Effects of experimental conditions on the sorption of organic compounds to soils and sediments

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Effects of experimental conditions on the sorption of organic compounds to soils and sediments

Abstract
Sorption is the basis for a number of techniques used to characterize solid particles. Because a number of techniques are based on sorptive interactions which are not fully understood, they are often plagued by experimental inconsistencies that are difficult to explain and frequently ignored. The purpose of this dissertation is to examine two techniques that are complicated by experimental inconsistencies--surface area measurements and the determination of distribution coefficients.

The apparent surface area of illite was measured by adsorption of a cationic fluorescent dye, Pyronin-y, from aqueous solutions in which pH and ionic strength were systematically varied. Estimates were highly dependent on pH, while ionic strength effects depended on the composition and pH of the buffer solutions. A complete lack of sorption of the anionic dye, New Coccine, to illite was also observed. Results indicated that the interactions between illite and dyes were primarily electrostatic.

Variations in experimental procedures frequently result in a wide range of distribution coefficients measured for a single compound. Distribution coefficients have been reported to vary inversely with the solid-to-solution ratio used to measure coefficients. One explanation attributes this effect to the production of microparticulates during batch equilibration and the subsequent inability to separate these particles from the aqueous phase. A mathematical model was developed which highlights the effect microparticulates can have on the measurement of distribution coefficients when different methods of analysis are used. Distribution coefficients measured using the counting of radiolabelled analytes will be underestimated and can vary significantly with sediment concentration. Distribution coefficients measured by fluorescence quenching will be overestimated and will only be slightly influenced by sediment concentration. These predictions were supported on a qualitative basis by distribution coefficients measured for the sorption of anthracene to sediment using radiolabelling and fluorescence quenching techniques. To further evaluate this theory, the effect of equilibration time, type of agitation, sediment concentration and separation efficiency on the production of microparticulates during a batch equilibration experiment were studied. Based on total organic carbon concentration and conductivity measurements for the aqueous phase, sediment concentration was found to be the only variable which significantly influenced the production of microparticulates.

Keywords
Chemistry, Analytical, Environmental Sciences

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EFFECTS OF EXPERIMENTAL CONDITIONS ON THE SORPTION OF ORGANIC COMPOUNDS TO SOILS AND SEDIMENTS

BY

KATHY BOOTH BRITTON
B.A., Wheaton College, 1982

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy

in

Chemistry

May, 1988

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This dissertation has been examined and approved.

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DEDICATION

To my family
ACKNOWLEDGEMENTS

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ABSTRACT

EFFECTS OF EXPERIMENTAL CONDITIONS ON THE SORPTION OF ORGANIC COMPOUNDS TO SOILS AND SEDIMENTS

by

Kathy Booth Britton
University of New Hampshire, May 1988

Sorption is the basis for a number of techniques used to characterize solid particles. Because a number of techniques are based on sorptive interactions which are not fully understood, they are often plagued by experimental inconsistencies that are difficult to explain and frequently ignored. The purpose of this dissertation is to examine two techniques that are complicated by experimental inconsistencies - surface area measurements and the determination of distribution coefficients.

The apparent surface area of illite was measured by adsorption of a cationic fluorescent dye, Pyronin-y, from aqueous solutions in which pH and ionic strength were systematically varied. Estimates were highly dependent on pH, while ionic strength effects depended on the composition and pH of the buffer solutions. A complete lack of sorption of the anionic dye, New Coccine, to illite was also observed. Results indicated that the interactions between illite and dyes were primarily electrostatic.

Variations in experimental procedures frequently result in a wide range of distribution coefficients measured for
a single compound. Distribution coefficients have been reported to vary inversely with the solid-to-solution ratio used to measure coefficients. One explanation attributes this effect to the production of microparticulates during batch equilibration and the subsequent inability to separate these particles from the aqueous phase. A mathematical model was developed which highlights the effect microparticulates can have on the measurement of distribution coefficients when different methods of analysis are used. Distribution coefficients measured using the counting of radiolabelled analytes will be underestimated and can vary significantly with sediment concentration. Distribution coefficients measured by fluorescence quenching will be overestimated and will only be slightly influenced by sediment concentration. These predictions were supported on a qualitative basis by distribution coefficients measured for the sorption of anthracene to sediment using radiolabelling and fluorescence quenching techniques. To further evaluate this theory, the effect of equilibration time, type of agitation, sediment concentration and separation efficiency on the production of microparticulates during a batch equilibration experiment were studied. Based on total organic carbon concentration and conductivity measurements for the aqueous phase, sediment concentration was found to be the only variable which significantly influenced the production of microparticulates.
CHAPTER I

GENERAL OVERVIEW OF SORPTION

Sorption (also called adsorption) is defined as the adhesion of molecules of a gas, liquid or dissolved substance to the surface of a solid. The solid is typically referred to as the sorbent (or adsorbent) and the sorbed molecules as the sorbate (or adsorbate). The release of sorbate molecules from the solid surface is called desorption. Desorption is often studied in conjunction with adsorption in order to determine the reversibility of the sorption reaction. Equilibrium sorption can be described by a sorption isotherm, a graph in which the concentration of sorbate bound to the solid is plotted versus the concentration of sorbate in solution. Sorption takes place in the interfacial region between a solid particle and the surrounding medium. The most important factors controlling the sorption process are the nature of the solid surface, the adsorbate molecules and the interfacial region in which sorption takes place.

Adsorption may be promoted by a strong adsorbate-adsorbent interaction or a weak solute-solvent interaction. The attractive forces between sorbate and sorbent can be classified as either physical, chemical or electrostatic. Physical sorption results from the action of van der Waals
forces which include dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. Electrostatic interactions will occur between a charged solid surface and ionic adsorbate molecules. Chemical interactions or chemisorption consists of specific interactions between the surface and adsorbate molecules, resulting in the formation of chemical bonds. Another force often contributing to the sorption of hydrophobic molecules is due to the interactions between the solvent and adsorbate molecules. A non-polar molecule is held in aqueous solution by an ordered, ice-like arrangement of water molecules around the solute. This solvation reaction is generally exothermic. The favorable enthalpy is counterbalanced by an unfavorable entropy of solution caused by the increased ordering of solvent molecules. Solvent molecules (especially non-polar molecules) will be driven from solution, promoting sorption due to the unfavorable entropy effect.

Measurements used to characterize soils and sediments are often based on the sorption phenomenon. Two examples are cation exchange capacity and surface area measurements. Sorption also plays a major role in predicting the fate and transport of chemicals in the environment and distribution coefficients are routinely measured to predict the distribution of a compound between sediment or soil and water. These measurements are complicated by the variability and complexity of sediment/soil composition because it allows for a variety of
sorptive interactions to take place within a single system. In addition, the majority of these sorptive interactions have not been fully characterized.

Consequently, measurement techniques based on sorption can be fraught with difficulties and they often produce inconsistent results. The objective of this work was to evaluate two such experimental techniques in detail. It was hoped that a quantitative understanding of the effects of experimental variables would lead to greater reliability of results or, at least, a recognition of the degree of uncertainty associated with such measurements. The variation in surface area measurements (by aqueous dye adsorption) with solution composition is systematically investigated with respect to solution pH and ionic strength. Also, the variation in distribution coefficients measured at different sediment concentrations is extensively studied in order to better understand the cause of this problem. A theoretical model, developed to predict this variation in measured distribution coefficients, is applied to results obtained under a variety of experimental conditions.
CHAPTER II

UNCERTAINTIES IN APPARENT SURFACE AREAS OF FINE PARTICULATES BY DYE ADSORPTION

Introduction

Surface area is an important measurement for soils and sediments due to its close relationship with the shrink-swell behavior of soil and soil water content (Mortland and Kemper, 1965; Newman, 1985). It is also related to cation exchange capacity and overall sorptive capacity.

Surface area is usually estimated from the amount of sorbate needed to form a monolayer over the surface of the particulates. Numerous methods have been developed to measure surface area. This is in large part due to the fact that no single technique yet has been found that can provide an absolute, unequivocal measurement of surface area regardless of the sample type. For example, techniques such as the BET method which require a dry particle are suitable for dry powder samples but yield questionable results when the sample of interest is normally in aqueous suspension. In particular, this is unacceptable for the measurement of the surface areas of environmental samples - soils and sediments - that normally exist in a hydrated state. In this instance, a technique that does not require dry particles is preferable, but even then each method has its own unique set of advantages and disadvantages. In many
cases, the factors which can influence measurements are not adequately considered.

The nature of the solid must be considered in relation to the measurement of its surface area. Structure and size distribution of pores is an important factor. For example, the surface area of a non-expanding clay is simply the sum of the areas of the external faces. However, both external and interlayer areas must be considered when measuring the surface area of an expanding lattice clay where the adsorbent molecules can reach the interlayer spaces. Evaluation of surface area measurements becomes even more complex when soils and sediments are considered because these particles are extremely heterogeneous. Some of the many constituents of soils and sediments are shown in Table 2.1. Besides the influence of porosity on the measurement, surface heterogeneity can also affect the nature of sorptive interactions (physical adsorption vs. chemisorption). It therefore becomes necessary to specify measurement technique and all experimental parameters when quoting an estimate of surface area.

Many methods are used to measure surface area (Table 2.2). Direct methods of surface area measurement include x-ray crystallography (van Olphen, 1963) and scanning electron microscopy (Kalb and Curry, 1969; Millette et al., 1978) that measure parameters of the particle from which surface area is then calculated. The remaining techniques can be classified as indirect methods because they are
Table 2.1. Composition of natural particulates.

<table>
<thead>
<tr>
<th>General component</th>
<th>Example</th>
</tr>
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<tr>
<td>Clay mineral</td>
<td>Illite</td>
</tr>
<tr>
<td>Hydrous metal oxide</td>
<td>Goethite</td>
</tr>
<tr>
<td>Organic matter</td>
<td>Humic acid</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>Skeletal remains of biota</td>
</tr>
</tbody>
</table>
Table 2.2. Techniques used to measure surface area.

- X-ray crystallography
- Scanning electron microscopy
- Adsorption of an inert gas
- Retention of polar molecules
- Heat of immersion
- Negative adsorption
- Adsorption of dye/surfactant from solution
based on properties such as adsorptive capacity, which are related to surface area. Each method can be classified as either a dry or wet technique, depending on whether the particulates are dried first or used in suspension. One common dry technique is the BET (Brunauer, Emmett, Teller) method, based on the adsorption of an inert gas, typically nitrogen or argon (Hang and Brindley, 1970; Kalb and Curry, 1969). Less frequently used methods include measurement of the heat evolved when a dry particle is immersed in water and another based on the retention of a polar molecule such as ethylene glycol. The primary disadvantage of dry particles in cases where the sample of interest is normally in suspension, such as estuarine suspended particulates, is that dehydration may irreversibly alter the particulate as well as its surface area.

To obtain a valid estimate of the surface area of a sample, it is advantageous to retain the natural environment as much as possible. Consequently, wet methods of surface area measurement are often preferred for environmental particles. The advantages of wet techniques are: (1) dry particles are not required, (2) the equipment used is generally inexpensive and widely available, (3) methods are usually rapid, (4) vacuums and high temperatures are not needed, and (5) measurement of both internal and external surface area is possible (Kalb and Curry, 1969). Two common methods are adsorption of an organic dye, such as methylene blue (Kipling and Wilson,
1960; Hang and Brindley, 1970), and adsorption of a surfactant such as dodecylamine hydrochloride (Kalb and Curry, 1969).

The adsorption of a cationic dye is frequently used since the solution concentration can be determined conveniently using absorbance spectrophotometry. Once the initial and equilibrium aqueous concentrations of dye are known, the amount of dye sorbed to the particulates is determined by the difference between the two values. Reliable use of this technique requires the establishment of conditions of monolayer coverage and cross-sectional areas of adsorbate molecules. If the area covered by each molecule is to be known accurately, then the orientation of dye molecules on the particle surface must be known as well as the form in which the molecule adsorbs (i.e. monomer or dimer). Because of their structure, the adsorption of dyes is energetically preferred and consequently, competition between solvent and dye molecules for adsorption sites is negligible. However, dyes also possess functional groups which can cause adsorption to be dominated by ion exchange with counter ions of the solid. In this way, surface area measurements may become more dependent on the surface charge than on the available area of the particulates.

The adsorption of pyridinium-type compounds on bentonite can be used to illustrate these points. Bentonite retains 86 meq of adsorbent per 100 g clay
regardless of whether pyridinium chloride or the 3,4,6-trimethylpyridinium cation is used (van Olphen, 1970). Having a cross-sectional area of 40 Å², the pyridinium ions are loosely packed on the bentonite surface while 3,4,6-trimethylpyridinium ions with cross-sectional areas of 60 Å² are more densely packed. In this case, surface area, if measured using pyridinium chloride would be seriously underestimated because adsorption is controlled by surface charge.

Despite reports of this nature, dye adsorption continues to be used as a technique for the determination of surface area of fine particulates. Therefore, the aim of this study was to evaluate the reliability of this method. Because solution composition can influence such exchange reactions, this research was designed to investigate the effects of pH and ionic strength on the measurement of surface area by aqueous dye adsorption.

**Literature Review**

Both cationic and anionic dyes have been used to measure the surface area of fine particulates. Predictably, adsorptive behavior differs dramatically for these two types of dyes. The effect of solution composition on aqueous dye adsorption has also been examined to a limited extent. In a number of cases, dye adsorption has been found to depend on solution composition, but explanations for this phenomenon vary.

Variations in the ionic strength and pH can alter the
surface charge of particulates and/or the charge of the species adsorbed (Bolan and Barrow, 1984; Bowden et al., 1973; Hunter and Liss, 1979; Loder and Liss, 1985; Madrid et al., 1983; Parker et al., 1979). Changes in surface charge of the solid can affect estimates of surface area in two different ways. First, solution conditions may influence the interactions between particles causing particle size to change as a result of coagulation or flocculation. Particles of like charge will repel one another and a highly dispersed particulate suspension will have a high surface area. However, if solution composition is changed so as to neutralize this surface charge, the particles will coagulate and the larger particles which result will possess a much lower surface area than the dispersed sample. Secondly, solution conditions may influence interactions between the particle surface and sorbate molecules. Adsorption is believed to occur as a result of two types of attractive forces (Kalb and Curry, 1969). Strong electrostatic attraction or repulsion will occur between charged surfaces and ionic dye molecules. This is primarily referred to as an ion exchange reaction. Physical sorption will also occur due to weaker van der Waals forces. Altering solution composition will change electrostatic interactions by changing the surface charge of the particulates. Consequently, the amount of dye adsorbed in this way can change with solution conditions.

Surface charge plays an important role in the
adsorption of methylene blue. In fact, methylene blue adsorption has been used to measure cation exchange capacity (CEC) as well as surface area (Hang and Brindley, 1970). Kipling and Wilson (1960) had little success measuring surface areas of carbon black and activated charcoal by methylene blue adsorption. Assuming that monolayer coverage corresponded to the plateau of the adsorption isotherm, and with particles of known surface areas, cross-sectional areas were calculated for methylene blue molecules. Because these values were much lower than previously published values, it was concluded that methylene blue adsorption could not be used for the accurate determination of surface areas of carbons.

Hang and Brindley (1970) proposed the measurement of both surface area and CEC of clay in a single experiment by constructing an isotherm for the adsorption of methylene blue. This was based on the assumption that adsorption occurs mainly through ion exchange. At low dye concentration, van der Waals forces cause the large methylene blue molecules to adsorb flat to the clay surface and thus block some of the exchange sites. When the clay particles are covered by a monolayer of dye molecules, optimum flocculation occurs. This is shown by the highest rate of sedimentation due to the size of the flocs forming. At this point of optimum flocculation, which corresponds to the point on adsorption isotherms where the curve begins to deviate from its initial slope, surface area is
measured. As methylene blue concentration is increased, the dye molecules reorient themselves on the surface and previously blocked exchange sites become saturated with dye. At this point, corresponding to the plateau of an adsorption isotherm, the CEC is determined. Results agreed acceptably with previously published results.

It remains unclear as to exactly what is measured by aqueous dye adsorption, but experimental conditions must play a very important role in these measurements. For example, Bodenheimer and Heller (1968) found that methylene blue sorption on montmorillonite was influenced by the degree of dispersion of the clay, which is influenced by solution composition as well as the interlayer cations initially present in the clay. Therefore, from this point on, the term apparent surface area will be used to indicate the uncertainty of this measurement.

As previously noted, both particle (adsorbent) and adsorbate characteristics can be affected by solution parameters. Hunter and Liss (1979) report that the negative charge associated with natural suspended particles decreased with increasing salinity. Okamura and Wada (1983) also found the surface charge of soils to vary predictably with pH and electrolyte concentration. In fact, theoretical models have been developed to try to explain the variation in surface charge with pH and ionic strength (Madrid et al., 1983; Bowden et al., 1973).

The influence of solution composition on adsorbate
characteristics has been reported by Padday (1970) in the formation of dimers and multimers by cyanine dyes. pH will also affect the dissociation equilibria of adsorbates of acidic or basic character. All of these effects could be manifested in the measurement of surface areas using aqueous dye adsorption.

In the measurement of the surface area of activated sludge using Lissamine Scarlet 4R, Smith and Coakley (1983) found it necessary to adjust solution pH to 2.5 in order to achieve dye adsorption. McKay (1982), in a study of the adsorption of dyes to activated carbon, reported that the adsorption of Direct Orange 39, an anionic dye, was promoted by adding sodium sulfate to the saturating solution. Also studying adsorption to activated carbon, Martin and Iwugo (1982) found pH to influence the removal of organics from wastewater. Increased adsorption in each case was attributed to neutralization on the charge on the solid, thereby reducing any electrostatic repulsion. Surface charge can therefore either promote or prevent dye adsorption. For example, adsorption of the negatively charged dye, erythrosin, to the negatively charged surface of silver halide will not occur (Padday, 1970).

The solvent can also have an effect on adsorption and, consequently, on apparent surface area. Chicco and Heijkoop (1978) used a homologous series of four alcohols as media for the adsorption of fluorescein and rhodamine B on a zinc oxide surface. They reported decreasing
adsorption with increasing polarity of the solvent and concluded that this was consistent with the general observation that highly polar molecules will exhibit great affinity for a polar surface. As solvent competition increased with solvent polarity, adsorption of dye molecules decreased. An increase in solvent polarity was also said to cause a decrease in specificity of adsorption based on the change in molar ratios of adsorbed fluorescein to rhodamine B from 5:1 in methanol to 1:2 in butanol.

The form in which the molecule is adsorbed can also be influenced by solution conditions. DeBussetti et al. (1980) reported pH dependence for the adsorption of orthophenanthroline onto various clays and oxides. Maximum adsorption occurred at approximately pH 6 regardless of sorbent. Based on acid dissociation equilibria of orthophenanthroline, maximum adsorption coincided with the pH at which the compound existed as a neutral species. In this case, adsorption of the uncharged molecule was favored over adsorption of the cationic species.

