated phases. Aldrich humic acids and bovine serum albumin were used as model OC to test the method. The sorption potential of OC in groundwater samples collected both within and outside the plume derived from a secondary sewage recharge facility was then investigated. Organic colloids capable of sorbing significant quantities of perylene (and by implication other contaminants with K<sub>OW</sub> values ≥10<sup>6</sup>) were present in the wells within the plume, but only at certain times of the year. The presence of these colloids could double the transport of very hydrophobic contaminants, but will have little effect on the transport of less hydrophobic species.

The importance of inorganic colloid/organic contaminant association was examined by investigating the sorption behavior of a series of hydrophobic organic compounds to several inorganic surfaces. The studies indicate sorption is complete within hours, isotherms are linear up to aqueous phase saturation, association increases with increasing organic compound aqueous activity coefficient, and sorption of a given compound to a series of surface types results in similar association constants for all surfaces if normalized by available surface area. These results have implications for both understanding the mechanism of inorganic surface-hydrophobic organic compound sorption and assessing the importance of inorganic colloid-associated transport. This study indicates that inorganic colloids like
kaolin can significantly augment the mobility of very hydrophobic contaminants (K_{ow} values \geq 10^6) if present in groundwaters at tens of mg/L.

The importance of colloid-associated contaminant transport was investigated at a field site contaminated by hydrophobic polycyclic aromatic hydrocarbons (PAHs) derived from coal tar. Carefully collected (at low flowrates, after extensive well purging, and maintaining in situ conditions throughout sampling and storage), groundwater samples were examined for colloids and PAHs. PAH levels in soil and coal tar samples were determined as well. Low levels of colloids (< 10 mg/L) were found in all three wells sampled. The role of these colloids was assessed by: (1) comparing observed groundwater PAH concentrations in the source area with concentrations expected based on dissolved phase partitioning of PAH between coal tar and groundwater, and (2) comparing observed groundwater PAH concentrations at downgradient wells with PAH concentrations expected based on dissolved phase alone or dissolved plus colloid-associated transport of these contaminants from the source area. Higher than expected concentrations of some PAHs were found at a downgradient well. The low levels of colloids observed in groundwater at this site were not sufficient to account for this observation. Colloids could not be implicated in the transport of PAH on the time and distance scales over which they were observed at this site.

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Chapter 1

Introduction
Large quantities of hydrophobic organic contaminants have entered the subsurface environment by waste disposal practices, spills and leaks. An understanding of the mobility of these contaminants in the subsurface is required to assess accurately the associated risks and design appropriate remediation or containment strategies. Contaminants may enter groundwater by direct input to the saturated zone of the aquifer or via the vadose zone. In the saturated zone, organic contaminants may be transported with the groundwater as dissolved species, spread along the water table as a non-aqueous liquid phase (for lighter than water phases), sink through the saturated zone as a dense non-aqueous liquid phase (Mackay et al., 1985), or, as suggested more recently (McCarthy and Zachara, 1989 and references therein), move with the groundwater as colloid-associated species. Away from the source area, organic contaminant transport was traditionally thought to be dominated by advection and dispersion of dissolved organic species (which may be retarded by partitioning to immobile aquifer material) with the groundwater. Such an approach predicts that organic contaminants with high partition coefficients for aquifer material (hydrophobic contaminants) will move through the subsurface very slowly as these contaminants are essentially immobilized by sorption to aquifer material. If, however, a mobile sorbing phase, colloids, exists in the aquifer, the mobility of hydrophobic organic contaminants may be substantially greater than predicted by the two phase (dissolved and mobile or sorbed and immobile) approach.

The importance of colloid-associated transport for a given contaminant depends on both the affinity of the contaminant for the colloidal sorbent and the concentration of mobile sorbent in the groundwater. This is illustrated by use of the retardation coefficient, R, used to model the transport of species
which sorb to aquifer material (Freeze and Cherry, 1979), which is modified to include the possibility of a mobile sorbent phase.

\[ R = 1 + \frac{\text{fraction immobilized in soil}}{\text{fraction dissolved + fraction colloid-associated}} \]

\[ = 1 + \frac{(p_b \cdot K_{\text{Soil}})}{(n + n \cdot (\text{colloids}) \cdot K_{\text{colloids}})} \quad (1) \]

The partition coefficients for soil and mobile colloids are indicated by their respective K values and \( p_b \) and \( n \) are the bulk density and porosity of the aquifer material, respectively. Organic contaminant sorptive equilibrium is assumed to apply between groundwater and both aquifer material and colloids. Additionally it is assumed that colloids move at the average linear velocity of the groundwater and are not themselves retarded or captured by the aquifer material. There is reason to believe some colloids are filtered by aquifer material (McDowell-Boyter et al., 1986) and some evidence that colloids may actually move faster than the average linear groundwater velocity due to size exclusion from small pores (Enfield and Bengsston, 1988; Harvey et al., 1989). Equation 1 indicates that colloids can enhance the transport of a contaminant by a factor of 2 or more if the product \((\text{colloid}) \cdot K_{\text{colloids}}\) is greater than 1. For nonpolar organic compounds, \( K_{\text{colloids}} \) generally increases with organic compound hydrophobicity. Colloids can enhance the transport of hydrophobic organic contaminants in groundwater if they exist in the subsurface as mobile species capable of sorbing a significant fraction of the contaminant mobile load.

Colloid-organic contaminant association is examined in this thesis. The sorption of hydrophobic organic compounds to both organic (model
macromolecules and groundwater organic colloids) and inorganic colloids (kaolin and other inorganic surfaces) was studied. In addition, the importance of colloid-associated transport at a site contaminated by coal tar (known to contain a variety of hydrophobic organic contaminants) was investigated by examination of groundwater samples (carefully collected to minimize sampling artifacts), soil, and coal tar source material. The following discussion provides a brief review of the existence of mobile colloids in groundwater and sorption of organic compounds to colloidal materials, indicating the contribution this thesis makes in these areas.

Existence of Mobile Colloids in Groundwater

A wide variety of colloidal materials have been found in groundwaters including: humic substances and other macromolecules (Leenheer et al., 1974; West, 1984; Thurman, 1985; Enfield et al., 1989) microorganisms (Keswick, et al. 1982; McGinnis and DeWalle, 1983; Harvey et al., 1989), mineral precipitates (Langmuir, 1969; Gschwend and Reynolds, 1986), and rock and mineral fragments (Nightingale and Bianchi, 1977; Ryan and Gschwend, 1990). The reader is referred to McCarthy and Zachara (1989) for a more detailed review of colloids found in groundwater. There is evidence in the literature that colloids can be transported hundreds of meters from their source. Reinhard (1984) reported the occurrence of chlorinated macromolecules derived from a wastewater reclamation facility 140 m from the source. Robertson et al. (1984) detected up to 780 mg/L of tannin and lignin in groundwater 900 m down-gradient of a waste pulp liquor disposal pit. Keswick et al. (1982) reported subsurface bacteria and viruses were transported up to 900 m and 1600 m, respectively, in groundwater. These examples indicate that colloids do exist as mobile species in groundwater. If
these colloids are capable of sorbing sufficient quantities of contaminants, they may play a role in contaminant transport in groundwater.

**Sorption to Colloids**

Colloidal humic substances and natural organic matter are known to be good sorbents for hydrophobic organic compounds (Boehm and Quinn, 1973; Carter and Suffet, 1982; Means and Wijayaratne, 1982; Landrum et al., 1984; West, 1984; McCarthy and Jiminez, 1985; Garbarini and Lion, 1986; Brownawell, 1986; Gauthier et al., 1986, 1987; Chiou et al., 1987). These studies collectively indicate that organic matter from various sources differ in ability to bind hydrophobic organic contaminants, and that pH and ionic strength of the solution in which sorption is measured can affect observed binding constants as well. Hence, binding constants for humic substances found in lakes and rivers may not apply to humic substances and other organic colloids found in groundwater, and sorption studies should be carried out under in situ solution chemistry conditions to determine relevant binding constants. Only a few studies examining the sorption of hydrophobic organic compounds to actual groundwater organic colloids have been reported in the literature (West, 1984; Enfield et al., 1989). These sorption studies were carried out, as is often the case, with colloidal material isolated from groundwater by fractionation procedures or concentrated via hollow fiber filter ultrafiltration. Such procedures may collect only a fraction of the organic colloids capable of sorbing contaminants or may change the character of these sorbents. It is preferable to conduct sorption experiments on unaltered groundwater samples under in situ groundwater chemistry conditions. In Chapter 2 a fluorescence quenching method is described which allows just that. The method was tested using model organic colloids (Aldrich humic acid and bovine serum albumin), then used to determine the ability of
groundwater colloids (collected from a site contaminated by the recharge of secondarily treated sewage) to associate with hydrophobic organic compounds, and thereby augment the mobile load of these compounds. This technique should be particularly useful in screening groundwaters for organic colloids capable of binding contaminants.

As indicated above, inorganic colloids may exist as mobile species in groundwater, as well. These colloids may be organic coated, in which case we would consider them organic colloids, as the dominant association of hydrophobic organic contaminants with these colloids is expected to be through sorption by the organic matter. Situations may exist where only very low levels of organic matter are present. Here, sorption of hydrophobic organic contaminant to the inorganic surface of colloids may be important. Far less information exists in the literature on this subject. Sorption of hydrophobic organic contaminants to inorganic surfaces has traditionally been thought to play a negligible role in aqueous systems. However as reported in Chapter 2, for perylene and laboratory glass surfaces, very hydrophobic species (e.g., $K_{ow} 10^6$), inorganic surfaces sorption may be more important than traditionally thought. In Chapter 3 the sorption of nonpolar hydrophobic organic compounds to inorganic surfaces including kaolin colloids, silica, and alumina surfaces is examined. Sorption studies were conducted to elucidate the sorption mechanism and provide a predictive framework for estimating sorption behavior of sorbate:sorbent pairs in the absence of measurements. This work brings us a step closer to understanding sorption of hydrophobic organic contaminants to inorganic surfaces and predicting the importance of this association in the environment.
Importance of Colloids to Subsurface Transport of Organic Contaminants

The discussion above indicates the potential for colloid associated hydrophobic organic contaminant transport in the subsurface, but to date the importance of this phenomenon has not been demonstrated on the field scale, for example, at a hazardous waste contaminated site. In Chapter 4, the effect of colloids on the transport of hydrophobic polycyclic aromatic hydrocarbons derived from the burial of coal tar was investigated. Groundwater samples were obtained from wells employing a sampling scheme designed to carefully collect groundwater samples representative of in situ conditions and devoid of colloidal artifacts (e.g., due to shearing of aquifer material, or precipitation resulting from water chemistry changes during sampling). These samples along with soil and coal tar source material samples were examined to determine the role of colloids in organic contaminant transport at this site. Such information is crucial for assessing exposure risks to contaminants and developing effective remediation or containment strategies.

The work reported in this thesis provides information to assess the role of groundwater colloids in hydrophobic organic contaminant transport at the sites examined in this work and methods to examine other sites. Though the application of this work is to transport of contaminants in groundwater, the information is generally applicable to other aquatic systems.
LITERATURE CITED


ABSTRACT

A fluorescence quenching method was developed to assess the hydrophobic organic pollutant binding potential of organic colloids (OC) in unaltered natural waters. This method allows (1) direct assessment of the importance of OC-enhanced pollutant transport for environmental samples under in situ water chemistry conditions, without requiring the isolation of OC or separation of equilibrate phases, (2) testing of chemicals which suffer substantial wall losses from aqueous solutions, and (3) examination of unstable water samples such as anoxic samples. Our experiments show that some OC (Aldrich humic acids) fully quench OC-associated perylene fluorescence, but others (bovine serum albumin) do not. This implies that fluorescence quenching results collected for a single [OC] or over a limited [OC] range provide only a lower limit estimate of the potential for OC-association. Tests with groundwater, recharged with secondary treated sewage and containing OC at about 1 mg C/L, showed temporal variation in the ability of OC present to quench or bind perylene.
INTRODUCTION

Organic colloids or inorganic colloids with organic coatings (both referred to herein as OC) may enhance the transport of hydrophobic organic pollutants in groundwater (McDowell-Boyer et al., 1986; Gschwend and Reynolds, 1987; Enfield and Bengtsson, 1988; McCarthy and Zachara, 1989). For such facilitated transport to be significant, not only must OC be present and mobile in the subsurface, but they must also be sufficiently capable of sorbing hydrophobic organic contaminants to augment the mobile load. Literature evidence suggests OC exist in uncontaminated groundwaters at approximately ppm levels (Leenheer et al., 1974; West, 1984; Thurman, 1985; Ryan, 1988) and in contaminated groundwaters at levels up to hundreds of ppm (Reinhard, 1984; Robertson et al., 1984). Some examples suggest that at least a portion of this OC may be mobile in groundwater. Reinhard (1984) reported mg/L quantities of OC (mw 500 - 10,000 g/mole) in groundwater, necessarily derived from a wastewater reclamation facility 140 m upgradient, as these macromolecules were chlorinated. Robertson et al. (1984) detected up to 780 mg/L of tannin and lignin in groundwater 900 m downgradient of a waste pulp liquor disposal pit, apparently traveling at the same rate as conservative constituents in the contaminant plume.

This paper focuses on the issue of sorption of hydrophobic organic pollutants to OC. For the purposes of this study, OC are operationally defined
as organic matter that will not pass through a 500 molecular weight cut-off (MWCO) ultrafiltration membrane (quantified as mass of organic carbon/sample volume, g C/L). Such matter may include humic and fulvic acids, other macromolecules commonly found in sewage effluents, aggregates of these, microorganisms or organic coatings on inorganic colloids. The first objective of this study was to develop a non-intrusive method that could be used to determine the extent of sorptive interactions between hydrophobic organic compounds and unaltered groundwater OC. After testing with model OC, the technique was applied to groundwater samples obtained from a site contaminated by the recharge of secondarily treated sewage and known to contain suspended colloids (Gschwend and Reynolds, 1987), thereby helping to assess the potential impact of colloid-facilitated transport at this site.

METHODS USED TO STUDY SORPTION OF ORGANIC POLLUTANTS TO NATURAL OC

Partitioning behavior of organic contaminants between natural waters and organic colloids has been investigated through a variety of methods. These include dialysis (Carter and Suffet, 1982; West, 1984), reverse phase separation (Landrum et al., 1984), ultrafiltration (Wijayaratne and Means, 1984), solubility enhancement (Chiou et al., 1987), static headspace analysis (Garbarini and Lion, 1986; Brownawell, 1986), and fluorescence quenching (Gauthier et al.,
1986, 1987). Methods not requiring the separation of equilibrated phases are preferred as equilibrium between OC and the organic contaminant may be disturbed during separation. Methods allowing the use of whole unaltered natural water samples for quantitation of \( K_{oc} \) values (Landrum et al., 1984; Chiou et al., 1987) have an additional advantage. Isolation and concentration steps could change the character of these colloidal sorbents or may collect only a fraction of the OC sorbents present. Further, since pH and ionic strength may affect the magnitude of the observed \( K_{oc} \) (Boehm and Quinn, 1973; Carter and Suffet, 1982; Means and Wijayaratne, 1982), if the isolated OC are not rediluted with ultrafiltrate with in situ pH and ionic strength conditions, the \( K_{oc} \) value may be incorrectly estimated. To avoid such difficulties, we propose a relatively simple adaptation of the fluorescence quenching method to provide direct assessment of OC-enhanced transport for a given pollutant using whole groundwater samples under in situ conditions.

FLUORESCENCE QUENCHING IN WHOLE WATER SAMPLES

The key to using fluorescence to determine OC-water partitioning behavior, and directly assess the importance of OC association in natural waters, is the observation that the fluorescence of a PAH is quenched on association with OC (Gauthier et al., 1986, 1987). This allows a distinction between dissolved PAH and OC-sorbed PAH without having to separate equilibrated phases. For the simple case in which the PAH exists as either
dissolved and fluorescent or as sorbed-to-OC and non-fluorescent, fluorescence can be used to examine the abundance of the species in a mixture where:

\[ [\text{PAH}_T] \ (g/mL) = [\text{PAH}_d] + [\text{PAH-OC}] \]  \hspace{1cm} (1)

with \([\text{PAH}_T]\) the total PAH mass per unit volume of sample, \([\text{PAH}_d]\) the dissolved PAH concentration of the sample, and \([\text{PAH-OC}]\) the mass of PAH associated with the OC per unit volume of sample. \([\text{PAH}_T]\) can be quantified by measuring the fluorescence, \(F_o\), of the PAH probe in an OC-void solution (e.g., ultrafiltered groundwater). \([\text{PAH}_d]\) can be obtained by measuring the PAH probe fluorescence, \(F\), in the presence of OC (e.g., an unaltered groundwater sample). Hence, the decrease in fluorescence in the presence of OC relative to that observed in the OC-void sample is a direct indication of OC-associated species.

Since we may define:

\[ K_{oc} = \frac{[\text{PAH-OC}]}{[\text{PAH}_d][\text{OC}]} \times \frac{mL}{g_c} \]  \hspace{1cm} (2)

and deduce the:
\[ \text{dissolved fraction} = \frac{[PAH_d]}{[PAH_T]} = (1 + K_{oc}[OC])^{-1} \]

(3)

then the observed fluorescence ratio \( F/F_0 = [PAH_d]/[PAH_T] \) is a function of both the sorbate's \( K_{oc} \) and the OC concentration in the groundwater. For a given groundwater sample, the OC concentration cannot be adjusted without altering the groundwater sample by concentration or dilution. Therefore, to observe a decrease in fluorescence, the PAH probe used must be carefully chosen. If an estimate of the sample's [OC] is available, the proper PAH can be chosen based on the compound's hydrophobicity. For example, to observe a \([PAH_d]/[PAH_T]\) ratio of at least 0.5, the PAH probe must have a \( K_{oc} \geq [OC]^{-1} \).

If the [OC] is unknown, a suite of PAH probes with a range of tendencies to sorb can be used to maximize the chance of observing quenching between the extremes of fully and insignificantly quenched. If there is no observable difference in PAH fluorescence between the ultrafiltered and unaltered samples, significant association with OC is probably not occurring for the probe compound of interest (with the caveat concerning quenching efficiency discussed below); and by implication there would be no association of OC with other nonpolar pollutants of similar hydrophobicity.
Assumptions of the Simple Fluorescence Quenching Expression

This simple approach entails a number of assumptions:

(1) quenching of the PAH probe fluorescence by OC is due to static quenching (indicative of association) rather than dynamic quenching;

(2) any observed decrease in PAH probe fluorescence is due only to PAH association with OC; (3) association of the PAH probe with OC results in complete quenching of PAH probe fluorescence. Gauthier et al. (1986) have discussed the reasonableness of the first assumption. The other two assumptions are discussed below.

Decreases in PAH Fluorescence

In addition to quenching on association with OC, observed decreases in PAH fluorescence could result from: PAH probe biodegradation, photodegradation, or volatilization during experimentation; the presence of other types of quenchers such as oxygen, aromatic amines, metals, or heavy atoms like I⁻; or adsorption of the probe to the sample vessel walls during experimentation. The first three possibilities can be minimized by suitable measures (poisoning, working in the dark, and choosing low headspace flasks). Provided that only OC are removed by the ultrafilter, using ultrafiltered samples as a reference for total PAH fluorescence will correct for the effect of other quenchers.

Partitioning of the PAH probe to the sample vessel surface can be minimized by choosing sample vessels with surfaces having a low affinity for
the PAH probe and minimal surface-area-to-volume ratio (SA/V). Preliminary experiments indicated that for very hydrophobic probes such as perylene, substantial wall losses occurred. To assess the magnitude of the OC-association for this probe required developing approaches to account for these additional losses. Sorption to walls can be accounted for by either equilibrium or kinetic methods. Both approaches rely on the assumption that the PAH probe itself, rather than the OC-associated probe, is partitioning to the vessel surface.

In the equilibrium approach, the mass balance equation is modified to allow for PAH partitioning to the vessel walls as well as to OC. Defining the equilibrium partition coefficient for the vessel wall as follows:

\[
K_w = \frac{[PAH_{wall}]}{[PAH_d](SA/V)} \quad (mL/cm^2)
\]

where \([PAH_{wall}]\) is the mass of PAH associated with the wall per unit volume of sample, the mass balance equation can be simplified and rearranged to:

\[
\frac{[PAH_d]}{[PAH_T]} = (1 + K_{oc}[OC] + K_w(SA/V))^{-1}
\]
Quantitation of OC-sorption now requires knowledge of $K_w$ and SA/V. For these purposes, SA/V can be estimated from the geometry of the sample vessel. $K_w$ can be obtained from a series of fluorescence measurements on wall-equilibrated aliquots of the sample following sequential exposure of the sample to new surfaces. If probe molecules are significantly lost to the vessel walls, the inverse of measured fluorescence, yielding measures of $1/[PAH_d]$, versus cumulative SA/V should decrease linearly with slope $K_w/[PAH_T]$ and intercept $\{1 + K_{oc}[OC])/[PAH_T]\}$. Note that [PAH$_T$] cannot be measured directly when wall loss is substantial, but can be estimated by back extrapolation of data from the ultrafiltered sample to SA/V = 0. If both the ultrafiltered and unaltered samples are spiked with the same quantity of PAH, then this estimate of [PAH$_T$] is valid for the OC-containing vessel as well. Substituting this value of [PAH$_T$] into the expressions for the slope and the intercept of the unaltered sample yields values for $K_w$ and $(1 + K_{oc}[OC])$.

