# THE SORPTION OF HYDROPHOBIC ORGANIC COMPOUNDS IN THE PRESENCE OF ENVIRONMENTAL CONCENTRATIONS OF DISSOLVED HUMIC AND FULVIC ACIDS AT VARIABLE pH VALUES

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of the
requirements for
the Degree of
DOCTOR OF PHILOSOPHY
May, 1990

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# ACKNOWLEDGEMENTS

I wish to express my thanks to Dr. Marcia H. Bates for serving as my principal advisor and for her guidance during the course of this research. I also wish to thank Dr. John N. Veenstra for serving on my committee and for his advice and suggestions. Thanks also go to Dr. Donald R. Snethen and Dr. Douglas C. Kent for serving as committee members.

A special note of thanks goes to Dr. Brian J. Carter and to Phillip Ward, III for their instruction and assistance during the characterization of the soils used in this study and for the generous use of the Soil Genesis and Morphology Laboratory. Also, thanks are extended to Dr. Lavoy I. Croy and Dave Ferris for the use of and instruction on their UV spectrophotometer.

My appreciation is also given to the University Center for Water Research for providing me with a Presidential Fellowship in Water Resources Research. Thanks also go to Dr. Robert K. Hughes of the Department of Civil Engineering for purchasing the fulvic acid used in this study. Without their financial support this research could not have been undertaken.

A sincere thanks is given to Kelly Whitfield for her careful and accurate preparation of this manuscript.

Finally, I wish to thank and acknowledge my colleagues, family, and many friends who were supportive, understanding, and helpful throughout this study. My greatest appreciation goes to my mother for her unwavering support throughout my career, for her constant belief in my capabilities, for her encouragement and love, and especially for waiting for the bicycle.

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# NOMENCLATURE

| | |
|---|---|
| AEC | anion exchange capacity |
| C | equilibrium concentration of solute in solution |
| C' | mass of solute sorbed |
| CEC | cation exchange capacity |
| $C_o$ | initial mass of solute |
| °C | degrees in Centigrade |
| cm | centimeter |
| DOC | dissolved organic carbon |
| DOM | dissolved organic matter |
| FA | fulvic acid |
| g | gram |
| HA | humic acid |
| HOC | hydrophobic organic compound |
| IHSS | International Humic Substances Society |
| $K_{ow}$ | octanol-water partition coefficient |
| $K_{soc}$ | Freundlich sorption capacity to soil organic carbon (used in the isotherm experiments) |
| $K'_{soc}$ | single-point partition coefficient (used in the DOM experiments) |
| l | liter |
| MA | Mulhall A-horizon soil |
| MB | Mulhall B-horizon soil |
| mg | milligram |
| ml | milliliter |

| | |
|---|---|
| mm | millimeter |
| MP | melting point |
| MW | molecular weight |
| n | slope of the Freundlich isotherm line |
| NB | Navina B-horizon soil |
| nm | nanometer |
| OC | organic carbon |
| OM | organic matter |
| pH | negative log of the hydrogen ion concentration in solution |
| ppb | part per billion (i.e., μg/l) |
| ppm | part per million (i.e., mg/l) |
| q | mass of solute sorbed per mass of adsorbent |
| $r^2$ | coefficient of determination |
| rpm | revolutions per minute |
| S | solubility of a compound |
| SOC | soil organic carbon |
| SOM | soil organic matter |
| μg | microgram |
| μl | microliter |
| μm | micrometer |
| umoles | micromoles |
| UV | ultraviolet |
| VP | vapor pressure |

# CHAPTER I

# INTRODUCTION

The quality of the environment continues to be a worldwide concern. The protection of air, water and biota from degradation due to the input of man-introduced chemicals has been the focus of considerable research. Much of this research has concentrated on the fate and transport of chemicals in surface waters, ground waters and soil systems. In particular, the focus has often been on pesticides and nutrients originating from agricultural practices and the plethora of organic and inorganic compounds introduced to the environment from industrial activities such as land disposal and wastewater discharge. The effort to reduce surface-water discharges has led to an increase in land disposal, thus adding to adverse impacts to soil and ground water from existing municipal and industrial landfills as well as previously unregulated and often now-abandoned hazardous waste disposal sites. The importance of ground water as a vital resource is of increasing concern to scientists as well as the general public.