In a preliminary study (Page, 1982), the effect of pH and ionic strength was studied using Pyronin-y, a fluorescent cationic dye, to measure the surface area of illite. Illite, a constituent of many soils and sediments, typically possesses a negative surface charge due to isomorphous substitution in its crystal lattice (Weaver and Pollard, 1973). The apparent surface area of illite was independent of pH and there was an approximate linear
relationship of positive slope between the apparent area and the square root of ionic strength. This result differs from the effect predicted by considering coagulation and competition for adsorption sites. As ionic strength is increased, coagulation should also increase and the apparent surface area of the particulates should decrease. Also, as ionic strength is increased, the concentration of ions competing for adsorption sites will increase causing apparent surface area to decrease.

The following study is a continuation of this work. In an effort to fully evaluate the potential utility of surface area measurement by aqueous dye adsorption, both cationic and anionic dyes were studied (Pyronin-\textsuperscript{y} and New Coccine). The effects of pH and ionic strength were extensively investigated with respect to the measurement of the apparent surface area of illite using Pyronin-\textsuperscript{y} adsorption.

**Experimental**

**Materials.** Pyronin-\textsuperscript{y} was purified according to the method described by Page (1982). New Coccine (also called Lissamine Scarlet 4R) was used without further purification. Illite, "IMt-1", from Silver Hill, Montana was purchased from The Clay Minerals Society, Source Clay Minerals Repository, Dept. of Geology, University of Missouri, Columbia, MO. It was purified according to the procedure of Page (1982) and size fractionated by sedimentation in deionized water. The 2 to 20 µm size
fraction was used in all adsorption isotherm and surface area measurements. The clay was stored as a suspension in deionized water and the concentration was determined by vacuum drying a known volume of the suspension at 60°C.

Acetate and tris(hydroxymethyl)aminomethane (THAM) buffer solutions were used as adsorption media with sodium chloride added to adjust the ionic strength. Ionic strength and pH were held constant throughout a single experiment by using a single batch of adjusted solution for all experiments. All Pyronin-y solutions were prepared using adjusted buffer solutions and stored in acid washed Teflon containers as much as possible to minimize adsorption of the dye to container walls.

Adsorption isotherms. Adsorption isotherms were constructed according to the method of Hang and Brindley (1970). To each of several 50 mL Teflon centrifuge tubes 1.0 mL of clay suspension was added, equivalent to approximately 1 mg of dried particles. Volumes ranging from 0.50 to 20.00 mL of a 3.0 x 10^{-4} M Pyronin-y solution were added to the clay samples using a buret, followed by buffer solution to bring the final volume of each sample to 30.0 mL. Samples were shaken overnight (room temperature) using a reciprocating shaker and then centrifuged (9000 rpm) for 10 minutes.

Pyronin-y solutions were analyzed using an excitation wavelength of 486 nm and a 518 nm long pass filter to limit the emission wavelengths monitored. Standards of
Pyronin-y were freshly prepared from a stock solution of 1.0 \times 10^{-5} \text{ M} \text{ Pyronin-y}, with concentrations ranging from 1.0 \times 10^{-7} \text{ M} to 6.0 \times 10^{-7} \text{ M}. Standards were prepared using the appropriate buffer solution in order to match the pH and ionic strength used in each experiment. The supernatant solutions after equilibration were diluted until the total absorbance of each was less than 0.05 and then fluorescence intensity was measured using a SLM 8000 fluorescence polarization instrument. Although fluorescence polarization measurements were not necessary, the polarization feature was used to help reduce any light scattering due to unseparated clay particles. All measurements were made using only one channel of the instrument. Five intensity readings (digital) were taken for each sample and standard solution. The amount of dye adsorbed was estimated by difference.

In a similar fashion, the construction of adsorption isotherms for New Coccine on illite was also investigated. New Coccine differs from Pyronin-y in that it does not fluoresce. Therefore, it was necessary to determine aqueous phase concentrations of New Coccine by absorbance spectrophotometry using a Model UV-2005 Shimadzu Double Beam Spectrophotometer at a wavelength of 506 nm. Standard solutions of New Coccine (1.0 \times 10^{-5} \text{ M} to 6.0 \times 10^{-5} \text{ M}) were prepared with pH and ionic strength of the solutions matching those used in isotherm experiments.

**Surface area measurements.** For the determination of
the apparent surface area of illite, concentrations of Pyronin-y were chosen to ensure saturation of the particulates by the dye. Three different concentrations of Pyronin-y were chosen based on adsorption isotherm measurements. These initial Pyronin-y concentrations yielded points on the plateaus of the adsorption isotherms. Samples were prepared for each of the three different concentrations of Pyronin-y by adding 10.0, 12.0, or 15.0 mL of \(3.0 \times 10^{-4}\) M Pyronin-y to a sample of approximately 1 mg of clay particles (contained in a Teflon centrifuge tube). Adjusted buffer solution was added to bring the final volume of each sample to 25.0 mL. Each point chosen from the adsorption isotherm was run in duplicate. A blank containing only the adjusted buffer solution and clay was prepared in the same manner. All samples were shaken overnight on a reciprocating shaker and later centrifuged (9000 rpm) for 10 minutes. The supernatant solution from each sample was diluted as necessary and dye concentration determined as previously described in the construction of adsorption isotherms.

Apparent surface areas were calculated using the following equation:

\[
\text{Apparent surface area} = \frac{A \times N \times C}{M}
\]

where \(A\) is the moles of adsorbed dye molecules, \(N\) is Avogadro's number, \(C\) equals the cross-sectional area per
dye molecule (m^2) and M is the mass of the sample in grams. In all calculations, Pyronin-y was assumed to have a cross-sectional area equal to that of methylene blue (130 Å^2) due to their similarity in structure (Hang and Brindley, 1970). The average surface area was then calculated for each sample and the values averaged.

**Cation exchange capacity.** A standard procedure was used to estimate the CEC of illite (Chapman, 1965). Illite was initially equilibrated with 1 M sodium acetate in acid washed polycarbonate centrifuge tubes. Samples were equilibrated overnight on a reciprocating shaker. Following centrifugation, the supernatant was removed and the sodium-saturated illite was washed with 3 aliquots of 95% ethanol. These samples were then equilibrated overnight with 1 M ammonium acetate on a reciprocating shaker in order to displace sodium ions. Samples were then centrifuged and the supernatants saved. Following a second equilibration with 1 M ammonium acetate, the supernatants were combined for analysis. Triplicate determinations of sodium concentration were done by flame atomic emission using an IL 951 AA/AE Spectrophotometer. Based on the sodium concentration and volume of supernatants, total milligrams of exchangeable sodium were calculated.

**Results and Discussion**

**Adsorption isotherms.** Adsorption isotherms were first determined for the adsorption of Pyronin-y (structure shown in Figure 2.1) on illite in order to determine the point
Figure 2.1. Structures of dye molecules.

Pyronin-y

New Coccine
at which dye saturation of the particulates was achieved. Shown in Figure 2.2 is the isotherm established at a pH of 7.96 and ionic strength of 0.25. The initial sharp increase in the amount of dye adsorbed is indicative of a high affinity of solute (Pyronin-y) for the adsorbent (Kahn, 1978; Stumm and Morgan, 1970). Adsorption was found to level off at an average value of 1.35 x 10^{-4} mole of Pyronin-y per gram of illite. At a pH of 6.95 and ionic strength equal to 0.25, a saturation value of 1.05 x 10^{-4} mole Pyronin-y per gram of illite was similarly determined. This saturation point is commonly used to measure the apparent surface area of fine particulates (DeBussetti et al., 1980; Giles et al., 1970; Kipling and Wilson, 1960; Padday, 1970; Smith and Coakley, 1983). It is assumed that this point corresponds to a monolayer of dye molecules covering the particulates. Based on the isotherms generated, points corresponding to initial dye concentrations of 1.20 x 10^{-4}, 1.44 x 10^{-4} and 1.80 x 10^{-4} M were chosen as points at which apparent surface areas were later measured.

Attempts were also made to construct isotherms for the adsorption of an anionic dye onto illite. New Coccine (structure shown in Figure 2.1) was chosen based on its previous use in surface area measurements (Smith and Coakley, 1983). All experiments conducted to determine adsorption isotherms were unsuccessful. Adsorption of New Coccine to the illite particulates was not observed.
Figure 2.2. Adsorption isotherm for the sorption of Pyronin-y on illite.

Equilibrium solution concentration (mole/g x 10^4)

Moles dye per gram illite (x 10^4)
regardless of the pH (ionic strength held constant at 0.25) of the saturating dye solution. Adjusted buffer solutions of pH 3.85 and 2.16 were used to try to promote adsorption of New Coccine on illite. Smith and Coakley (1983) also observed this lack of adsorption for saturating dye solutions having a pH close to that of natural waters (pH 7 to 8); however, at pH equal to 2.5 they were able to promote the adsorption of New Coccine to activated sludge due to neutralization of the negative surface charge of the solid. This was not observed for New Coccine on illite.

The behavior of Pyronin-y and New Coccine with respect to illite suggests that electrostatic interactions dominate the adsorption process. In addition to the lack of adsorption of New Coccine to illite, adsorption isotherms for Pyronin-y show that the quantity of dye adsorbed at the point of maximum adsorption (plateau of isotherm) differs with pH. Illite is a non-expanding three layer clay composed primarily of oxygen and metal (silicon, iron, magnesium and aluminum) atoms. Substitutions of aluminum for silicon within its crystal lattice result in a net layer charge of approximately -0.7 per unit cell (Weaver and Pollard, 1973; Velds, 1977).

Examination of the importance of electrostatic interactions in relation to other adsorptive forces such as van der Waals forces requires that the energy of the interaction as well as the distance over which it occurs be considered. Electrostatic (coulombic) interactions are
characteristically high in energy (greater than 10 kcal/mole) and operate over relatively long distances (Adamson, 1979). The coulombic force varies inversely with the square root of the distance whereas van der Waals forces vary inversely with the distance raised to the sixth power. It is therefore possible that electrostatic forces will dominate in the interaction between ionic dyes and negatively charged clay particulates. The cationic dye, Pyronin-y, is attracted to the negatively charged surface of illite whereas New Coccine, an anionic dye, is repelled by it. It therefore is necessary to choose a cationic dye such as Pyronin-y in order to obtain an estimate of the apparent surface area of illite. However, even with Pyronin-y, adsorption will vary with the composition of the saturating dye solution. Consequently, the influence of solution pH and ionic strength must be investigated for the measurement of apparent surface area by aqueous dye adsorption.

**Apparent surface area.** A systematic study was conducted to determine the variation in apparent surface area with changes in pH and ionic strength. Apparent surface areas of illite were measured by the adsorption of Pyronin-y from aqueous solution. Measured areas varied from 73.9 to 148 m²/g with standard deviations ranging from 3% to 16%.

pH was varied from 3.71 to 9.98 with ionic strength held constant at 0.25. The effect of pH on apparent
surface area is shown in Figure 2.3. Four different adjusted buffer solutions were used to cover this wide range of pH's. A trend of increasing surface area with increasing pH was observed from pH 3.17 to 6.19, all within the pH range of the acetate buffer system. The apparent surface area then dropped dramatically to 101 and 103 m²/g at pH values of 7.41 and 7.96, respectively. Finally, increasing pH to 9.98 caused a jump in surface area to 138 m²/g.

The effect of ionic strength (at constant pH) was also examined. Results are summarized in Table 2.3. Ionic strength had very little influence on the apparent surface area of illite at pH 7.96. However, at pH 4.13, a decrease of 0.20 in ionic strength caused the apparent surface area to increase by 62 m²/g.

DeBussetti et al. (1980) found surface areas, as measured by the adsorption of 1,10-phenanthroline, to increase as solution pH was increased from 3 to 6 for several different types of solids, including clay minerals. In each case, the maximum surface area was measured around a pH of 6. This variation was explained using the acid-base equilibria of 1,10-phenanthroline. At pH equal to 6, the molecular form of orthophenanthroline predominates and was said to be preferred over the cationic species by the sorbents.

Okamura and Wada (1983), in studying the cation exchange capacity of soil found cation retention to
Figure 2.3. Influence of pH on the apparent surface area of illite at constant ionic strength (0.25).
Table 2.3. Effect of ionic strength on the apparent surface area of illite.

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>pH = 4.13</th>
<th>pH = 7.96</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>85.9</td>
<td>103</td>
</tr>
<tr>
<td>0.15</td>
<td></td>
<td>112</td>
</tr>
<tr>
<td>0.05</td>
<td>148</td>
<td>108</td>
</tr>
</tbody>
</table>
decrease with decreasing pH and electrolyte concentration. Martin and Iwugo (1982) also found solutions of low pH (3-5) to enhance the removal of organics from wastewater, by increasing their adsorption to activated carbon. In both cases, improved adsorption at low pH's was attributed to neutralization of the negative surface charge of the adsorbent.

Page (1982) studied the adsorption of Pyronin-y on illite from aqueous solutions with pH varying from 3.81 to 6.74. No measures were taken to hold ionic strength constant. Apparent surface area did vary with pH; however, no trend was distinguishable. Ionic strength calculations based on the dissociation equilibrium of the acetate buffer system used, revealed that apparent surface area actually varied directly with the square root of the ionic strength. Page was able to explain this behavior based on charge interactions between the cationic dye and negatively charged clay surface.

McKay (1982) also reported an ionic strength effect for the adsorption of the anionic dye, Direct Orange 39, on activated carbon. As the concentration of sodium sulfate in the aqueous dye solution was increased, the rate of adsorption and amount of dye adsorbed increased. This was attributed to a reduction in the electrostatic repulsion between the dye and carbon surface.

Several possible explanations for the variation in apparent surface area with solution pH and ionic strength
observed here will be explored. Factors that will be considered include speciation of the dye, electrostatic interactions, and competition for adsorption sites between the dye and other ions present in solution. Solution composition can have an effect on the apparent surface area by influencing any of the items listed above.

Ionic strength and pH can affect the species of dye adsorbed by the clay. pH will influence the acid-base equilibrium as was the case with 1,10-phenanthroline (DeBussetti et al., 1980). In the case of Pyronin-y, increasing hydrogen ion concentration may cause protonation of the functional group, \(-N(CH_3)_2\); however, the equilibrium constant for this process has not been measured. If protonation did occur, this would cause the charge associated with Pyronin-y to change from +1 to +2. Therefore, as pH is increased, electrostatic attraction would increase causing apparent surface area to increase. However, this does not explain the anomalous results observed at pH 7-8; nor does it explain the ionic strength effect observed. It is also possible that solution composition may promote the formation of dimers or multimers. Padday (1970) reported that the aggregation of dye molecules can occur both in solution and at the surface of the sorbent. Narine (1980) noted that dimerization increased as a function of ionic strength. Dimerization could also be facilitated by increasing the concentration of hydroxyl ions in solution. However, according to Page
(1982), estimates for the dimerization constant of Pyronin-y indicate that surface area measurements will not be complicated by the presence of dimers for the dye concentration range used.

It is also necessary to examine changes in the clay particles that may result from changes in pH and ionic strength. As already discussed, illite has a constant negative charge due to substitution within its crystal lattice. In order to maintain electroneutrality of the surface, this net negative charge is balanced by an excess of positive charge (cations) in the solution close to the particle surface. Consequently, the concentration of cations will be greater close to the clay surface than in the bulk solution. This area of excess charge in solution is called the diffuse double layer (Adamson, 1979; Bard and Faulkner, 1980). Provided that there are only electrostatic interactions between the surface and ions in solution (no chemisorption), the actual surface charge of the clay will be independent of solution composition. However, pH and electrolyte concentration can affect the diffuse double layer and in this way influence dye adsorption.

Increasing ionic strength will allow for a higher concentration of sodium ions (from NaCl) at the clay surface thereby neutralizing the negative surface charge and compressing the electrical double layer (McKay, 1982). This can affect interactions between clay and Pyronin-y as
well as between individual clay particles. Dye molecules can approach the clay surface more closely so that in addition to far reaching coulombic forces, other forces (such as van der Waals forces) will also contribute to adsorption. Dye adsorption and apparent surface area should increase with increasing NaCl concentration. However, ionic strength was found to either have no effect (pH 7.96) or, as ionic strength increased, apparent surface area decreased (pH 4.13).

Electrostatic interactions also occur between clay particles. Dispersion of the clay particles is due largely to electrostatic repulsion between negatively charged particles. As ionic strength is increased, compression of the electrical double layer will bring particles closer together. Other attractive forces will have the opportunity to operate as the distance between particles decreases, thereby causing flocculation. Therefore, as ionic strength increases, particle size will also increase. Because surface area varies inversely with particle size, surface area will decrease. Bodenheimer and Heller (1968) found methylene blue adsorption to vary depending on the degree of dispersion of particulate samples. This can explain the effect of ionic strength at pH 4.13 but not at pH 7.96. The decrease in apparent surface area with decreasing pH can be similarly accounted for.

Finally, the effect of pH and ionic strength on apparent surface area can be viewed with respect to
competition between ions for cation exchange sites. Dye adsorption has been used previously to measure the cation exchange capacity of solids in addition to their apparent surface area (Hang and Brindley, 1970). Pyronin-y will compete with hydrogen and sodium ions for illite exchange sites. This is best illustrated using the following equilibrium:

\[
(S^-)(H^+)_x(Na^+)_y + zD^+ \rightleftharpoons (S^-)(H^+)_{x-a}(Na^+)_{y-b}(D^+)_z + a(H^+) + b(Na^+).
\]

In this case, \(S^-\) represents the illite surface and \(D^+\) represents Pyronin-y. The total number of hydrogen and sodium ions displaced by Pyronin-y is assumed to equal the number of dye cations adsorbed \((a + b = z)\). Simply by applying LeChatelier's Principle, the effect of pH and ionic strength can be predicted. As NaCl concentration is increased, the reverse reaction is favored. Therefore, as ionic strength is increased, desorption of Pyronin-y will be favored, resulting in a decrease in apparent surface area. This was observed for a constant pH of 4.13, but not at pH 7.96 (Table 2.3). As pH is increased, the forward reaction with the adsorption of Pyronin-y should be favored. As pH is increased, apparent surface area is predicted to increase as was observed. At the point where pH begins to level off \((\text{pH} \geq 9)\), the concentration of \(H^+\) becomes negligible and cannot compete effectively for
exchange sites. Because ionic strength is held constant, competition between sodium ions and Pyronin-y will not change, resulting in the observed "plateau" (Figure 2.3).