An alternative approach to quantitation of PAH-OC association in the presence of losses to vessel surfaces is to use observations of the kinetics of this wall loss. This approach requires the additional assumption that the kinetics of PAH partitioning to OC is fast relative to the kinetics of PAH adsorption to the vessel wall. Assume that the sorption process can be represented as:
\[ \begin{align*}
  k_w \\
  PAH_d &= \frac{k_w}{k_{-w}} \cdot PAH_{-\text{wall}}
\end{align*} \]

(6)

where \( k_w \) and \( k_{-w} \) are first-order forward and backward rate constants for wall adsorption. At sorptive equilibrium,

\[ \frac{[PAH_{-\text{wall}}]}{[PAH_d]} = \frac{k_w}{k_{-w}} - K_w \left( \frac{SA}{V} \right) \]

(7)

The change in \([PAH_d]\) in time due to adsorption of PAH to the vessel walls can be observed by monitoring the time-varying solution fluorescence, \( F(t) \), and thus:

\[ \frac{d[PAH_d]}{dt} = \frac{dF}{dt} \]
Integration of Equation 8 with the initial condition

\[ F(t)|_{t=0} = [\text{PAH}_T] - [\text{PAH-OC}] = F_0 \]

yields:

\[
F = \frac{k_{-w}F_0^*}{k_w + k_{-w}} + \frac{k_w F_0^*}{k_w + k_{-w}} e^{-(k_w + k_{-w})t}
\]

(9)

This equation is of the form \( F = c + ae^{bt} \). Hence, a nonlinear least squares curve fitting program can be used to determine \( a, b, \) and \( c \) from fluorescence measurements obtained as a function of time. These estimates allow determination of \( ([\text{PAH}_T] - [\text{PAH-OC}]), k_{-w}, k_w \) and \( K_w \). The ratio of fluorescence values extrapolated to \( t = 0 \) for the unaltered sample relative to that for the ultrafiltered sample allows calculation of the quantity \( K_{oc}[\text{OC}] \).

**Efficiency of Static Quenching by OC**

The analysis thus far has also relied on the assumption that only the \([\text{PAH}_d]\) species is quantified by measured fluorescence. This assumption is valid if static quenching of PAH fluorescence by OC results in complete quenching of PAH fluorescence. If this is not the case, the formulation must incorporate the possibility that the OC-associated PAH contributes to the observed fluorescence. Ignoring wall losses for the purposes of this derivation, and assuming only one type of OC exists in the sample:
\[ F = [PAH_T] \left( (\text{fraction dissolved}) + (\text{fraction sorbed})\phi \right) \]

(10)

where \( \phi \) is the fluorescence quantum yield of OC-bound PAH. Since we may write

\[ \text{fraction sorbed} = \frac{K_{oc}[OC]}{1 + K_{oc}[OC]} \]

(11)

use of Equations 3 and 10 yields:

\[ \frac{F}{[PAH_T]} = \frac{1 + \phi K_{oc}[OC]}{1 + K_{oc}[OC]} \]

(12)

For groundwaters with a given quantity of OC of unknown composition, \( \phi \) cannot be determined directly. If, however, the groundwater OC are concentrated, \( \phi \) and \( K_{oc} \) can be determined by observing fluorescence as a function of [OC]. Unfortunately, it is uncertain how the concentration procedure
might affect the sorbent properties of the OC or how estimation of the $K_{oc}$ under other than \textit{in situ} conditions may affect the magnitude of the product, $K_{oc}[OC]$. We have examined this issue indirectly by using model OC (Aldrich humic acids and bovine serum albumin, BSA), as discussed in the results section. Measuring fluorescence as a function of [OC] for these model compounds allows determination of the $\phi$ values for these two model OC. These experiments allow us to assess the error that might be associated with assuming complete quenching in quantifying partitioning of PAH to OC using whole water samples.
METHODS AND MATERIALS

APPARATUS

Fluorescence measurements were obtained on a Perkin Elmer LS-5 spectrofluorimeter with slit widths set at 3nm\textsubscript{ex}/10nm\textsubscript{em}. Fluorescence data were collected at the following wavelength pairs (nm) (ex/em): 434/466, 250/350, 340/460, 492/519, and 605/600. These wavelengths monitor perylene, phenanthrene, OC, rhodamine 110, and light scattering, respectively. The wavelength pairs were chosen to maximize each fluorophore signal and minimize background interference. Absorbance measurements were obtained on a Beckman DU-7 spectrophotometer. Data were collected at the following wavelengths (nm): 519, 492, 466, 460, 434, 350, 340, and 250 to allow for inner-filter-effect correction of fluorescence data.

MATERIALS

TEST SOLUTION

Concentrated stock solutions of PAH were made up in methanol. Experimental solutions for fluorescence studies were spiked with 10-25 \textmu L of the stock PAH solution per 20-50 mL test solution. The resulting spiked test solutions contained combinations of the following: 0.3-1 \textmu g/L perylene (Aldrich, 99%, gold label), 26-65 \textmu g/L phenanthrene (Eastman), 10-26 \textmu g/L rhodamine 110 (Kodak, lasergrade), and 200-500 mg/L methanol (EM Science, Omnisolve
glass distilled). We do not believe such low levels of methanol \((5 \times 10^{-3}\) volume fraction) will significantly affect PAH aqueous activities (Yalkowsky et al., 1976; Munz and Roberts, 1986; Morris et al., 1988), and therefore do not anticipate effects on PAH sorption by OC. Note the resulting perylene concentration of some test solutions exceeded the reported solubility of 0.4 \(\mu g/L\) (Mackay and Shiu, 1977). Substantial losses to glass walls were expected, so some samples were overspiked to maximize the fluorescent signal remaining after equilibration. For most experiments, perylene, phenanthrene and rhodamine 110 were spiked concurrently. The fluorescence spectra of these probes do not overlap substantially. Partition coefficients observed for perylene to OC in the presence and absence of the other two probes were indistinguishable. Some test solutions received only methanol. These solutions allowed for background subtraction of fluorescence due to sample components. Rhodamine 110 was included in test solutions to normalize probe responses to account for slight differences in spike level. Rhodamine 110 has a strong fluorescence signal at wavelengths which do not interfere with the PAH used in this study, and is soluble enough that sorption to glass walls and OC was not expected.

**SAMPLES**

Initial equilibrium-approach experiments were carried out using distilled water and 5 mg/L Aldrich humic acid solutions (techgrade, Aldrich, Milwaukee, WI) at pH 4.5. Aldrich humic acids were used as received.
Subsequent kinetic experiments were carried out with Norganic water (Millipore Corp., Bedford, MA) at pH 7, and 1.3 mg/L Aldrich humic acid solutions at pH 7. For these experiments Aldrich humic acid was cleaned prior to use by repeated dissolution in base, precipitation in acid, centrifugation, redissolution, and filtration through a 100 nm Nuclepore filter.

Groundwater samples used in experiments were collected from three U.S. Geological Survey monitoring wells located near Otis Air Base, Cape Cod, MA. At this site, recharge of secondarily treated sewage to a sand and gravel aquifer for more than 50 years (LeBlanc, 1984) has created an extensive plume of dissolved organic carbon (DOC), a portion of which is expected to be OC (Figure 1). Well F242-77 is outside the plume, and so low levels of DOC and OC would be expected. Well F343-57 is near the contamination source, where higher levels of OC were anticipated. Well F350-77 is in the middle of a detergent plume. Half of the total DOC at the latter well consists of detergents (Thurman et al., 1986); we expected a portion of the remainder to consist of OC. Groundwater samples were obtained from the three wells with a submersible gear-driven pump (Fultz Pump Inc., Lewistown, PA) at very low flow rates (100 mL/min) to minimize shearing of aquifer material. Samples were pumped to the surface through polypropylene tubing and collected in glass LuerlokR syringes or in argon-filled biological oxygen demand (BOD) bottles in argon-filled zipper-lock bags. Samples were stored in the dark at slightly below groundwater temperature. Subsequent sample transfers were made in a glove
Figure 1: Map showing the location of infiltration bed and monitoring wells sampled. Location of DOC plume contours (in mg C/L) are from Thurman et al., 1986. Arrows indicate the general direction of groundwater flow.
box in which commercial grade argon (< 2 ppm O₂) was used to maintain an inert atmosphere. The pH, Eh, conductivity, dissolved oxygen (DO), and laser light scattering intensity (N4 Submicron Particle Analyzer, Coulter Electronics, Hialeah, FL) of the samples were measured while sampling in the field, on subsampling in the laboratory, and after fluorescence quenching studies were conducted to determine whether groundwater samples maintained their in situ conditions through storage and experimentation. These parameters are reported for each well in Table I. For a given sample, these parameters were found to remain constant throughout storage and experimentation.

GLASSWARE

Fluorescence quenching experiments were carried out in 100 ml round bottom flasks with ground glass stoppers or 50 mL glass Luerlok R syringes. Reverse phase separation equilibrations were carried out in 20 mL glass syringes. Quartz cuvettes 1 cm × 1 cm × 4 cm were used for both fluorescence and absorbance measurements. Flasks and cuvettes were cleaned for use by soaking in concentrated chromic/sulfuric acid followed by rinsing with distilled water. Glass syringes were cleaned by soaking in persulfate solution (5 g/L potassium persulfate and 0.5% phosphoric acid in distilled water) at 90°C-100°C for at least one hour. This was followed by rinsing and soaking in distilled water.
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<th>Well #</th>
<th>pH</th>
<th>Eh mV</th>
<th>O₂ ppm</th>
<th>Conductivity μS</th>
<th>[TOC] mg C/L</th>
<th>[OC] * mg C/L</th>
<th>Laser Light</th>
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<td>1.5</td>
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* Established as the decrease in TOC after ultrafiltration
ULTRAFILTRATION

Groundwater samples were ultrafiltered using an Amicon ultrafiltration cell with a 76 mm 500 MWCO YCO5 ultrafiltration membrane. Ultrafilters were prepared for use by: soaking overnight in Norganic water, rinsing with 100 mL Norganic water, and then rinsing with 50 mL of the sample. A new filter was used for samples from each well. Roughly 350 kPa argon backpressure forced the sample through the membrane.

ORGANIC CARBON ANALYSIS

Samples were acidified with phosphoric acid and purged of inorganic carbon by a nitrogen stream. Aliquots (50 - 200 μL) of purged samples were injected directly into the high temperature combustion chamber of an Ionics Total Carbon Analyzer (Watertown, MA). This instrument utilizes a platinum catalyst to facilitate organic matter oxidation at 900°C and an infrared detector to measure CO₂ which is produced. Dilutions of a 1000 mg C/L potassium biphthalate (Mallinckrodt, reagent grade) solution prepared with Norganic water were used to obtain a calibration curve. The [OC] was obtained from the difference between organic carbon measured in the whole and ultrafiltered samples.

TYPICAL PROCEDURE

KINETIC APPROACH

A 50 mL glass syringe containing either a humic acid solution,
ultrafiltered humic acid solution, Norganic water, whole groundwater, or ultrafiltered groundwater and a small teflon stir bar was spiked with 10 μL of a methanol solution containing perylene, phenanthrene and rhodamine 110 or 10 μL of methanol. Immediately after spiking the syringe was placed on a stir plate. Syringes were covered with foil during experiments to minimize photodegradation of PAH and samples were spiked with sodium azide to minimize biodegradation where required. The sample was allowed to mix 3 minutes; then aliquots were withdrawn sequentially in time for fluorescence and absorbance measurements. At each time point, 5 mL of sample were withdrawn from the syringe for rinsing and filling the cuvette. Four integrated fluorescence readings were immediately recorded for each of the wavelength pairs listed. Readings were recorded first for the least soluble PAH to minimize the effect of losses to the cuvette walls. After all the fluorescence measurements were obtained the cuvette was transferred to the spectrophotometer for absorbance measurements. Absorbance measurements were used to calculate inner-filter-effect correction factors for fluorescence measurements (Gauthier et al., 1986). This correction was largest for fluorescence wavelengths used to monitor phenanthrene, but never exceeded 1.4. Corrected fluorescence measurements were normalized by rhodamine 110 fluorescence measurements for a given data set to account for slight variation in spiking volume. These data along with measured organic carbon concentrations for both whole and ultrafiltered samples allow determination of
\( K_{oc} \) values as previously described.

EQUILIBRIUM APPROACH

Samples were transferred from BOD bottles to 100 mL flasks and spiked under an argon atmosphere in a glove box. These flasks were then incubated in the dark at 22°C for 3 days. Preliminary experiments indicated that PAH sorptive equilibrium between flask walls and sample was reached in less than 3 days. Following this equilibration period, an aliquot of the sample was removed from the flask in the glove box. A portion of this subsample was used to rinse the pipette and cuvette, and then the remainder was transferred to the cuvette for measurement of fluorescence and absorbance. The remainder of the sample in the 100 mL flask was transferred to a clean flask. The sample was then allowed to re-equilibrate with this fresh gas surface for 3 days. This procedure was repeated to obtain at least 4 fluorescence observations as function of cumulative SA/V.

REVERSE PHASE SEPARATION

For comparative purposes partition coefficients were determined using the method of Landrum et al. (1984). The basis for the method is that dissolved PAH are retained by a C\textsubscript{18} cartridge while OC (humic materials in particular) and associated PAH pass through the cartridge. Glass syringes (20 or 50 mL) were filled with Aldrich humic acid or BSA solutions, distilled water, or groundwater samples. Syringes were spiked with 10 - 25 \( \mu \)L of the PAH spiking solutions or methanol (for determination of background fluorescence)
and 10 μL of saturated sodium azide solution. Syringes containing distilled water were used to ensure PAH were retained by the cartridge in the absence of OC. Samples in syringes were equilibrated with PAH spikes in the dark with a stirbar on a stirplate for several hours or without stirbar for at least 18 hours. An 8 mL aliquot was then taken to obtain a measure of total PAH (dissolved + OC-associated). The sample was then passed through the C18 cartridge (Maxi Clean cartridge, Alltech Associates cleaned with 10 mL methanol and at least 30 mL distilled water before use) and an 8 mL aliquot of the effluent was taken to determine OC-associated PAH content. These aliquots were extracted with 4 mL of hexane (EM Science, Omnisolve, glass distilled) and analyzed by fluorimetry. The dissolved PAH content was determined by difference. The $K_{oc}$ (mL/g C) was calculated as: $[\text{PAH-OC}] / ([\text{PAH}_d][\text{OC}])$. 
RESULTS/DISCUSSION

METHOD VERIFICATION USING MODEL OC

Aldrich humic acids and bovine serum albumin were used as model OC to test the fluorescence quenching method, verifying assumptions inherent in the derivation, as well as to allow comparison of partitioning data obtained by fluorescence quenching with results obtained by more traditional methods.

PERYLENE/ALDRICH HUMIC ACIDS: EQUILIBRIUM APPROACH

According to Equation 5, the reciprocal of observed perylene fluorescence obtained via the equilibrium approach should vary directly with the vessel SAV ratio. This is observed for perylene fluorescence in the presence of 1.4 mg C/L Aldrich humic acids as well as for distilled water samples (Figure 2a). The fluorescence measurements obtained in the presence of Aldrich humic acids lie on a distinctly different line than those obtained for the distilled water sample indicating fluorescence quenching is occurring presumably due to association of perylene with the humic acids. As previously described, the fluorescence value associated with [PAH_T] is determined from the intercept of the OC-void sample. This value can be substituted into the expression for the intercept for the humic acid sample [(1/[PAH_T]) (1 + K_{oc}[OC])] to determine K_{oc}[OC]. This estimate of [PAH_T] can also be used to determine K_w from the slope of the linear regression. The average K_w obtained from the slopes of the replicate Aldrich humic acid samples (K_w = 0.36 mL/cm^2) is virtually identical to
Figure 2: Partitioning data for Aldrich humic acids

a) The flask-wall equilibrium approach: perylene
   • solid symbols indicate replicate Aldrich humic acid solutions, 1.4 mg C/L.
   ○ open symbols indicate replicate distilled water samples.

b) the kinetic approach: perylene
   • solid symbols indicate 0.47 mg C/L clean Aldrich humic acid solutions
   ■ spiked with perylene/phenanthrene/rhodamine
   • spiked with perylene only
   ○ Norganic water spiked with perylene
   □ ultrafiltered humic acid solution spiked with perylene/phenanthrene/rhodamine

c) the kinetic approach: phenanthrene
   • 0.47 mg C/L clean and filtered humic acids
   ○ ultrafiltered humic acid solution
that obtained for the replicate distilled water samples ($K_w = 0.39 \text{ mL/cm}^2$). This supports the assumption that the PAH probe is partitioning directly to the glass surface. The Aldrich humic acid OC show no tendency to associate with the glass surface. Fluorescence measurements (ex $= 340/\text{em} = 460$, indicative of humic acid concentration) on aliquots removed from a glass syringe filled with humic acids at time $= 0$ showed no decrease in humic acid concentration when measured every 5 - 10 minutes over the course of an hour. Perylene fluorescence, on the other hand, decreased and approached the glass surface-solution equilibrium value within the same time frame. This is contrary to the results of Brownawell (1986) in experiments with marine organic colloids and PCBs, who attributed significant losses of PCBs from solution to partitioning to glass-surface-associated OC. Aldrich humic acids may interact with glass surfaces differently than marine OC or seawater ions may facilitate such OC-glass associations.

**PERYLENE/ALDRICH HUMIC ACIDS: KINETIC APPROACH**

Using the kinetic approach, perylene fluorescence measurements for both the OC-void and humic acid samples show decrease in time, asymptotically approaching the solution-glass surface equilibrium value (Figure 2b). The fluorescence value associated with [PAH$_T$] is obtained from the intercept of Equation 9 for the OC-void sample. The ratio of this [PAH$_T$] value and the intercept of Equation 9 for the humic acid sample provide an estimate of
$K_{oc}[OC]$. The fluorescence measurements obtained for the OC-void and humic acid samples lie on distinct curves indicating quenching occurs in the presence of OC. The similarity of the average $K_w$ values for replicates calculated from the ratio of the rate constants obtained from the curve fitting program

$$(K_w = \frac{k_w}{k_{-w}(SA/V)})$$

for the distilled water samples ($K_w = 0.35 \text{ mL/cm}^2$) and humic acid samples ($K_w = 0.33 \text{ mL/cm}^2$) support both the assumptions that OC is not partitioning to the glass surface and that PAH-OC partitioning is fast relative to PAH-wall partitioning.

Further evidence that PAH-OC partitioning is fast relative to PAH partitioning to the glass surface was provided by the following experiment. A syringe containing Aldrich humic acids was spiked with perylene and allowed to equilibrate with OC and the glass surface. After several hours the solution was transferred to a second clean syringe, and perylene fluorescence was monitored over time. Perylene fluorescence decreased at the same rate as in experiments without prior perylene-OC equilibration, suggesting that the initial 3 minute mixing time prior to the first fluorescence measurement is adequate for PAH-OC equilibration. Fast equilibration times for PAH association with OC were also
obtained by Gauthier et al. (1986) for pyrene, phenanthrene and anthracene and by McCarthy and Jimenez (1985) for benzo(a)pyrene. Hassett and Milacic (1985), however, reported a much slower binding rate constant \( t_{1/2} \approx 3 \text{ days} \) for tetrachlorobiphenyl using a gas purging technique to monitor free compound activities.

**PHENANTHRENE/ALDRICH HUMIC ACIDS**

Current concepts of hydrophobic organic compound partitioning to OC predict that partitioning behavior is proportional to the hydrophobicity of the organic compound, for example, as reflected by \( K_{ow} \). To test this assumption, phenanthrene was included as a second probe in some samples. At low OC levels (0.47 mg C/L) the phenanthrene fluorescence measured for the Aldrich humic acid samples is virtually identical to that measured for the OC-void samples (Figure 2c), indicating that phenanthrene, unlike the more hydrophobic perylene, shows little if any association to OC. This result could be predicted from the expected ratio of dissolved-to-total phenanthrene of 0.996 calculated from the \( K_{oc} \) of \( 7.9 \times 10^3 \text{mL/g C} \) (Landrum et al., 1984). Not only does phenanthrene show less tendency to associate with OC, but the fluorescence readings in Figure 2c show no significant decrease with time, suggesting no interactions with glass surfaces. This allows the use of phenanthrene to further verify our assumptions regarding the absence of dynamic quenching and losses due to volatilization or biodegradation.
FLUORESCENCE QUENCHING EFFICIENCY

One final assumption inherent in the derivation of both the equilibrium and kinetic approaches is that the probe fluorescence is totally quenched on association with OC, i.e., $\phi = 0$. This assumption can be tested by measuring fluorescence as a function of time at various model compound concentrations. The intercepts of fluorescence data obtained by the kinetic approach for various OC concentrations versus [OC] should fit a curve described by Equation 12, where [PAH$_T$] is obtained from the intercept of the fluorescence data for the OC-void sample using the kinetic approach. The curve should asymptotically approach $\phi$ as $[OC] \to \infty$. The $K_{oc}$ estimate from these data can be deduced from the curve as the inverse of the [OC] where $F/F_o = (1 + \phi)/2$. Data obtained in this manner for perylene with clean and filtered Aldrich humic acids and with BSA are shown in Figures 3a and 3b. For the Aldrich humic acids, the curve asymptotically approaches a $\phi$ value of -0.033, which is not significantly different from zero; the fit $K_{oc}$ is $2.4 \times 10^6$. This $K_{oc}$ is similar to the $K_{oc}$ value obtained by the kinetic approach for clean unfiltered Aldrich humic acids at a single [OC] (Table II). For BSA, however, the curve asymptotically approaches a $\phi$ value of 0.58, which is significantly different from zero, and $K_{oc}$ is found to be $3.4 \times 10^5$. This non-zero value of $\phi$ may reflect the diminished overlap of BSA’s allowed electronic transitions (e.g., as exhibited by its shorter wavelength absorption spectrum as compared to Aldrich humic acids, Figure 4) with perylene’s fluorescent emission energies.
Figure 3: Determination of $\phi$ and $K_{oc}$ for model OC
   a) clean and filtered Aldrich humic acids
   b) BSA

(each data point obtained by backextrapolation to SA=0
using kinetic approach)
(a) $K_{oc} = 2.4 \times 10^6$
$\phi = -0.033$

(b) $K_{oc} = 3.4 \times 10^5$
$\phi = 0.58$
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<td><strong>Table II</strong>: $K_{oc}$'s (± rel. std. error) Found Using Model OC in This Work and Reported Previously</td>
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<tr>
<td>Aldrich humic acid as received</td>
<td>phenanthrene: $8.8 \times 10^5$ (± 55%)</td>
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<tr>
<td>1.4 mg C/L by equilibrium approach</td>
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<tr>
<td>Aldrich humic acid after cleanup</td>
<td>$&lt; 6 \times 10^4$</td>
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<td>0.47 mg C/L by kinetic approach</td>
<td>(± 8.2%)</td>
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<td>0 to 1.9 mg C/L by kinetic approach</td>
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<td>1.15 mg C/L by reverse phase approach</td>
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<td>(Landrum et al., 1984)</td>
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<td>0 to 66 mg C/L by kinetic approach</td>
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<td>2.8 mg C/L by reverse phase approach</td>
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<tr>
<td>$K_w$ (27)</td>
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* Indicates no quenching observed and calculated upper limit $K_{oc}$ value based on the [OC] present and the precision of the fluorescence measurements (generally < 3% for phenanthrene estimates and perylene reverse phase estimates) or the standard deviation of the backextrapolated fluorescence estimates for perylene (generally < 6%).
Figure 4: \(A_{\text{abs vs. wavelength}}\) scans for model OC and groundwaters at 1.5 mg C/L. Perylene fluorescence emission wavelength scan excitation \(\lambda = 434\).
Determining a $K_{oc}$ value for perylene partitioning to BSA using the equilibrium or kinetic approach and a single concentration of [BSA] would give too small a result if the nonzero value of $\phi$ were not taken into account. Similarly, since $\phi$ may not be zero for all types of OC found in groundwaters, $K_{oc}[OC]$ estimates obtained by observing diminished probe fluorescence due to quenching by groundwater [OC] yields only a lower limit on probe-OC association. If concentration and dilution steps do not affect the OC sorbent properties, groundwater OC could be diluted or concentrated to various [OC] levels to allow direct assessment of $\phi$ and $K_{oc}$.