Research has explored the transport and fate of compounds associated with sediments in surface water, and with soil and geologic materials beneath the surface of the land. One area of interest has been the sorption of neutral organic compounds to sediments and soils. Of particular concern is that these typically sparingly soluble, high molecular weight compounds sorb strongly to soils, are persistent, and are transported greater distances in the environment than would be expected. Several researchers have proposed that transport of these hydrophobic organic compounds is facilitated through binding to other materials in the water such as colloids, macromolecules, microorganisms, cosolvents and dissolved organic matter. This type of transport mechanism would help to explain why compounds with a high affinity for soil sorption are being detected much farther downgradient than predicted, since some of the compound could be sorbed and some could be moved through facilitated transport.

The purpose of this study is to evaluate the sorption of three hydrophobic organic compounds (HOCs) to three soils in the presence and absence of dissolved organic matter (DOM) over a range of environmental pH values. The materials used are HOCs covering a range of very low solubility. The soils have varying soil properties and two types of DOM were added in increasing concentrations. The objectives of this study are to correlate the effects of HOC binding to DOM with soil sorption, soil properties, compound properties, aqueous pH and organic matter type and concentration. The results should help environmental scientists better understand and predict the fate of HOCs in aqueous systems containing both dissolved organic carbon and soil or sediment.

# CHAPTER II

# REVIEW OF THE LITERATURE

## Introduction

Chemical contaminants are found throughout the aqueous environment in surface waters, ground waters, oceans and in rain, snow and fog. Sources of contaminants in the environment are numerous. Agricultural sources of contaminants include feedlots and pesticide and fertilizer application. Industrial contaminant sources such as industrial landfills, illegal dumping, and land treatment of industrial wastes also impact the environment. Municipal sources of contaminant input to the environment include landfills, rapid infiltration basins for sewage effluent disposal, and land treatment of sewage sludge. Contaminants can also find their way to surface and ground waters via aerial distribution and deposition from atmospheric emissions by industry and automobiles, and through volatilization of chemicals from treated cropland.

The fate and transport of contaminants in aqueous environments depend on a variety of physical and chemical characteristics of the contaminant and the environmental system to which the contaminant is input (Seiber, 1987). These contaminant factors include compound-related properties such as solubility, volatility, bioconcentration and biotransformation potential, and photodegradation. System properties include the solution pH, the type and composition of the soil and the indigenous microbial population (Callahan, et al, 1979).

Environmental contaminants can be classified as either inorganic or organic compounds. Substantial research has focused on inorganic contaminants such as metals, radionuclides and non-metal inorganics (nitrates, sulfur dioxide, sulfate). Recently, concern has increased regarding the dominant organic compounds found in the environment such as hydrocarbons, insecticides, nematicides, herbicides and industrial solvents. Hundreds of these compounds have been identified in various ground waters (Dunlap, et al, 1984).

The organic contaminants can be divided into polar or charged compounds, and nonpolar or uncharged compounds. The focus of this literature review will be on the nonpolar compounds, especially those of low solubility, and their interaction with soil and water. These low solubility, nonpolar compounds are known as hydrophobic organic compounds (HOCs) and are generally high molecular weight compounds lacking charged functional groups. Many herbicides and pesticides are classified as HOCs.

## Solubility of Hydrophobic Organic Compounds

### Mechanisms of Solvation

The mechanisms governing the aqueous solubility of HOCs and that of inorganic and polar organic compounds differ. Inorganic compounds are generally solvated by dissociation into ions. On the other hand, interactions between charged portions or functional groups and water molecules are responsible for the solvation of polar organic molecules. These interactions are dependent on water molecules being slightly polar.

Solvation of HOCs, which are sparingly soluble in water and nonionic or nonpolar, can be described using various models. These models generally depend on thermodynamic approaches involving fugacity, activity coefficient, and surface area of the solute.