In order to further evaluate the role of ion exchange in the adsorption of Pyronin-y on illite, the cation exchange capacity (CEC) of illite was determined by the exchange of NH$_4^+$ for Na$^+$. A cation exchange capacity of 15.4 meq/100g illite was measured. This was compared to cation exchange capacities calculated from Pyronin-y adsorption data, assuming that saturation of illite by dye molecules corresponds to saturation of all ion exchange sites. These calculations are summarized in Table 2.4 with values ranging from 9.43 meq/100g to 18.9 meq/100g, depending on pH and ionic strength. At an ionic strength of 0.25 and pH 5.21 to 6.29 (similar to the conditions under which cation exchange capacity was measured), the computed CEC's of 15.1 and 16.1 meq/100g correspond closely to the CEC measured by Na$^+$ displacement. The agreement of these values indicates that Pyronin-y adsorption on illite is due to primarily ion exchange and the dye molecules will effectively compete with sodium ions for exchange sites.

The one obvious exception in the results occurs at pH 7.96. Ionic strength was found to have no effect at this pH and looking at apparent surface area versus pH (Figure 2.3), surface area is significantly less than what would be predicted based on the surrounding experimental data. This is not due simply to the change in buffer systems.
Table 2.4. Cation exchange capacities of illite calculated based on the adsorption of Pyronin-y.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ionic strength</th>
<th>CEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.71</td>
<td>0.25</td>
<td>9.43</td>
</tr>
<tr>
<td>4.14</td>
<td>0.25</td>
<td>11.0</td>
</tr>
<tr>
<td>4.57</td>
<td>0.25</td>
<td>12.6</td>
</tr>
<tr>
<td>5.21</td>
<td>0.25</td>
<td>15.1</td>
</tr>
<tr>
<td>6.19</td>
<td>0.25</td>
<td>16.1</td>
</tr>
<tr>
<td>7.41</td>
<td>0.25</td>
<td>13.0</td>
</tr>
<tr>
<td>7.96</td>
<td>0.25</td>
<td>13.2</td>
</tr>
<tr>
<td>9.98</td>
<td>0.25</td>
<td>17.6</td>
</tr>
<tr>
<td>7.96</td>
<td>0.15</td>
<td>15.1</td>
</tr>
<tr>
<td>4.12</td>
<td>0.05</td>
<td>18.9</td>
</tr>
<tr>
<td>7.96</td>
<td>0.05</td>
<td>13.8</td>
</tr>
</tbody>
</table>
Use of THAM and phosphate buffers in surface area measurements gave similar values for apparent surface area; with THAM a value of 103 m$^2$/g was measured (pH 7.96) and with phosphate, a value of 101 m$^2$/g was measured (pH 7.44). This anomaly can be related to the point of zero salt effect (PZSE). Hydrogen and hydroxyl ions will be specifically adsorbed (chemisorbed) at the edges of the clay particles and non-specifically adsorbed (due to electrostatic attraction) on the clay faces. The net proton charge density is defined as the surface charge density due to specific adsorption of hydrogen and hydroxyl ions. The point of zero salt effect is defined as the pH at which there is no change in the net proton charge density with changes in pH (Parker et al., 1979). It is measured by the acid-base titration of a suspension at a variety of ionic strengths. By plotting net proton charge density (calculated from pH and acid/base concentrations in suspension) versus pH at several different ionic strengths, the PZSE is determined by the pH at which the curves intersect. Page (1982) measured the PZSE for illite at pH 7.2. This may account for the absence of an ionic strength at pH 7.96. Also, at the point of zero salt effect, colloid stability will be at a minimum or rather, maximum flocculation will occur. Associated with the formation of large flocs at this pH will be a drop in apparent surface area as was seen between pH 7 and 8.
Conclusion

The results presented here indicate that both ionic strength and pH of the saturating dye (Pyronin-y) solution will influence the measurement of apparent surface area. Several possible explanations for this behavior have been presented; however, the exact mechanism for Pyronin-y adsorption on illite is not known and hence the explanations remain speculative. Nevertheless, it is very clear from the data that the measurement of apparent surface area of fine particulates by aqueous dye adsorption is highly dependent on experimental conditions.

Measurements were made using a very simple particulate sample - illite which was stripped of metal oxides and organic matter. Dye adsorption is often used to measure surface areas of natural particulates (soils and sediments) which are much more complex than pure clay and will consist of a mixture of metal oxides and organic matter as well as clay minerals. These additional components further complicate dye adsorption due to a variety of additional surface reactions that can occur. For example, metal oxides can undergo the following dissociation reactions (M = metal):

\[
\begin{align*}
\text{MOH}_2(\text{s}) & \rightleftharpoons \text{MOH}(\text{s}) + \text{H}^+(\text{aq}) \\
\text{MOH}(\text{s}) & \rightleftharpoons \text{MO}^-(\text{s}) + \text{H}^+(\text{aq})
\end{align*}
\]

Because these reactions are pH dependent, the properties of
the particle surface will also vary with pH. Surface area measurements are influenced by the nature of the particulate surface and consequently will depend on solution composition.

The results presented here introduce questions as to the validity of the values obtained if measured surface area can be manipulated simply by changing solution conditions. It also emphasizes the need to duplicate environmental conditions if reasonable estimates of the adsorptive capacity of natural particulates are to be determined using aqueous dye adsorption.
References


CHAPTER III

THE EFFECTS OF COMMON LABORATORY PROCEDURES ON THE MEASUREMENT OF DISTRIBUTION COEFFICIENTS

Introduction

Widespread contamination by chemicals that pose a threat to public health has led to numerous studies devoted to the fate and transport of these substances in the environment. Heavy metals such as mercury, pesticides such as DDT and polycyclic aromatic hydrocarbons such as benzo(a)pyrene have received attention due to their toxic, carcinogenic and mutagenic properties. The ultimate fate of these chemicals in the environment is dictated by processes such as sorption, volatilization, dissolution, photolysis, hydrolysis and biodegradation. The micro and bulk distribution of organic pollutants in soils and sediments significantly influences the rates of these processes thereby modifying transport, lifetimes, and toxic impact.

In soils and aquatic environments, adsorption is favored for a number of pollutants due to their hydrophobic nature. For example, Armstrong et al. (1977) studied the effects of an oil field brine effluent on a shallow Texas bay and found concentrations of polycyclic aromatic hydrocarbons in the sediment at least 1000 times greater than in the overlying water. Sediment-associated
pollutants usually degrade at different rates than dissolved compounds, sometimes faster and sometimes slower. For example, the microbial degradation of chlorpropham and di-n-butyl phthalate was found to decrease when associated with sediment (Steen et al., 1980). For 3,4-dichloroaniline, 1,1-bis(p-chlorophenyl)-2,2-dichloroethylene, and m-trifluoromethylpentadecanophenone, different photoreactivities were exhibited when sorbed than when dissolved in water (Miller and Zepp, 1979). Therefore, in order to develop models which will reliably predict the transport and fate of pollutants in the environment, a large amount of information is required concerning the distribution of compounds between water and sediment or soil and their behavior in these different phases.

Coefficients developed to express the distribution of a compound between sediment or soil and an aqueous phase have been used as a major predictive tool in environmental fate models. Assuming that the following equilibrium

\[ K_d \quad \text{M}_{\text{solid}} \xleftrightarrow{M_{\text{aqueous}}} \]

situation exists, the equilibrium distribution coefficient, \( K_d \), is defined by:

\[ K_d = \frac{C_s}{C_{aq}} . \]  \hspace{1cm} (1)

\( C_s \) and \( C_{aq} \) are the equilibrium concentrations associated
with sediment (or soil) and solution, respectively. This simple linear model which assumes both dynamic equilibrium and complete reversibility, has been found experimentally valid only for dilute solutions. Other sorption models including the Freundlich, Langmuir, BET and Gibbs models all tend to predict linear partitioning at low sorption concentrations (Voice and Weber, 1983).

Experimental estimates of \( K_d \) for a given pollutant have been found to vary depending on the sediment or soil used to determine the coefficient. These differences can be attributed to the organic carbon content of the sediment. Lambert (1965, 1966, 1967, 1968) was able to correlate \( K_d \) estimates with the organic carbon content of sediments, resulting in the definition of a new distribution coefficient, \( K_{oc} \), which is normalized to the fraction of organic carbon in the sediment, \( f_{oc} \):

\[
K_{oc} = \frac{K_d}{f_{oc}}.
\]  

(2)

This new term was shown to remain virtually constant for a particular compound, regardless of the soil or sediment studied. Numerous studies have since shown that \( K_{oc} \) values are not nearly as reproducible between labs as they are within a single lab.

For a number of compounds, \( K_{oc} \) has been correlated with solubility (Karickhoff, 1981) and with octanol-water partition coefficients (Karickhoff et al., 1979). The
octanol-water partition coefficient, $K_{ow}$, is defined as:

$$K_{ow} = \frac{C_o}{C_{aq}}$$

(3)

where $C_o$ and $C_{aq}$ are the equilibrium concentrations associated with the octanol and aqueous phases, respectively. Here also, however, the correlations are good within labs but differ widely between labs.

The actual mechanism by which a pollutant is concentrated in sediment has not been established conclusively. With respect to the accumulation of nonionic hydrophobic compounds in sediments, Chiou et al. (1979) proposed that sorption occurs by equilibrium partitioning into the organic matter of the sediment, analogous to the partitioning of a chemical in a liquid-liquid system such as octanol-water. Others argue in favor of an adsorption model in which molecules are bound at specific binding sites on the sediment surface (MacIntyre and Smith, 1984; Mingelgrin and Gerstl, 1983). In this case, pollutant will associate with the mineral matrix as well as the organic matter of the sediment. This theory could also apply to ionic compounds such as organic acids and metal ions. In the absence of definitive evidence to support either mechanism, the terms, partitioning and sorption, as used in the following discussion, do not denote any particular mechanism, but rather describe only the accumulation of pollutant in the sediment phase.
Under the equilibrium conditions previously described, the equilibrium constant or distribution coefficient, $K_d$, is related to the free energy of partitioning/adsorption, $\Delta G^0$, by the following equation:

$$\ln K_d = -\frac{\Delta G^0}{RT}$$  \hspace{1cm} (4)

where $R$ is the gas constant and $T$ is the absolute temperature. Thermodynamic theory also predicts that $K_d$ should remain constant regardless of the relative amounts of sediment and water used to experimentally measure the distribution coefficient. However, this is not supported by experimental evidence; rather $K_d$ has often been found to vary inversely with the solid-to-solution ratio (O'Connor and Connolly, 1980).

Distribution coefficients have been measured for a wide variety of compounds and a number of different solids including clay minerals, natural soils and sediments, and suspended organic colloids (humic and fulvic acids). Included in the list of compounds studied (Table 3.1) are aromatic hydrocarbons, pesticides, metals and radionuclides. The effect of solid-to-solution ratio has been observed for all of these compounds and several possible explanations have been proposed. Competitive binding (Curl and Keoleian, 1984), irreversible adsorption (DiToro and Horzempa, 1982) and experimental artifacts (Gschwend and Wu, 1985; Voice et al., 1983) are three of
Table 3.1. Compounds for which solids concentration effect has been reported.

Arochlor 1254
chlorobenzene
cobalt
DDT
dieldrin
heptachlor
kepone
lindane
manganese
naphthalene
ruthenium
strontium
2,4,5,2',4',5'-hexachlorobiphenyl
2,5,2'-trichlorobiphenyl
the more common explanations proposed. The goal of this research is to examine more closely the possibility that this effect may be accounted for by the experimental procedure used.

Several methods are used to determine distribution coefficients. The particular procedure will depend on both the analyte (pollutant) and sorbent. Distribution coefficients for a water-colloidal organic matter system are determined much differently than coefficients for a sediment-water system. For instance, a fluorescence quenching method has been developed by Gauthier et al. (1986) to determine the binding of polycyclic aromatic hydrocarbons to dissolved humic and fulvic acids. This is based on the principle that the fluorescence of the molecule is quenched when associated with humic material and does not require a separation step. Measurement of $K_{oc}$ in a water-sediment system usually involves agitation of a mixture containing a known quantity of soil or sediment and a known volume of an aqueous solution of pollutant. Following equilibration, the solid and solution phases are separated either by centrifugation or filtration, and the aqueous phase pollutant concentration is measured. Typical methods of analysis include liquid scintillation counting for radiolabelled pollutants, gas chromatography, and various spectroscopic techniques. Concentration estimates in the sorbent are usually calculated by difference using mass balance.
To date, no widely accepted standard laboratory protocol has evolved for the estimation of $K_{oc}$. Batch equilibrations often use solutions with ionic strengths and pH values that differ considerably from the natural environment. Various types of agitation have been used to promote a rapid approach to equilibrium. Also, the separation of solid and solution phases has been achieved by various centrifugation or filtration conditions. Unfortunately, these laboratory experiments often subject the sediment to much more rigorous conditions than in a natural water system, thereby causing abnormal and variable disruption of the sediment particulates. The microparticulates produced are inefficiently separated from the aqueous phase and these very fine particulates often have a much higher concentration of organic pollutant than the true solution or bulk sediment. Depending on the analytical methodology, the microparticulate bound pollutant may be entirely or partially included in the aqueous phase, or it may be totally excluded. This has implications for experimental estimates of the distribution of organic pollutants between sediment and an aqueous phase and even greater implications when the data are extrapolated to a natural system. It also can explain the poor agreement of estimates from different investigators. The work described here is designed to shed further light on this subject.
Literature Review

Several anomalies have been observed when measuring distribution coefficients. Variations in coefficients with sediment concentration, "unfavorable adsorption" conditions observed in Freundlich adsorption isotherms, and adsorption-desorption hysteresis have all led to inquiries into the validity of current theories of sorption and partitioning. Most researchers believe that these irregularities all have the same cause; however, differences of opinion exist as to exactly what this cause is.

Effect of solids concentration. The inverse relationship between distribution coefficients and solids concentration (or solid-to-solution ratio) is the most often observed anomaly. This relationship has been found for a wide variety of sorbates and a number of different solids. For example, distribution coefficients for radioactive substances (Higgo and Rees, 1986), heavy metals (DiToro et al., 1986), pesticides (Lotse et al., 1968), polychlorinated biphenyls (Horzempa and DiToro, 1983), and polycyclic aromatic hydrocarbons (Voice et al., 1983) have all been found to depend on sediment concentration. Solids studied include various types of sediment, clays such as montmorillonite (Weber et al., 1983) and living organisms such as phytoplankton (Harding and Phillips, 1978).

In a study of the adsorption of lindane by lake sediments, Lotse et al. (1968) investigated the influence
of a number of variables including sediment concentration, organic matter content and lindane-to-sediment ratio. Statistical analysis of the data revealed sediment concentration to be the most important variable influencing lindane adsorption. Horzempa and DiToro (1983) in studying the distribution of 2,4,5,2',4',5'-hexachlorobiphenyl in lake sediment, measured coefficients of 9900, 12300, and 17100 L/kg for sediment concentrations of 1100, 220 and 55 mg/L, respectively. Koskinen and Cheng (1983) also investigated the effect of solids concentration on the sediment distribution coefficients of 2,4,5-trichlorophenoxyacetic acid. They found that changing the soil-to-solution ratio from 1:1 to 1:3.3 caused the measured coefficient to increase from 7.4 to 10.5 (a factor of 1.4); however, no further change in $K_d$ was observed by increasing the ratio from 1:3.3 to 1:33.

O'Connor and Connolly (1980) recently reviewed this problem, compiling an extensive list of studies in which this effect has been reported. For solids concentrations representative of natural systems (10 to 10,000 mg/L), a linear relationship was found to exist between log $K_d$ and the log of solids concentration. In general, the solids concentration was found to have the greatest influence on distribution coefficients determined for compounds having high affinities for the sediment or solid. In studying the effect of solids concentration on distribution coefficients of several hydrophobic compounds, Weber et al. (1983) found
that coefficients decreased by approximately one order of magnitude as sediment concentration was increased by 2 to 2½ orders of magnitude.

As a result of these findings, empirical relationships have been derived to describe the dependence of distribution coefficients on solids concentration. Voice et al. (1983) derived the following expression based on data collected for 10 different solid-solute combinations of three sediments and four priority pollutants:

\[
\log K_d = 0.748(\log K_{ow}) - 0.648(\log S) - 0.131 (f_{oc}) + 0.364.
\]  

(5)

In their survey of the literature, O'Connor and Connolly (1980) were able to derive a more generalized equation of the form:

\[
K_d = K_d^0 + \frac{b}{S_o + S_a}
\]  

(6)

where \(K_d^0\) is the limiting distribution coefficient at high solids concentration, \(S\) is the concentration of solids, and \(S_o\), \(a\) and \(b\) are empirical constants that must be evaluated for each solid/solute combination. For both equations, an inverse relationship is predicted between \(\log K_d\) and \(\log S\).
Freundlich isotherm - "unfavorable adsorption".

Sorption data is often expressed in terms of a Freundlich adsorption isotherm, an empirically derived relationship:

\[ \frac{x}{m} = K_f C^{1/n} \]  \hspace{1cm} (7)

where \( x \) is the amount of sorbate associated with a solid of mass \( m \). \( K_f \) is the distribution coefficient, \( C \) is the concentration of sorbate in the aqueous phase, and \( 1/n \) is indicative of the intensity of the sorption reaction (Khan, 1978; Moore, 1972; Voice and Weber, 1983). The above equation will reduce to a linear relationship for \( n \) equal to one:

\[ \frac{x}{m} = K_f C. \]  \hspace{1cm} (8)

Although these circumstances are often found to hold true for low aqueous concentrations of pollutant, some researchers have reported \( 1/n \) to be greater than one. This can be referred to as "unfavorable adsorption" (Weber, 1972).

Weber et al. (1983) determined the distribution of Aroclor 1254 in sediments, clay minerals and algae, finding in most cases that isotherms exhibited a shape characteristic of the Freundlich model with \( 1/n \) greater than one. However, this irregularity in adsorption is observed much less frequently than the solids concentration
Figure 3.1. Sample isotherm (Solid line corresponds to ideal conditions; dashed line corresponds to "unfavorable adsorption").

Concentration of pollutant in sediment (mg/g) vs Concentration of pollutant in aqueous phase (mg/L)
effect. For example, Koskinen and Cheng (1983) report the Freundlich distribution coefficient to vary with solids concentration, but found $1/n$ to vary only between 0.84 and 0.92. 

"Unfavorable adsorption" is believed to be related to the effect of solids concentration (Weber et al., 1983). The points that make up an isotherm are measured using a series of individual partitioning experiments. Equilibrium conditions can be controlled over the entire isotherm by either gradually increasing the initial concentration of pollutant in solution or decreasing the amount of solids used to measure each point. If the isotherm is constructed by gradually decreasing the concentration of solids in each batch, then the solids concentration effect noted previously will influence the shape of the isotherm. As solids concentration is decreased, more pollutant than is expected under ideal conditions is measured in the solid phase. This causes the isotherm to curve upward as the equilibrium solution concentration increases (Figure 3.1). When data are interpreted in terms of the Freundlich model, $1/n$ will be greater than one. This will not be observed if solids concentration is held constant when constructing the isotherm.