It would be useful to identify a correlation between an easily measured OC property and the $\phi$ value for that OC. The overlap of the OC absorbance spectrum with PAH probe fluorescence emission spectrum could provide such a correlation. Static quenching in general can occur if there is significant overlap of the quencher absorbance spectrum and the fluorescent probe emission spectrum (Shulman, 1977). Perhaps there is a correlation between degree of overlap and $\phi$. There was a greater degree of overlap for perylene fluorescence energies with the absorption spectra from Aldrich humic acids than with BSA (Figure 4). Measurement of absorbance, $\phi$, and $K_{oc}$ values for a greater variety of OC and probes is required to substantiate such a correlation.
SUMMARY OF $K_{oc}$ RESULTS AND COMPARISONS WITH OTHER INVESTIGATORS

Having tested the main assumptions inherent in the equilibrium and kinetic approach derivations and determined that $\phi = 0$ for Aldrich humic acids, $K_{oc}$ values can be calculated from the data presented in Figure 2. These $K_{oc}$ estimates for perylene and upper estimates for phenanthrene are reported in Table II. The standard deviations reported are based on variability of replicates. Both the kinetic and equilibrium approaches provide reproducible $K_{oc}$ estimates (Table II and Figure 2a and 2b). Concurrent spiking of perylene, phenanthrene, and rhodamine did not affect the estimated perylene-OC partitioning constants (Figure 2b). Since fluorescence measurements for perylene in ultrafiltered humic acid solutions are the same as those obtained in Norganic water, either insignificant quantities of quenchers other than OC are present in the OC-containing samples or ultrafiltration removes only OC from the Aldrich humic acid solutions.

Though the data obtained by a given approach are reproducible, the $K_{oc}$ values obtained in our early experiments using the vessel-wall equilibrium approach differed from those obtained later using the kinetic approach (Table II). We believe this is due to a difference in the OC used. The early equilibrium approach experiments were performed using Aldrich humic acids without prior cleanup (old stock), while for the kinetic approach experiments Aldrich humic acid stock solutions were cleaned and filtered as described in the Method
section of this paper. The old stock seems to contain a portion of OC which is not as good a sorbent as the humic acids in the clean stock (e.g., fulvic materials). Evidence of this difference in stock solutions can be seen in the fluorescence emission scans of the old and clean stocks (Figure 5). The fluorescence maximum for the clean humic acids is at a higher wavelength than that for the old humic/fulvic stock. The difference in fluorescence maxima observed for the old and clean stocks is similar to the difference observed by Miano et al. (1988) between humic and fulvic materials. This is consistent with presence of a lower molecular weight fulvic fraction in the old stock which is removed by the cleaning procedure. If this fraction had a lower \( K_{oc} \) value for perylene, then we would expect to measure an overall lower \( K_{oc} \) for the old stock solution relative to the clean material. There is evidence in the literature indicating the \( K_{oc} \) values measured for PAH and chlorinated hydrocarbons are higher for soil-derived humic materials than for soil-derived fulvic materials (Gauthier et al., 1986, 1987; Chiou et al., 1986), although Chiou has also reported similar \( K_{oc} \) values for river humic and fulvic materials.

A comparison of these \( K_{oc} \) values obtained by fluorescence quenching with \( K_{oc} \) obtained by other techniques provides further verification of our method. \( K_{oc} \) values for perylene and phenanthrene with Aldrich humic acids were measured using a reverse phase separation technique (Table II). The \( K_{oc} \) value for perylene with clean Aldrich humic acids measured by the reverse phase technique is only 1/2 to 1/3 that obtained by the fluorescence
Figure 5: Fluorescence emission wavelength scans (excitation wavelength = 290) for model OC and groundwater OC. Note groundwater scans represents the difference between the whole and ultrafiltered scans.
quenching method. Invalid assumptions in the fluorescence quenching method, should lead to underestimation rather than overestimation of the $K_{oc}$ value; problems involved in the separation of equilibrated phases using reverse phase cartridges may account for the observed discrepancy in $K_{oc}$ values. Though no data exist in the literature regarding perylene partitioning to Aldrich humic acids, comparison of our results with those obtained by others for benzo(a)pyrene (B(a)P), a five ring PAH of similar hydrophobicity (but markedly greater carcinogenicity) is instructive. The $K_{oc}$ values obtained for perylene by the fluorescence quenching method are in the same range as those obtained by others for B(a)P (Table II). The $K_{oc}$ value obtained by the reverse phase method for phenanthrene is consistent with the upper limit $K_{oc}$ estimated by considering the precision of the fluorescence quenching method and matches the $K_{oc}$ value obtained by Landrum et al. (1984) using a reverse phase method. Thus, the fluorescence quenching method appears consistent with other approaches.

The data obtained for Aldrich humic acids ($\phi = 0$) and perylene indicate the validity of the fluorescence quenching method for humic-like OC. Partitioning data for very hydrophobic probes can be obtained even in the presence of losses to vessel walls by adopting either the equilibrium or the kinetic approach. The kinetic approach has the advantage of being quicker and involves less sample manipulation, and this approach can successfully be applied to groundwater samples for which in situ water chemistry conditions
must be maintained throughout experimentation. In addition to providing an estimate of partition coefficients for groundwater OC, these approaches provide K_w estimates. All K_w's measured for perylene to flask or syringe glass surfaces fall in the range of 0.1 to 0.6 mL/cm².

The fluorescence data obtained for BSA indicate that some types of OC which may be found in groundwater will not totally quench perylene fluorescence on association (ϕ ≠ 0). If this is the case, fluorescence data obtained for the existing groundwater [OC] could underestimate the true value of K_{oc}[OC]. Unfortunately, the alternative method (reverse phase separation), chosen for comparative purposes, seems to underestimate (by a factor of ~ 10) the true K_{oc} value for perylene-OC as well. The studies with BSA suggests that using fluorescence data from a single [OC] (e.g., unconcentrated groundwater) with the assumption that ϕ = 0 may underestimate the magnitude of OC-association by about a factor of 2 to 3 for ϕ = 0.6.

**FLUORESCENCE QUENCHING TO QUANTIFY THE IMPACT OF OC IN GROUNDWATER**

The fluorescence quenching method was applied to several groundwater samples to investigate the potential importance of OC-sorbed species in such waters. Three wells were tested on two separate occasions to evaluate the magnitude of sorption to OC. The groundwater properties vary substantially between these wells (Table I); most notably wells F343-57 and
F350-77 contain water with about ten times more OC than the background well F242-77. The groundwater nearest the infiltration beds had the highest pH, the lowest $E_h$, and the highest conductivity. Oxygen was present at or near detection limits in groundwater from both wells in the contamination plume, and laser light scattering intensity was greatest near the sewage beds. This level of light scattering, a few times above our background, suggests less than 1 mg/L of inorganic colloids, possibly organic coated, were present (based on a polystyrene bead standard). Previous samples recovered from this particular site contained greater inorganic colloid concentrations (Gschwend and Reynolds, 1987). Both wells F343-57 and F350-77 showed significant temporal changes in conductivity, further indicating the variable nature of the groundwater plume.

Maintenance of in situ conditions, especially anoxia, was especially challenging for samples from the groundwater contamination plume. Introduction of even slight amounts of oxygen into these samples quickly led to precipitation of iron oxides. By filling 50 mL glass syringes in the field, and using the kinetic approach for determining partitioning, we were able to observe fluorescence quenching while avoiding such water chemistry changes. With the most sensitive samples from well F343-57, the transfer steps involved in the equilibrium-approach resulted in precipitation of ferric oxides. Hence, for well F343-57 only data obtained with the kinetic approach are reported here.

Fluorescence quenching results for perylene for these three wells are
shown in Figures 6 - 8. Using the measured OC concentration and assuming $\phi = 0$, $K_{oc}$ values for these samples can be calculated. No evidence for any association of either perylene or phenanthrene with OC was ever observed for samples obtained from the background well F242-77, either via fluorescence quenching (Figure 6) or via reverse phase separation (Table III). Similarly no association of the more water soluble probe, phenanthrene, was observed for any sample obtained from wells F343-57 or F350-77 regardless of the method used to quantify partitioning (Table III). The results for the more hydrophobic probe, perylene, for the wells within the contaminant plume demonstrate a puzzling temporal variability. Fluorescence measurements for the October 1987 samples from well F350-77 exhibited perylene quenching by OC (Figure 7(a)). The April 1988 samples from well F343-57 also demonstrated perylene association with OC both via fluorescence quenching (Figure 8(a)) and via reverse phase methods (Table III); the two $K_{oc}$ estimates agree reasonably well. In contrast, perylene showed no tendency to associate with OC in the July 1988 samples obtained from either of these wells, when measured by fluorescence quenching (Figures 7(b) and 8(b)) or by reverse phase methods (Table III).

The magnitudes of the computed $K_{oc}$ values for most cases seem reasonable. The lack of association of phenanthrene or perylene with OC in samples from the background well could have been predicted given the low OC concentrations. Calculations suggest only 5 - 9% of the perylene and less than 0.2% of the phenanthrene would be associated with OC in these samples.
Figure 6: Perylene partitioning data for groundwater samples from well F242-77.

- solid symbols indicate whole groundwater samples.
- open symbols indicate ultrafiltered groundwater samples.
  a) equilibrium approach: samples collected in October, 1987.
  b) kinetic approach: samples collected in April, 1988.
Figure 7: Perylene partitioning data for groundwater from well F350-77

- solid symbols indicate whole groundwater samples
- open symbols indicate ultrafiltered groundwater samples
  a) equilibrium approach: sample collected in October, 1987
Figure 8: Perylene partitioning data for groundwater from well F343-57: kinetic approach.

- solid symbols indicate whole groundwater samples
- open symbols indicate ultrafiltered groundwater samples
  a) sample collected in April, 1988
**TABLE III: PAH Partitioning Behavior to Groundwater OC**

<table>
<thead>
<tr>
<th>sample and method</th>
<th>[OC] mg C/L</th>
<th>perylene $K_{oc}$ (mL/g C)</th>
<th>phenanthrene $K_{oc}$ (mL/g C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F343–67 Apr. 88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetic</td>
<td>1.1</td>
<td>$6.7 \times 10^5 \pm 3.6 \times 10^5$</td>
<td>$&lt;1.8 \times 10^5$*</td>
</tr>
<tr>
<td>reverse phase</td>
<td>1.1</td>
<td>$2.6 \times 10^5 \pm 2 \times 10^4$</td>
<td>$&lt;2 \times 10^3$*</td>
</tr>
<tr>
<td>July 88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetic</td>
<td>1.5</td>
<td>$&lt;4.1 \times 10^4$*</td>
<td>$&lt;6.5 \times 10^4$*</td>
</tr>
<tr>
<td>reverse phase</td>
<td>1.5</td>
<td>$&lt;1.7 \times 10^4$*</td>
<td>$&lt;1.2 \times 10^4$*</td>
</tr>
</tbody>
</table>

* Indicates no quenching observed and calculated upper limit $K_{oc}$ value based on the [OC] present and the precision of the fluorescence measurements (generally $< 3\%$ for phenanthrene estimates and perylene reverse phase estimates) or the standard deviation of the backextrapolated fluorescence estimates for perylene (generally $< 6\%$).
**TABLE III** (continued)

<table>
<thead>
<tr>
<th>sample and method</th>
<th>[OC] mg C/L</th>
<th>perylene K&lt;sub&gt;oc&lt;/sub&gt; (mL/g C)</th>
<th>phenanthrene K&lt;sub&gt;oc&lt;/sub&gt; (mL/g C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F350—77 Oct. 87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>1.4</td>
<td>$1.1 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>July 88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetic</td>
<td>1.3</td>
<td>$&lt;4 \times 10^4$</td>
<td>$&lt;4.2 \times 10^4$</td>
</tr>
<tr>
<td>reverse phase</td>
<td>1.3</td>
<td>$&lt;1.6 \times 10^4$</td>
<td>$&lt;7 \times 10^3$</td>
</tr>
<tr>
<td>F242—77 Oct. 87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.1</td>
<td>$&lt;5.5 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>April 88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>kinetic</td>
<td>0.2</td>
<td>$&lt;3 \times 10^5$</td>
<td>$&lt;8.4 \times 10^4$</td>
</tr>
<tr>
<td>reverse phase</td>
<td>0.2</td>
<td>$&lt;1.4 \times 10^5$</td>
<td>$&lt;8.1 \times 10^4$</td>
</tr>
</tbody>
</table>
(assuming $K_{oc}$ values of $5 \times 10^5$ and $8 \times 10^3$, respectively). Similarly, phenanthrene is insufficiently hydrophobic to be significantly bound even at the higher OC concentrations found in wells F343-57 and F350-77 (less than 1% association predicted).

For the first set of samples collected from wells F343-57 (April 1988) and F350-77 (October 1987), the perylene $K_{oc}$ estimates agree with values which might have been predicted. Both proteins and humic materials can be important components of secondary sewage effluent (Rebhun and Manka, 1971; Manka et al., 1974), leading us to expect $K_{oc}$ values somewhere between those measured for the two model OC; the measured groundwater $K_{oc}$ values are comparable to those measured for BSA and about half that measured for the clean Aldrich humic acids. If, however, the $\phi$ values for the groundwater OC were greater than zero, the true $K_{oc}$ values would be greater than those reported in Table III. Using the $K_{ow}$ value for perylene as an upper estimate of the true $K_{oc}$ for OC in these groundwaters indicates that the $\phi = 0$ assumption leads to at most a factor of 3 - 5 underestimation of the true $K_{oc}$ value.

It is difficult to interpret the temporal variability in the $K_{oc}$ values measured for samples from wells F343-57 and F350-77. Conceivably, the OC in the July 1988 samples differed in composition and $\phi$ value from that previously collected from these wells; for example, they could have been rich in hydrophilic polysaccharides or consisted of quite small macromolecules. Other workers have previously shown how differences in the character of OC, for
example C/O ratios or aliphatic/aromatic proportions can significantly affect $K_{oc}$ (Chiou et al., 1986; Garbarini and Lion, 1986; Gauthier et al., 1987). We briefly examined this possibility by comparing the fluorescence emission spectra of the July samples with the earlier samples (Figure 5). Both the fluorescent intensities and the overall spectral response did not appear significantly different for the samples collected at any one well, tending to counter the hypothesis that the OC was compositionally different. Another possibility is that the groundwater composition was varying so as to effect differential OC-perylene interactions. For both July 1988 samples, the electrical conductivity was lower than previously seen. Although this decrease in salt content would increase the solubility of perylene in the water, the Setchenow relationship (e.g., May, 1980; Whitehouse, 1984) suggests this effect would be quite small. Using a value of the Setchenow constant, $K_s$, similar to that reported for other PAH ($0.4 \text{ M}^{-1}$) and converting conductivity measures to ionic strengths ($10^{-2}\text{M}$) using Langmuir's equation (1969), we find:

$$\frac{\text{Solubility}_{\text{saltwater}2}}{\text{Solubility}_{\text{saltwater}1}} = 10^{-(K_s(\Delta[Salt]))} = 10^{-0.004} \approx 0.99$$

(13)

The corresponding change in perylene’s aqueous activity coefficient due to these changing concentrations is insufficient to explain the observed lack of
OC-association. The observed differences in conductivities could also signal a shift in the macromolecular configuration of the OC. Increasing ionic strength has been shown to cause organic polyelectrolytes like humic acids and proteins to take on a more globular configuration (Ghosh and Schnitzer, 1980). Chiou et al. (1986) have demonstrated that organic macromolecules occurring in a stretched out configuration (e.g., polyacrylic acid) do not act as sorbents for hydrophobic chemicals. Conceivably, the OC present in the July 1988 groundwaters, although present at roughly the same concentrations and composed of similar structural elements as in the early samples, were simply "denatured" and unable to bind perylene. Further work is necessary to substantiate this hypothesis or other explanations.

**IMPLICATION TO SUBSURFACE TRANSPORT**

The quenching results for groundwater obtained within the plume at Otis Air Base suggest that sufficient OC is at least sometimes present to augment the mobile load of very hydrophobic chemicals. Assuming that OC moves at the groundwater seepage velocity, and that immobile organic matter has a $K_{oc}$ value similar to mobile OC, an adjusted retardation coefficient can be calculated for such OC-interactive species:

\[
\text{retardation factor} = 1 + \frac{\text{fraction immobilized by soil}}{\text{fraction dissolved} + \text{fraction OC-bound}}
\]
\[ -1 + \frac{\rho_b f_{oc} K_{oc}}{n + n[OC]K_{oc}} \]

where \( \rho_b \) is the soil bulk density, \( f_{oc} \) is the organic carbon content of the soil, and \( n \) is the soil porosity. Obviously, for cases where the product \([OC]K_{oc}\) is small compared to 1, that is, when the mobile OC concentration is low or pollutants of concern exhibit low \( K_{oc} \) values, the retardation expression simplifies to that derived for the two-phase transport case (e.g., Freeze and Cherry, 1979).

The significance of OC association to transport of compounds like perylene in the sewage plume at Otis Air Base can be illustrated as follows. Barber et al. (1988) have found for these aquifer solids, \( n = 0.3 \), \( \rho_b = 1.8 \text{ g/cm}^3 \), and \( f_{oc} = 5\% \) fines at 0.1\% organic content = \( 5 \times 10^{-5} \). For perylene with \( K_{oc} = 7 \times 10^5 \) and groundwater \([OC] \approx 1 \text{ mg C/L}\), we find:

\[
\text{retardation factor} = 1 + \frac{63}{0.3 + 0.2} \approx 130
\]

(15)

In other words, the presence of OC in the flowing groundwater approximately doubles the mobile load (halves the retardation factor calculated in the absence
of OC) of a contaminant with hydrophobicity similar to perylene. The presence of OC could be even more important than the retardation coefficient predicts if size exclusion effects allow colloids to travel faster than the seepage velocity (Harvey et al., 1988).
CONCLUSION

The fluorescence quenching method described in this paper provides an alternative method for determination of partition coefficients between OC and fluorescent sorbates in environmental samples, allowing direct assessment of the possibility of OC-enhanced pollutant transport. The advantages of this method are that it requires no separation of equilibrated phases, and partition coefficients can be determined under in situ conditions. The method allows determination of partition coefficients for all OC which quench the fluorescence of PAH probes on association. Partition coefficients and the possibility of enhanced transport for non-fluorescent pollutants can be determined by inference. The main limitation of this method is the assumption that probe fluorescence is completely quenched on association with OC ($\phi = 0$). Bounds can be placed on the true $K_{oc}$ value using the probe $K_{ow}$, as an upper limit, and the $K_{oc}$ calculated assuming $\phi = 0$, as the lower bound. Determination of the actual groundwater [OC] $\cdot K_{oc}$ requires further sample manipulation by dilution or OC concentration to determine $\phi$. The limitation of this method imposed by this assumption (factor of 3 - 5 underestimation of $K_{oc}$) must be weighed against the possible errors in other methods due to OC concentration and separation schemes that may change the nature of the OC or collect only a fraction of the OC present and capable of sorbing organic contaminants. The fluorescence quenching method described is useful for
screening/determining the $K_{ow}$ range of contaminants for which OC in the sample will significantly increase the mobile load. The method was used successfully on samples from an aquifer contaminated by recharge of secondarily treated sewage. The data indicate the presence of OC in this case will approximately double the mobile load of hydrophobic pollutants such as perylene or B(a)P, but will have little effect on the mobility of less hydrophobic pollutants. The temporal variability observed in PAH-OC association in these groundwaters indicates that unlike organic contaminant partitioning to soil organic matter, partition coefficients for OC may not be a simple function of OC organic carbon content. Understanding this variability will be necessary to estimate accurately the transport of OC-associated hydrophobic organic pollutants through the subsurface. Additionally, groundwater samples from this site indicate that OC may represent a significant fraction of the TOC in environmental samples (e.g., 40 - 60% for groundwater within the plume) or a minor fraction (e.g., 10 - 20% at well F242-77). This indicates that use of TOC in calculation of $K_{oc}$ values will underestimate the true $K_{oc}$ as ultrafilterable DOC (for the samples in this study) does not quench PAH fluorescence and therefore does not appear to bind.
ACKNOWLEDGMENT

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LITERATURE CITED


Chapter 3

Sorption of Hydrophobic Organic Compounds to Inorganic Surfaces
INTRODUCTION

Situations exist where hydrophobic organic compounds (HOC) in aqueous systems may be exposed to low organic carbon content inorganic soils and sediments. For instance, hazardous HOC wastes may be disposed of in low organic carbon aquifers ($f_{OC} = 0.002$, Abdul and Gibson, 1986; Banerjee et al., 1988). An understanding of HOC sorption to inorganic surfaces is required for accurate prediction of the movement of HOC through these materials. Sorption of HOC to inorganic colloids, with relatively high surface area/$g_{colloid}$, could enhance their transport through the subsurface. On the other hand, HOC association with inorganic surfaces of aquifer material or protective clay liners (with high inorganic surface areas and relatively low $f_{OC}$ Johnson et al., 1989) may retard the transport of these species. Unfortunately, far less information exist in the literature reporting on the sorption of HOC to inorganic surfaces than is the case with organic matter. The wealth of literature on the sorption of pesticides to inorganic surfaces relates mainly to polar organic compound sorption rather than HOC sorption. Much of the data and interpretation reported in the literature suffers from one or more of the following: (1) the organic carbon content of the inorganic materials is not measured rather, it is often assumed to be zero. This assumption may lead to misinterpretation of the role of inorganic surfaces in HOC sorption, (2) partition coefficients for the inorganic surfaces ($K_i$) are reported on a mL/g basis rather than on a mL/cm$^2$ basis which would allow better comparison with data on other particle sizes, (3) the analytical procedures suffer from incomplete separation of equilibrated phases, and (4) lack of mass balance datc. These problems and the absence of thorough studies attempting to understand the mechanism of HOC/inorganic surface sorption in general has
resulted in lack of a proposed, let alone, widely accepted and tested sorption mechanism and inability to predict the sorptive behavior of a given HOC/inorganic surface pair. Despite these difficulties, previous studies yield several insights. The data in general suggest that HOC sorption to inorganic surfaces, on a mL/g basis, occurs to a far lesser extent than is the case with organic matter. The amount of a given HOC sorbed may be a function of the surface area (SA) of the inorganic particle. Sorption to some inorganic surfaces appears to correlate with sorbate \( K_{OW} \) (Schwarzenbach and Westall, 1981).