#### Fugacity Model

The solvation of a HOC is often considered in terms of its fugacity using the Raoult's law convention in which the fugacity of the compound is equal to the mole fraction of the compound in water multiplied by its aqueous activity coefficient and its reference fugacity at the system temperature. The reference fugacity for solid compounds is the extrapolated liquid fugacity, i.e., below the triple point of the compound (Hildebrand and Scott, 1964; MacKay, 1977). In systems where the solvent has a relatively high molecular weight, Chiou and Manes (1986) recommend the use of the Flory-Huggins model which uses the volume fraction rather than the mole fraction of the compound in solution for estimating compound solubility.

### Cavity Model

Another model used to describe solvation of HOCs is known as the "hole" or "cavity" model. This is a conceptual model involving two steps. In the first step of this model, a hole or cavity must be made to accommodate the solute molecule in the solvent by displacement of the solvent molecules. In the second step, the compound interacts with the solvent once placed in the cavity (Belfort, 1981). The energy necessary to develop the cavity is thought to be the main determinant of solubility for both polar and nonpolar solutes (Amidon, et al, 1974; Yalkowsky, et al, 1975). This energy is dependent on the hydrocarbonaceous molecular surface area of the nonpolar solute and the solute-solvent surface tension. Thus, the larger the HOC molecule, the greater the energy required to create a cavity and solvate the HOC. This results in the low solubilities observed for HOCs and helps explain their strong tendency to leave the solution and to be sorbed at liquid-solid interfaces. In otherwords, HOCs tend to be solvophobic, in terms of solvent-solute interactions (Woodburn, et al, 1986).

### Factors Affecting Solubility

Regardless of which model is used to describe solvation, the solubilities of HOCs are related to several factors including temperature, molecular weight, polarity, and octanol-water partition coefficient. Other components in solution such as dissolved ions, cosolvents, and dissolved organic matter (DOM) are also known to influence HOC solubility.

### Temperature, Molecular Weight, and Polarity

An increase in temperature has been shown to increase the solution concentration of HOCs (Bowman and Sans, 1979; Bigger and Riggs, 1974). Compounds with low molecular weight and high polarity (ionic species or charged functional groups) are more soluble than high molecular weight, nonpolar compounds (Seiber, 1987).

### Octanol-Water Partition Coefficient

The solubility of a compound has been shown to be inversely correlated in a linear fashion to its log octanol-water partition coefficient (log $K_{ow}$). Numerous researchers including Chiou, et al (1979), Chiou and Schmedding (1982), Griffin and Chou (1980), Karickhoff (1981), Miller, et al (1985), Chiou and Freed (1977) and Marple, et al (1986) have described this relationship. Leo, et al (1971) related solubilities of compounds in various solvents and presented an extensive compilation of their results. Hounslow (1983) summarized the results of several investigators relating solubility to $K_{ow}$. Isnard and Lambert (1989) report and discuss at least 18 correlations between solubility (S) and log $K_{ow}$. Salient equations describing these relationships are given below.

Chiou, et al (1977) related $K_{ow}$ values covering six orders of magnitude with solubility values over a range of eight orders of magnitude using:

$$\log K_{ow} = 5.00 - 0.670 \log S$$

where, $K_{ow}$ = octanol-water partition coefficient.

S = aqueous solubility (μmoles/l).

Also, Doucette and Andren (1987) reported a correlation between the total molecular surface area (TSA) of HOCs to $K_{ow}$ using:

$$\log K_{ow} = 0.0238 \text{ (TSA)} - 0.142$$

Solubility and $K_{ow}$ have also been related to HOC bioconcentration in fish (Kenaga and Goring, 1980; Thurman, 1985). Also, Chiou, et al (1977) presented:

$$\log (BF) = 3.41 - 0.508 \log S$$

where, BF = bioconcentration factor in rainbow trout.

S = aqueous solubility in μmoles/l.

## Bisolutes, Impurities and Dissolved Ions

Other components in a solution can also affect the solubility of HOCs. Bowman and Sans (1979) report lowered solubilities of insecticides when equilibrated together in solution as bisolutes compared to their individual solubilities in separate solutions. Solubilities were also lowered when individual insecticide compounds were found to contain impurities (Bowman and Sans, 1979). In addition, as the ionic strength of the solution increases, the aqueous solubility of HOCs decreases (Thurman, 1985).