**Adsorption-desorption hysteresis.** A number of systems have been shown to display adsorption-desorption hysteresis or "nonsingularity". Desorption experiments are typically carried out using batch equilibration. Following initial
adsorption of the pollutant, solid and aqueous phases are separated and the supernatant replaced with "clean", pollutant-free solution. The sample is then re-equilibrated and equilibrium concentrations of the pollutant in aqueous and solid phases are measured. In this way, desorption isotherms and coefficients can be determined. Hysteresis exists in cases where the desorption and adsorption isotherms do not coincide. Consequently, different conditions are measured by desorption and adsorption experiments.

DiToro and Horzempa (1982) studied the adsorption-desorption behavior of 2,4,5,2',4',5'-hexachlorobiphenyl on clays and lake sediments. They estimated distribution coefficients to be 2½ to 3½ times greater for desorption than for adsorption. For example, coefficients of 18,100 L/kg and 60,900 L/kg were determined by adsorption and desorption, respectively. Koskinen and Cheng (1983) similarly observed nonsingularity of adsorption and desorption isotherms for the association of 2,4,5-trichlorophenoxyacetic acid on Palouse silt loam soil.

A direct relationship between adsorption-desorption hysteresis and the effect of solids concentration is not evident; however, both phenomena are believed to be manifestations of the same cause.

A number of explanations have been proposed for these observations. These can be separated into two categories. The first, experimental artifacts, includes (a) the
production of nonseparable microparticulates and (b) the
presence of radiochemical impurities in radiolabelled
analytes. The second category is based on the actual
mechanism of binding. This includes (c) irreversible
sorption, (d) particle-particle interactions, and
(e) competitive adsorption. In all cases, mathematical
models have also been developed and will be presented
briefly here.

**Nonseparable microparticulates.** Most experiments
designed to measure distribution coefficients employ batch
equilibration techniques. It is believed that typical
agitation conditions cause the release of sorbing or
solute-binding material from the solid into solution.
Furthermore, typical separation methods (centrifugation
and filtration) cannot adequately remove this material from
solution.

The exact composition of this solute-binding material,
often described as nonseparable microparticulates (Gschwend
and Wu, 1985; Voice et al., 1983), remains ambiguous. On
the basis of dissolved organic carbon and the weight of
dissolved solids of equilibrated solutions, Gschwend and Wu
(1985) concluded that the suspended material had a
composition similar to the corresponding parent sediment.
In a detailed field study of PCB partitioning in Lake
Superior, Baker et al. (1986) reported suspended material
to contain 5 to 10 times more organic carbon than the bulk
sediment.
Regardless of the actual composition of this material (dissolved, colloidal organic matter or microparticulate), it may often contain a much higher concentration of the pollutant than either water or bulk solid. For example, atrazine and linuron have been found to bind 10 to 35 times more strongly on natural colloids than on soils or sediments, suggesting that microparticulates should be treated with enhanced $K_{oc}$'s (Means and Wijayaratne, 1982). It has also been demonstrated that the water solubilities of some pollutants are enhanced by dissolved humic and fulvic acids (Chiou et al., 1986). Distribution coefficients have been reported to vary with particle size, generally increasing as particle size decreases (Karickhoff and Brown, 1978; Nkedi-Kizza et al., 1983). This may be due to the fact that surface area is greatest for fine particulates and colloidal matter and thus, more surface area is available for pollutant binding. Particle composition has also been correlated with particle size (Nkedi-Kizza et al., 1983; Watson and Parsons, 1974). Therefore, changes in distribution coefficients could also be related to composition changes that accompany changes in particle size.

It is believed that a three-phase system results from batch equilibration; this consists of water, bulk solid and a third phase not separated from water but possessing a higher capacity for the solute than water alone (Voice et al., 1983). Furthermore, the ability of the aqueous phase
to "accomodate" pollutant will depend on the concentration of bulk solid, provided a relationship exists between solids concentration and the concentration of microparticulates. Therefore, speciation of the solute must be taken into account. Normally it is assumed that only two forms of the pollutant will exist after equilibration - bound (solid phase) and free (solution phase). Pollutant bound to microparticulates is not accounted for separately but is frequently included in the solution phase (free) concentration. Several mathematical models demonstrating the effect this can have on measured distribution coefficients have been developed.

Four slightly different models that express the observed or measured distribution coefficient in terms of the "true" distribution coefficients have been derived. The "true" and observed coefficients ($K_d^{\text{true}}$ and $K_d^{\text{obsd}}$, respectively) can be defined as:

$$K_d^{\text{true}} = \frac{P/m}{D/v} \quad \text{and}$$

$$K_d^{\text{obsd}} = \frac{P/m}{(D+N)/v}$$

where $P$ is the mass of compound sorbed to separable solid, $D$ is the mass of free or dissolved compound, $N$ is the mass of compound sorbed to nonseparable particulates, $v$ equals the volume of aqueous phase and $m$ equals mass of bulk
solid. Using these definitions, Gschwend and Wu (1985) derived the following:

\[ K_{d}^{\text{obsd}} = K_d^{\text{true}} (1 + K_{NSP}^{\text{true}} \text{DOC})^{-1} \]  
(11)

where \( K_{NSP}^{\text{true}} \) is the distribution coefficient that describes pollutant binding to nonseparable particulates and DOC is the concentration of organic carbon in the aqueous phase.

Baker et al. (1986) modified the above equation, assuming that linear relationships exist between (a) the concentration of nonseparable microparticulates (\( m_{NSP}/v \) or DOC) and solid concentration (\( m/v \)):

\[ m_{NSP}/v = f_{NSP}(m/v), \]  
(12)

and (b) \( K_{d}^{\text{true}} \) and \( K_{NSP}^{\text{true}} \):

\[ K_{NSP}^{\text{true}} = x_{NSP} K_d^{\text{true}}. \]  
(13)

where \( f_{NSP} \) and \( x_{NSP} \) are proportionality constants. It was demonstrated that:

\[ K_{d}^{\text{obsd}} = K_d^{\text{true}} (1 + x_{NSP} K_d^{\text{true}} f_{NSP}(m/v))^{-1} \]  
(14)

Higgo and Rees (1986) also present a two species model in which the pollutant or solute is present in two stable forms - bound to sediment and bound to microparticulates.
Figure 3.2. Models proposed to explain the variation in measured distribution coefficients with sediment concentration (M = pollutant or analyte molecule, FREE = freely dissolved, SED = bound to bulk sediment, NSP = bound to nonseparable microparticulates).


\[
\begin{align*}
K_d & \quad M_{FREE} \rightleftharpoons M_{SED} \\
& \quad K_{NSP} \quad M_{FREE} \rightleftharpoons M_{NSP}
\end{align*}
\]


\[
\begin{align*}
K_2 & \quad M_{FREE} \rightarrow M_{NSP} \\
& \quad K_1 \quad M_{SED} \rightarrow M_{SED}
\end{align*}
\]

c. Radiochemical impurities (I = impurity molecule) (McCarthy et al., 1986).

\[
\begin{align*}
K_d & \quad M_{FREE} \rightleftharpoons M_{SED} \\
& \quad I_{FREE} \rightleftharpoons I_{SED}
\end{align*}
\]

d. Irreversible sorption (S_{REV} = reversible binding site, S_{IRREV} = irreversible binding site) (DiToro and Horzempa, 1982).

\[
\begin{align*}
K_x & \quad M + S_{REV} \rightleftharpoons MS_{REV} \\
& \quad K_0 \quad M + S_{IRREV} \rightleftharpoons MS_{IRREV}
\end{align*}
\]
e. Particle-particle interaction (DiToro et al., 1986)

\[
\begin{align*}
M + S_{\text{REV}} & \underset{K_X}{\overset{K_X}{\rightleftharpoons}} MS_{\text{REV}} \\
MS_{\text{REV}} + M & \rightarrow S_{\text{REV}} + 2M \\
M + S_{\text{IRREV}} & \rightarrow MS_{\text{IRREV}}
\end{align*}
\]


\[
\begin{align*}
A + S & \underset{K_A}{\overset{K_A}{\rightleftharpoons}} AS \\
B + S & \underset{K_B}{\overset{K_B}{\rightleftharpoons}} BS \\
B + R & \underset{K_B'}{\overset{K_B'}{\rightleftharpoons}} BR
\end{align*}
\]
Assuming that the pollutant has a high affinity for the sediment ($K_H$) and a low affinity for microparticulates ($K_L$) and the concentration of microparticulates is proportional to sediment concentration:

$$K_{\text{obsd}} = \frac{(v/m) (K_H + v/m) (K_L + v/m)}{(v/m - k) (K_L - K_H) + K_H + v/m}$$  \hspace{1cm} (15)

where $k$ is a proportionality constant.

Figure 3.2 illustrates several possible equilibrium situations that could exist. The first (Figure 3.2a), which assumes reversible exchange between free and bound forms of the pollutant, is the basis for the models presented above. Voice and Weber (1985) proposed a model based on the equilibria depicted in Figure 3.2b in which irreversible binding of the pollutant by microparticulates ($K_x$) occurs initially, followed by binding of either microparticulate bound or free pollutant to the bulk solid ($K_1$ and $K_2$). The following log-linear relationship is also assumed:

$$\text{DOC} = A(m/v)^B = AS^B$$  \hspace{1cm} (16)

where $A$ and $B$ are empirically derived. The observed distribution coefficient can then be expressed as:

$$K_{\text{obsd}} = \frac{1/(S + 1/K_1) + K_x AS^B/(S + 1/K_2)}{1/(K_1S + 1) + K_x AS^B/(K_2S + 1)}$$  \hspace{1cm} (17)
The presence of nonseparable microparticulates will result in an overestimation of the aqueous phase concentration of pollutant. The most common methods of analysis used (counting of radiolabelled sorbates, gas chromatography) measure only the total aqueous phase concentration and will not discriminate between freely dissolved and microparticulate bound forms of the analyte. The solids concentration effect has been reported in experiments using both liquid scintillation counting (Horzempa and DiToro, 1983; Koskinen and Cheng, 1983; Voice et al., 1983) and gas chromatography (Baker et al., 1986; Gschwend and Wu, 1985; Weber et al., 1983) as the method of analysis. As sediment concentration increases, the amount of microparticulate material released into solution will also increase. This will be accompanied by an increase in the amount of pollutant bound to microparticulates and its aqueous phase concentration. Finally, as aqueous phase concentration increases, the observed distribution coefficient will decrease.

Adsorption-desorption hysteresis can be similarly explained. These experiments typically consist of an initial adsorption step followed by a desorption step. In both cases, batch equilibration techniques are normally used. Microparticulates, released into solution during adsorption, are removed when the equilibrated aqueous phase is replaced with fresh solution prior to desorption. When the sample is re-equilibrated, a smaller amount of
nonseparable material is released into solution. This is reasonable since the "most fragile" part of the solid has been removed during the first equilibration and the remaining solid is therefore less susceptible to disruption when shaken. The decrease in concentration of suspended material is accompanied by a decrease in the concentration of solute bound to suspended particles. As a result, the observed aqueous phase concentration will decrease and the observed distribution coefficient will increase. Consequently, $K_{d}^{obsd}$ (desorption) is predicted to be greater than $K_{d}^{obsd}$ (adsorption), agreeing with experimental results.

Radiochemical impurities. Most partitioning/sorption experiments use liquid scintillation counting of radiolabelled solutes as the method of analysis. McCarthy et al. (1986) have suggested that the presence of radiolabelled impurities in the analyte will cause the observed variations in distribution coefficients.

In order to simplify the derivation, only one impurity was assumed to be present, possessing its own unique distribution coefficient. The equilibria are shown in Figure 3.2c. Because the counting of radiolabelled compounds measures total radioactivity and will not distinguish between different compounds, the apparent concentration of analyte measured includes both analyte and impurity. Therefore the observed distribution coefficient can be expressed as follows:
\[
K_{\text{obsd}} = \frac{C_s}{C_{aq} + I_{aq}} + I_s
\]

where \(C_s\) and \(I_s\) are the concentrations of analyte and impurity bound to sediment, respectively, and \(C_{aq}\) and \(I_{aq}\) are aqueous concentrations of analyte and impurity, respectively. If the analyte is 100% pure then \(I_s = I_{aq} = 0\) and:

\[
K_{\text{obsd}} = \frac{C_s}{C_{aq}} = K_{\text{true}}.
\]

The solids concentration effect can be explained by assuming that the impurity has a lower affinity for the sediment than the analyte (smaller distribution coefficient). The concentration of impurity would then be greatest in the aqueous phase (\(I_{aq} > I_s\)) resulting in an overestimated aqueous phase concentration of analyte and a smaller observed distribution coefficient relative to the true value. As the concentration of sorbent increases, more of the analyte will be bound than the impurity and \(C_{aq}\) will decrease; the decrease in \(C_{aq}\) enhances the error caused by summing \(C_{aq}\) and \(I_{aq}\) in the denominator and leads to lower estimates of the distribution coefficient.

Adsorption-desorption hysteresis can also be explained via this concept. A significant amount of impurity is discarded when the aqueous phase is removed following the initial equilibration step. Therefore, aqueous phase
concentration of the impurity will be lower in the desorption step and the error in the desorption coefficient will decrease. Following this rationale, the desorption coefficient will be greater than the adsorption coefficient (as $I_{aq}$ decreases, $k_{obsd}^d$ increases) which agrees with experimental observations.

This theory has two limitations. First, the impurities present may not always possess a lower affinity for the sediment than the analyte itself. This theory will not hold if the reverse situation were to occur. More importantly, it can only explain anomalies in distribution coefficients measured by radioactivity. It cannot explain why a solids concentration effect has also been observed in experiments using gas chromatography as the method of analysis.

**Irreversible sorption.** The fundamental assumption made in all adsorption-desorption studies is that the analyte is reversibly bound by the soil or sediment. DiToro and Horzempa (1982) have proposed that this basic assumption is incorrect and instead suggest that two distinct fractions of sorbed analyte exist—one bound reversibly and another more strongly bound, irreversible fraction (Figure 3.2d). Therefore, the total equilibrium concentration of sorbed pollutant, $r$, can be expressed as:

$$ r = r_x + r_o $$  \hspace{1cm} (20)
where \( r_x \) is the reversibly bound fraction and \( r_o \) is the resistant, irreversibly bound fraction.

Assuming that the isotherms are linear in all cases, four distinct coefficients are defined: \( K_{ads} \), the adsorption coefficient; \( K_{des} \), the desorption coefficient; \( K_x \), the coefficient of the reversible fraction; and \( K_o \), the coefficient of the resistant fraction. The following equations have been derived to predict the amounts of reversibly and irreversibly bound analyte:

\[
K_x = \frac{K_{ads}}{1 + m(K_{des} - K_{ads})} \quad \text{and} \quad (21)
\]

\[
K_o = \frac{mK_{ads}(K_{des} - K_{ads})}{1 + m(K_{des} - K_{ads})} \quad (22)
\]

\((m = \text{mass of solid})\). These relationships demonstrate the connection between conventional adsorption and desorption coefficients and the coefficients of the reversible and irreversible fractions.

In an adsorption–desorption experiment, the first step involves both reversible and irreversible binding of the analyte and so in subsequent equilibration, only a fraction of the sorbed analyte is available to be desorbed. Following desorption, the aqueous concentration is much less than what is predicted with completely reversible binding. Therefore, the measured desorption coefficient will be greater than the adsorption coefficient. A
comparable explanation for the effect of solids concentration does not exist based only on this model.

Particle-particle interaction. DiToro et al. (1986) build on the idea of irreversible sorption in order to explain the effect of solids concentration as well as adsorption-desorption hysteresis. It is assumed that only the reversible distribution coefficient will vary with solids concentration and a model based on particle-particle induced desorption is proposed to explain the phenomenon.

Once sorbed, they suggest that analyte molecules can desorb in two different ways. The first is simply the reverse of adsorption, while the second assumes that a binary interaction occurs between sediment particles causing desorption to occur. The importance of the second desorption reaction will vary with solids concentration. Figure 3.2e illustrates the reactions involved.

In this model, adsorption-desorption hysteresis can still be explained in terms of reversible and irreversible sorption. The solids concentration effect is explained in terms of particle-particle interaction. As the concentration of sediment in the system increases, the number of particle-particle interactions will also increase causing a greater amount of desorption to occur. Consequently, the aqueous phase concentration will be greater at high solids concentration than at low solids concentration and an inverse relationship between solids concentration and the measured distribution coefficient
is predicted.

McKay and Powers (1987) have presented a similar model based on the ideas of DiToro et al. (1986). The models differ in that McKay and Powers postulate that the adsorption of hydrophobic organic compounds is primarily reversible ("loose sorption") and not a combination of reversible and irreversible binding. The process of "loose sorption" is said to be readily reversible due to particle collisions and so the distribution coefficient will decrease as particle concentration and the collision rate increases.

In both cases, predicted distribution coefficients were found to be consistent with experimentally measured coefficients. However, there is no direct experimental evidence for particle-particle interactions and the models are not widely accepted.

**Competitive adsorption.** Curl and Keoleian (1984) argue that competitive adsorption occurs between the analyte, A, and an "implicit adsorbate", B, originally present on the solid (Figure 3.2f). The implicit adsorbate is loosely defined as a natural organic substance which becomes associated with soil, clay or sediment in the environment. During batch adsorption-desorption experiments, B desorbs and uncovers sites for binding A and in this way will produce an increase in the apparent distribution coefficient.

In the simplest case presented, the following
expression was derived for the observed distribution coefficient, $K_{d}^{\text{obsd}}$:  

$$K_{d}^{\text{obsd}} = \frac{aK_A}{1 + K_A C_A + K_B C_B}. \quad (23)$$

$K_A$ and $K_B$ equal adsorption equilibrium constants for A and B, respectively. $C_A$ and $C_B$ are equilibrium solution concentrations of A and B, respectively, and $a$ equals the maximum adsorbed concentration of A. In this derivation, A and B are assumed to exhibit a competitive Langmuir isotherm so that

$$C_A' = \frac{aK_A C_A}{1 + K_A C_A + K_B C_B}, \quad \text{and}$$

$$C_B' = \frac{bK_B C_B}{1 + K_A C_A + K_B C_B} \quad (25)$$

where $C_A'$ and $C_B'$ equal the sorbed concentrations of A and B, respectively and $b$ is the maximum adsorbed concentration of implicit adsorbate. If $K_A C_A \ll 1 + K_B C_B$, and $K_B C_B$ is constant, then equation (21) corresponds to the linear model commonly used to describe the adsorption of A and $K_{d}^{\text{obsd}}$ will then be less than the true distribution coefficient, $aK_A$, due to the presence of implicit adsorbate, B.