In this chapter, the sorptive behavior of several HOC to three inorganic solids is examined. First, to provide a conceptual framework for interpretation of sorption results, the structure of water in bulk solution, and near hydrophobic solutes and inorganic surfaces is discussed. Then, sorption studies are described. These studies involve examination of the sorption of a series of HOC (polycyclic aromatic hydrocarbons (PAH) and chlorinated benzenes) to a given surface (kaolin or silica) and comparison of the sorption of a given HOC to a series of surfaces (kaolin, silica, and alumina). Sorption isotherms are examined as well. The goals of this work were to gain a better understanding of the general mechanism governing the sorption of HOC to inorganic surfaces and to develop a physically based predictive model consistent with this mechanism. This would allow estimation of \( K_i \) values for HOC/inorganic surface pairs from readily available parameters in the absence of experimental sorption data.
CONCEPTUALIZATION OF THE WATER: HOC: INORGANIC SURFACE SYSTEM

Water is not a "normal" liquid. There exists some structure in liquid water which is affected by the presence of both HOC and inorganic surfaces. This liquid water structure allows for the possibility of sorption resulting from an energetically favorable restructuring of solvent molecules not available with sorption from unstructured solvents "normal" liquids.

Bulk Water Structure

Following the work of Frank and Evans (1945) and Nemethy and Shegara (1962a), bulk water is described as follows. Unlike "normal" liquids, water is thought to exist as groups of hydrogen bonded molecules surrounded by nonhydrogen bonded individual water molecules. A water molecule can exist as an individual nonhydrogen bonded species, or in a group connected by hydrogen bonds. The distribution of these various species of water at a given temperature is determined by the energy levels of these various species (which is a function of the energy of the hydrogen bond). The energy levels and hence distribution of these species is a function of temperature and is affected by the presence of both hydrophobic solutes and inorganic surfaces.

Hydrophobic Solute in Water

The theory presented by Frank and Evans (1945) and extended by Nemethy and Shegara (1962a) was developed in part to explain the negative enthalpy of solution, low solubilities, and large heat capacities observed for aqueous solutions of nonpolar solutes (inert gases, and some low molecular weight nonpolar organic compounds). The interaction of nonpolar or hydrophobic solutes with the various species of water indicated above is thought to result in changes in the energy levels of these species.
leading to an overall change in the distribution of these species and hence a 
change in the energy level of the system. A hydrophobic solute can lower 
the energy level of tetra-hydrogen bonded species by interacting with the 
central water molecule, increasing its coordination number, lowering the 
overall energy level of the cluster, thereby stabilizing it. When the 
hydrophobic solute interacts with any of the other species, it may do so at the 
expense of an interaction between this water species and another water 
molecule. As hydrogen bond interactions between water molecules are 
much stronger than the van der Waals interactions between the water 
molecule and the hydrophobic solute, this interaction of the hydrophobic 
solute with any of the nonfully hydrogen bonded species leads to an 
increase in the energy level of that particular species. Hence there is a shift in 
the distribution of water species near a hydrophobic solute, relative to that in 
the bulk, toward the more highly hydrogen bonded water clusters, the tetra-
bonded in particular. Consequently, the water near a hydrophobic solute is 
more “icelike” than the bulk water and hence the concept of “icebergs” 
proposed by Frank and Evans (1945). These stabilized clusters or icebergs 
near HOC are not thought to encompass the solute, but rather form a partial 
cage. This cage should not be thought of as a permanent cage, but rather 
as clusters that are rapidly forming and melting away due to local fluctuations.

The degree of icelikeness about a hydrophobic solute, and hence the 
distribution of water species in the system in general, is determined by the size 
of the solute as this determines both the number of clusters that can fit around 
the solute and the strength of the particular solute’s van der Waals interactions 
with the water clusters. Aliphatic and aromatic HOC of similar size and 
molecular weight may differ in their ability to form icebergs due to differences 
in the strength of their interactions with water. Nemethy and Shegara (1962a)
suggest that aromatic solutes may preferentially stabilize tetra-bonded clusters at edges of rings and interact preferentially with the individual water molecules on the top and bottom of the rings. Pi bond interactions with the unbonded water species is thought to lead to less of an increase in the energy level of this species than is the case with aliphatic species or aromatic ring edges. They further suggest the preferential interaction of tetra-bonded species at edges is due to the possibility of cluster-structure disruption at the faces of rings due to the stronger pi bond interactions. The intermediate hydrogen bonded species (water bonded to 1 - 3 other water molecules) show less preference for faces and edges as both factors affect these species.

The overall effect of the hydrophobic solute is then to stabilize tetra-bonded species, increasing the likelihood of finding them in the vicinity of the solute and increasing the representation of this species over that found in the absence of hydrophobic solute. This leads to an increase in the overall level of hydrogen bonding in the system as the tetra-bonded species are stabilized. This is used to explain the observed negative enthalpy of solution for low molecular weight (e.g., methane, ethane, propane and butane) hydrophobic solutes. Positive enthalpies of solution (of liquid solutes or hypothetical liquid for solid solutes) for higher molecular weight hydrophobic organic solutes (May et al., 1983; Dickhut et al., 1986; Shiu et al., 1988 and Friesen and Webster, 1990) indicate that the increase in interaction, decrease in enthalpy, of the tetra-bonded species is outweighed by positive enthalpy of the other water species forced to associate with the organic species at the expense of more favorable associations with other water molecules. The increased representation of the more icelike tetra-bonded species in the presence of the hydrophobic solute leads to a decrease in the entropy of
the system as well. A positive $\Delta G$ and hence low liquid solubility of even low molecular weight HOC indicates the importance of the entropy term. The large heat capacity of these solutions (larger than that of water itself) is due to the melting of the icebergs as the thermal energy of the water molecules increases. The structure of water breaks down as temperature increases and the water starts to behave more like a "normal" liquid.

**Inorganic Surfaces in Water**

Inorganic surfaces can be thought of as of combinations of several types of surface groups. A silica surface, for instance, is composed of siloxane and silanol groups. Alumina is made up of analogous groups where alumina is connected to the oxygen and hydroxyl groups. Kaolin contains both silicon and aluminum oxide surfaces. One face of kaolin is primarily siloxane with occasional (1 - 10 mequiv/100g kaolin. Swartz-Allen and Matijevik, 1974) substitutions of aluminum atoms for silicon leading to a charge deficiency about these isomorphic substitution sites. The other face is primarily composed of hydroxylated alumina. The edges, which are essentially broken edges of silicon dioxide and aluminum oxide crystalline sheets, present combinations of siloxane and silanol and the analogous alumina groups. The surfaces of glassware and glassbeads can be thought of as an amorphous silicon dioxide surface containing both types of groups with occasional impurities (e.g., boron, sodium, or calcium) which may create a charge imbalance at the surface.

The structure of bulk water is affected by the presence of each of these groups. The more polar sites (silanol, hydroxylated alumina, and isomorphic substitution sites), which may be charged depending on the acid/base conditions of the solution, interact strongly with water molecules. Water in the vicinity of these charged sites is organized in a manner similar to water about
ions described by Frank and Evans (1945). Ions in aqueous solution can line up the dipoles of water molecules extending a number of layers away from the ion, disrupting the structure of water found in the bulk solution. The extent of the interaction and distance of organization depends on the size and charge of the ion. The charge on silanol and hydroxylated alumina groups is pH dependant. Siloxane type groups are charge satisfied, and present only a weakly polar surface to the water. For instance, the oxygen atoms in a siloxane group have a partial negative charge, whereas the silicon atoms have a partial positive charge. Though this partial charge orients water dipoles at the interface, the interaction with water at these sites is not as strong and the organization probably does not extend past the first layer of water molecules. Organization of water near a surface is confirmed by the evidence for vicinal water (Drost-Hansen, 1978).

METHODS AND MATERIALS

MATERIALS

Sorbates

Perylene (Aldrich, 99%, gold label), pyrene (Aldrich, 99+%), phenanthrene (Eastman), naphthalene (J.T. Baker, Reagent grade), 1,2,4-trichlorobenzene (Aldrich, 99+%), 1,4-dichlorobenzene (Aldrich, 99+%), chlorobenzene (Aldrich, 99%), and methyl perylene (provided by R. J. Liukkonen, Dept. of Chem., Univ. Minn., Duluth, MN, > 95% purity as determined by GC-FID, GCMS) were used in sorption experiments. Stock solutions of individual or combinations of these HOC were made up in methanol (EM science, Omnisolve glass distilled) containing some methylene
chloride (EM science, Omnisolve glass distilled) if necessary to solubilize the higher molecular weight HOC. Small quantities (< 250 µL/L) of these stock solutions were spiked into distilled water containing NaN₃ (300 µL of saturated NaN₃ solution / L distilled water) with or without sorbent. The total masses of sorbate added resulted in dissolved sorbate concentrations less than or equal to the sorbate aqueous solubilities (Table I).

**Sorbents**

Kaolin (EM Sciences, colloidal powder), glass beads (Scientific Instrum. Serv., 200 mesh), neutral alumina (Alltech, 80/200 mesh neutral alumina), and in some cases the experimental vessel interior glass (Pyrex) surface were used as sorbents in this work. These surfaces were prepared by baking in a muffle furnace at 450°C for 3 hours to remove organic matter. Sorbents were prewashed a number of times to remove unseattlable fines and prevent separation of phases problems (Gschwend and Wu, 1985). Between washings, the sorbent was settled by gravity (glass beads and alumina) or centrifugation (kaolin) and the supernatant containing unseattlable fines was discarded and replaced with fresh NaN₃ solution. Sorbent characteristics are listed in Table I.

**Glassware**

Several types of experimental vessels were used in this work. For sorbates which sorb to the vessel glass walls to an appreciable extent (methyl perylene and perylene), 15 mL or 50 mL glass centrifuge tubes with ground glass stoppers were used. For the other sorbates either the above glassware or 12 mL, 35 mL, or 50 mL centrifuge tubes with screw caps lined with solvent rinsed aluminum foil were used. The glass surfaces of all these vessels were cleaned by baking in a muffle furnace at 450°C for 3 hours, then filled with distilled water to soak at least overnight. The vessels used in supernatant
## TABLE 1: Sorbate and Sorbent Properties

<table>
<thead>
<tr>
<th>Sorbates</th>
<th>Aqueous Solubility (μg/L)</th>
<th>T_m,p (°K)</th>
<th>Log ( \gamma_w ) (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chlorobenzene</td>
<td>3.0 x 10^5</td>
<td>227</td>
<td>4.3</td>
</tr>
<tr>
<td>1,4 - dichlorobenzene</td>
<td>9.0 x 10^4</td>
<td>326</td>
<td>5.1</td>
</tr>
<tr>
<td>1,2,4 - trichlorobenzene</td>
<td>3.5 x 10^4</td>
<td>290</td>
<td>5.3</td>
</tr>
<tr>
<td>naphthalene</td>
<td>3.2 x 10^4</td>
<td>353</td>
<td>4.8</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>1 x 10^3</td>
<td>374</td>
<td>6.2</td>
</tr>
<tr>
<td>pyrene</td>
<td>130</td>
<td>429</td>
<td>6.6</td>
</tr>
<tr>
<td>perylene</td>
<td>0.4</td>
<td>550</td>
<td>8.1</td>
</tr>
<tr>
<td>methyl perylene</td>
<td>4</td>
<td>386</td>
<td>8.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET* Surface Area (cm²/g)</th>
<th>Geometrically** Calculated Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin</td>
<td>1.2 x 10^5</td>
<td></td>
</tr>
<tr>
<td>alumina, Al₂O₃</td>
<td>1.3 x 10^6</td>
<td>90 - 210 cm²/g</td>
</tr>
<tr>
<td>amorphous 80 - 200 mesh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>glass beads 200 mesh</td>
<td>6.1 x 10^3</td>
<td>250 cm²/g</td>
</tr>
<tr>
<td>glass walls 15 mL (Pyrex)</td>
<td></td>
<td>3.0 cm²/mL</td>
</tr>
<tr>
<td>50 mL (Pyrex)</td>
<td></td>
<td>1.7 cm²/mL</td>
</tr>
</tbody>
</table>

*BET analysis by Porous Materials Inc., N2, 308.16 °K, samples outgassed to 20 microns at 200 °C.
**assuming no microporosity
extractions were 20 mL foil-lined screw-cap test tubes or the above listed glassware. These vessels were prepared for use by soaking in chromic/sulfuric acid solution overnight, soaking in distilled water at least overnight, then solvent rinsing with methanol, methylene chloride and hexane (EM science, Omnisolve glass distilled). Quartz cuvettes used for fluorimetry were similarly prepared.

GENERAL EXPERIMENTAL PROCEDURE

Known quantities of glass beads or alumina were added to a set of experimental vessels. In sorption experiments involving HOC which do not sorb appreciably to glassware walls, two sets of tubes were equilibrated to obtain sorption data. One set contained sorbent, the other did not. For experiments involving sorbates which were found to sorb appreciably to glassware walls (perylene and methyl perylene), a third set of tubes was required to quantify total sorbate. This set of tubes was filled with one of the filling solutions, then immediately extracted into hexane or methylene chloride to quantify the total sorbate added corrected for extraction efficiency.

Three types of filling solutions (all containing NaN₃ to inhibit microbial growth) were used in sorption experiments. First, solutions of sorbate (to distribute amongst a set of tubes) were used to quantify sorption. These solutions often contained two HOC, the HOC under study and a second HOC (e.g., naphthalene or phenanthrene) not expected to sorb appreciably to the quantity of sorbent used to allow monitoring of losses due volatilization and degradation. Next, solutions of the spike carrier (methanol, in some cases containing a small portion of methylene chloride) plus the second HOC, where utilized, as blanks. Finally, for isotherm experiments, sorbate was
added on a tube by tube basis to NaN₃ solutions. The filled sets of tubes were stoppered or capped, sealed with teflon tape, covered with foil, then equilibrated on a wrist action shaker at room temperature (~22° C). For the chlorobenzenes/kaolin experiments, a small teflon stir bar was added, and the tubes were equilibrated on a stir plate as the ratio of water to sorbent was too low to allow effective mixing on the shaker. Control tubes containing a stir bar but no kaolin were not statistically different from standards containing the same quantity of sorbate indicating the stir bar did not sorb significant amounts of sorbate. After the equilibration period (see kinetics section), the tubes were centrifuged using centrifugal force exceeding that used to wash out fines, to separate the equilibrated phases. The supernatant was then either analyzed directly, or after extraction into hexane or methylene chloride, by fluorimetry (Beckman, DU-7), or direct aqueous injection gas chromatography with flame ionization detection (98° C isothermal; 15 m, SE 54) for the chlorobenzenes. In some experiments, solvent extracted methyl perylene was analyzed by gas chromatography-mass spectrometry (HP 5995, splitless, 66° C (1 min) - 280° C (20 min) @ 16° C/min, 30 m, DB-5) after a concentration step. The excitation and emission wavelengths used for the PAH were 400/436, 434/466, 239/394, 250/350, 268/324, and 605/600 nm to monitor for methyl perylene, perylene, pyrene, phenanthrene, naphthalene, and light scattering, respectively. In some cases the settled sorbent and glass vessel walls were extracted with methanol/methylene chloride and analyzed by fluorimetry or gas chromatography-mass spectrometry allowing mass balance determination and direct observation of wall and kaolin-sorbed concentrations. Sorption coefficients (Kj) were calculated in general by measuring the total added and dissolved sorbate concentrations and calculating the amount sorbed by difference.
Sorption kinetics experiments were conducted by harvesting, centrifuging, and extracting sets of tubes as a function of time. Time zero was taken as the moment of sorbate addition to the suspensions. For sorption isotherm experiments, tubes contained a common level of sorbent and a range of total sorbate concentrations.

RESULTS AND DISCUSSION

SORPTION KINETICS

Sorption kinetics were examined for several sorbate:sorbent pairs to determine required equilibration times. The data in Figure 1 indicate that equilibrium between dissolved and sorbed phases is reached within ~10 hr. The curves shown in Figure 1 represent model fits \( C_{\text{eq}} + (C_0 - C_{\text{eq}}) \cdot e^{-kt} \) to the data. \( C_0 \) and \( C_{\text{eq}} \) are the initial and equilibrium dissolved phase concentrations measured by fluorescence, and \( k \) indicates the overall rate of approach to equilibrium. The sorption kinetics for kaolin, indicated by dotted curve with no symbols, were deduced from the observed fluorescence in vessels containing no clay (sorption to glass walls only) and those containing clay (sorption to both kaolin and glass walls). Kinetics experiments involving perylene sorption to glass walls in the absence of shaking, indicate that equilibrium is reached faster with shaking than without. Unlike perylene and methyl perylene, phenanthrene included in these experiments showed no solid surface association and hence, no change in fluorescence over time. This substantiates the assumption that the observed decreases in perylene and methyl perylene are due to sorption rather than volatilization, as this process is expected to affect the lower molecular weight
Figure 1: Sorption kinetics

(a) perylene sorption data and model fits for glass tube (50 mL) walls and kaolin.
(b) methyl perylene sorption data for glass tube walls (50 mL) walls and kaolin.
phenanthrene more heavily than the other two sorbates. This is indicated as well by the good mass balances obtained in the few instances where both dissolved and sorbed (to walls and added sorbent) phase concentrations were measured. Thorough kinetics studies were not performed for all sorbate/sorbent pairs used in this study. Equilibration times of 3 days were used for all other sorbate/sorbent pairs.

In general, kinetics data in the literature are presented only to assure adequacy of equilibration times. A wide range of equilibration times have been used (2 hours to 4 days). In most cases adequacy of equilibration times was indicated by showing that dissolved and/or sorbed phase concentrations at widely spaced time points, for instance, 24 hr and 48 hr, do not differ. Hence, these data, at least the longer equilibration data, do not lend themselves to pinpointing differences in kinetics on shorter time scales. In addition, in some cases it seems kinetics were checked for one sample, generally one containing organic matter, and equilibration times for this sample were applied to inorganic surface sorption as well. Sorption kinetics of HOC to organic and inorganic surfaces may not be the same. Two studies (Keoleian and Curl, 1989, and Rogers et al., 1980) did look at kinetics in a detailed way for inorganic surfaces in particular. Keoleian and Curl (1989) using tetrachlorobiphenyl/kaolin found that equilibrium was reached within 2 hours. Rogers et al. (1980), on the other hand, found equilibration times of 16 hours were required for benzene/montmorillonite. Our data certainly fall within this wide range. Differences observed could be due to different sorbents used (montmorillonite is an expandable clay; kaolin is not), presence of organic matter, and/or differences in shaking speeds.
SORPTION ISOTHERMS

Sorption isotherms were constructed for methyl perylene sorption to both glassware and kaolin and for pyrene sorption to kaolin (Figure 2). If a linear partitioning model (sorbed) = K_j · (dissolved) is valid, the log (sorbec) regressed against log (dissolved) should yield a slope of 1 with the intercept indicating the log K_j value. Examined in this way, the sorption isotherm for methyl perylene:glassware has a slope and intercept of 1.0 and -0.08, respectively (Figure 2a). Both the slope of 1 and the lack of any trend in the data (plotted as insert of Figure 2a) indicate that the partition coefficient for methyl perylene to the glassware surface is independent of the total sorbate concentration up to saturation (indicated by the arrow in Figure 2a).

Although there is more scatter in the two isotherms where kaolin is the sorbent (Figures 2b and c), it appears that these isotherms are also linear. For methyl perylene sorption to kaolin, the log-log plot has a slope of 1.1 ± 0.12, not significantly greater than 1.0. Further there is no obvious trend in K_kaol with sorbate concentration (Figure 2b). For the pyrene:kaolin isotherm, including all data, results in a slope of 0.87 ± 0.09 (Figure 2c). The lower pyrene concentration points are less reliable than the higher concentration points. At the high kaolin concentration (22 g/L) required to observe measurable reductions in dissolved phase pyrene concentrations, some kaolin fines remained in the supernatant despite repeated prewashing. This resulted in light scattering interference in the dissolved phase fluorescence readings for the low pyrene concentrations. This was not a problem for the higher pyrene concentrations as these samples required dilution to keep fluorescence readings on scale. If the lower pyrene concentration points are left out of the isotherm regression (Figure 2c, solid line), the slope and intercept become
Figure 2: Sorption isotherms

(a) methyl perylene/glass wall isotherm.
(b) methyl perylene/kaolin isotherm.
(c) pyrene/kaolin isotherm.

Arrows on graphs indicate HOC solubility (µg/L).
Inserts indicate log K_d as a function of HOC (dissolved).
METHYL PERYLENE/GLASS WALL ISOTHERM

\[ y \text{ int} = -0.08 \]
\[ \text{slope} = 1.00 \]
\[ r^2 = 0.9822 \]

METHYL PERYLENE/KAOLIN ISOTHERM

10 mg/L kaolin

\[ y \text{ int} = 0.22 \pm 0.006 \]
\[ \text{slope} = 1.1 \pm 0.12 \]
\[ r^2 = 0.9409 \]

PYRENE/KAOLIN ISOTHERM

22 g/L kaolin

\[ y \text{ int} = -3.28 \pm 0.26 \]
\[ \text{slope} = 0.87 \pm 0.09 \]
\[ r^2 = 0.9109 \]

\[ y \text{ int} = -3.64 \pm 0.48 \]
\[ \text{slope} = 1.08 \pm 0.11 \]
\[ r^2 = 0.9247 \]
1.08 ± 0.11 and 1.4 ± 0.19. As shown in the insert (Figure 2c), the calculated 
K_{kaol} is not obviously a function of the sorbate concentration.

Linear isotherms are reported in the literature for many HOC:inorganic 
sorbent pairs (Table II). Unfortunately, in most cases the isotherm data were 
collected over a rather limited range of HOC concentrations which often did 
not extend to the particular NOC's saturation level. Though literature data in 
general support our findings, without data extending over a wide range of 
concentrations approaching saturation it is not certain this observed linearity 
reported in the literature can be extrapolated over the entire HOC 
concentration range. The few cases where nonlinear isotherms were 
reported ( Table II) may be due to analytical problems, including 
incomplete separation of phases characterized by decreasing K_j values with 
increasing sorbent concentration, and isotherms constructed almost entirely 
above saturation conditions.

The linearity of isotherms (slope of 1 on a log-log plot) indicates that the 
portion of solute molecules (relative to the total number of solute molecules) 
associated with the sorbent remains constant no matter the total 
concentration of solute (up to saturation). Isotherm linearity has been used in 
the context of HOC:organic matter partitioning to distinguish between 
possible sorption mechanisms (Chiou et al., 1979 and 1985). Linear isotherms 
are consistent with absorption mechanisms, whereas, nonlinearity is used to 
confirm adsorption mechanisms. Sorption by absorption involves distribution 
of the sorbate into different phases. For example, the phases involved in 
HOC:organic matter association in aqueous solution are the organic-solvent-
like organic matter phase and the aqueous phase. Absorption is a function of 
the volume of the sorbent phases. Though consistent with the observed linear
TABLE II: Summary of HOC:inorganic surface pairs reported in the literature, indicating isotherm linearity and pairs plotted in Figure 5

<table>
<thead>
<tr>
<th>SORBENT:SORBATE</th>
<th>ISOHERMS BEHAVIOR</th>
<th>DATA USED IN FIGURES</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>kaolin, SiO2 &amp; Al2O3: substituted benzenes (aliphatic and chloro) tetrachloroethylene</td>
<td>NR</td>
<td>✓</td>
<td>Schwarzenbach and Westall, 1981</td>
</tr>
<tr>
<td>kaolin:tetrachlorobiphenyl</td>
<td>linear</td>
<td>✓</td>
<td>Keoleian and Curl, 1989</td>
</tr>
<tr>
<td>kaolin &amp; montmorillonite: hexachlorobiphenyl</td>
<td>linear</td>
<td>✓</td>
<td>Di Toro and Horzempa, 1982</td>
</tr>
<tr>
<td>kaolin, illite, &amp;montmorillonite: DDT, heptachlor, and dieldrin</td>
<td>nonlinear</td>
<td></td>
<td>Huang and Liao, 1973</td>
</tr>
<tr>
<td>montmorillonite: jet fuel oil components</td>
<td>NR</td>
<td>✓</td>
<td>MacIntyre and deFur, 1985</td>
</tr>
<tr>
<td>Al- and Ca-montmorillonite: benzene</td>
<td>linear</td>
<td></td>
<td>Rogers et al., 1980</td>
</tr>
<tr>
<td>H, Na, and Ca-montmorillonite: 1,2-dibromo-3-chloro-propane</td>
<td>nonlinear</td>
<td></td>
<td>Singhal and Singh, 1976</td>
</tr>
<tr>
<td>bentonite: lindane</td>
<td>linear</td>
<td>✓</td>
<td>Kay and Elrick, 1967</td>
</tr>
<tr>
<td>SiO2 &amp; Al2O3: benzene</td>
<td>NR</td>
<td>✓</td>
<td>Noll, 1987</td>
</tr>
<tr>
<td>80 - 120 &amp; 20 - 30 mesh silica sand: lindane and dieldrin</td>
<td>linear</td>
<td></td>
<td>Boucher and Lee, 1972</td>
</tr>
<tr>
<td>low carbon aquifer material: 2,3, and 4 ring PAH</td>
<td>linear</td>
<td>✓</td>
<td>Abdul and Gibson, 1986</td>
</tr>
<tr>
<td>low carbon aquifer material: trichlorobenzene and ortho-chlorotoluene</td>
<td>linear</td>
<td>✓</td>
<td>Banerjee et al., 1988</td>
</tr>
</tbody>
</table>

NR = not reported
isotherms, it is hard to imagine partitioning into an inorganic sorbent phase unless we envision vicinal water (Drost-Hansen, 1978) as a separate phase located between the inorganic surface and the bulk water phase.

Adsorption, on the other hand, involves association of the sorbate with the surface or interface of the sorbent. The competitive adsorption reaction involving HOC and solvent (water) molecules competing for association with the inorganic surface can be written as follows.

\[ \text{HOC:} \text{H}_2\text{O} + \text{Surf:} \text{H}_2\text{O} = \text{Surf:HOC} + \text{H}_2\text{O:} \text{H}_2\text{O} \]  

(1)

at equilibrium:

\[ \Delta G^\circ = -RT \ln \frac{[\text{Surf:HOC}][\text{H}_2\text{O:} \text{H}_2\text{O}]}{[\text{HOC:} \text{H}_2\text{O}][\text{Surf:H}_2\text{O}]} \]  

(2)

where the activities of these species, \([]\), are defined as the product of their respective activity coefficients and mole fractions in the water or on the surface. The degree of HOC association with the surface is determined by the mole fraction of HOC in solution (limited by its aqueous solubility) and the relative interaction energies of the component pairs in Equations 1 and 2. Nonlinear isotherms are often reported for adsorption processes. The nonlinearity is observed when \(\Delta G^\circ\) changes with HOC surface coverage, if the properties of the surface change with HOC surface coverage, or specific interaction sites become saturated. The observed isotherm linearity along with the results of sorption experiments described below provide clues to the HOC:inorganic surface sorption mechanism.
SORPTION OF A SERIES OF HOC TO KAOLIN AND SILICA

A correlation between \( \log K_i \) and \( \log \gamma_W \) is expected from the picture presented of HOC in water. Sorption can be thought of as a partial reversal of HOC aqueous solubilization. Absorption of HOC from water into a sorbent phase is directly analogous to aqueous solubilization of HOC (hypothetical liquid HOC solubilization in the case of HOC which are solids at room temperature). Adsorption could result from a partial reversal of HOC solubilization on association with a surface. The aqueous activity coefficient of a given HOC is exactly what quantifies the free energy of liquid solubilization. Hence the observed relationship between sorption and \( \gamma_W \) is expected to provide information on the sorption mechanism.

The sorption coefficients for a series of HOC (methyl perylene, perylene, pyrene, 1,2,4-trichlorobenzene, and 1,4-dichlorobenzene) with widely varying aqueous activity coefficients (\( \gamma_W \)) were determined for kaolin (Figure 3a). Partition coefficients for sorption to silica (glassware and glass beads) were determined for a smaller set of HOC, methyl perylene, perylene, and pyrene (Figure 3b). \( \log \gamma_W \) values (Table I) were calculated from published HOC aqueous solubility data (Miller et al., 1985) by summing the melting term (\( \Delta S_f (T - Tmp)/2.303 RT \)) and the log of the inverse of the NOC’s solubility (on a mole fraction basis) for HOC which are solids at room temperature (\( T = 295^\circ K \)). The entropy of fusion, \( \Delta S_f \), is assumed to be 13.5 cal/mole deg for all HOC n this study (Yalkowsky and Valvani, 1980). \( Tmp \) is the NOC’s melting point in \(^\circ K\), and \( R \) is the universal gas constant (1.98 cal/mole deg). The aqueous solubility of methyl perylene was estimated as 4 \( \mu g/L \) and melting point data was obtained from Peake et al. (1983). There is a strong correlation between
Figure 3: Correlation between HOC partition coefficients and aqueous activity coefficients.

(a) kaolin: dichlorobenzene, trichlorobenzene, pyrene, perylene, and methyl perylene.
(b) glass beads and walls: pyrene, perylene, and methyl perylene.
KAOLIN

\[ \log K_{\text{Kaol}} \text{ (mL/cm}^2 \text{)} \]

\[ \log \gamma_W \]

\[
y \text{ int } = -15.3 \\
\text{slope } = 1.83 \\
r^2 = 0.9873
\]

glass beads and walls

\[ \log K_{\text{Sil}} \text{ (mL/cm}^2 \text{)} \]

\[ \log \gamma_W \]

\[
y \text{ int } = -10.2 \\
\text{slope } = 1.17 \\
r = 0.9821
\]

\[
y \text{ int } = -15.9 \\
\text{slope } = 1.84 \\
r = 0.9721
\]
log $K_{Kao1}$ values observed for kaolin and HOC log $\gamma_W$, with slope and intercept of 1.33 and -15.3, respectively (Figure 3a). The $K_{Kao1}$ value for 1,4-dichlorobenzene (the lowest $\gamma_W$ point) is an upper estimate as very little 1,4-dichlorobenzene was sorbed even at the high kaolin concentration (625 g/L) used in the chlorobenzene:kaolin experiments.

Sorption data for HOC to silica surfaces (glass beads and walls) provided a similar relationship (Figure 3b). However, the interpretation of the slope and intercept is complicated as $K_{Sil}$ values for methyl perylene and perylene are calculated using geometric estimates of the surface area of vessel walls (as the BET surface area of the inside wall of the vessel could not be determined), whereas, the glass bead surface area was determined by BET analysis. Geometric estimation of surface area could lead to underestimation of true surface area if imperfections or pores exist in the inorganic surface. However, if small pores included in BET measures of surface area are not accessible to HOC, geometric surface area estimates may provide a better estimate of surface available for HOC sorption. To allow comparison of HOC sorption to glass walls and beads, geometric estimates of bead surface areas can be used in calculation of $K_{Sil}$ values on a mL/cm$^2$ basis. Assuming beads are nonporous spheres of radius 50 $\mu$m (estimated by microscopic examination), sorption data on a mL/cm$^2$ basis for this limited set of HOC on silica are regressed against log $\gamma_W$. The slope and intercept of this regression are 1.17 and -10.2, respectively, when geometric estimates of surface areas are used for both glass walls and beads. If the BET surface area estimate is used for the glass beads, a slope of 1.84 and intercept of -15.9 are found (Figure 3b). The difference between these lines reflects the difference in surface area estimates (BET vs geometry) for the glass beads (Table I). The BET estimate is close to 25 times larger than
the geometric estimate indicating either the beads are somewhat porous or the assumed shape and estimated bead radius do not represent the entire population of beads. Which estimate most accurately reflects surface area accessible for HOC sorption to glass beads is not known. The accuracy (in terms of HOC accessible surface area) of the geometric estimate of the glass tube surface area, for that matter, is uncertain as well. Further studies, involving a series of HOC on a common sorbent (glass beads), are required to determine useful slopes and intercepts.

A correlation between log $K_i$ and log $\gamma_w$ with slope greater than one provides information about sorption mechanisms. The magnitude of the HOC $\gamma_w$ imposes a limit on the amount of solubilization energy that can be recovered on partitioning out of the water phase. If the energy driving sorption is associated mainly with the state of the HOC, and the proportion of the liquid HOC solubilization energy recovered on partitioning out of the water phase were constant for all HOC, the slope of log $K_i$ vs log $\gamma_w$ would reflect that proportion, imposing a limit of 1 on the magnitude of the slope. If however, the proportion of solubilization energy recovered on sorption varies from one HOC to the next, with higher $\gamma_w$ HOC recovering a greater proportion of energy on sorption, the slope of the log $K_i$ vs log $\gamma_w$ regression could be greater than one. The slope in this case reflects not only the proportion of solubilization energy recovered for a given HOC but the manner in which that proportion changes from one HOC to another. If the energy driving sorption is not dominated by the state of the HOC, but additional energy changes in the system contribute, such as the freeing of water molecules associated with the inorganic surface (hydration energy) on sorption, slopes greater than one may result as well.
EFFECT OF SORBENT TYPE ON HOC $K_l$

The manner in which $K_l$ values vary for a given HOC as a function of surface type may provide clues as to the mechanism of HOC sorption to inorganic surfaces, as well as indicate whether predictive relationships must be developed for each surface type encountered or whether a general relationship can be found. $K_l$ values were measured for perylene on kaolin, silica (glass walls), and aluminum oxide, for methyl perylene on kaolin and silica (glass walls), and for pyrene on kaolin and silica (glass beads). The effect of surface type on sorption of these HOC can be seen in Figure 4a where $K_l$ values (on a mL/cm$^2$ basis) for all HOC and surfaces studied are plotted as a function of inorganic surface type. The $K_l$ values for kaolin, alumina, and glass beads with units of mL/g kaolin have been converted to an area basis with BET surface area measurements (Table I) to allow direct comparison of $K_l$ values for all surfaces. The observed differences in $K_l$ values for perylene and methyl perylene on silica and kaolin are within the error (one standard deviation) of $K_l$ measurements for kaolin on an area basis (Figure 4a). The $K_l$ values for pyrene on silica (both BET and geometric) are within 0.5 log units of that for kaolin. The observed $K_l$ for perylene on alumina is however, very different from that observed for the other two sorbents (Figure 4a). This could be due to the difference in surface type or overestimation of the available surface area for HOC sorption. The BET surface area for alumina is quite high for its nominal radius (37 - 125 μm) indicating the material is quite porous. If these pores are small relative to the size of perylene and methyl perylene, much of the surface may be unavailable for sorption. Pore sizes for some chromatographic grade aluminas are reported to be on the order of 10's of angstroms in diameter (Snyder; 1968, Aldrich Chemicals reports
Figure 4: $K_i$ values observed for HOC to kaolin, silica, and alumina

(a) observed $K_i$ values for methyl perylene, perylene, and pyrene on silica, kaolin, and alumina.

(b) Correlation of surface area normalized partition coefficients and aqueous activities coefficients for kaolin, glass beads and walls, and alumina.

solid symbols indicate data normalized by BET SA estimates for the various sorbents.
open symbols indicate data normalized by geometric SA estimates for glass and alumina
a

![Graph of Log $K_i$ vs. Log $\gamma_W$](image)

- methyl perylene
- perylene
- pyrene

silica  kaolin  alumina

b

![Graph of Log $K_i$ vs. Log $\gamma_W$](image)

- $y$ int = -14.8
- slope = 1.74
- $r^2 = 0.9762$

kaolin
- silica
- alumina

- SA by geometry
- SA by BET

Log $K_i$ (mL/cm²)

Log $\gamma_W$

116
average micropore sizes of 58 angstroms) whereas the length of perylene is probably closer to 10 angstroms. Inaccessibility of pore space to perylene may not be because perylene cannot physically fit into the pores, but rather may be due to the state of water in these pores. It is conceivable (and evident in the vicinal water literature, Braun and Drost-Hansen, 1976) that water is more icelike in confined pores, hence intrusion of perylene into a pore would probably involve breaking of hydrogen bonds which is energetically unfavorable. If we assume for simplicity that the alumina particles are spheres with range of radii of 37 µm to 89 µm reflecting the range of mesh sizes, a geometric surface area, excluding pores, of 90 - 210 cm²/g can be estimated. Using these surface area estimates to calculate K_f for perylene on an area basis puts the K_f for alumina in the same range as that observed for silica and kaolin (Figure 4a and b).

The observed similarity in sorption (normalized by sorbent surface area) between sorbents may be useful in determining sorption mechanisms. The fact that sorption is a function of surface area rather than sorbent volume or mass is suggestive of an adsorption process. Though, because the volume of vicinal water that may surround a surface is proportional to sorbent surface area, absorption into this type of phase cannot be ruled out simply because of the correlation with surface area. The apparent independence of sorption on inorganic surface type suggests that (1) the surfaces used in this study are very similar in the specific ways that matter for HOC sorption, (2) kaolin and glass baked at 450°C are similar and differences observed for alumina are due to this surface type rather than microporosity, or (3) there are different ways for a sorbent to interact with an inorganic surface and differences in surfaces are compensated for by these different options for interaction. Any proposed sorption mechanism will have to allow for one of these possibilities.
The similarity of observed sorption coefficients for a given HOC on a surface area basis (BET or geometric surface area for nonporous materials and geometric surface area for microporous materials) between the surfaces used in this study indicates that data for all sorbents can be combined and regressed against the log $\gamma_w$ values of the sorbates to obtain a common inorganic surface predictive relationship. The line obtained on regressing all the data (excluding the aluminum:BET point), is Figure 4b).

$$\log K_i \text{ (mL/cm}^2\text{)} = 1.74 \log \gamma_w - 14.8$$

may be useful in predicting $K_i$'s for other HOC on these surfaces.

Most of the literature data for $K_i$ are reported on a mL/g basis. Some authors however report surface area/g information for the sorbents in which can be used to calculate $K_i$ values on a mL/cm$^2$ basis allowing direct comparison between literature data sets and our data. This compilation of literature data is presented in Figure 5a. These data include a wide range of surfaces including kaolin, SiO$_2$, aluminum, low carbon aquifer materials, florisil, and montmorillonite (sorbate:sorbent pairs plotted in Figure 5a are indicated in Table II). The slope and intercept of the literature data regression (Figure 5a) differ substantially from that obtained for the HOC and sorbents used in this study (Figure 5b). The difference between the slope of the log $K_i$ vs. log $\gamma_w$ regression for literature data and data presented in this study can in part be explained by experimental problems namely, presence of organic matter and separation of equilibrated phases. The presence of organic matter affects low $\gamma_w$ HOC more than high $\gamma_w$ HOC. This is due to the difference in
Figure 5: Ki values for various surfaces reported in the literature.

(a) on a mL/cm² basis for studies (indicated in Table II) reporting surface area data.
(b) studies reporting data for a series of HOC on a given sorbent (indicated in Table II).
(c) data reported in b excluding low γw points
slopes between log $K_I$ and log $K_{OC}$ vs. log $\gamma_W$. This can best be seen by comparing the expected (predicted from the regression in Figure 4a) contribution of HOC sorption to the inorganic surface to the total sorption

$$K_p = K_{OC} \cdot f_{OC} + K_I \text{ (mL/cm}^2\text{)} \cdot f_i$$

(4)

where $f_i$, the fraction of available inorganic surface, is estimated by the measured surface area/gram sorbent. For example, if the kaolin $f_{OC}$ of 0.0006 and $K_{OC}$ values calculated using the regression for kaolin presented in Schwarzenbach and Westall (1981) are used in this calculation, the inorganic surface contribution to total sorption for chlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,4,5-tetrachlorobenzene are 0.9, 5.7, 29, and 73%, respectively. The presence of even 0.06% organic carbon has a substantial effect on sorption of the lower molecular weight chlorinated hydrocarbons. This differential effect of organic matter on observed sorption to inorganic materials affects the slope of log $K_I$ vs. log $\gamma_W$ regressions. This can be seen in Figure 6b and c. Sorption data from the three literature studies which included data for more than two HOC on a given surface (indicated in Table II) are plotted as a function of log $\gamma_W$ of the HOC. $K_I$ values are plotted on a mL/g basis as surface area estimates for sorbents are not reported in all studies. The slope of the log $K_I$ vs log $\gamma_W$ regressions remain unchanged on normalization by surface area, only intercepts change. If we assume that organic matter present on sorbents biases the true magnitude of observed $K_I$ values in all the studies presented in Figure 5b, especially the HOC with lower $\gamma_W$, and therefore remove all HOC with $\gamma_W$ less than 5 from the regressions, we find in most cases the slopes double (Figure 5c). In particular, the slope of the chlorinated benzene data for kaolin (indicated by solid triangles in Figures 6b
and c) increases from 0.68 to 1.5 when just the chlorobenzene point is removed from the regression. Still more increase in slope is obtained, 0.87 - 1.5, for the data from the Abdul and Gibson (1986) indicated by open circles in Figures 6b and c, if the next lowest log γᵦ point is removed. In addition to this overestimation of Kᵢ values for HOC with low γᵦ due to the presence of organic matter, separation of phases problems may lead to erroneously low Kᵢ values for high γᵦ HOC. Both of these biases lead to underestimation of log Kᵢ vs. log γᵦ regression slopes. In sum it appears that literature data suggest a slope of at least one for log Kᵢ vs. log γᵦ.

SORPTION MECHANISM

Combining the images of water, HOC:water, and inorganic surface:water interactions detailed in the introduction with the knowledge gained from the data, we can develop a picture of HOC sorption to inorganic surfaces. This sorption can be described as a competitive adsorption process (Equation 1). The primary driving force, however, is not attraction of the HOC for the surface, but rather, preferential association of water with itself rather than with HOC or the inorganic surface. Sorption results in large part from the energetically favorable restructuring of water molecules as HOC associate with an inorganic surface allowing water molecules previously in association with both the HOC and inorganic surface to interact with other water molecules. The fact that water is not a "normal" liquid allows for the possibility of water:water interactions being the a driving force. Water molecules forced to associate (with some cost or little energetic advantage) with HOC or some areas of inorganic surfaces (e.g., siloxane sites), and thereby prevented from fully associating with other water molecules, may be
freed on the sorption of HOC to an inorganic surface. An energetic advantage can be derived from this association if interactions between the water molecules are stronger than water:HOC and water: inorganic (siloxane) surface interactions. As indicated above, the energy levels of all but the fully hydrogen bonded (tetra-bonded) species increases relative to its energy level in the bulk on association with a HOC as this association prevents the more favorable water:water interaction. An enthalpic advantage can be derived from freeing these species, allowing them to fully interact with other water molecules. Though the tetra-bonded species is stabilized by interaction with HOC with resultant energy level decrease for this species, the entropy level of the system is increased, due to the higher level of organization of this species. Hence, an entropic advantage can be derived from freeing these species.

Similar advantages may be found at the inorganic surface water interface, for example, at siloxane type sites. At these sites though there is a favorable enthalpic interaction between water and the oxygen atom of the siloxane group, this interaction may not be as strong as the water:water interaction which is prevented by association with the surface. The energy level of the system may be lowered (favorable ΔG) by association of HOC with siloxane type surface groups even though the interaction between HOC:siloxane is not expected to be as strong as that between water:siloxane. This is similar to the situation described and modeled by Nemethy and Shegara (1962b) for association of protein side chains in aqueous solution.