As solids concentration is increased, $C_B$ will increase as more B is dissolved, resulting in a decrease in the
observed distribution coefficient. In an adsorption-desorption experiment, B is desorbed and removed during the first batch equilibration step. This results in a smaller concentration of dissolved B in the second desorption step and therefore $K_{d}^{\text{obsd}}$ is greater when measured by desorption than by adsorption.

However, if $K_{B}C_{B}$ is much less than 1, none of the above effects will be observed since $K_{d}^{\text{obsd}} = aK_{A}$. Curl and Keoleian (1984) have further derived a much more complex model which assumes that there exists a second "reservoir" for B. B is then bound to two types of binding sites, each described by a unique distribution coefficient. The effect of solids concentration is no longer represented by a simple inverse relationship between solids concentration and $K_{d}^{\text{obsd}}$, but also depends on the amount of B and the binding sites involved.

Current status of theories. Conclusive evidence has not yet been presented for any of the above theories. The two most widely discussed theories are based on nonseparable microparticulates and particle-particle interactions with irreversible sorption. Each model has been shown to adequately describe experimental data and arguments have been presented for and against both.

Based on experiments designed to eliminate any possible effects caused by microparticulates, DiToro et al. (1986) concluded that the solids concentration effect could not be explained by microparticulates. In studying the
adsorption of nickel to montmorillonite, solids concentration was varied by adding or removing equilibrated solution from sample vessels. Samples were then reequilibrated and aqueous nickel concentrations measured. Experiments were designed to exclude any interference of a dissolved third phase by using control vessels in which solids concentration was not changed. Precautions were taken to ensure that the concentration of suspended microparticulates was the same for control and experimental sample vessels. Comparison of aqueous nickel concentrations in experimental and control vessels showed an increase in aqueous nickel concentration as solids concentration was increased. DiToro and Horzempa (1982) obtained similar results for the sorption of 2,4,5,2',4',5'-hexachlorobiphenyl to lake sediments. Despite this evidence disputing the microparticulate theory, no data have been collected that support the theory of particle-particle interactions.

Gschwend and Wu (1985) argue against the theory of particle-particle interactions and irreversible sorption, stating that "unless either some unusual chemical bond between these nonreactive compounds (PCB's/PAH's) and natural organic matter or mineral surfaces is forming or some deformation of the natural organic matter around the sorbates to form a "cagelike" structure is occurring, we do not understand how such an irreversible uptake could take place (especially on the time scale of hours to days)."
Fundamental to their argument is the assumption that binding of organic compounds to sediment primarily involves hydrophobic association with the organic matter of the sediment. Evidence has not been presented that disputes particle-particle interactions or irreversible sorption; however, a significant amount of data does exist that supports the microparticulate theory.

The production of nonseparable microparticulates has been followed by measuring organic carbon content, turbidity and weight of dissolved solids of the aqueous phase after equilibration with sediment or soil (Gschwend and Wu, 1985; Voice et al., 1983). The concentration of nonseparable material was found to increase with increasing solids concentration. The amount of suspended material remaining after separation has also been followed as a function of the duration and force of centrifugation. Although microparticulates cannot be completely removed from solution, their concentration can be decreased using stringent centrifugal conditions (Gschwend and Wu, 1985). Using a technique that distinguishes between free paraquat and paraquat sorbed to suspended particulates, Karickhoff and Brown (1978) were able to follow the concentration of sorbed paraquat as a function of centrifugation time. The amount of sorbed paraquat was found to gradually decrease over a centrifugation period of 4 hours; however, it should be noted that after 1 hour of centrifuging, the aqueous phase still contained more sorbed than "free" paraquat.
Although the exact composition of the microparticulate material produced during batch equilibration is not known, it is very possible that it contains a high percentage of natural organic matter. Madhun et al. (1986) used ordinary batch equilibration to obtain natural organic matter from a 1:5 soil:water mixture. They found that the aqueous phase contained over 200 ppm total organic carbon following agitation and centrifugation of the soil-water mixture. The presence of natural organic matter (such as that mentioned above) in the aqueous phase has been shown to influence measured distribution coefficients for several sorbates. In the binding of cholesterol and 2,2',5,5'-tetrachlorobiphenyl by river and sewage-borne solids, Hassett and Anderson (1982) found that as dissolved organic carbon concentrations of sewage and river waters are increased by ultrafiltration, adsorption ($K_d^{obsd}$) decreases. Similar results were reported for the binding of $^{244}$Cm to sediments (Sibley and Alberts, 1984). If a large percentage of microparticulate material is indeed organic in nature, then based on the results discussed above, distribution coefficients will be influenced by the production of microparticulates during batch equilibrations.

If the solids concentration effect and adsorption-desorption hysteresis can be explained by the production of nonseparable microparticulates, experimental details may greatly affect the measurement of distribution coefficients.
and therefore, should be specified. For example, washing sediments prior to batch equilibration has been found to result in increased distribution coefficients when compared to unwashed sediments (Gschwend and Wu, 1985; Koskinen and Cheng, 1983; Sibley and Alberts, 1984). Conditions of agitation and separation can also affect results.

The method of analysis also becomes a very important factor when there is incomplete separation of microparticulates. Techniques such as the counting of radiolabelled analytes will not distinguish between freely dissolved analyte and analyte bound to microparticulates. There are, however, several methods that can distinguish between the two species. Karickhoff and Brown (1978) used UV absorption to detect paraquat bound to hectorite (maximum absorbance at 275 nm) and "free" paraquat (maximum absorbance at 260-262 nm). A reverse-phase separation technique (Landrum et al., 1984) separates "free" analyte from analyte associated with dissolved or suspended organic matter. The analyte is first equilibrated with a solution containing humic material, as in the measurement of distribution coefficients with sediment. Analyte bound to humic material is then separated from "free" analyte in solution using a Sep-Pak cartridge that retains the "free" analyte but allows analyte bound to humic material to pass through. Analyte sorbed to the column is later eluted and analyzed. Radiolabelled compounds are used and the final analysis done using liquid scintillation counting. The
problem here is that the proportion of each specie can be altered during the separation step. In fact, Landrum notes that results vary with flow rate through the column. Finally, a fluorescence quenching technique developed by Gauthier et al. (1986) will detect only freely dissolved analyte. This method is based on the principle that fluorescence of a molecule is quenched when associated with organic material and so no separation step is required. Therefore, there is no disturbance of the equilibrium concentrations. This technique has been successfully used in determining binding constants for pyrene, anthracene and phenanthrene.

It is the purpose of the research presented here to more closely examine the influence of experimental variables such as the degree of agitation, separation efficiency and method of analysis. Batch equilibrations using liquid scintillation counting, with and without Sep-Pak separations, as well as fluorescence quenching will be compared. A theoretical model is also presented that predicts the bias in measured distribution coefficients introduced by the method of analysis when microparticulates are produced.

**Theory**

Batch equilibration involves agitation of a mixture containing a known quantity, a, of sediment or soil and a known volume, v, of an aqueous solution of the sorbate of interest. Following separation of the solid and solution
phases, the concentration of analyte X in each phase is determined and the distribution coefficient ($K_d$) is calculated.

In the following derivation, a "true" or ideal value for $K_{oc}$ (coefficient normalized to fraction of organic carbon of the soil or sediment) is assumed, from which distribution coefficients can then be calculated. The "true" value refers to the ideal situation where no microparticulates are produced and therefore reflects the actual distribution between free and bound X.

The non-ideal case involves the production of microparticulates. Here it is necessary to distinguish between three different forms of X that can exist at equilibrium: (1) X free in solution, (2) X bound to microparticulates suspended in solution, and (3) X bound to bulk sediment which is readily separated from the aqueous phase. It is assumed that two equilibrium situations exist: (1) X can partition between bottom sediment and water. The corresponding distribution coefficient, $K_1$, is expressed as:

$$K_1 = \frac{x_{SED}/a}{x_{FREE}/v} \quad (26)$$

where $x_{SED}$ and $x_{FREE}$ are the quantities of X (grams) sorbed to bulk sediment and free in solution, respectively. (2) X can also distribute between water and suspended microparticulates where b is the mass of suspended
microparticulates. In this case, the distribution coefficient, $K_2$, can be expressed as:

$$K_2 = \frac{x_{\text{SUS}}/b}{x_{\text{FREE}}/v}$$  \hspace{1cm} (27)

where $x_{\text{SUS}}$ is the amount of X bound to microparticulates and $b$ is the mass of suspended microparticulates. These assumptions are also made in the model proposed by Gschwend and Wu (1985).

Using mass balance for X:

$$x_{\text{TOTAL}} = x_{\text{SUS}} + x_{\text{SED}} + x_{\text{FREE}}$$  \hspace{1cm} (28)

the distribution of X between bulk sediment, microparticulates and solution (free) can be derived. Simultaneous solution of equations 26, 27, and 28 yields:

$$x_{\text{FREE}} = \frac{x_{\text{TOTAL}}v}{K_1a + K_2b + v}$$  \hspace{1cm} (29)

$$x_{\text{SED}} = \frac{K_1ax_{\text{FREE}}}{v}, \text{ and}$$  \hspace{1cm} (30)

$$x_{\text{SUS}} = \frac{K_2bx_{\text{FREE}}}{v}$$  \hspace{1cm} (31)

In all cases it is assumed that the mass of microparticulates produced is negligible in relation to the initial mass of bulk sediment and so there is no
observable change in bulk sediment mass over the course of an experiment. This assumption is reasonable based on the results of Gschwend and Wu (1985) and Voice and Weber (1985). For example, in a batch equilibration using 0.5 g sediment in 40 mL water, the organic carbon content of the aqueous phase was determined to be approximately 10 mg/L (Gschwend and Wu, 1985). For microparticulates containing 100% organic material, this corresponds to 0.4 mg in 40 mL or 0.08% of the bulk sediment mass. For microparticulates containing only 2.5% organic matter (similar to bulk sediment), this corresponds to 16 mg in 40 mL or 3.2% of bulk sediment mass.

A radiolabelling experiment uses activity determination to measure the aqueous phase concentration. The amount of X bound to sediment is determined by difference. Because the measured concentration of the aqueous phase includes both free X and X bound to microparticulates, the experimental distribution coefficient, $K_d^R$, is expressed as:

$$K_d^R = \frac{x_{SED}/a}{(x_{SUS} + x_{FREE})/v} \quad (32)$$

Substitution of equations 30 and 31 into equation 32 yields:
\[ K_d^R = \frac{vK_1}{v + K_2b} \]  

(33)

If \( x_{\text{SUS}} \ll x_{\text{FREE}} \) or \( K_2b \ll v \), then \( K_d^R \) will closely approach \( K_1 \), the true distribution coefficient. Radiolabelling is specified here as the analytical technique because it is so frequently used in the measurement of distribution coefficients. This is not to say that this model will apply only to experiments using the activity determination of radiolabelled compounds. It will also hold for any analytical technique which cannot distinguish between sorbate which is freely dissolved and sorbate bound to suspended microparticulates.

Fluorescence quenching also measures the concentration of \( X \) in the aqueous phase. Fluorescence is quenched for \( X \) bound to soil or suspended microparticulates and therefore only free \( X \) is detected. The amount of \( X \) associated with the sediment is determined by difference and represents \( X \) bound to bulk sediment as well as microparticulates. The distribution coefficient, \( K_d^F \), now becomes:

\[ K_d^F = \frac{(x_{\text{SED}} + x_{\text{SUS}})/a}{x_{\text{FREE}}/v} \]  

(34)

Substitution of equations 30 and 31 into equation 34 yields:
\[ K_d^F = \frac{K_1 a + K_2 b}{a} \]  \hspace{1cm} (35)

\( K_d^F \) will approach the true distribution coefficient \((K_1)\) if \( x_{SUS} \ll x_{SOIL} \) or \( K_2 b \ll K_1 a \). As in the case of \( K_d^R \), \( K_d^F \) could also apply to any experiment in which the analytical technique is capable of distinguishing between freely dissolved sorbate and sorbate bound to suspended microparticulates.

Further derivation yields:

\[
\frac{K_d^F}{K_d^R} = \left[ 1 + \frac{x_{SUS}}{x_{SED}} \right] \left[ 1 + \frac{x_{SUS}}{x_{FREE}} \right] \hspace{1cm} (36)
\]

\[
= \left[ 1 + \frac{K_2 b}{K_1 a} \right] \left[ 1 + \frac{K_2 b}{v} \right]. \hspace{1cm} (37)
\]

Using the definitions for \( K_1 \), \( K_2 \) and total organic carbon concentration (TOC) of the aqueous phase:

\[ K_1 = (OC) (K_{oc}) \]  \hspace{1cm} (38)

\[ K_2 = (OC') (K_{oc}) \]  \hspace{1cm} and \hspace{1cm} (39)

\[ TOC = \frac{(OC') (b)}{v} \]  \hspace{1cm} (40)

\((OC = \text{fraction of organic carbon in sediment}; \ OC' = \text{fraction of organic carbon in microparticulates, this ratio})\)
can be expressed as:

\[
\frac{K_d^F}{K_d^R} = \left[ 1 + \frac{(v)(TOC)}{(a)(OC)} \right] \left[ 1 + (TOC)(K_{oc}) \right]. \tag{41}
\]

This theoretical treatment demonstrates the influence of sediment concentration, suspended microparticulates and the magnitude of \(K_{oc}\) on measured distribution coefficients. Equations 33, 35, and 41 were used to calculate values for \(K_d^F\), \(K_d^R\) and \(K_d^F/K_d^R\) under hypothetical laboratory conditions. Conditions were chosen to mimic those typically encountered in batch equilibrations.

To simplify calculations, \(K_{oc}\) was assumed to be the same for both sediment and microparticulates, and so values of \(K_1\) and \(K_2\) will differ only when sediment and microparticulates contain different percentages of organic carbon. This assumption is reasonable although there could be some difference in the composition of organic matter between bulk sediment and microparticulates and this would be likely to produce some differences in \(K_{oc}\). Initially, a "true" value of \(K_{oc}\) of 80,000 mL/g was assumed, with bulk sediment containing 2.5% organic carbon (\(K_1 = 2000\) mL/g) and microparticulates containing 10% organic carbon (\(K_2 = 8000\) mL/g). It was also assumed that all organic carbon in solution is associated with microparticulates. Therefore, the concentration of suspended microparticulates is expressed in terms of total organic carbon concentration.
(TOC) of the aqueous phase.

TOC was varied in order to evaluate the effect of microparticulates on predicted distribution coefficients. As can be seen in Table 3.2, $K_d^R$ is more strongly influenced by TOC than is $K_d^F$. At a level of 25 ppm organic carbon, $K_d^F$ deviates only 1% from the "true" value of 2000 mL/g while $K_d^R$ differs by 67%; $K_d^F$ is approximately three times greater than $K_d^R$. Over the range of TOC concentrations assumed (0 to 25.0 ppm C), the relationship between $K_d^F/K_d^R$ and TOC was found to be linear for a constant value of $K_{oc}$. For $K_{oc} = 80,000$ mL/g (0.08 L/mg), linear regression gave an equation of the form:

$$\frac{K_d^F}{K_d^R} = 0.998 + (0.81)(TOC).$$

(42)

By assuming that $K_2b/K_1a \ll 1$, equation 37 reduces to:

$$\frac{K_d^F}{K_d^R} = 1 + \frac{K_2b}{v}.$$  

(43)

Combined with the definitions for $K_2$ and total organic carbon (equations 39 and 40), this equation becomes:

$$\frac{K_d^F}{K_d^R} = 1 + (TOC)(K_{oc}),$$  

(44)

very similar to that calculated using linear regression. Comparison of values calculated for $K_d^F/K_d^R$ using equations
Table 3.2. Calculated distribution coefficients $K_d^R$ and $K_d^{F*}$.

<table>
<thead>
<tr>
<th>TOC (mg/L)</th>
<th>$K_d^R$ (mL/g)</th>
<th>$K_d^{F*}$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>0.5</td>
<td>1923</td>
<td>2000.4</td>
</tr>
<tr>
<td>1.0</td>
<td>1852</td>
<td>2000.8</td>
</tr>
<tr>
<td>2.5</td>
<td>1666</td>
<td>2002</td>
</tr>
<tr>
<td>5.0</td>
<td>1429</td>
<td>2004</td>
</tr>
<tr>
<td>10.0</td>
<td>1111</td>
<td>2008</td>
</tr>
<tr>
<td>15.0</td>
<td>909</td>
<td>2012</td>
</tr>
<tr>
<td>25.0</td>
<td>666</td>
<td>2020</td>
</tr>
</tbody>
</table>

* Hypothetical experimental conditions:

10 mL : 1 g = solution-to-solid ratio  
80,000 mL/g = "true" $K_{oc}$

bulk sediment contains 2.5% organic carbon  
microparticulates contain 10% organic carbon
41 and 44 reveals that for the hypothetical conditions listed in Table 3.2 \((K_{oc} = 80,000 \text{ mL/g})\), the difference between approximate and exact values increases with increasing TOC. A TOC concentration of 25.0 ppm results in a 1% difference between exact and approximate values. Also, for a constant TOC of 10.0 ppm C, the discrepancy increases with increasing \(K_{oc}\) and decreasing sediment concentration. There is a 4% difference between approximate and exact values of \(K_d^F/K_d^R\) for \(K_{oc} = 80,000 \text{ mL/g}\) and a sediment-to-water ratio of 0.1 g: 10 mL, or for \(K_{oc} = 800,000 \text{ mL/g}\) and a sediment-to-water ratio of 1 g: 10 mL.

The assumption that \(K_{2b}/K_1a \ll 1\) is equivalent to assuming that \(x_{\text{SUS}}/x_{\text{SED}} \ll 1\) or \(x_{\text{SUS}} \ll x_{\text{SED}}\). With this assumption, equation 36 reduces to:

\[
\frac{K_d^F}{K_d^R} = 1 + \frac{x_{\text{SUS}}}{x_{\text{FREE}}}.
\]  

(45)

This approximation will be valid in cases where the amount of microparticulates produced is negligible relative to total solids and the analyte is not greatly enriched in the suspended material relative to the bulk solid. As already stated, for \(x_{\text{SUS}} \ll x_{\text{SED}}\), \(K_d^F\) will equal the "true" distribution coefficient (equation 34). Similarly, for \(x_{\text{SUS}} \ll x_{\text{FREE}}\), \(K_d^R\) will equal the "true" distribution coefficient (equation 32). Figure 3.3a shows the relative
amounts of the three species of X at equilibrium. For compounds having a high affinity for the solid (such as pyrene), dissolved (free) aqueous concentrations will be very low and the amount of X associated with suspended microparticulates will significantly add to the concentration of X in the aqueous phase. Therefore, $K_d^R$ will be greatly influenced by the production of nonseparable microparticulates during an experiment. Conversely, the relative amount of X associated with the sediment is very high and the contribution of X from suspended microparticulates is negligible. This causes $K_d^F$ to remain essentially constant regardless of TOC.

Figure 3.3b corresponds to the case where $K_{oc}$ is small and the compound has a low affinity for the sediment (e.g. acetophenone). In this case, the contribution of $x_{SUS}$ to both $x_{FREE}$ and $x_{SED}$ is essentially negligible; neither $K_d^F$ or $K_d^R$ is greatly affected by the production of microparticulates during an experiment.

Calculations using TOC values ranging from 0 to 25.0 ppm carbon indicate that for $K_{oc} = 80$ mL/g, $K_d^F$ and $K_d^R$ are approximately equal while for $K_{oc} = 80,000$ mL/g, $K_d^F$ and $K_d^R$ can differ significantly (Figure 3.4). Calculations show a linear relationship to exist between $K_{oc}$ and $K_d^F/K_d^R$ (constant TOC), in agreement with the approximate relationship represented by equation 44 (Figure 3.5). This prediction is consistent with the observation of O'Connor and Connolly (1980) that the solids effect is greatest for
Figure 3.3. Speciation of analyte in a three phase system (solid:solution ratio = 1:10, 10% organic carbon in microparticulates, 2.5% organic carbon in bulk sediment.

a. $K_{oc} = 80,000 \text{ mL/g}$. 

- Bound to sediment
- Bound to microparticulates
- Freely dissolved

% of Total Analyte

TOC (mg/L)
b. $K_{oc} = 80 \text{ mL/g.}$
Figure 3.4. Influence of TOC on $K_d^F/K_d^R$.

$K_{oc} = 80,000 \text{ mL/g}$

$K_{oc} = 80 \text{ mL/g}$
Figure 3.5. Influence of "true" $K_{oc}$ on $K_d^F/K_d^R$ (solid:solution ratio = 1 g: 10 mL).

TOC = 25.0 ppm

TOC = 10.0 ppm

TOC = 1.0 ppm
compounds characterized by large distribution coefficients whereas the measured coefficient approaches a constant value for substances of low partitioning.

Equation 41 shows that while TOC concentration of the aqueous phase is important, the percent organic carbon in the microparticulates will not directly affect the ratio, \( K_d^F / K_d^R \). Calculations show that for a given concentration of TOC, distribution coefficients predicted by the model remain constant regardless of the percent of organic carbon present in the microparticulates. Conversely, the percent organic carbon present in the sediment will influence \( K_d^F / K_d^R \). However, this effect is small — increasing organic carbon from 2.5% to 25% results in a decrease in \( K_d^F / K_d^R \) from 1.81 to 1.80 (other parameters given in Table 3.2).

Theoretical calculations also predict that the solid-to-solution ratio should not greatly influence the magnitude of distribution coefficients. Predicted values for \( K_d^F \) and \( K_d^R \) did not change significantly (less than 1%) when solid-to-solution ratio was decreased from 1:10 to 1:5, all other parameters held constant. According to this model, the primary way in which solids concentration can noticeably affect measured distribution coefficients is through TOC concentration with the production of microparticulates. Experimental evidence is required to link solids concentration with the concentration of microparticulates.
**Experimental**

Two types of experiments were conducted. The batch equilibration method was first examined to determine the effect of procedural variations on aqueous phase composition and sediment integrity. Distribution coefficients were then determined for anthracene binding to sediment. Several different methods of analysis were used in order to investigate their effects on coefficient estimates.

A. **Batch equilibration - Effect of experimental variables.**

**Procedure.** The batch equilibration procedure consisted of three basic steps: equilibration of sediment with aqueous solution, separation of sediment and solution phases, and analysis/examination of the separated phases. Samples were prepared by adding a known mass of sediment followed by 25.0 mL of an aqueous solution to a 50 mL Teflon centrifuge tube. Duplicate samples were run under each set of conditions.

Sediment concentration was varied from 10 g/L to 250 g/L. Both distilled water and a solution of 0.5 M NaCl, 0.05 M MgSO$_4$·7H$_2$O (major components of seawater) were used to evaluate the effect of solution composition. Samples were agitated during the equilibration procedure using either a wrist-action shaker, reciprocating shaker or sonicator. Equilibration times of 0.25, 2, 8 and 24 hours were evaluated. The two phases were separated by centrifugation, filtration or a combination of the two.
The influence of ultrafiltration of the aqueous phase was also examined. Following separation, conductivity of the aqueous phase was measured and the solution immediately frozen for later TOC (total organic carbon) analysis. Sediment was freeze-dried for examination by scanning electron microscopy.

**Materials and apparatus.** Core samples (0" to 10" below surface) of sediment were obtained from the Oyster River in Dover, New Hampshire. Sediment was air-dried and passed through a 2 mm sieve to remove any large particles. Carbon, hydrogen and nitrogen contents of sediment samples were determined on a Perkin Elmer 240B Elemental Analyzer.

Glass-distilled (Kontes WS-2 continuous still), deionized (research grade mixed bed demineralizer, Barnstead D0809) water was used in all solution preparation. All glass and plasticware was washed with 20% H$_2$SO$_4$, rinsed thoroughly with deionized water and air-dried.

Batch equilibration samples were centrifuged using an International Clinical Centrifuge, Model CL, or they were filtered through 0.45 μ Nucleopore filters (47 mm in diameter). Ultrafiltration was performed using Amicon UM-2 (molecular weight cutoff = 2000), PM-10 (molecular weight cutoff = 10,000) and XM-50 (molecular weight cutoff = 50,000) membranes. Prior to use, all filters were washed thoroughly with distilled, deionized water.

Total organic carbon (TOC) concentrations of
supernatants were determined using an Oceanography International Total Organic Carbon Analyzer equipped with a Horiba PIR-2000 Infrared Analyzer and a Model 526 integrator. Calibration curves were constructed using standard carbon solutions prepared with potassium hydrogen phthalate (A.C.S. primary standard). Prior to analysis, all samples were digested by the persulfate oxidation technique of Menzel and Vaccaro (1964). Digestion reagents, potassium persulfate (analytical reagent, Sigma Chemical Company) and phosphoric acid (85% solution, Fisher Scientific) were used without further purification.

Conductivities of supernatants were measured using a Wheatstone bridge assembly.

Sediment was freeze-dried using a Labconco bench top freeze-dryer and later examined using an AMR 1000 Scanning Electron Microscope. Samples were mounted on aluminum studs using double-sided tape to secure sediment particles. Samples were then coated with a 200 Å gold-palladium coat using a Hummer-V Sputter Coater.

B. Determination of Distribution Coefficient.

Procedure. Distribution coefficients of radiolabelled anthracene were first measured using the batch equilibration technique. A known weight of sediment was equilibrated for 24 hours with 25.0 mL of a phosphate buffer solution (pH = 6.5) containing radiolabelled anthracene. The effect of sediment concentration on measured coefficients was examined using two sediment
concentrations, 10 and 100 g/L. Samples were centrifuged for one hour and the aqueous phase was analyzed by liquid scintillation counting.

Anthracene distribution coefficients were also determined using a second set of samples prepared as described above. However, an attempt was made to separate free from microparticulate bound anthracene by passing the aqueous supernatants through C-18 Sep-Pak cartridges prior to analysis. This procedure was adapted from that developed by Landrum et al. (1984).

Distribution coefficients for anthracene were also determined by fluorescence quenching using the procedure of Gauthier et al. (1986).

Duplicate measurements were made in all cases.

Materials and Apparatus. Sediment described in the previous section was used in all measurements. Fluorescence quenching experiments were conducted using 99+% pure anthracene (Aldrich, gold label). Radiolabelled 9(10)-14C anthracene (15.1 mCi/m mole) from Amersham was purified by preparative thin-layer chromatography before use. Column separations were performed using C-18 Sep-Pak Cartridges (Waters Associates).

Fluorescence measurements were made with a Perkin Elmer Model 204 Fluorescence Spectrophotometer. Excitation and emission wavelengths of 250 and 380 nm, respectively, were used to monitor anthracene fluorescence. Measurements were made as a function of added sediment. Samples were
centrifuged before each reading to reduce the effects of scatter. Data averaging was performed with an Apple IIe Computer so that each measured fluorescence value corresponded to an average of 225 data points. Absorbance measurements were made using a Bausch and Lomb Spectronic 200 Recording Spectrophotometer. A Beckman LS-7000 Liquid Scintillation Counter equipped with automatic quench compensation was used to measure radioactivity.

Results and Discussion

A. Batch equilibration - An overview of experimental variables.

The effects of sediment concentration, type of agitation, equilibration time, method of separation and composition of the aqueous phase were examined using statistically designed experiments. The sediment used in all these experiments contained 2.44% organic carbon. Total organic carbon (TOC) concentration was used as the primary indicator of the release of microparticulate material into the aqueous phase. Conductivity was also monitored in order to provide an indication of the extent to which salts were released into the aqueous phase. Data interpretation relied on analysis of variance (ANOVA) and regression analysis (RAT).

Various methods were compared for efficiency in separating out microparticulate material. The effectiveness of ultrafiltration was also investigated with membranes of various pore sizes. Evaluation of the effects
of aqueous phase composition was limited to the comparison of distilled water with a solution designed to mimic the ionic strength of sea water.

The effects of sediment concentration and type of agitation were investigated using a 3x6 factorial design and 24 hour equilibration time. Samples were separated by centrifuging at 9000 rpm. Total organic carbon (TOC) and conductivity measurements are summarized in Tables 3.3a and 3.4a. ANOVA calculations for each complete data set are shown in 3.3b and 3.4b. Similarly, the effects of equilibration time and type of agitation were studied using a 3x4 factorial experiment at a constant sediment concentration of 100 g/L (solid-to-solution ratio = 2.5g: 25.0 mL; samples centrifuged at 9000 rpm). TOC concentration and conductivities are summarized in Tables 3.5a and 3.6a, respectively, and statistical analyses are shown in Tables 3.5b and 3.6b. According to TOC and conductivity results, no significant interactions (0.05 significance level) were found between sediment concentration and agitation type or equilibration time and agitation type. Therefore, the effects of each variable can be considered separately.

All results will be evaluated in terms of the microparticulate theory previously presented.

Separation efficiency. Of the literature surveyed, it was found that centrifugation has been used in approximately 90% of all experiments designed to measure
Table 3.3. Effect of sediment concentration and type of agitation on TOC concentration of aqueous phase.

a. TOC results (ppm C).*

<table>
<thead>
<tr>
<th>Sediment Concentration (g/L)</th>
<th>Wrist Action</th>
<th>Reciprocating</th>
<th>Sonication</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.01</td>
<td>5.36</td>
<td>8.02</td>
</tr>
<tr>
<td>50</td>
<td>14.5</td>
<td>13.2</td>
<td>14.5**</td>
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<tr>
<td>100</td>
<td>17.2</td>
<td>20.4</td>
<td>15.6</td>
</tr>
<tr>
<td>150</td>
<td>32.0</td>
<td>37.6</td>
<td>30.6</td>
</tr>
<tr>
<td>200</td>
<td>37.5</td>
<td>37.5</td>
<td>34.0</td>
</tr>
<tr>
<td>250</td>
<td>33.3</td>
<td>38.2</td>
<td>36.2</td>
</tr>
</tbody>
</table>

* Each point represents the average of two values.

** Only one value - not duplicated.

b. ANOVA.

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>25831.05</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>20491.108</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>4951.0295</td>
<td>5</td>
<td>990.2059</td>
<td>60.53</td>
</tr>
<tr>
<td>Agitation</td>
<td>27.8696</td>
<td>2</td>
<td>13.9348</td>
<td>0.85</td>
</tr>
<tr>
<td>Error</td>
<td>278.1002</td>
<td>17</td>
<td>16.3588</td>
<td></td>
</tr>
<tr>
<td>Interaction</td>
<td>82.9427</td>
<td>10</td>
<td>8.2943</td>
<td>0.51</td>
</tr>
</tbody>
</table>

*** At the 0.05 significance level, required F values for 2 and 17, 5 and 17, and 10 and 17 df are 3.59, 2.81, and 2.45, respectively.
Table 3.4. Effect of sediment concentration and type of agitation on conductivity of aqueous phase.

a. Conductivity (μmho).*

<table>
<thead>
<tr>
<th>Sediment Concentration (g/L)</th>
<th>Wrist Action</th>
<th>Reciprocating</th>
<th>Sonication</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2426</td>
<td>2625</td>
<td>2200</td>
</tr>
<tr>
<td>50</td>
<td>12000</td>
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<td>100</td>
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<td>18700</td>
</tr>
<tr>
<td>150</td>
<td>31700</td>
<td>27100</td>
<td>31400</td>
</tr>
<tr>
<td>200</td>
<td>35600</td>
<td>33700</td>
<td>30700</td>
</tr>
</tbody>
</table>

* Each point represents the average of two values.

b. ANOVA.**

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)***</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>11248.16</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
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</tr>
<tr>
<td>Agitation</td>
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<td>14.710</td>
<td>0.69</td>
</tr>
<tr>
<td>Error</td>
<td>321.171</td>
<td>15</td>
<td>21.4114</td>
<td></td>
</tr>
<tr>
<td>Interaction</td>
<td>46.9475</td>
<td>8</td>
<td>5.868</td>
<td>0.27</td>
</tr>
</tbody>
</table>

** ANOVA calculated using coded values. Values divided by 1000.

*** At the 0.05 significance level, required F values for 2 and 15, 4 and 15, and 8 and 15 df are 3.68, 3.06, and 2.64, respectively.
Table 3.5. Effect of equilibration time and type of agitation on TOC concentration of aqueous phase.

a. TOC results (ppm C).*

<table>
<thead>
<tr>
<th>Equilibration Time (hours)</th>
<th>Wrist Action</th>
<th>Reciprocating</th>
<th>Sonication</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>20.6</td>
<td>22.0</td>
<td>16.9</td>
</tr>
<tr>
<td>2</td>
<td>20.0</td>
<td>17.2**</td>
<td>18.3</td>
</tr>
<tr>
<td>8</td>
<td>19.5</td>
<td>20.6</td>
<td>20.7</td>
</tr>
<tr>
<td>24</td>
<td>17.2</td>
<td>20.4</td>
<td>15.6</td>
</tr>
</tbody>
</table>

* Each point represents the average of two values.
** Only one value - not duplicated.

b. ANOVA.

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)***</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>CF</td>
<td>8440.364</td>
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</tr>
<tr>
<td>Time</td>
<td>23.574</td>
<td>3</td>
<td>7.858</td>
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<tr>
<td>Agitation</td>
<td>24.915</td>
<td>2</td>
<td>12.457</td>
<td>3.212</td>
</tr>
<tr>
<td>Error</td>
<td>42.66</td>
<td>11</td>
<td>3.878</td>
<td></td>
</tr>
<tr>
<td>Interaction</td>
<td>34.407</td>
<td>6</td>
<td>5.734</td>
<td>1.479</td>
</tr>
</tbody>
</table>

*** At the 0.05 significance level, required F values for 2 and 11, 3 and 11, and 6 and 11 df are 3.98, 3.59, and 3.09, respectively.
Table 3.6. Effect of equilibration time and type of agitation on conductivity of aqueous phase.

a. Conductivity (μmho)*.

<table>
<thead>
<tr>
<th>Equilibration Time (hours)**</th>
<th>Wrist Action</th>
<th>Reciprocating</th>
<th>Sonication</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10750</td>
<td>15000</td>
<td>14300</td>
</tr>
<tr>
<td>8</td>
<td>19950</td>
<td>21700</td>
<td>19900</td>
</tr>
<tr>
<td>24</td>
<td>21600</td>
<td>17000</td>
<td>18700</td>
</tr>
</tbody>
</table>

* Each point corresponds to the average of two values.

** Conductivity measurements for equilibration time of 0.25 hours inadvertently omitted.

b. ANOVA.***

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)****</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>5870.82</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>5610.936</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>172.861</td>
<td>2</td>
<td>86.43</td>
<td>9.62</td>
</tr>
<tr>
<td>Agitation</td>
<td>0.657</td>
<td>2</td>
<td>0.328</td>
<td>0.036</td>
</tr>
<tr>
<td>Error</td>
<td>80.82</td>
<td>9</td>
<td>8.98</td>
<td></td>
</tr>
<tr>
<td>Interaction</td>
<td>5.546</td>
<td>4</td>
<td>1.386</td>
<td>0.154</td>
</tr>
</tbody>
</table>

*** ANOVA calculated using coded values. Values divided by 1000.

**** At the 0.05 significance level, required F values for 2 and 9, and 4 and 9 df are 4.26 and 3.63, respectively. At the 0.01 significance level, the required value for 2 and 9 df is 8.02.
distribution coefficients for soils and sediments; filtration was used in the remaining 10% of experiments. Filtration is more often used for collection of suspended particulate matter from the aquatic environment and removal of particulate material in wastewater treatment (Lal, 1977; Levine et al., 1985). However, Baker et al. (1986) point out that neither filtration or centrifugation (with operational size cutoffs) are able to completely remove all particulate material from suspension due to its naturally occurring continuous size distribution. Furthermore, Karickhoff and Brown (1978) have shown that separation efficiency can play a role in the determination of distribution coefficients. In the adsorption of paraquat to clay, the concentration of sorbed paraquat remaining in suspension decreased over the course of 4 hours centrifugation time. As a result, it is concluded that sediment-water phase concentrations are not absolute.

Several separation techniques were evaluated using a constant sediment concentration of 100 g/L and equilibration time of 24 hours with reciprocating shaking. The following methods of separation were studied: (a) centrifugation for one hour at 9000 rpm, (b) filtration through 0.45 μm Nucleopore filters (filters first washed with 250 mL deionized water), (c) centrifugation followed by filtration, (d) centrifugation after samples were allowed to settle for 24 hours, and (e) filtration (0.45 μm Nucleopore filters) after samples were allowed to settle
for 24 hours. The amount of carbon contributed by the filters was negligible; organic carbon levels in filtration blanks were less than 0.3 ppm carbon.

Results of this experiment are summarized in Table 3.7a and ANOVA is shown in Table 3.7b. No significant difference was found between the different separation techniques (0.05 significance level); however, TOC concentrations tended to be slightly higher when samples were allowed to stand for 24 hours (significant at 0.10 level). Samples were left to settle for 24 hours in order to see if this would promote reaggregation of the particulates and thereby decrease microparticulate (TOC) concentration. Instead, small additional amounts of organic material were released into solution upon standing or filterable aggregates broke down further. Consequently, it appears best to centrifuge or filter samples as soon as possible after equilibration in order to avoid further biasing of distribution coefficient measurements. Otherwise, differences in these methods of separation are not an important consideration in the batch equilibration procedure. This is in agreement with the findings of Karickhoff et al. (1979). Distribution coefficients measured for pyrene and methoxychlor on medium and coarse sediments were indistinguishable within experimental error regardless of whether samples were filtered through halocarbon membranes (2-5 \( \mu \)m pore size) or centrifuged (20,000 rpm, 1 hour).
Table 3.7  Effect of separation technique on TOC concentration of the aqueous phase.

a. TOC results (ppm C).