**Sorption Isotherms**

The isotherm data indicate that the ΔG° of sorption does not vary as a function of surface coverage (Equation 2, ΔG° = constant). This indicates that
all inorganic surface site types available for sorption yield the same sum of interaction energies on HOC association with the site. Otherwise, isotherm nonlinearity would be observed. Additionally, linear isotherms up to HOC aqueous solubility indicate that HOC cannot out-compete water for all available sites at the low HOC mole fraction (limited by aqueous solubility) even though some energy may be recovered as new water:water interactions on association of HOC with the surface. The upper limit of linearity is expected to occur on saturation of the dissolved phase or surface coverage. At this point a new option for lowering the free energy of the system arises, that being association of the solute with itself and precipitation or formation of a pure HOC phase. Nonlinear isotherms would only be expected if the number of solute molecules present could actually disrupt the structure of the bulk water as a whole not just locally, or significantly affect the entire structure of the water at the sorbent water interface. With the low solubility HOC dealt with in this study, the small portion of HOC (\(< 2.5 \times 10^{-4}\) moles/L) relative to the number of water molecules present (55.5 M/L) precludes such effects.

Kl vs qw of HOC

Slopes greater than one indicate that the fraction of liquid solubilization energy recovered on sorption is not a constant function of \(\gamma_W\). This may indicate that an increasing fraction of solubilization energy is recovered with increasing \(\gamma_W\), or a fraction of the inorganic surface hydration energy is gained on sorption. The energy levels of the various water species surrounding a given HOC, which can be freed on sorption, is determined by the specific interaction between the HOC and these water species. The number of water groups affected by the presence of the HOC is determined by the size of the HOC. Hence, the proportion of solubilization energy
recovered could well vary from one HOC to another. As indicated above, there are differences in the energy levels of water species organized about aliphatic and aromatic species of similar size. This indicates the slopes of log $K_J$ vs log $\gamma_W$ regressions may well vary from one HOC family to another.

**$K_J$ vs Surface Type**

The similar $K_J$ values observed for a given HOC on the various surfaces tested indicated that the $\Delta G^\circ$ (Equation 2) of sorption is not very different for the oxides tested in this study. This indicates that the HOC:surface interaction sites are similar on all surfaces, different HOC:surface site types exist on different surfaces but the total sum of interaction energies is the same, or surface site interactions represent only a small contribution to the total $\Delta G_{ads}$.

**IMPLICATION OF THE RESULTS TO TRANSPORT OF HOC IN GROUNDWATER**

The correlations found in this work together with Equation 4 can be used to determine where HOC sorption to inorganic surfaces will be important. The predictive relationships (Equations 3 and 4) indicate inorganic surfaces will have the greatest effect where high $\gamma_W$ HOC coexist with high concentrations of low organic carbon inorganic solids (aquifers) and high surface area inorganic particles (colloids). Applications of this work to hydrophobic organic contaminant transport in groundwater are readily apparent. Ignoring the possibility of sorption of HOC to inorganic surfaces could lead to substantial underestimation of the retardation of HOC with high $\gamma_W$ values in low organic carbon aquifers. This can best be shown by calculating the contribution of inorganic sorption ($K_J \cdot SA$) for several HOC to total sorption ($K_p$total) for low organic carbon aquifer material. Using estimates $f_{oc} = 0.0002$ and $SA = 1 \times 10^4$ cm$^2$/g (similar to that found at the Bordon site, Mackay
et al., 1986) along with $K_{OC}$ values obtained from Karickhoff (1981) and log $\gamma_W$ values calculated from mole fraction solubilities reported in Karickhoff (1981), the contribution of inorganic sorption can be calculated from Equations 3 and 4. For HOC with $K_{OC}$ and $\gamma_W$ values like perylene, inorganic sorption accounts for 87% of the total sorption in an aquifer like this. For HOC like pyrene and tetrachloroethylene, the contributions are lower, 20% and 0.03% respectively. This translates to a retardation coefficient ($R = 1 + (\rho_b \cdot K_{total})/n$, where $\rho_b$ is the bulk density of the aquifer material, and $n$ is the aquifer porosity) when inorganic sorption is considered for perylene of almost 8 times that calculated for organic carbon sorption only. If log $K_{OC}$ is expressed as a linear function of log $\gamma_W$ (using data from Karickhoff (1981), for benzene, naphthalene, anthracene, phenanthrene, and pyrene, log $K_{OC} = 0.86 \log \gamma_W - 1.15$, $r^2 = 0.9878$), Equation 4 can be rearranged to determine log $\gamma_W$ values required to produce greater than a 50% contribution of inorganic sorption to total sorption for a material of known foc and SA (Equation 5).

$$\log \gamma_W > (14.4 + \log (foc/SA))/0.94 \quad (5)$$

SA is in units of cm$^2$/g and $\gamma_W$ is on a mole fraction basis. For Bordon aquifer material the log $\gamma_W$ required for 50% inorganic sorption contribution is 6.9. For reference, pyrene’s log $\gamma_W$ is 6.6, perylene’s is 8.05. The implications for retardation are even greater in a higher surface area material such as a clay liner.

Similar calculations can be done to determine mobile inorganic colloid concentrations required to enhance the transport of HOC in an aquifer. In this case the retardation coefficient can be reformulated to include a mobile colloidal phase ($R = 1 + (\rho_b \cdot K_{total})/(n + n \cdot (colloid) \cdot K_p_{colloid})$, where the
denominator now includes terms for the mobile colloid concentration in the groundwater and a total partition coefficient for HOC to colloids. If we assume for simplicity that only kaolin colloids exist, and use the regression for kaolin specifically (Figure 3a), log $\gamma_w$ values for which greater than a 50% reduction in the retardation coefficient and hence, potential doubling of HOC groundwater transport can be calculated (Equation 6).

$$\log \gamma_w > (11 - \log \text{(kaolin colloids)})/1.9$$

For mobile kaolin colloid concentrations of 1, 10, 50, and 100 g/mL, HOC with log $\gamma_w$ values of 8.95, 8.4, 8.05, and 7.9, respectively, are required to cause a 50% reduction in R due to the presence of kaolin colloids. These are not unreasonably high colloid concentrations. Ryan (1988) found dispersed clay colloids in groundwater at concentrations as high as 60 mg/L. These examples clearly indicate the importance of considering sorption of HOC to inorganic surfaces and including it's contribution in groundwater transport models.

**CONCLUSIONS**

Situations exist in the environment where HOC coexist with inorganic surfaces. It is important to understand interactions between HOC and inorganic surfaces, as well as the magnitude of HOC:inorganic interactions relative to HOC:organic interactions. The goal of this work was to gain a better understanding of the mechanism of HOC:inorganic surface interaction in aqueous systems and develop a predictive relationship which can be applied to situations where HOC and inorganic surfaces coexist. The sorption
behavior (including kinetic and isotherm behavior) of a series of HOC was studied on a series of surfaces. These studies were carried out in such a manner to minimize problems identified in the literature which have complicated interpretation of HOC:inorganic surface sorption data namely, incomplete separation of phases and presence of organic matter. The data collected indicate: (1) HOC:inorganic sorption is complete within hours, (2) sorption isotherms are linear over wide (up to saturation) HOC concentration ranges, (3) HOC sorption is a function of $\gamma_w$ for a series of HOC on a given surface, and (5) the differences in HOC sorption between the sorbents studied may be explained by differences in surface area alone.

These features are consistent with an adsorption mechanism where association of HOC with the inorganic surface is primarily driven by changes in the interactions and organization of the solvent water, rather than by the specific enthalpic interaction of the HOC with the inorganic surface. This possibility arises because water is not a "normal" liquid. Sorption results from the reorganization of the aqueous system including changes in the distribution of the various species of water in the system and preferential association of HOC with the inorganic surface and water with water species. Such a model suggests: (1) linear sorption isotherms up to dissolved phase saturation conditions for all surfaces, (2) dependence of $K_j$ values on $\gamma_w$, though this dependence may vary from one HOC family to another, and (3) dependence of HOC sorption on sorbent surface area.

The success of normalization of observed $K_j$ values for different surfaces by sorbent surface area is very useful in that it provides the semiempirical predictive relationship in Figure 4b and Equation 3. This predictive relationship requires only knowledge of the NOC's $\gamma_w$ and the sorbent's surface area, and is expected to apply to HOC and surfaces similar to those used in this study.
This predictive relationship suggests that sorption of HOC to inorganic surfaces will be important for high concentrations of low floc inorganic particles, high surface area inorganic materials, and HOC with high $\gamma_W$. The implications of this work lie in the areas of inorganic colloid (high SA/g) enhanced transport of HOC with high $\gamma_W$, retarded transport of these contaminants in low organic carbon aquifers, and retention of HOC by clay liners. This study suggests more work should be done to elucidate the sorption mechanism, and broaden the applicability of the semiempirical predictive relationship presented in this paper before this relationship is widely applied outside the bounds of this work.
Literature Cited


CHAPTER 4

INVESTIGATION OF A COAL TAR CONTAMINATED AQUIFER:
SAMPLING GROUNDWATER FOR DISSOLVED AND
COLLOID-ASSOCIATED ORGANIC CONTAMINANTS
INTRODUCTION

The need to consider the possibility of colloid-enhanced organic contaminant transport at hazardous waste sites has only recently become apparent. This mode of transport is expected to be important if sufficient quantities of colloids, capable of sorbing contaminants, exist within the contaminant plume. Mobile colloids, including organic macromolecules, microorganisms, mineral precipitates, and rock and mineral fragments, have been found in groundwaters (Keswick et al., 1982; Reinhard, 1984; Robertson et al., 1984; Gschwend and Reynolds, 1987; Ryan and Gschwend, 1990). Some types of colloids, microorganisms and macromolecules, have been found hundreds of meters from their source (Keswick et al., 1982; Reinhard 1984; Robertson et al., 1984) indicating that colloids can be transported significant distances in the subsurface. Organic colloids (e.g., humic substances) are known to be good sorbents for hydrophobic organic compounds (Carter and Suffet, 1982; Means and Wijayaratne, 1982; Landrum et al., 1984; McCarthy and Jiminez, 1985; Brownawell, 1986; Chiou et al., 1986; Gauthier et al., 1986, 1987; Backhus and Gschwend, 1990). Colloidal inorganic species, such as clays, can sorb significant quantities of very hydrophobic (e.g., \( K_{ow} > 10^6 \)) organic compounds as well (Chapter 3). The importance of colloid-associated transport for a given contaminant is expected to be a function of both the chemical's affinity for the colloidal sorbent and the concentration of mobile sorbent in the groundwater. The contaminant's affinity for the colloidal sorbent is expected to increase with increasing chemical hydrophobicity. Hence, colloid-associated transport in the subsurface is expected to be most important for very hydrophobic contaminants.
To date, the impact of colloids on organic contaminant transport at actual hazardous waste sites has not been examined. Some evidence exists implicating colloids in the transport of radionuclides through the subsurface. Penrose et al. (1990) found colloid-associated plutonium and americium as far as 3390 m downgradient of the waste discharge area. In the absence of colloids, these contaminants, which have high partition coefficients for aquifer material, were not expected to have traveled more than meters from their source. Comparable studies at sites contaminated by hydrophobic organic compounds are required to determine whether colloids significantly influence the transport of these hazardous species.

The purpose of this work is to evaluate the importance of colloid-associated organic contaminant transport at a hazardous waste site. To this end we sought a site known to contain very hydrophobic organic species. Preferably these contaminants would be geochemically stable to simplify interpretation and modeling of contaminant distributions. In addition, some evidence supporting the existence of mobile colloids at this site was desired. Light scattering material in groundwater samples or observed contaminant concentrations in excess of those expected based on dissolved phase alone would suggest colloids may be present.

Coal tar contaminated sites fulfill some of these requirements. Coal tar, created as a byproduct of coal gasification and often disposed of by subsurface burial, is a known source of hydrophobic organic contaminants in groundwater (Eng, 1985). Polycyclic aromatic hydrocarbons (PAHs), exhibiting a wide range of hydrophobicity, comprise a substantial fraction of coal tar. A number of PAHs are known carcinogens (e.g., benzo(a)pyrene) and many are found on the U.S. Environmental Protection Agency's hazardous substances list. These contaminants are expected to be
geochemically stable especially in anoxic groundwaters. The presence of a range PAHs with varying physical properties, including hydrophobicity and volatility in this waste material, provides a means to sort out processes (e.g., sorption and volatilization) by observed fractionation. PAH concentrations exceeding those expected for dissolved phase transport alone have been observed in groundwaters contaminated by coal tar (Villaume et al., 1983; Gschwend et al., 1988; Groher, 1989). This could indicate that colloid-associated transport is important at these sites. Alternatively, these results may be an artifact of the groundwater sampling method employed (Gschwend et al., 1988; Groher, 1989).

In this chapter, we seek to determine whether colloids play a role in transporting PAHs in groundwater at a coal tar contaminated field site. To accomplish this goal, estimates of mobile groundwater colloid concentrations were obtained from wells in the source area and downgradient. To assess accurately mobile colloid concentrations, groundwater was carefully sampled to insure that observed colloids were present as mobile species in the groundwater and not sheared from aquifer material or precipitated during sampling or storage. Additionally, the spatial distribution of hydrophobic organic contaminants in the aquifer was determined from groundwater and soil samples. These observations were compared to predicted spatial contaminant distributions based on either dissolved phase transport alone or combined dissolved and colloid-associated transport to determine the importance of colloids at this site.
MATERIALS AND METHODS

SITE DESCRIPTION

The site chosen for this investigation housed a coal gasification plant in operation from 1853 - 1923. An estimated 12,000 m$^3$ of this coal tar was buried on the site. Tar deposits up to 2.6 m thick cover 0.44 hectares at depths to 7.6 m below the ground surface. A liquid tar layer was found at approximately 1.8 m below the surface in some source areas. Though the time and exact location of coal tar burial at this site is not known, the time frame of plant operation provides an estimate of the maximum amount of time the groundwater at this site has been exposed to the coal tar. The locations of the coal tar source boundaries were defined by observations at 90 soil borings across the site (Figure 1).

The aquifer material at this site is of glacial-fluvial origin and ranges from fine to coarse grained sands to gravel. Much of the site is covered with fill to depths of ~1.5 m. The bedrock, found at depths of 12 - 33 m below the ground surface, is composed of granitic gneisses and schists. The topography across the site is quite flat. With the exception of a few concrete pads and old building foundations the ground surface is uncovered, and the site is only sparsely vegetated. A river bounds the property on one side. The water table is located around 5 m below the ground surface. The general direction of the groundwater flow across the site is toward the river in the direction the river flow (Figure 1). The average linear groundwater velocity estimated from slug tests and observed hydraulic gradients is about 0.3 m/day.
Figure 1: Site map

(a) areal view indicating location of the coal tar source, monitoring wells sampled, and general direction of groundwater flow

(b) vertical view of wells indicating depth of source material at well cluster A/D, pump head location in wells sampled and soil sample depths
Figure 1a
- monitoring wells sampled
- monitoring wells
- soil boring locations

...coal tar deposits
...direction of gw flow
...concrete structure

Figure 1b

...elevation above mean sea level (meters)

...A/D source area

...B

...C

...water level

...pump inlet

...well casing

...screened well intervals

...tar deposits

...1.2 m soil extract intervals

...1.5 (meters below surface)
MATERIALS

To study hydrophobic organic contaminants, expected to be present in very low concentrations in groundwater, care must be taken in choosing and cleaning sampling materials to avoid contamination and prevent losses. All materials (glassware, pump, aluminum tubing, packers) used in the collection and analysis of samples for PAHs were solvent rinsed with methanol and methylene chloride (EM Science, Omnisolve glass distilled) prior to use. Glassware was soaked in a chromic/sulfuric acid solution (Fisher Scientific) then rinsed and soaked in distilled water before solvent rinsing. Between wells (sampled in order of least contaminated to most contaminated) the pump and packers were thoroughly solvent rinsed to prevent cross-contamination. Separate reels of aluminum tubing were used for each well. Glass, aluminum, and stainless steel materials were used to minimize sorptive losses of hydrophobic contaminants (Reynolds et al., 1989).

SAMPLING

Groundwater/Mobile Colloid

A groundwater sampling protocol incorporating prolonged slow pumping and measures to maintain in situ groundwater chemistry conditions through sampling and storage was used to sample wells at this site (Figure 2). Samples were pumped to the ground surface with a submersible, gear-driven, positive-displacement pump, 4.45 cm in diameter and 17.8 cm in length (model SP-202, Fultz, Inc., Lewistown, PA). This pump has a low sample contact surface area constructed of inert materials (stainless steel body and inlet with teflon gears). A variable voltage AC-DC convertor powered by a generator controlled the pump. Purging and sampling flow rates of 97 ± 20 mL/min, 140 ± 60 mL/min and 80 ± 33 mL/min (measured using a stopwatch
Figure 2: Groundwater sampling apparatus.
Figure 2

SAMPLING GROUNDWATER FOR COLLOIDS

0.48 cm x 15.24 m aluminum tubing

AC generator
AC to DC Power
Supply

Turbidimeter

3 Way Stopcock

Flow cell—Calibrating
solutions

Flow cell—
Measurements

Graduated cylinder
for measuring flow rate

Stopwatch

4L Glass Sampling Bottle

Glass
Turbidimeter
Cell

Inflatable
Packer

Screened
Interval

Pump inlet

Pump

Screed

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and 100 mL graduated cylinder), respectively, were maintained at wells A, B, and C. The groundwater sampling zone was isolated by use of inflatable packers constructed of polyvinyl chloride and viton (QED Environmental Systems, Inc., Ann Arbor, MI) which straddled the pump inlet (placed 20 cm above and below the pump inlet). The packers were inflated with compressed argon gas. Groundwater was pumped to the surface through a continuous piece of 0.48 cm (id) aluminum tubing (Alltech Assoc., Deerfield, IL).

Each well was purged until water expected to be representative of formation water was being sampled. Water chemistry parameters were monitored during well purging to determine required purging times. This was accomplished by connecting the aluminum sampling tubing to a flow-through cell equipped with electrodes for monitoring groundwater pH, Eh, dissolved oxygen, temperature, and specific conductivity, or a flow-through sampling cell for collection of discrete samples for light scattering measurements (Turbidimeter, Hach Company, Loveland, CO). Electrodes for pH, Eh and conductivity measurements were calibrated at the groundwater temperature in the calibration chamber of the flow-through cell.

Samples for laboratory analysis of colloids were collected in biological oxygen demand (BOD) bottles or on 30 nm pore size filters. The BOD bottles, which were initially filled with argon and enclosed in argon-filled zipper-lock bags, were filled with groundwater by cracking the zipper open enough to insert the sampling tubing, shaking the stopper off the bottle in the bag, inserting the tubing into the bottom of the bottle, overfilling the bottle (by at least 1/2 the volume of the bottle), removing the tubing from the bottle, replacing the stopper, and finally removing the tubing from the bag and sealing the bag. These water samples were stored in a cooler in the field.
Field filters for scanning electron microscopy and energy-dispersive x-ray (SEM/EDX) analysis were collected in 5-mL disposable plastic syringes by joining the end of the sampling tubing to the syringe tip. The syringe was rinsed several times with groundwater, any bubbles were displaced, and the syringe was connected to a Millipore Swinnex filter holder containing a 30 nm pore size Nuclepore polycarbonate filter. The sample was forced through the filter by the pressure provided by weights (0.8 Kg/cm²). The filter was rinsed with 5 mL of distilled, deionized water (QH2O, Milli-Q system, Millipore Corp., Bedford, MA) prior to drying and stored in small petri plates in a desiccator.

Samples for PAH analysis were collected in 4-L amber bottles with foil-lined screw caps. These bottles were filled by threading the sampling tubing through a silicone stopper, placed in the neck of the bottle, to the bottom of the bottle (Figure 2). The stopper held a section of outlet aluminum tubing about a centimeter below the stopper for overfilling the bottle (by at least 1 L). After overfilling, a 150 mL aliquot of the water was poured off and replaced with a 100 mL aliquot of methylene chloride. The 4 L bottle was capped with a foil-lined screw cap and briefly shaken to begin the PAH extraction.

**Soil**

Soil samples, for determination of PAH concentrations and general soil properties, were collected with a split spoon sampler during the hollow stem auger drilling of well B. Samples were scooped from the center of the split spoon into acid soaked/solvent rinsed jars with foil-lined screw caps. Samples were stored at -14 °C in the dark for 30 months prior to analysis.

**Coal Tar**

A sample of the liquid coal tar was obtained from the bottom of well D (Figure 1) to provide information about the composition of the source.
material. A dipstick was used to collect the tar sample and allow visual
examination of the contents of this well and other wells. This dipstick consisted
of a 1.2 m section of 1.3 cm (id) glass tubing equipped with a polypropylene
check valve at the bottom. The glass tubing was connected to a 9 m section
of tygon tubing, which could be plugged with a stopper at the surface to
provide suction as the dipstick containing sample was brought to the surface.
On the first attempt to sample the tar in this well, the check valve failed and
much of the coal tar collected in the bottom foot of the dipstick leaked past
the check valve as the dipstick was brought to the surface. The sample
collected in the dipstick on the second attempt provided about 0.3 m of
liquid coal tar in the bottom of the dipstick, clear water above the tar and
several cm of tar (visually the same as the bottom tar) floating on the surface.
The floating tar could be compositionally different from the bottom tar or may
be bottom tar which leaked from the dipstick in the first sampling attempt.
During previous groundwater sampling efforts at this well, tar was found only at
the bottom of this well. The entire content of the dipstick was drained into a 60-
mL BOD bottle. The tar sample was stored in the dark at 8 °C until analysis.

LABORATORY ANALYSIS

Groundwater

Polycyclic Aromatic Hydrocarbons

The methylene chloride extraction of PAHs from groundwater samples
started in the field was continued in the laboratory. PAH were extracted from
the groundwater and the wall of the collection vessel to which very
hydrophobic PAH may sorb (Chapter 3) by adding a glass-coated stir bar to
the sample, then securing the bottle, on its side, to a stir plate. The contents
were stirred for 15 min after which the bottle was rotated allowing the
methylene chloride to contact directly a second portion of the vessel wall. Stirring was then continued another 15 minutes. The 4-L bottle was rotated and stirred a total of five times with a total laboratory extraction time of at least 75 min. Following this first extraction, the methylene chloride was allowed to settle to the bottom of the vessel, then withdrawn using a 100 mL glass LuerlokR syringe connected to a needle of 0.48 cm (id) aluminum tubing via a metal Luer stopcock . Any water drawn into the syringe was allowed to separate, then the methylene chloride was drained into a glass flask. The amount of methylene chloride recovered was determined by weight. A second aliquot of methylene chloride was then added to the groundwater and the extraction sequence repeated two more times.