<table>
<thead>
<tr>
<th>Separation Technique</th>
<th>C (1)</th>
<th>F (2)</th>
<th>C-F (3)</th>
<th>St-C (4)</th>
<th>St-F (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.5</td>
<td>19.0</td>
<td>22.6</td>
<td>23.8</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>21.4</td>
<td>21.0</td>
<td>20.4</td>
<td>24.0</td>
<td>23.6</td>
<td></td>
</tr>
</tbody>
</table>

(1) C = Centrifugation.
(2) F = Filtration.
(3) C-F = Centrifugation followed by filtration.
(4) St-C = Centrifuged after 24 hours of standing.
(5) St-F = Filtered after 24 hours of standing.

b. ANOVA – One variable of classification.

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>4799.37</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>4774.225</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation</td>
<td>19.32</td>
<td>4</td>
<td>4.83</td>
<td>4.14</td>
</tr>
<tr>
<td>Residual</td>
<td>5.825</td>
<td>5</td>
<td>1.165</td>
<td></td>
</tr>
</tbody>
</table>

* At the 0.05 significance level, required F value for 4 and 5 df is 5.19; at the 0.10 significance level, it is 3.52.
Ultrafiltration is another separation technique that has been used to collect and fractionate high molecular weight organic matter found in natural water samples (Buffle et al., 1978; Hassett and Anderson, 1982; Wijayaratne and Means, 1984). In ultrafiltration, hydrostatic pressure is used to force molecules smaller than the size cutoff of the membrane through the micropores of the membrane while larger molecules are retained (Aiken, 1984). Bengtsson et al. (1986) have suggested an ultrafiltration procedure to separate macromolecules and particulates when determining distribution coefficients of radiolabelled compounds. They have demonstrated that the ultrafiltration cell will retain polymer and particle suspensions while allowing low molecular weight radiolabelled organic compounds to pass through the membrane. Therefore, ultrafiltration was investigated.

Ultrafiltration was used in conjunction with centrifugation. Batch equilibrations (reciprocating shaker for 24 hours) were carried out with a sediment concentration of 100 g/L. Samples were then centrifuged for 1 hour (9000 rpm) and the aqueous phase was passed through the appropriate ultrafiltration membrane. Three different membranes were evaluated: (a) XM-50, molecular weight cutoff of 50,000, (b) PM-10, molecular weight cutoff of 10,000, and (c) UM-2, molecular weight cutoff of 1000. Blanks were prepared by passing 25 mL of distilled-deionized water through each membrane.
The results of TOC analyses are summarized in Table 3.8a and the corresponding ANOVA is shown in Table 3.8b. Although TOC concentration decreased by approximately 30% in going from a XM-50 membrane to a UM-2 membrane, the differences were not real even at the 0.10 level of significance.

These results can also be compared to those obtained by centrifugation only. From Table 3.7a, equilibrated sediment-water samples separated using centrifugation contain an average of 20.6 ppm carbon. Ultrafiltration following centrifugation did not significantly change TOC concentration for any of the membranes. Using only centrifugation to separate sediment from water, aqueous phase TOC concentrations have varied from 13.4 to 21.0 ppm carbon. Clearly, ultrafiltration through the membranes studied here does not improve separation efficiency.

Typical soluble organic matter derived from soils and sediments will have molecular weights in the range 10,000 to 1000 daltons. Buffie et al. (1978) evaluated the use of ultrafiltration for the separation and fractionation of organic ligands in fresh waters. Most humic and fulvic acids were retained between the PM-10 and UM-05 ultrafiltration membranes (35 to 50% falling in the molecular weight range of 10,000 to 1000 daltons). In a study by Madhun et al. (1986), water soluble soil organic materials (WSSOM) from soil were chromatographed on two Sephadex gels, G-10 and G-25, with exclusion limits of 700
Table 3.8. Effect of ultrafiltration on TOC concentration of the aqueous phase.

a. TOC results (ppm C).

<table>
<thead>
<tr>
<th>Ultrafiltration Membrane</th>
<th>XM-50 (50,000 MW)</th>
<th>PM-10 (10,000 MW)</th>
<th>UM-2 (1000 MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.8</td>
<td>18.4</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>28.1</td>
<td>22.8</td>
<td>16.9</td>
</tr>
</tbody>
</table>

b. ANOVA — One variable of classification.

<table>
<thead>
<tr>
<th></th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F(calc)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>2512.06</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>2400.00</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>57.33</td>
<td>2</td>
<td>28.665</td>
<td>1.57</td>
</tr>
<tr>
<td>Residual</td>
<td>54.73</td>
<td>3</td>
<td>18.24</td>
<td></td>
</tr>
</tbody>
</table>

* At the 0.10 significance level, required F value for 2 and 3 df is 5.46.
and 5000 daltons, respectively. Approximately 17% of WSSOM components were found to have relative molecular masses greater than or equal to 5000, 36% with molecular masses in the range 1000 to 5000, and 47% with molecular masses less than or equal to 1000. Finally, light scattering measurements show fulvic acid to have an average molecular weight of 5850 daltons (Underdown et al., 1981). Consequently, it is not surprising to find that TOC concentrations were not decreased when aqueous phases were passed through XM-50 and PM-10 membranes; however, it is surprising to find that the efficiency of separation was not improved by ultrafiltration through the UM-2 membrane. Perhaps a more extensively replicated experiment would show a statistically significant decrease of TOC in filtrates from the UM-2 membranes, especially considering the trend in this data. Considering the increased experimental complexity, the time, and the cost of using ultrafiltration, there seemed to be inadequate promise of improvement to justify pursuit of this approach as an alternative to more conventional separation methods.

**Solution composition.** In measuring distribution coefficients, the effect of aqueous phase ionic strength is of interest due to the variety of media used for laboratory measurements and the wide range of ionic strengths encountered in natural waters. Salinity can vary from less than 0.05% in fresh water (lakes, streams) to 3.5% in sea water. Often, changes in ionic strength have
been reported to cause large variations in measured distribution coefficients. For example, Koskinen and Cheng (1983) found that coefficients measured for 2,4,5-trichlorophenoxyacetic acid on soil approximately doubled when 0.01 N CaSO$_4$ or CaCl$_2$ was used in place of distilled water and increased 4-fold with 0.1 N CaSO$_4$. Similarly, in a study of the sorption of pyrene to river sediment, Karickhoff et al. (1979) reported the distribution coefficient to increase by 15% when salt concentration was increased from 0 to 20 mg/mL NaCl.

Frequently, the effect of aqueous phase composition is not taken into account when determining distribution coefficients. Solutions used for laboratory measurements include distilled water, natural water samples which have been filtered, and various buffer and salt solutions. This could have serious implications when these results are compared or extrapolated to the environment. For example, distribution coefficients determined in distilled water probably won't accurately predict the behavior of pollutants in salt water.

The effect of ionic strength has been explained in several ways. Some researchers (Farmer and Aochi, 1974; Moreale and Van Bladel, 1980) believe variations in ionic strength are accompanied by pH changes and it is the fluctuations in pH that are reflected in the changing distribution coefficients. In the case of an organic acid, pH will influence its speciation (ionized vs. molecular
form) and hence its binding to soil or sediment. A second possibility is that with increased ionic strength, there is also an increase in competition for binding sites; however, this can only explain decreases in coefficients caused by increasing ionic strength. Increases in distribution coefficients of hydrophobic compounds with increasing ionic strength have been explained by the "salting out effect". Increasing the salt concentration reduces the solubility of hydrophobic compounds, thus favoring sorption to sediment and increasing distribution coefficients.

Ionic strength could also have an influence on the sediment or soil itself. For example, Horzempa and DiToro (1983) found that the distribution coefficient of 2,4,5,2',4',5'-hexachlorobiphenyl (HCBP) on montmorillonite more than doubled when the concentration of CaCl$_2$ was increased from $10^{-4}$ M to $10^{-2}$ M (without exceeding the solubility limit of HCBP). It was suggested that increasing the salt concentration may influence the surface charge of the particles, promoting flocculation. This would reduce the amount of microparticulate material which cannot be removed by typical separation techniques. Thus, the apparent aqueous phase concentration would decrease and the distribution coefficient would increase as ionic strength increased. This possibility was investigated. Batch equilibrations were carried out at a sediment concentration of 100 g/L and equilibration time of 24 hours with reciprocating shaking. Samples were then centrifuged
(9000 rpm, 1 hour). Aqueous phases were chosen to represent the two extremes encountered in the environment. In one case, distilled-deionized water was used. In the second case, a solution of 0.5 M NaCl, 0.05 M MgSO₄·7H₂O was used because sodium, chloride, sulfate and magnesium ions are four of the main constituents of sea water (Martin, 1968). Following equilibration and centrifugation, the high ionic strength solution was found to contain an average of 25.5 ppm organic carbon and distilled-deionized water contained 20.0 ppm carbon. Clearly, the concentration of nonseparable microparticulates did not decrease at high ionic strength as was postulated.

These findings are supported in part by the results of Hunter and Liss (1979). Using particles collected in coastal and estuarine waters, it was determined that the particles remained negatively charged at all salinities. Flocculation will not be an important consideration at high ionic strengths if charge neutralization does not occur as salt concentration is increased. The ions added to the aqueous phase appear to, instead, stabilize the microparticulates in solution thereby decreasing separation efficiency. A more detailed study is required in order to address this question fully.

Tables 3.4a and 3.6a show that significant quantities of salt were released during equilibration of the sediment used in this study. Conductivities measured for the aqueous phase varied from 2200 to 35,600 µmhos, depending
on experimental conditions used. Based on these results and published data demonstrating that apparent distribution coefficients will vary with ionic strength, it is recommended that steps be taken to either remove or account for possible fluctuations caused by the release of salts during batch equilibration. One possible solution is to first wash soil or sediment samples to reduce the release of salts during batch equilibration; however, it is possible that the measured $K_d$ then will not relate to the actual environmental state. A second possibility is to apply a correction for ionic strength (if one can be found to apply consistently). This would be analogous to the correction which has been developed to account for the varying organic carbon content of soils and sediments.

**Type of agitation.** Batch equilibration procedures typically employ some form of agitation to help attain equilibrium. It is possible that agitation of a sediment-water mixture actually produces grinding action between the sediment particles. This grinding would result in the partial disintegration of the bulk particles and simultaneous production of microparticulates. Many particles of bulk sediment are aggregates of smaller particulates or structural units that are held together by various types of chemical bonds. With sufficient mechanical energy, it is possible to rupture these bonds (Edwards and Bremner, 1967a; Moen and Richardson, 1984). If different forms of agitation provide different amounts
of mechanical energy, this should be reflected by different degrees of disruption of the sediment particles and varying amounts of microparticulates.

Two common forms of agitation used during batch equilibrations are reciprocating and wrist action agitation. Often, the form of agitation is not specified. Because of these variations in procedures used, as well as the lack of such details in some cases, it is important to ascertain if they could contribute to the observed discrepancies in distribution coefficients. The three forms of agitation investigated here were wrist action shaking, reciprocating shaking and sonication. Sonication was investigated because it has been shown to be very effective in extracting soluble organic matter from sediment (Jenkins and Grant, 1987; McIver, 1962) and in producing stable particulate suspensions (Watson and Parsons, 1974; Edwards and Bremner, 1967a and 1967b). Centrifuge tubes were clamped in an upright position during wrist action agitation and sonication, while centrifuge tubes were held horizontally on the reciprocating shaker.

The extent of sediment disruption (microparticulate production) was based on TOC concentrations of the aqueous phases following equilibration and centrifugation (9000 rpm). Results are shown in Tables 3.3a and 3.5a. The type of agitation was found to have no significant influence on the amount of microparticulate material produced during equilibration (0.05 significance level).
This conclusion was reached in the study of sediment concentration with type of agitation (Table 3.3b) as well as in the investigation of equilibration time with type of agitation (Table 3.5b). Similarly, type of agitation was found to have no influence on the amount of salt released, as reflected by the conductivities of equilibrated aqueous phases (Tables 3.4b and 3.6b).

Agitation is not solely responsible for the release of organic carbon into solution. A significant amount of carbon is released even when the sample is not agitated at all. Samples containing 100 g/L sediment were allowed to equilibrate for 24 hours with no agitation; following centrifugation the aqueous phase was found to contain 14.8 ppm carbon. This suggests that most of the organic matter released into solution is readily soluble.

Pictures obtained with scanning electron microscopy (SEM) (Figures 3.6 and 3.7) reveal that while sediment is altered by agitation, the extent of particle disruption does not differ when different types of agitation are used. In Figure 3.6, a representative sample of the original sediment is compared with sediment agitated for 24 hours using a reciprocating shaker. The majority of large particles found in the original sediment were disrupted during equilibration. This agrees with TOC results for agitated samples. SEM pictures were also obtained for sediment samples equilibrated under a variety of other experimental conditions (type of agitation,
Figure 3.6. Comparison of original and agitated sediment using scanning electron microscopy.
Figure 3.7. Comparison of sonicated sediment at two different sediment concentrations. (top photo = 10 g/L, bottom photo = 100 g/L)
equilibration time and sediment concentrations). On a qualitative basis, SEM pictures showed no obvious, consistent differences between the various types of agitation regardless of the equilibration time or sediment concentration used. The only exception was for a sediment concentration of 10 g/L where sonication caused severe breakdown of the original particles, much more so than wrist action or reciprocating shaking. This also agrees with TOC results. Type of agitation was found to have no effect on microparticulate production, but when 10 g/L sediment was used, TOC concentrations were slightly higher with sonication.

It therefore appears that agitation is not a critical variable in the production of microparticulates. When these results are considered in terms of microparticulate theory presented, any variations in distribution coefficients cannot be attributed to the different types of agitation in common use. These results also show that the type of agitation will not cause variations in distribution coefficients due to fluctuations in the salt content (ionic strength) of the aqueous phase because salt release does not vary with type of agitation.

**Equilibration time.** Another experimental parameter that varies from experiment to experiment is the time of equilibration. A brief survey of the literature shows that times from 15 minutes (Karickhoff and Brown, 1978) to 4 days (Carter and Suffet, 1982) have been used with 24 hours
Hassett and Anderson, 1982; Koskinen and Cheng, 1983; Lotse et al., 1968; Moen and Richardson, 1984; Voice et al., 1983; Weber et al., 1983) being the most common. Equilibration times are chosen primarily on the basis of kinetics of the distribution process to ensure equilibrium has been reached. Previous studies have shown sorption kinetics to be rapid, with equilibrium reached in less than 2 to 4 hours (DiToro and Horzempa, 1982; Lotse et al., 1968; Nau-Ritter et al., 1982; Voice et al., 1983; Weber et al., 1983), suggesting that agitation times employed may often be longer than necessary. While this ensures that equilibrium has been reached, the additional agitation could result in sediment disruption and microparticulate production. Edwards and Bremner (1967a, 1967b) investigated the effect of agitation time on the production of stable dispersions of soil in water in two separate studies. Quantities of clay-size particles (less than 0.002 mm in diameter) were found to increase with increasing equilibration time for both sonication and reciprocating agitation.

Consequently, equilibration time was examined to determine any possible effect it may have on the production of microparticulates. Equilibration time was varied from 15 minutes to 24 hours (sediment concentration = 100 g/L). TOC and conductivity results are summarized in Tables 3.5a and 3.6a. According to the analysis of variance (Tables 3.5b and 3.6b), the effect of
equilibration time on TOC concentration is not significant (0.05 significance level); however, the amount of salt (conductivity) released by the sediment is influenced by equilibration time. Conductivity increased by an average of 7150 μmhos as equilibration time was increased from 2 to 8 hours, leveling off as equilibration time was increased to 24 hours. SEM pictures were in agreement with TOC results showing no noticeable difference between sediment samples equilibrated for different times.

Based on these results and microparticulate theory, equilibration time should have no influence on the measurement of distribution coefficients insofar as the concentration of microparticulates remained constant. In relation to microparticulate production, it appears that equilibration times typically used are appropriate and kinetics remain the major consideration when deciding how long to equilibrate a sample. Conductivity results indicate a possible difficulty in that the ionic strength of the aqueous phase, which has been shown to have an effect on measured coefficients in some cases, will vary with equilibration time. Because conductivity levels off for equilibration times of 8 hours or more, it may be advantageous to use equilibration times of at least 8 hours.

**Sediment concentration.** The variable of greatest concern is sediment concentration. As discussed previously, numerous cases exist in which measured
distribution coefficients vary inversely with sediment concentration. O'Connor and Connolly (1980) have demonstrated that distribution coefficients vary linearly with solids concentration, over a range of 0.01 to 10 g/L. This poses a problem in the comparison of results between laboratories or in the extrapolation of results to the environment since sediment concentrations used in batch equilibrations vary from 0.005 (DiToro et al., 1986) to 1000 g/L (Koskinen and Cheng, 1983).

The theory based on the presence of nonseparable microparticulates suggests that the quantity of microparticulates produced should vary linearly with solids concentration. This is not unreasonable considering that the continuous size distribution of sediment and soil particles extends both above and below the size cutoffs of typical separation techniques. It is also possible that disruption of the sediment occurs due to grinding between the individual particles. For example, Nau-Ritter et al. (1982) observed the formation of fine particulates at the water surface resulting from disintegration of the original clay particles when agitated. As sediment concentration increases, this grinding action will be enhanced producing increased amounts of nonseparable microparticulates.

The aqueous phase composition has been studied as a function of solids concentration using TOC analysis, turbidity and weight of dissolved solids. Gschwend and Wu (1985) found nonseparable microparticulates to increase in
a fixed proportion to total solids. Voice et al. (1983) came to the same conclusion, finding TOC and turbidity to increase with increasing solids concentration. However, in both studies, sediment concentrations investigated were less than 10 g/L and a large number of batch equilibrations employ concentrations much greater than this. Consequently, it is the purpose of this investigation to examine aqueous phase compositions when sediment concentrations greater than 10 g/L are used.

Six sediment concentrations, varying from 10 to 250 g/L, were used with a constant equilibration time of 24 hours. TOC and conductivity results are summarized in Tables 3.3a and 3.4a, respectively. Analysis of variance (Tables 3.3b and 3.4b) showed sediment concentration to be significant in both cases (0.01 significance level).

Figure 3.8 illustrates the relationship between conductivity and sediment concentration. Using regression analysis, the following linear relationship was derived (lack of fit not significant at 0.01 significance level):

\[(1000)(\text{CON}) = (0.166)(\text{S}) + 2.44\] (46)

where CON equals conductivity (\(\mu\text{mhos}\)) and S is the concentration of sediment (g/L). As already discussed, distribution coefficients can vary with the ionic strength of the solution. An increase in ionic strength with sediment concentration can therefore bias measurements and
Figure 3.8. Effect of sediment concentration on conductivity of aqueous phase.
must either be eliminated or accounted for.