The extracts obtained by this procedure were subdivided for analysis of the more volatile PAHs present at high enough concentrations to allow analysis without further concentration and the other PAHs present at low concentrations. Three extracts were obtained from each sample bottle. The three extracts were analyzed separately for only one of the 4 - 5 samples collected from each well. Extraction efficiencies were determined from these sets of extracts. Analysis of the third extract of one sample bottle from each well indicated, for each of the PAH quantified, that less than 0.6% of the total amount of each PAH recovered in three extractions remained after the second extraction. Thus, three extractions appear sufficient. For all other samples, the three extracts were combined prior to analysis. The portion of the extracts examined without further concentration were analyzed by direct injection capillary gas chromatography with flame ionization detection (GC-FID, DB5, 30 m, 0.25 μm film thickness capillary column; 45 °C - 270 °C (20 min) @ 8 °C/min). Individual PAH concentrations were quantitated using peak heights of the corresponding PAH in an external standard. The remainder of
the extracts for each bottle were spiked with a set of deuterated PAH internal standards (d10 phenanthrene, d10 pyrene, d12 chrysene, and d12 perylene) and concentrated by rotary evaporation to several mL. Just prior to analysis, the extract was further concentrated under a stream of argon to 0.5 mL. These samples were analyzed by selected ion monitoring gas chromatography mass spectrometry (SIM-GCMS, HP 5995, splitless injection, DB5, 30 m, 0.25 μm film thickness capillary column; 40 °C - 270 °C (20 min) @ 12 or 16 °C/min). Individual PAH concentrations were determined using peak heights of the corresponding PAH in external standards. PAH concentrations quantitated in this manner were corrected to account for any losses during sample concentration steps using the observed recovery of the nearest eluting internal standard. Methylene chloride samples concentrated to 0.5 mL served as blanks. All extracts were stored in the dark at -14°C.

Colloids

Estimates of groundwater colloid concentrations and size distributions were obtained with a laser light scattering (LLS) apparatus (N4 Submicron Particle Analyzer, Coulter Electronics, Hialeah, FL). Colloid concentrations were estimated by comparing observed laser light scattering intensities (counts/sec) with those obtained for known concentrations of colloidal materials of similar size and optical properties. Insufficient quantities of scattering material in all samples prevented size distribution determinations by photon correlation spectroscopy. Instead, the light scattering material size was estimated by measuring LLS intensity of both unfiltered samples and filtered samples. A reduction in scattering intensity of the sample after filtration through a 3 μm or 100 nm pore diameter filter (Nuclepore) suggested that a portion of the scattering material was excluded by the filter pores.
To examine visually colloid size distributions and determine elemental composition of colloids, field filtered groundwater were analyzed by SEM/EDX. Desiccated filters were attached to stubs with double-sided adhesive tape, then coated with gold. These samples were examined with a Cambridge Stereoscan 240 SEM and Link Analytical QX200 EDX system.

**Total (nonvolatile) Organic Carbon**

An estimate of the maximum concentration of organic colloids present in groundwater samples was obtained from total nonvolatile organic carbon analysis (T(nv)OC). Groundwater samples were acidified with phosphoric acid (100 μL of 10% v/v phosphoric acid per 4 mL sample) and purged of inorganic carbon (and unavoidably of some volatile organic constituents as well) by a stream of nitrogen for 5 minutes. Aliquots (50 μL) of purged samples were injected directly into the high temperature (900 °C) combustion chamber of an Ionics Total Carbon Analyzer (Watertown, MA). This instrument utilizes a platinum catalyst to facilitate organic matter oxidation and an infrared detector to measure CO₂ produced. Dilutions of a 1 g/L potassium bipthalate (Mallinckrodt, reagent grade) solution prepared with distilled water were used as standards to quantitate the instrument response.

**Soil**

**Polycyclic Aromatic Hydrocarbons**

PAH concentrations present in soil samples were determined for subsamples of soil from which rocks greater than ~1 cm in length were excluded. These samples were spiked with deuterated internal standards (d10 phenanthrene and d12 perylene) and soxhlet extracted for 24 hr with 10% methanol/90% methylene chloride. The extracts were concentrated by rotary evaporation to ~10 mL and analyzed by GC-FID and SIM-GCMS as above. Spiked solvent blanks were carried through the same procedure.
Soil properties

Soil properties required for prediction of PAH sorption to aquifer material were determined as follows. The fraction of organic carbon (foc) present in the soil was determined on subsamples of soil which were dried, then passed through a # 12 sieve (1680 μm openings). Organic carbon content was determined with a Perkin Elmer 2400 CHN analyzer (925°C combustion temperature) after removal of inorganic carbon by exposure to HCl fumes in a dessicator for 3 days and overnight drying at 60°C (analysis performed by Sue McGroddy at Univ. of Mass., Boston). Multipoint BET analysis with nitrogen was used to determine the surface area of dried and sieved soil samples after outgassing to 20 microns at 200°C (analysis was preformed by Porous Materials Inc., Ithaca, NY). The mineralogy of the soil was determined to be primarily quartz by X-ray diffraction of soil samples which were dried, sieved as above, then ground to pass through a 74 μm sieve. Random powder mounts of this ground material were scanned from 3° - 70° 2θ at 1° 2θ/min with a Diano X-ray generator and a Phillips diffractometer using Ni-filtered Cu Kα radiation. Divergence and receiving slits were 3° and 0.2 mm, respectively.

Coal Tar

The chromatographable composition of the coal tar from the source area was determined for a 100 μL aliquot of the tar (ρ = 1.09 g/mL) diluted to 100 mL with methylene chloride. This sample was analyzed by GC-FID and GC-MS, as above.
RESULTS AND DISCUSSION

GROUNDWATER SAMPLE INTEGRITY

Prior to purging and sampling, the contents of each well were visually examined, using a dipstick, to provide information on the presence and location of tar and sediment. Visual inspection of the contents of well A, within the source area, indicated that no tar or sediment was present in the upper portion of this well (the 12 m dipstick did not sample the bottom 1.5 m of this well). The water in this well was clear. In contrast, well B contained a very floccy orange material (most likely precipitated iron oxide) both in the bottom ~ 0.3 m of the well and ~ 5 cm floating at the water surface. No tar was evident in this well either. Water from well C was clear except for a few centimeters of sediment at the bottom of the well. These materials may not represent in situ groundwater conditions, and must be purged or isolated prior to groundwater sampling. The information provided by the dipstick samples was useful in positioning the pump head and packers within the well to minimize collection of these materials.

Each well was purged at a low flow rate for a prolonged period until water thought to be representative of the formation was being sampled. A well is generally considered sufficiently purged when bulk water chemistry measurements (e.g., pH, Eh, specific conductivity) are observed to level off (Barcelona et al., 1985). Given that the objective of this work was to sample colloids and colloid-associated contaminants, a parameter more indicative of these species, light scattering, was monitored during purging.

Laser light scattering intensity was found to be a good surrogate for monitoring variation in the concentrations of the more hydrophobic PAHs during the purging of well D on our March, 1988 reconnaissance trip (Figure 3).
Figure 3:

The other parameters monitored during the purging of well D did not mimic the PAH concentration variations in time as closely and hence were less indicative of sufficient purging times for organic contaminants and colloids (Figure 4). The pH, Eh, and dissolved oxygen content of the water withdrawn from the well reached a stable value in less than 1 hr of pumping at ~ 150 mL/min (Figure 4). In contrast, the laser light scattering observations did not level off until approximately 2 hr (Figure 3). The jump in scattering intensity at ~ 210 minutes we believe was due to a temporary, unintentional, increase in the pumping rate. This source well was sampled without the benefit of a bottom packer, and so these increases in both light scattering intensity and PAH concentrations may be due to either suspension of bottom materials or increased aquifer material shearing at the higher flow rate. This sampling experience indicated that light scattering intensity was the most useful indicator of required purging times or volumes for both colloids and the more hydrophobic PAHs.

This purging procedure was repeated at wells A, B, and C with the benefit of a bottom packer to determine whether required purging times and volumes were generally applicable from one well to the next. At well A all monitored parameters except light scattering and specific conductivity were found to be relatively constant in time (Figure 5). Little variation in light scattering intensity (Nephelometric Turbidity Units, NTU) was observed after 2 hr of purging at about 100 mL/min. The final values of all parameters monitored are listed in Table 1. All parameters monitored during the purging of well B varied as a function of time; light scattering, Eh, and O2 decreased in time and pH and conductivity increased in time (Figure 6). Light scattering levels appeared to have leveled off after 3 hr of purging at 140 mL/min. Unlike well A however, this parameter did not remain constant throughout the sampling
Figure 4:

Figure 5:

Well A, December 1989: groundwater chemistry parameters observed as a function of time during purging. Light scattering intensity is reported in nephelometric turbidity units (NTU). The dotted line indicates the average background light scatter intensity based on QH20. The time well purging ended and groundwater sampling began is indicated by the arrow on the light scattering intensity graph.
Figures 6:

Well B, December, 1989: groundwater chemistry parameters observed as a function of time during purging. Light scattering intensity is reported in nephelometric turbidity units (NTU). The dotted line indicates the average background light scatter intensity based on QH20. The time well purging ended and groundwater sampling began is indicated by the arrow on the light scattering intensity graph.
period but rather began to decrease again after about 5 hr, then it appeared to level off again before the sampling period ended. This may indicate heterogeneity in groundwater colloid distributions within the aquifer. At well C, light scattering (obtained in the lab as the turbidimeter malfunctioned in the field), Eh, and O2 decreased in time, while pH and conductivity showed no trend (Figure 7).

Some generalizations can be drawn from the purging experience from these three wells. First, parameters other than light scattering intensity did not provide a reliable basis for judging sufficient purging times for collection of groundwater colloids and colloid-associated contaminants representative of conditions within the aquifer. Purging a volume of about 20 L prior to sampling appeared sufficient for all wells except B, which only temporarily leveled off within this purging volume. Required purging volume may be a function of pumping rate as light scattering observations from the wells sampled at less than 100 mL/min (wells A and C) seemed to level off after about 12 L were removed whereas 20 L had to be pumped before scattering intensity leveled off at wells purged at closer to 150 mL/min (B and D). Finally, light scattering intensity appears to provide a good indication of required purging volumes to obtain samples representative of PAH concentrations in formation water. This was supported by both the observed correlation between light scattering intensity and groundwater concentrations for the more hydrophobic PAHs at well D and by the lack of a discernable trend in PAH concentrations in the 4 - 5 samples collected from the other wells after scattering intensity had leveled off.
Figures 7:

Well C, December, 1989: groundwater chemistry parameters observed as a function of time during purging. Light scattering intensity is reported in nephelometric turbidity units (NTU). The dotted line indicates the average background light scatter intensity based on QH20. The time well purging ended and groundwater sampling began is indicated by the arrow on the light scattering intensity graph.
GROUNDWATER COLLOID CONCENTRATIONS

The maximum concentrations of mobile groundwater colloids present near the source and in the downgradient wells were determined by both light scattering intensity and T(nv)OC measurements. Light scattering observations for all groundwater samples analyzed in the field leveled off above those observed for QH2O (Figures 5-7 and Table I). This scattering intensity can be converted to colloid concentrations using colloidal standards with similar size and optical properties. An indication of the size of the colloids present in these groundwater samples was provided by comparison of LLS intensity measurements of unfiltered subsamples and samples filtered through 3 μm and 100 nm pore size filters. These results are reported in Table I for samples collected after approximately 4 hr of purging from well A and B and a set of samples collected after 1, 1.7, 2.8, and 3.5 hr of purging well C. Unlike NTU levels observed in subsamples for this series from well C (Figure 7), LLS results showed no trend in time. Hence averaged values for the four samples are reported. This suggests that the two light scattering instruments on average sample different light scattering populations. The turbidimeter measures the intensity from a much larger window than the LLS analyzer. The variation in turbidimeter response in this series of samples suggests that the change in intensity as a function of time is probably due to the larger but rare particles in the sample which are represented in the large window of the turbidimeter but only occasionally intersect the laser beam. Most of the light scattering in groundwater from wells B and C was attributable to colloids in the size range between 3 μm and 100 nm. The observed light scatter intensity in the sample from well A was due predominantly to colloids less than 100 nm in diameter. SEM of field filters qualitatively confirm these size distributions. The particles analyzed by SEM/EDX were predominantly silica or clay-like (silicon
<table>
<thead>
<tr>
<th>Parameter</th>
<th>well A</th>
<th>well B</th>
<th>well C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>1.5</td>
<td>2.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Eh (volts)</td>
<td>-0.3</td>
<td>0.3</td>
<td>0.78</td>
</tr>
<tr>
<td>pH</td>
<td>6.4</td>
<td>6.2</td>
<td>6.2</td>
</tr>
<tr>
<td>O₂ (ppm)</td>
<td>1.2</td>
<td>0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Conductivity (μmhos)</td>
<td>1700</td>
<td>260</td>
<td>550</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>9.5</td>
<td>13</td>
<td>11</td>
</tr>
<tr>
<td>T(nv)OC (mg C/L)</td>
<td>5.0</td>
<td>4.8</td>
<td>6.1 ± 0.7 (n=7)</td>
</tr>
</tbody>
</table>

| LLS (counts/sec)        |        |        |            |
| unfiltered sample       | 440    | 2200   | 2500       |
| % remaining after       |        |        |            |
| 3 μm filtration         | NA     | 100    | 76         |
| % remaining after       |        |        |            |
| 100 nm filtration       | 93     | 17     | 18         |

NA = not analysed
and aluminum with minor potassium and iron peaks). These observations of
groundwater colloid size and composition justify the use of kaolin standards to
quantify colloid concentrations. Kaolin concentration in units of mg/L
correspond very closely to NTUs. Hence only a few mg/L of light scattering
colloids were found in these groundwater samples. Both colloid size and
composition observations were consistent with their existence as mobile
species in groundwater.

Organic colloids such as humic materials at low levels (mg/L) are not
detectable by light scattering and are too small to be resolved by SEM. The
maximum quantity of these materials present in groundwater samples was
determined from T(nv)OC (dissolved + colloidal organic carbon)
measurements (Table I). As with the light scattering colloids, at very most
several 5 - 6 mg/L of macromolecular organic colloids were present in these
groundwater samples. Organic macromolecules were probably not present
in concentrations very different than the ~ mg/L levels commonly observed
for uncontaminated groundwaters (Leenheer et al., 1974)). Apparently coal
tar does not contribute substantial quantities of organic macromolecules to
the surrounding groundwater.

A concern in interpreting groundwater colloid data is that observed
colloids are artifacts of the well construction and sampling procedures. One
way to test this concern is to compare colloid results obtained from wells within
the contaminant plume with those from "background" wells. If colloid
formation and mobilization were a result of the contamination, and no
colloids were observed in a similarly constructed and sampled well outside
the contaminant plume, then one might conclude that observed colloids
were not artifacts. As colloids were found in all wells sampled at this site we
cannot be certain they were not artifacts. On the other hand, great care was
taken in sampling the groundwater to minimize sampling artifacts. Further, wells were constructed using the least disruptive well construction method, hollow stem augur drilling, requiring no drilling muds which could add artifact colloids to the near well environment (Buddemeier, 1986; Ryan, 1988). Though bentonite was used in the construction of well A, we have some confidence that colloids observed at this well were not artifacts of the bentonite seal as colloids were observed in wells not constructed with this material. Nonetheless, the colloid observations do provide an estimate of the maximum mobile colloid load in the groundwater, and this maximum was was found to be quite low (< 10 mg/L).

POLYCYCLIC AROMATIC HYDROCARBONS DISTRIBUTIONS

Near the Source

Observed PAH concentrations in the source area groundwater can be used to determine whether the colloids present sorb significant quantities of these contaminants, thereby increasing the mobile PAH load. This was accomplished by comparing observations with expected PAH concentrations based on dissolved phase partitioning between the coal tar and the groundwater. Measured PAH concentrations higher than those expected could suggest colloid-associated PAHs were present.

The expected concentrations of individual PAHs in groundwater equilibrated with coal tar were estimated as the product of the mole fraction of the PAH present in the coal tar and the aqueous solubility (hypothetical liquid solubility in the case of PAHs which are solids at groundwater temperature) of the PAH. The weight fractions of some of the PAH present in the coal tar were quantitated (Table II). These PAH represent the range of PAH present in this coal tar (Figure 8). Approximately 30% of the tar by weight
TABLE II: PAH concentrations in coal tar and expected aqueous concentrations in equilibrium with coal tar

<table>
<thead>
<tr>
<th>PAH</th>
<th>(PAH) in coal tar (mg/g tar)</th>
<th>hypothetical liquid solubility (10°C) (µg/L)</th>
<th>expected (PAH) in water equilibrated with coal tar (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>140±78</td>
<td>8.9 x 10^4</td>
<td>1.2 x 10^4 (1.4 x 10^4)**</td>
</tr>
<tr>
<td>1-Methyl Naphthalene</td>
<td>27</td>
<td>2.8 x 10^4*</td>
<td>770 (810)*</td>
</tr>
<tr>
<td>Di-Methyl Naphthalene</td>
<td>12</td>
<td>8 x 10^3*</td>
<td>96 (92)*</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>17±1.1</td>
<td>3.3 x 10^3</td>
<td>56 (47)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>7.4±2</td>
<td>2.0 x 10^3</td>
<td>15 (11)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>4.0±1.4</td>
<td>200</td>
<td>1.1 (0.75)</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>2.5±1.3</td>
<td>30</td>
<td>0.073 (0.044)</td>
</tr>
</tbody>
</table>

n = 2 for all means and std dev.

Solubility data from May et al., 1978 and ΔSt values from Yalkowsky and Valvani, 1980 or if unknown 13.5 cal/mole was used in calculation of hypothetical liquid solubilities.

* 25 °C solubility data (Miller et al., 1985) used in calculations.

** calculated assuming PAH wt fraction = mole fraction in the tar or assuming the molecular weight of the tar is 150 g/mole, in parentheses.
Figure 8:

Chromatogram of coal tar; attenuation changes are indicated.
was chromatographable. Most of the chromatographed peaks were identified as PAH and alkyl substituted PAHs. Naphthalene represented 14 percent of the tar by weight. The weight fractions of the individual PAH quantitated in Table II are very similar to those reported for a coal tar by Groher (1989) and are within a factor of 5 for other coal tars and coal oils reported in the literature (McNeil, 1985; Nishioka et al., 1986; Picel et al., 1988). The mean molecular weight of coal tar is not known, so the mole fractions of individual PAHs in the tar were estimated either by assuming the mole fraction and weight fraction were equal or assuming a molecular weight for the tar (e.g., 150 g/mole, Picel et al., 1988). The expected concentrations of PAHs estimated using both these assumptions and estimates of the liquid solubilities of these PAH at 10 °C are reported in Table II.

To use these estimates of expected PAH concentrations in determining the role of colloids, we must have some confidence that this calculation provides accurate predictions. This is provided by comparing literature observations of PAH concentrations reported in water equilibrated with coal tars or oils with expectations calculated as above. Picel et al. (1988) reported both concentrations of a number of PAHs in a coal oil and in water equilibrated with that material. The calculated concentrations of naphthalene, phenanthrene, and pyrene in equilibrium with a coal oil, assuming the weight fraction of these PAH in the tar reflects the mole fraction, were 64%, 91%, and 28% of the values observed by Picel et al. (1988). If the mole fraction of these PAHs in the tar was calculated using an estimated molecular weight for the tar of 150 g/mole, calculated equilibrium concentrations were 55%, 77%, and 38% of those observed for naphthalene, phenanthrene, and pyrene, respectively. Calculated concentrations are within a factor of ~3 of those observed. Groher (1989) too found that estimates
assuming a molecular weight for coal tar of 150 g/mole were within a factor of 2 - 3 of the observed aqueous concentrations of a series of PAH equilibrated with coal tar.

PAH concentrations exceeding predictions (Table II) by more than a factor of 3 could indicate that colloid association is important. Additionally, as colloids are expected to have an increasing influence with increasing contaminant hydrophobicity, the relative concentration ratios of a series of PAH may be indicative of colloid-PAH association as well. The PAH concentrations observed at well A were not in excess of those expected based on dissolved phase partitioning of PAH from coal tar (Tables II and III). Further, the groundwater was not systematically enriched in the more hydrophobic species relative to more soluble species as would be expected if colloids affected PAH mobile load. The same general conclusions can be drawn from groundwater sampled from well D on the reconnaissance trip. The PAH concentrations observed in this groundwater (Figure 3, minimum points), however, were much higher than those observed at well A. In fact, observed PAH concentrations were quite close to those predicted for groundwater equilibrated with coal tar. The observed concentrations of all PAH quantitated with the exception of chrysene were within a factor of two of those predicted assuming weight fraction of naphthalene in the tar represents its mole fraction (Figure 3 and Table II). The minimum combined chrysene and benzoanthracene concentration (these peaks were not resolved in these analyses) is 4 times that expected. The more hydrophobic PAH levels observed were more suspect than those for the more soluble PAH. This well contains tar and was sampled without the benefit of a bottom packer to isolate fully the tar from the pump inlet. Entrainment of just 1 μL of tar in a liter of groundwater would account for most
<table>
<thead>
<tr>
<th>PAH</th>
<th>well A</th>
<th>well B</th>
<th>well C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>1000 ± 280</td>
<td>1800 ± 200</td>
<td>0.32 ± 0.17</td>
</tr>
<tr>
<td>1-Methyl Naphthalene</td>
<td>470</td>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>Di-Methyl Naphthalene</td>
<td>200</td>
<td>160</td>
<td>1</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>84 ± 32</td>
<td>15 ± 1.6</td>
<td>0.87 ± 0.22</td>
</tr>
<tr>
<td>Pyrene</td>
<td>5.4 ± 1.2</td>
<td>0.6 ± 0.09</td>
<td>0.71 ± 0.11</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.16 ± 0.06</td>
<td>0.13 ± 0.05</td>
<td>0.18 ± 0.06</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.057 ± 0.007</td>
<td>0.064 ± 0.01</td>
<td>0.11 ± 0.03</td>
</tr>
</tbody>
</table>

n = 3 - 7 for all means and std deviation
of the pyrene and chrysene in this sample. The most soluble PAHs were less susceptible to such sampling artifacts. The quantitative differences between groundwater sampled from the two source wells suggest there is some variability in the source region. These observations indicate that the low concentrations of colloids present in source area groundwater were not sufficient to significantly augment the PAH mobile load.

**Downgradient Wells**

Predictions based on dissolved phase alone or dissolved plus colloid-associated transport of PAHs from the source region to downgradient wells can be used to assess the role of colloids at this site. Colloids were expected to both increase the distance a contaminant traveled in a given amount of time and change the fingerprint of a series of PAHs relative to that expected for dissolved phase transport alone. As groundwater is advected and dispersed away from the source area, PAHs are selectively (based on hydrophobicity) removed from the groundwater by sorption to aquifer material. Colloids increase the mobile fraction of the contaminant and thereby reduce contaminant retardation due to sorption to aquifer material. The degree of colloid-association is a function of contaminant hydrophobicity. Hence, if colloids were present, an enrichment in the more hydrophobic PAH would be expected at downgradient locations.

A 1-dimensional contaminant transport model was used to predict PAH concentrations at downgradient locations. This model allows for contaminant advection and dispersion with the groundwater (as dissolved and colloid-associated species) and retardation by sorption to aquifer material (Table IV, Equations 1 and 2). The possibility of contaminant losses by volatilization or degradation were not accounted for in this simple model. Volatilization to the unsaturated zone may affect naphthalene concentrations in groundwater.
TABLE IV: Modeling Equations and Parameter Definition

ONE DIMENSIONAL CONTAMINANT TRANSPORT IN POROUS MEDIA

\[ \frac{dC}{dt} = \left( \frac{D_x}{R} \right) \frac{d^2C}{dx^2} - \left( \frac{V_x}{R} \right) \frac{dC}{dx} \quad (IV - 1) \]

RETARDATION COEFFICIENT

\[ R = 1 + \frac{p_b}{n} \left[ \frac{f_{oc} \cdot K_{oc} + f_i \cdot K_i}{1 + [(OC)K_{ocoll} + (IC)K_{ic}]} \right] \quad (IV - 2) \]

SOLUTION FOR ADVECTION AND DISPERSION IN THE DIRECTION OF GROUNDWATER FLOW WITH A CONTINUOUS PLANE SOURCE

BOUNDARY CONDITIONS:

\[ C(x,0) = 0 \text{ for } x \geq 0 \]
\[ C(0,t) = C_0 \text{ for } t \geq 0 \]
\[ C(\alpha,t) = 0 \text{ for } t \geq 0 \]

\[ \frac{C}{C_0} = \frac{1}{2} \left[ \text{erfc} \left( \frac{x - V_x/R}{2 \sqrt{D_x \cdot t/R}} \right) + \exp \left( \frac{X \cdot V_x/R}{D_x / R} \right) \text{erfc} \left( \frac{x + V_x/R}{2 \sqrt{D_x \cdot t/R}} \right) \right] \quad (IV - 3) \]

SOLUTION FOR LATERAL DISPERSION OF CONTAMINANTS \( V = 0 \)

\[ \frac{C}{C_0} = \text{erfc} \left[ \frac{Z}{2 \sqrt{D_z \cdot t/R}} \right] \quad (IV - 4) \]
TABLE IV cont.

PARAMETER DEFINITION:

\( C \) = groundwater contaminant concentration
\( t \) = time, maximum time of source exposure = 50,000 days
\( x \) = distance from the source, well 7s = 46 m, well 9s = 76 m
\( V \) = average linear groundwater velocity, 0.3 m/day
\( D \) = coefficient of hydrodynamic dispersion = \( \alpha_x V + D_m^* \)
\( \alpha_L \) = longitudinal dispersivity
\( \alpha_z \) = transverse downward dispersivity
\( D_m^* \) = tortuous molecular diffusion coefficient
\( \rho_B \) = aquifer material bulk density = 1.85 g/mL
\( n \) = aquifer porosity = 0.3
\( f_{oc} \) = fraction of organic carbon of the soil = 0.005
\( f_i \) = fraction of available inorganic soil surface = 0.9 m²/g
\( (OC) \) = organic colloid concentration, maximum = 6 mgOC/L
\( (IC) \) = inorganic colloid concentration, maximum = 2 mg kaolin/L
\( K_{OC} \) = partition coefficient to organic carbon, calculated from a regression using PAH \( K_{OW} \) (Karickhoff et al., 1979; Miller et al., 1985)
\( K_I \) = partition coefficient to inorganic surface, calculated from regression using aqueous activity coefficients (Chapter 3; this thesis; Miller et al., 1985)
\( K_{OColl} \) = partition coefficient to organic carbon fraction of the organic colloids estimated as PAH \( K_{OW} \) (Karickhoff et al.)
\( K_{IC} \) = partition coefficient to inorganic surface, calculated from regression using aqueous activity coefficients assuming the colloids are kaolin-like (Chapter 3; this thesis; Miller et al., 1985)
near the water table but was not expected to be as important for the other 
PAHs. The Henry's Law constants for phenanthrene and pyrene, for example, 
are 8% and and 2% of that for naphthalene. PAHs were assumed to be 
geochemically stable. This is not a bad assumption for most PAHs in anoxic 
(as suggested by Eh measurements) groundwater, though there is some 
evidence that naphthalene is degraded under denitrifying conditions 
(Mihelcic and Lathy, 1988). Expected PAH concentrations in groundwater at 
downgradient locations from the source material were obtained from the 
solution to Equation 1 using boundary and initial conditions representing a 
continuous plane source (Table IV).

Predictions based on dissolved phase transport alone provide a 
basis for determining the role of colloid-associated transport between the 
source and downgradient wells. The predicted groundwater concentrations 
relative to source groundwater concentrations are plotted as a function of 
distance from the source for a series of PAHs at t = 50,000 days after source input 
(Figure 9a). This is a maximum estimate of input time given the plant operation 
dates. An average linear groundwater velocity of 0.3 m/day, consistent with 
hydraulic conductivity and head measurements at this site, and a longitudinal 
dispersivity, \( \alpha_L \), of 1 m were used for these predictions. The field scale 
longitudinal dispersivity for this site is unknown. The longitudinal dispersivity used 
for predictions in Figure 9 was estimated from a correlation of observed 
dispersivity as a function of distance over which it was determined (Anderson, 
1979). This estimate is on the same order as those observed for other sandy 
aquitifers over similar distances (Egboka et al., 1983; Sudicky et al., 1983; 
Garabedian et al., 1987). Using these parameters, naphthalene and methyl 
naphthalene concentrations at or close to those in the source area (C0) were 
expected at distances from the source corresponding to the locations of
Figure 9: Model predictions of C/Co values as a function of distance (in the direction of groundwater flow) from the source at well cluster A/D at $t = 50,000$ days

(a) dissolved phase transport only
   (insert) model sensitivity to $\alpha_L$ value for phenanthrene

(b) dissolved plus colloid-associated transport
   (insert) comparison of dissolved and dissolved plus colloid-associated predictions

a  naphthalene
a1 methyl naphthalene
a2 di-methyl naphthalene
b  phenanthrene
c  pyrene
d  chrysene
e  b(a)p

observed groundwater concentrations at well B relative those measured at source well A are indicated by the open symbols
wells B (46 m) and C (76 m). Di-methyl naphthalene concentrations less than 1/10 of groundwater concentrations leaving the source area were predicted at well B. Observable levels of the more hydrophobic PAHs were not expected at these distances from the source even after 137 years.

Observed concentrations of the series of PAHs quantitated in groundwater at well C did not match predicted concentrations based on dissolved phase transport. Naphthalene and methyl naphthalene levels at this well were only a fraction of a percent of those predicted using any of the three estimates of $C_0$ (Tables II and III and Figure 3). Though higher than PAH concentrations generally reported for uncontaminated groundwaters (0.001 - 0.01 μg/L, Dzombak and Lethy, 1984), these low concentrations of all PAHs in groundwater from this well may represent "background" levels at this site. PAHs are components of most fuels and are ubiquitous byproducts of combustion. This site is located in an industrial area, hence PAH concentrations exceeding those in uncontaminated groundwater are not surprising. If well C water did represent background levels across the site, there is little chance of distinguishing coal tar contaminated (e.g., expected in equilibrium with pure coal tar) groundwater from uncontaminated (e.g., well C) groundwater by observed b(a)p concentrations. All other PAHs quantitated were expected to be above "background" levels in water in equilibrium with tar. The discrepancy between observed and predicted PAH concentrations at this well indicate that either loss mechanisms not accounted for in the model depleted the groundwater of naphthalene and methyl naphthalene or that well C is not in the direct flowpath of the contaminant plume.

There was a discrepancy between observed and predicted levels of PAHs at well B as well. Higher than expected levels of naphthalene, methyl naphthalene, dimethyl naphthalene, and phenanthrene, based on $C_0$
values estimated as observed PAH concentrations at well A (Table III) were found at well B. Naphthalene and methyl naphthalene were found at levels nearly twice those expected. Dimethyl naphthalene was found at 16 times the expected value. Phenanthrene, not expected to be present at observable levels at this distance from the source, was present at a concentration nearly 20% of that in the source area at well A (Figure 9a). With the exception of naphthalene, similar findings were obtained using PAH concentration observations at well D as C₀ values (Table III and Figure 3). In this case naphthalene is found to be only 1/10 that expected, while the other three PAH were at levels in excess of that expected. If the assumed C₀ value in this case was correct, the lower-than-predicted naphthalene level could indicate that this PAH is lost by mechanisms not accounted for in the simple model. Possible explanations for the observations in excess of predicted levels include underestimation of the groundwater velocity and dispersion coefficient or colloid enhanced transport.

The longitudinal dispersivity was the least known parameter used in the model. The value of 1 m used in the preceding predictions is reasonable based on literature values as indicated above. It is possible that a higher dispersivity was more appropriate for this aquifer. The aquifer material at this site is not homogeneous. Observations during drilling and digging at this site indicate the aquifer material is quite heterogeneous. Material ranging from clay flakes and sand grains to boulders were found. Higher dispersivities are expected for more heterogeneous aquifers. The effect of increasing the longitudinal dispersivity on model predictions of phenanthrene concentrations are indicated in the insert if Figure 9a. An αₐ value of about 10 m is required to match the observed phenanthrene concentration at well B.
Another possible explanation for higher-than-expected concentrations of PAHs at well B is that colloids have enhanced the transport of these contaminants. This possibility can be added to the transport model by including estimates of colloid-association in the calculation of the retardation coefficient (Table IV, Equation 2). Both the levels of colloids and contaminant partition coefficients were assumed to be constants both temporally and spatially. Colloid-associated contaminants were assumed to be advected and dispersed in the same manner as dissolved species, and sorptive equilibrium is assumed to apply to both colloids and aquifer material.

Estimates of maximum colloid levels from light scattering ([IC] = 2 mg/L) and T(nv)OC ([OC] = 6 mg/L) measurements were used to determine whether colloid-associated transport could be used to explain observations at well B. Partition coefficient for organic colloids were estimated as the PAH K_{OW}. For inorganic colloids (light scattering material) the partition coefficient, K_{IC}, was estimated from a regression for kaolin (Chapter 3). Both of these estimates err on the side of overestimation of colloid-PAH association. Predictions of PAH concentrations at well B using these assumptions were not very different from those found for dissolved phase transport alone (Figure 9). These levels of colloids can significantly enhance the transport of the more hydrophobic PAH (Figure 9b, insert), but their effect is only noticeable at closer distances to the source. Hence, present day levels of colloids in the groundwater at this site cannot be used to explain higher-than-expected concentrations of PAH at well B.
SUMMARY AND SPECULATION

SUMMARY

Low levels (< 10 mg/L) of colloids were observed in groundwater near the source and at downgradient wells using a sampling protocol designed to minimize creation of artifactual colloids. The presence of colloid-associated PAHs were not required to explain observed PAH concentrations in the source region. PAH concentrations at or below levels expected based on dissolved phase partitioning of these contaminants between the coal tar and groundwater were found at the source area. This is contrary to previously obtained observations at this site and others using less careful sampling methods (Villaume et al., 1983; Gschwend et al., 1988; Groher, 1989).

Predictions of PAH concentrations at well B using maximum observed concentrations of colloids in groundwater at this site were not found to be noticeably different from predictions based on dissolved phase transport alone. Though colloids at these levels were expected to significantly enhance the transport of the more hydrophobic PAHs, their effect would only be observable at locations nearer the source. Our attempts to install wells to obtain groundwater from these locations were unsuccessful. Hence, the importance of colloids at shorter distances cannot be ruled out at this point.

SPECULATION

The higher-than-expected levels of PAHs observed at well B remain to be explained. As noted above, a longitudinal dispersivity 10 times that typically observed on similar field scales could explain observations. Another possibility is suggested by observations of PAH concentrations observed in soil samples collected during the drilling of well B. Soil samples from depths
above, below ground level with the source material location were analyzed for PAHs (Figure 1). From predictions and observations of PAH concentrations at well B we did not expect to find pyrene, chrysene or b(a)P concentrations above background levels. If soil from 7.9 - 8.5 meters below the ground surface represents background PAH levels in aquifer material, we found all PAHs at levels exceeding the background in at depths between 4.3 and 6.7 m below the ground surface at well B (Figure 10). We note that reported depths for these soil samples, obtained by split spoon sampling during drilling, may not accurately reflect the true depth at which they resided in the aquifer. Reported depths probably overestimate the true depths. Additionally, we cannot be absolutely certain that PAH levels found at depths below the peak at 4.9 - 5.5 m were not due to downward smearing of contaminants during drilling and sampling. It is certain however that higher than expected levels of PAHs were found in soil near the water table at this well.

The levels of PAH found in this soil are suggestive of the presence of pure coal tar at this location. This can be seen by comparing the fingerprints of PAH distributions found in soil to those of coal tar itself and groundwater equilibrated with coal tar (Figure 11). The expected fingerprints of PAH in soil equilibrated with groundwater from wells B and C are provided for comparativ,. purposes as well. Qualitatively the fingerprints of both coal tar itself and that expected for soil equilibrated with source area groundwater are quite similar to that observed at soil depths from 4.9 - 6.7 m. Quantitatively, the observed soil concentrations exceed those expected for soil equilibrated with groundwater from well B and surprisingly, even that equilibrated with source area groundwater (Figure 11). These observations are consistent with the presence of coal tar in the soil at B. PAHs were expected to partition to a greater extent into coal tar than a comparable
Figure 10:

Depth profiles of PAH concentrations in soil samples and soil foc and surface area measurements.
Figure 11:

PAH fingerprints observed in soil samples collected from the depths indicated, and in pure coal tar and predicted for soil in equilibrium with groundwater equilibrated with coal tar (pred. tar/gw), groundwater collected from well B (pred. B gw), and groundwater collected from the "background" well (pred. C gw).

a  naphthalene
b  phenanthrene
c  pyrene
d  chrysene
e  b(a)P
SOIL FINGERPRINTS

[PAH] (µg/g Soil) or (mg/g Tar)

soil depth below ground surface (m)

pred tar/gw pred B gw pred C gw

tar 1.2-1.8 4.3-4.9 4.9-5.5 5.5-6.1 6.1-6.7 7.9-8.5

c d e a b c d e

1E-2 1E-1 10 100 1000
quantity on an organic carbon basis of natural soil organic matter. The
presence of coal tar near well B could be due to migration of tar from the
source area to well B via spreading along the water table.

The contribution of this additional source of PAHs to contamination of
groundwater collected from about 6 m below the ground surface can be
determined from model predictions of downward diffusion or dispersion of
contaminants. In this case, the transport equation is solved assuming the
downward groundwater velocity is zero (Table IV Equations 1 and 4). If the tar
source at well B was confined to the water table depth ~ 5 m below the
ground surface, the likelihood of groundwater contamination observed at 6
m below the surface by this source can be determined. This source is not
expected to contribute significant quantities of any PAH to groundwater 1 m
below the source if the downward dispersion coefficient was near that
expected for tortuous molecular diffusion (Figure 12a). This source was
expected to contribute naphthalene and methyl naphthalene to the
groundwater at 6 m if a vertical dispersivity similar to that observed in a sandy
aquifer on Cape Cod (Garabedian et al., 1987) was more appropriate
(Figure 12b). Using this dispersivity, this source at B will only contribute dimethyl
naphthalene and phenanthrene to groundwater at 6 m if the source is closer
than 1 m. This is entirely possible if the observed depth profiles in the soil truly
exist in the aquifer. Coal tar migrating across the water table which may
fluctuate seasonally could distribute tar over a range of soil depths. The
existence of coal tar sources at both well cluster A/D and in the soil at well B
can be used to provide a reasonable explanation for observed
concentrations of PAH at well B. The combination of dissolved phase
transport of PAH by advection and dispersion of groundwater, initially
containing PAHs at levels near those observed at well A, and vertical
Figure 12: Model predictions of C/Co values as a function of depth below the source (assumed to be at the water table) at t = 50,000 days

(a) predictions for tortuous molecular diffusion

(b) predictions with transverse dispersion similar to that found near Otis Air Base, Cape Cod, MA

a naphthalene  
a1 methyl naphthalene  
a2 di-methyl naphthalene  
b phenanthrene  
c pyrene  
d chrysene  
e b(a)p

Observed groundwater concentrations at well B relative those measured at source well A are indicated by the open symbols.

x on a given curve indicates the observed PAH value in groundwater collected from well B relative to that measured in groundwater from source well A for the corresponding PAH
MOLECULAR DIFFUSION
\[ D = 8.6 \times 10^{-6} \text{ m}^2/\text{day} \]

HYDRODYNAMIC DISPERSION
\[ D = 4.5 \times 10^{-4} \text{ m}^2/\text{day} \]
dispersion of PAH from source material near the water table at well B may be responsible for observed groundwater PAH concentrations from well B.
LITERATURE CITED


for polycyclic aromatic hydrocarbon binding to dissolved humic materials. ES&T 20: 1162-1166.


Chapter 5

Conclusions
In this thesis, the importance of colloids in the transport of hydrophobic organic contaminant was examined. The findings of this work are as follows.

**Summary**

A fluorescence quenching method useful for screening groundwater samples for organic colloids capable of sorbing hydrophobic organic compounds was described. The advantages of this method are that binding can be examined under *in situ* conditions without isolation, fractionation, or equilibrated phase separation steps. The limitation of this method is our limited knowledge of the quenching efficiency of groundwater OC for PAH probes. Two types of OC Aldrich humic acids and bovine serum albumin were found to have different quenching efficiencies. This method was used to determine the potential for colloid-associated transport of hydrophobic organic contaminants in groundwater downgradient of a secondary sewage recharge facility. Organic colloids capable of sorbing significant quantities of perylene (and by implication other contaminants with $K_{ow}$ values on the order of $\geq 10^6$) were present in two downgradient wells, but only at certain times of the year. The presence of these colloids could double the transport of very hydrophobic contaminants, but will have little effect on the transport of less hydrophobic species. The organic colloids present within the plume represented a major fraction of the TOC. This work indicates that colloids capable of binding hydrophobic organic contaminants do exist in groundwaters.

The sorption of nonpolar hydrophobic organic compounds to inorganic surfaces was investigated. The sorption studies indicate sorption is complete within hours, sorption isotherms are linear up to aqueous phase saturation.
sorption increases with increasing organic compound aqueous activity coefficient, and sorption of a given compound to a series of surface types results in similar association constants for all surfaces if normalized by available surface area. These features are consistent with an adsorption mechanism where association of the organic compound is primarily driven by the interactions and organization of the solvent water rather than by specific enthalpic interaction of the organic compound and the inorganic surface. This work provides a predictive relationship for sorption of organic compounds to inorganic surfaces. Caution must be exercised in using such a predictive correlation outside the bounds (compound family and sorbent types) of this work. This correlation suggests that sorption to inorganic surfaces will be important for low organic carbon materials with high available surface areas and very hydrophobic organic compounds. The implications of this work lie in the areas of inorganic colloid-enhanced transport of hydrophobic contaminants in low organic carbon environments, and retardation of hydrophobic contaminants by low organic carbon aquifer materials or in high surface area clay liners.

The carefully collected (at low flowrates, after extensive well purging, and maintaining in situ conditions throughout sampling and storage) groundwater samples, soil, and coal tar samples examined from a coal tar waste site indicate that concentrations observed in soil and groundwater from wells downgradient of the coal tar source are not consistent with dissolved phase advection and dispersion (using typical longitudinal dispersion coefficients) of organic contaminants with the groundwater. Though colloids were found in the carefully collected groundwater samples from all wells sampled, the low concentrations observed were not sufficient to
account for the higher than expected concentrations of the more hydrophobic polycyclic aromatic contaminants found at the downgradient well. The distribution of contaminants in this aquifer downgradient of the source are best attributed to the lateral spreading of coal tar source material downgradient along the water table or past transport of colloidal coal tar packets with subsequent capture of at least a portion of the tar by aquifer material at the downgradient well. The study suggests that determination of the dominant mode of contaminant transport using a limited set of groundwater samples only could yield misleading results.

Questions Remaining and Possibilities for Future Work

In general this work indicates that colloids capable of sorbing hydrophobic organic contaminants do exist in groundwater. At the two sites examined in this study, low concentrations (~mg/L) were found. These low levels are expected to enhance the transport of only very hydrophobic contaminants. It would be very useful to examine additional contaminated sites to determine whether low colloids levels are common or the exception, and whether all colloids found can significantly sorb contaminants present.

Though relatively simple and elegant, the fluorescence quenching method described in Chapter 2 has the main limitation that the fluorescence quenching efficiency of all organic colloids is not known and may not be 100%. Examination of fluorescence quenching efficiency of groundwater organic colloids or a means of predicting the efficiency would be useful. Static quenching of a fluorophore is a result of the quencher providing an alternative pathway for return from the excited to the ground state. If the time scale of this pathway is much faster than the release of a photon, quenching will be observed on association. The quenching efficiency is expected to be
a function the effectiveness of functional groups in close proximity to the 
"binding region" to provide for fast return to the ground state. Hence 
qualitative information on the nature of groundwater OC would be useful both 
to gain a better understanding of quenching efficiency and to understand 
the reasons for the temporal variability observed in quenching and 
association. Groundwater sampling should be conducted temporally at 
other sites to determine whether this complicating phenomenon is a 
common occurrence.

The work reported in Chapter 3 provides a basis for understanding 
inorganic surface: nonpolar organic compound association but, further work 
must be done to fully elucidate the sorption mechanism. This work could 
include examination of sorption at different temperatures to determine 
sorption enthalpies, and investigation of surfaces with very different surface 
characteristics.