The effect of sediment concentration on TOC is illustrated in Figure 3.9. Based on regression analysis (0.01 significance level), it was found that for sediment concentration ≤ 150 g/L, the data are best described by a linear relationship:

\[ TOC = (0.183)(S) + 3.549. \] (47)

The concentration of organic carbon then levels off at sediment concentrations greater than 150 g/L (TOC = 36.2 ppm). Analysis of variance revealed no significant difference between TOC concentrations measured for sediment concentrations of 150 to 250 g/L. For sediment concentrations less than or equal to 150 g/L, results are in agreement with the findings of Gschwend and Wu (1985) and Voice et al., (1983); the concentration of microparticulate material increases linearly with solids concentration.

SEM pictures showed no obvious differences between samples equilibrated at different sediment concentrations with one exception. Sonication of 10 g/L sediment (Figure 3.7) caused severe disruption of the original particles; at all other concentrations studied, many of the larger sediment particles remained intact. This can be explained by the dependence of sonication energy on sediment concentration. Edwards and Bremner (1967b) were able to
Figure 3.9. Effect of sediment concentration on total organic carbon concentration of aqueous phase.
control the intensity of sonication by using different sediment concentrations. As sediment concentration is decreased, the intensity of sonication is increased. This high intensity of sonication for 10 g/L sediment results in the breakdown of sediment particles as was observed. SEM pictures also indicate that the increase in TOC with sediment concentration is not accompanied by a corresponding increase in particle breakdown. Consequently, fluctuations in distribution coefficients cannot be accounted for solely by increased disintegration of sediment (increased "grinding action") with increased sediment concentration.

Figure 3.10 shows the percent of total organic carbon removed from the bulk sediment as a function of sediment concentration. At no point is the sediment stripped of all its organic carbon; for the conditions used, the bulk sediment loses at most 2.5% of its organic carbon during equilibration. As sediment concentration increases, the amount of organic carbon available for release into solution also increases; however as seen in Figure 3.10, the actual amount of carbon released into solution does not increase in direct proportion to the amount of available carbon. This suggests that there are factors other than the availability of organic carbon which will influence its release into solution.

To more fully evaluate the effect sediment concentration has on the measurement of distribution
Figure 3.10. Dependence of carbon removal from bulk sediment on sediment concentration.
coefficients, TOC data was combined with the microparticulate model developed earlier. Using the model fitted to experimental data with equations 33 and 35, $K_d^R$ and $K_d^F$ were calculated (Table 3.9). Because it was not possible to fully characterize the microparticulate material produced, it was assumed that it contained 10% organic carbon. A $K_{oc}$ value of 80,000 mL/g was used in all calculations. Experimental conditions are listed in Table 3.9.

$K_d^F$ and $K_d^R$ are both predicted to decrease with increasing sediment concentration. As seen in Table 3.9, fluorescence quenching (and similar analytical techniques) will produce a small overestimation of the "true" distribution coefficient while techniques such as the activity determination of radiolabelled compounds will cause the distribution coefficient to be greatly underestimated. In addition, $K_d^F$ approaches the "true" distribution coefficient as sediment concentration is decreased.

These observations are best explained by examining the amount of analyte bound to microparticulate material in relation to the amounts of analyte dissolved plus sediment-bound. When considered as a percentage of total sediment weight (Figure 3.10), the relative amount of microparticulates is greatest at low sediment concentrations. Therefore, the ratio of analyte sorbed to microparticulates relative to the amount of sediment-bound
Table 3.9. Distribution coefficients predicted using experimental TOC results. *

<table>
<thead>
<tr>
<th>Sediment Concentration (g/L)</th>
<th>Predicted TOC (ppm) **</th>
<th>$K_d^F$ (mL/g)</th>
<th>$K_d^R$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.38</td>
<td>1995</td>
<td>1365</td>
</tr>
<tr>
<td>50</td>
<td>12.7</td>
<td>1972</td>
<td>968</td>
</tr>
<tr>
<td>100</td>
<td>21.8</td>
<td>1969</td>
<td>711</td>
</tr>
<tr>
<td>150</td>
<td>31.0</td>
<td>1968</td>
<td>561</td>
</tr>
<tr>
<td>200</td>
<td>36.2</td>
<td>1966</td>
<td>501</td>
</tr>
<tr>
<td>250</td>
<td>36.2</td>
<td>1964</td>
<td>501</td>
</tr>
</tbody>
</table>

* Experimental conditions:
  Total aqueous volume = 25.0 mL
  "True" $K_{oc} = 80,000$ mL/g (assumed value)
  Bulk sediment contains 2.44% C, $K_1 = 1952$ mL/g
  Microparticulates contain 10.0% C (assumed value, $K_2 = 8000$ mL/g)

** Calculated using the following model fitted to experimental data:
  For $\leq 150$ g/L sediment: TOC = $(0.183)(S) + 3.549$.
  For $> 150$ g/L sediment: TOC = 36.2 (average value).
analyte will be greatest at low sediment concentrations. Because fluorescence quenching does not distinguish between sediment and microparticulate-bound analyte, the amount of error in $K_d^F$ will increase as sediment concentration is decreased. However, it is only at extremely low sediment concentrations that there will be a considerable amount of error in $K_d^F$. Conversely, the error in $K_d^R$ is lowest at low sediment concentrations. In this case, the contribution of analyte from the microparticulates must be considered relative to the amount of analyte dissolved in solution. Because TOC increases directly with sediment concentration, the contribution of analyte associated with the microparticulates also increases with sediment concentration. Simultaneously, the amount of freely dissolved analyte decreases as more sediment is added to the mixture. Consequently, it is a combination of these two effects that causes $K_d^R$ to be underestimated, decreasing with increasing sediment concentration.

The solids concentration effect is much more dramatic for $K_d^R$ than $K_d^F$. $K_d^R$ decreases by more than half of its original value as sediment concentration increases from 10 to 250 g/L while $K_d^F$ decreases by less than 2%. Plotted as a function of sediment concentration (Figures 3.11 and 3.12), both $K_d^R$ and $K_d^F$ show significant decreases initially, leveling off as sediment concentration increases. The inverse relationship predicted here agrees with experimental results reported in the literature. Baker et
Figure 3.11. Effect of sediment concentration on the distribution coefficient predicted for radiolabelling.
Figure 3.12. Effect of sediment concentration on the distribution coefficient predicted for fluorescence quenching.
al. (1986) and Voice et al. (1983), have derived linear relationships between log $K_d$ and log $S$ ($S$ = sediment concentration). For the data presented in Table 3.9, linear regression yields:

$$\log K_d^R = (-0.314)(\log S) + 3.470, \ r = 0.974 \quad (48)$$
and
$$\log K_d^F = (-0.0052)(\log S) + 3.305, \ r = 0.968 \quad (49)$$

for sediment concentrations of 150 g/L or lower. O'Connell and Connolly (1980) described a similar relationship between solids concentration and $K_d$ for a limited range of solids concentrations (0.01 to 10 g/L). They also suggested that $K_d$ may reach a constant limiting value at a solids concentration somewhat greater than 10 g/L. However, they could not specify the exact solids concentration without additional measurements of $K_d$. This constant limiting value is predicted by the model presented here - $K_d^R$ becomes constant for sediment concentrations greater than 150 g/L. 

Values for $K_d^F/K_d^R$ were also calculated and are shown in Figure 3.13 as a function of sediment concentration. The relationship between $K_d^F/K_d^R$ and sediment concentration ($S$) is best described by the line:

$$K_d^F/K_d^R = (0.0146)(S) + 1.31 \quad (50)$$

for sediment concentrations less than or equal to 150 g/L;
Figure 3.13. Effect of sediment concentration on $\frac{K^F_d}{K^R_d}$.
\( K_d^F/K_d^R \) becomes constant at sediment concentrations greater than 150 g/L \( (K_d^F/K_d^R = 3.92) \). Because \( K_d^F/K_d^R \) depends primarily on TOC, this relationship closely resembles that which exists between TOC and solids concentration.

This application of microparticulate theory to empirical data indicates that at extremely low sediment concentrations (much less than 10 g/L), use of analytical techniques such as the counting of radiolabelled analytes should provide a reliable estimate of the distribution coefficient. However, in all other cases, fluorescence quenching or a technique similar in principle is the better choice, being much less subject to the influence of microparticulates. Such methods will provide a more accurate estimate of the distribution coefficient for a wide range of sediment concentrations. At this point, more experimental evidence is needed to demonstrate the bias in measured values of \( K_d \) that can be introduced by different analytical techniques in the presence of microparticulates.

**B. Determination of distribution coefficient.**

The distribution coefficient for the association of anthracene with sediment was measured in three different ways in order to determine if the method of analysis is an important variable, as postulated. If the method of analysis is not important then all coefficients should be the same regardless of the analytical technique used. In the first case, \( K_d \) was determined using radiolabelled anthracene in a typical batch equilibration experiment.


\( K_{OC}^R = \text{measured distribution coefficient} \). In the second case, one step was added to the above procedure; the supernatant was passed through a C-18 Sep-Pak column to remove any freely dissolved anthracene which should leave only anthracene bound to microparticulates in solution \( K_{OC}^{sp} = \text{measured distribution coefficient} \). Finally, \( K_d \) was measured by fluorescence quenching which involves the titration of an anthracene solution with a suspension of the sediment and monitoring the changes in fluorescence intensity of anthracene \( K_{OC}^F = \text{measured distribution coefficient} \). Measured distribution coefficients are summarized in Table 3.10. All values have been normalized to the fraction of organic carbon in the sediment.

The effect of sediment concentration was investigated for the typical radiolabelling experiment and Sep-Pak experiment using concentrations of 10 g/L and 100 g/L sediment. As expected \( K_{OC}^R \) decreased approximately 20% as sediment concentration increased 10-fold. The distribution coefficient measured using the Sep-Pak technique does not show the influence of sediment concentration as \( K_{OC}^R \) does. \( K_{OC}^{sp} \) increased slightly with the increase in sediment concentration but the difference in values is within experimental error. \( K_{OC}^{sp} \) is 1.4 to 1.9 times greater than \( K_{OC}^R \).

These results can be accounted for by the production of microparticulates during batch equilibration. As already discussed, it is possible to account for the
Table 3.10. Coefficients measured for the distribution of anthracene between sediment and water.

<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>0.5 g/L Sediment</th>
<th>10 g/L Sediment</th>
<th>100 g/L Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Radiolabelling*</td>
<td>17,000</td>
<td>8855</td>
<td>6730</td>
</tr>
<tr>
<td>Sep-Pak**</td>
<td></td>
<td>12,050</td>
<td>12,550</td>
</tr>
<tr>
<td>Fluorescence Quenching</td>
<td></td>
<td>39,400***</td>
<td></td>
</tr>
</tbody>
</table>

* % Relative Standard Deviation = 5.8%.
** % Relative Standard Deviation = 2.3%.
*** Determined for sediment concentration ranging from 0 to 0.27 g/L; Relative Standard Deviation = 7.0%.
inverse relationship between $K_{oc}^R$ and sediment concentration using microparticulate theory. Furthermore, if the Sep-Pak technique does indeed separate dissolved anthracene from anthracene bound to microparticulates, then $K_{oc}^{sp}$ will not show a sediment concentration effect. $K_{oc}^{sp}$ will also be greater than $K_{oc}^R$ since anthracene bound to microparticulates can be subtracted from the total amount of anthracene in the aqueous phase following equilibration. The concentration of dissolved anthracene is therefore lower when determined using the Sep-Pak technique and $K_{oc}^{sp}$ is greater than $K_{oc}^R$.

The distribution coefficient for anthracene was also measured using a technique based on fluorescence quenching where the intensity of anthracene fluorescence decreases in the presence of humic and fulvic acids (microparticulate material). $K_d$ is calculated using the equation:

$$\frac{F_0}{F} = 1 + K_d S \tag{51}$$

where $F_0$ is the fluorescence intensity before adding any sediment, $F$ is the fluorescence intensity of centrifuged supernatant after the addition of sediment, and $S$ is the sediment concentration (Gauthier et al., 1986). Plotting $F_0/F$ as a function of sediment concentration should give a line with slope equal to the distribution coefficient. $K_{oc}^F = 39.000$ mL/g was determined in this way. It was not possible to investigate the effect of high sediment
concentration on $K_{oc}^F$ as was done for radiolabelling and Sep-Pak experiments. However, sediment concentration was varied from 0 to 0.27 g/L over the course of a single fluorescence quenching experiment. If $K_{oc}^F$ did vary with sediment concentration, this would be reflected in non-linear plots of $F_o/F$ vs. $S$ (Gauthier et al., 1986); this was not observed. $K_{oc}^F$ is 4.4 to 5.7 times greater than $K_{oc}^R$ for these high concentrations. In order to be sure that the difference between $K_{oc}^F$ and $K_{oc}^R$ was not due solely to the difference in sediment concentrations used, $K_{oc}^F$ was compared to $K_{oc}^R$ measured at a sediment concentration much closer to the concentration used in a fluorescence quenching experiment. For 0.5 g/L sediment $K_{oc}^R = 17,000$ mL/g, which is still less than half the magnitude of $K_{oc}^F$. As solids concentration is decreased, microparticulate theory predicts that the difference between distribution coefficients ($K_{oc}^F$ and $K_{oc}^R$) will decrease.

If both fluorescence quenching and Sep-Pak techniques can distinguish between dissolved and microparticulate-bound anthracene, then theoretically, $K_{oc}^F$ and $K_{oc}^{sp}$ should be equal. This was not found experimentally; $K_{oc}^F$ was over three times greater than $K_{oc}^{sp}$. It is possible that the Sep-Pak technique does not distinguish between the two forms of anthracene as effectively as fluorescence quenching. If microparticulates were trapped in the Sep-Pak column, this would inflate the apparent
concentration of dissolved anthracene and cause $K_{oc}^{sp}$ to be less than the "true" distribution coefficient and less than $K_{oc}^{F}$. The Sep-Pak technique was developed to measure the binding of hydrophobic compounds to dissolved humic and fulvic acids (Landrum et al., 1984). Therefore, while dissolved organic material will pass through quantitatively, it is possible that larger microparticulate material may become trapped and not all pass through the column.

Karickhoff et al. (1979) report $K_{oc} = 26,000$ mL/g for anthracene binding to river sediment (at a sediment concentration of 20 g/L). Distribution coefficients measured using the Sep-Pak and fluorescence quenching techniques are closest to this value. These values are of the same order of magnitude as the published value with Sep-Pak values being less and the fluorescence quenching value being greater than 26,000 mL/g.

These measured coefficients can also be compared to theoretical predictions from microparticulate theory. Assuming the "true" $K_{oc}$ for anthracene is 40,000 mL/g, values of 1.24 and 1.89 are calculated for $K_{d}^{F}/K_{d}^{R}$ at sediment concentrations of 10 and 100 g/L, respectively. Experimental values of $K_{d}^{F}/K_{d}^{R}$ equal to 4.4 (10 g/L sediment) and 5.6 (100 g/L sediment) do increase with increasing sediment concentration as microparticulate theory predicts, but they differ significantly from theoretical values. $K_{d}^{F}/K_{d}^{R}$ is calculated here using the assumption that both
bulk sediment and microparticulate material have the same sorptive characteristics (same $K_{OC}'s$). However, if the sorption of anthracene to microparticulates is enhanced relative to bulk sediment, there is better agreement between theoretical and experimental values. This assumption is in keeping with experimental results; Means and Wijayaratne (1982) report the sorption of atrazine and linuron on colloidal organic material to be enhanced relative to bulk sediment. If $K_{OC}$ for the microparticulates is assumed to be 10.2 times greater than for bulk sediment, a value of 4.4 is calculated for $K_d^F/K_d^R$ at a sediment concentration of 10 g/L, in agreement with the experimentally determined value. Calculations for 100 g/L sediment do not show the same agreement. $K_d^F/K_d^R$ is predicted to be 8.8 when enhanced sorption by microparticulate material is considered; this is 1½ times greater than the value found experimentally.

Clearly, analytical technique does influence the measurement of distribution coefficients in a manner consistent with microparticulate theory on a qualitative basis. However, the discrepancy between quantitative predictions and experimental results indicates that the microparticulate theory presented here may not be the sole answer to the problem of variable distribution coefficients. Several other theories, discussed previously, have been developed to explain variations of coefficients. It is possible that a combination of
several theories may be required to explain the observed effects.

Conclusion

The mathematical model developed here highlights the effect nonseparable microparticulates can have on the measurement of distribution coefficients when different methods of analysis are used. Distribution coefficients can vary significantly with sediment concentration when using a technique that does not distinguish between analyte bound to nonseparable microparticulates and freely dissolved analyte. One common example of this is the counting of radiolabelled analytes. This is compared to fluorescence quenching, a technique that doesn't distinguish between analyte bound to microparticulates and analyte bound to sediment. The model predicts that distribution coefficients measured in this way will be only slightly influenced by sediment concentration. The distribution coefficient will be underestimated using radiolabelling and overestimated using fluorescence quenching. In addition, it is predicted that the sediment concentration effect will be greatest for those compounds with a high affinity for the sediment. The model agrees with the inverse relationship empirically found to exist between distribution coefficients and sediment concentration.

The importance of experimental details in a batch equilibration experiment were also investigated and
evaluated in relation to microparticulate theory. The experimental variable of primary importance is sediment concentration. Other variables investigated - equilibration time, type of agitation, separation efficiency, and solution composition - were found to have very little or no effect on the production of microparticulates during batch equilibration. Experiments also revealed differences in distribution coefficients for the binding of anthracene to sediment when three different methods of analysis were used. Three techniques were compared: batch equilibration with the counting of radiolabelled analytes, separation of dissolved and microparticulate-bound analyte using a Sep-Pak column, and fluorescence quenching. Distribution coefficients for liquid scintillation counting in a typical batch equilibration experiment showed the greatest amount of variation with sediment concentration. Distribution coefficients measured by the other two techniques were much less dependent on sediment concentration and therefore, variability of estimates might be reduced by wider use of these techniques. A standardized protocol with respect to equilibration might also be helpful.

The results presented here support the theory that fluctuations in distribution coefficients with sediment concentration are caused in part by the production of nonseparable microparticulate material during typical batch equilibrations. This effect must be considered when laboratory estimates of distribution coefficients are
extrapolated to the environment. Microparticulates are
produced and will influence distribution coefficients both
in the laboratory and in nature. In predicting the
transport of pollutants in the environment, it must be
remembered that pollutant bound to microparticulates is
much more mobile than pollutant bound to bottom sediment.
The extrapolation of microparticulate theory to the
environment remains to be done.
References