## Cosolvents

The effects of cosolvents, such as acetone and methanol, on HOC solubility have been investigated by several researchers (Yalkowsky, et al, 1976; Fu and Luthy 1985, 1986a, 1986b; Amidon, et al, 1974; Munz and Roberts, 1986; Tewari, et al, 1982; Bowman and Sans, 1979). In general, a direct correlation between the fraction of organic solvent present in solution and an increase in solute solubility concentration was found. That is, there appears to be a semi-lograrithmic increase in solubility with an increase in solvent volume (Fu and Luthy, 1986a). This effect has been proposed as a means in which transport of HOCs may be enhanced at hazardous waste sites where solvents and HOCs may both be present.

## Dissolved Organic Matter

Dissolved organic matter (DOM) such as humic and fulvic acids has also been noted to increase the solubility of HOCs in aqueous solution. Wershaw, et al (1969) showed that DOM lowered the surface tension of water and caused the solubility of DDT to increase 20 times in a solution containing 0.5% sodium humate. Ogner and Schnitzer (1970) and Matsuda and Schnitzer (1971) reported fulvic acid solubilizing hydrophobic dialkyl phthalates and suggested that DOM could mediate HOC mobilization and transport. Leachate from a landfill and river water containing DOM were shown by Griffin and Chou (1980) to increase the solubility of HOCs from 2.5 to 200 times greater than the solubility of the compounds in deionized water. Chiou, et al (1986) showed that DOM increases HOC solubility and that there was no competition between solutes for binding to DOM. This solubility enhancement effect was related in a linear fashion to the solute's solubility in pure water and its $K_{ow}$. The partitioning of the HOCs into the DOM was shown to increase as the solute's solubility decreased. The partitioning was also shown to increase as the solute's $K_{ow}$ increased. The effect was attributed to be controlled by the DOM molecular size, molecular structure, and polarity. Chiou, et al (1987) went on to calculate partition coefficients on a dissolved organic carbon (DOC) basis and stated that these partition coefficients are variable, are primarily dependent on the molecular composition and polarity of the DOM, and that DOM molecular size was a secondary determinant. The observed enhancement of the HOC solubility was expressed using:

$$S_w^* = S_w(1 + XK_{dom})$$

or,

$$S_w^* = S_w(1 + XK_{doc})$$

where, $S_w^*$ = apparent water solubility in a solution containing DOM.

$S_w$ = apparent water solubility in pure water.

$X$ = concentration of DOM or DOC in g/ml water.

$K_{dom}$ = partition coefficient based on DOM.

$K_{doc}$ = partition coefficient based on DOC.

Chiou, et al (1986) also showed that the effect of DOM on increasing the solubility of HOCs increased with an increase in DOM concentration. This effect was approximately four times more pronounced for humic acids than for fulvic acids, and about five to seven times greater for soil organic matter sources than for river-derived humics. The increase in effectiveness of various DOM sources at enhancing HOC solubility was attributed to their greater molecular size and lower polarity allowing for a larger intramolecular nonpolar environment into which the HOCs could partition (Chiou, 1986). In addition, the effect was found to be the greatest for the most hydrophobic compounds (i.e., the least water soluble) and had no effect on compounds whose solubilities were greater than 1 mg/l. Chiou, et al (1987) later report that the solubility enhancement effect was greater for commercially supplied humic acids (Aldrich and Fluka-Tridom) than for humic acids prepared by the researchers. They attributed this effect to the relatively greater carbon content and lower oxygen content of the commercial humic acids.

## Sorption and Binding of Compounds

### Factors Affecting Sorption and Binding

Numerous researchers have investigated the reactions of inorganic and organic compounds in soil and water. These investigations have generally centered on sorption to soil and soil fractions, and the binding of compounds to components in water such as DOM and colloids. The sorption and binding of compounds are dependent on the properties of the compounds, the soil properties, the aqueous solution properties and sorption and binding mechanisms.

### Compound Properties

The properties of a compound which influence sorption and binding include charge, polarity, number and character of functional groups, and molecular weight and solubility. Unlike inorganic and ionic organic compounds, HOCs are nonpolar, nonionic, and are not charge dependent. Therefore, HOCs are generally unaffected by processes involving electrical forces. Thus, the principal compound properties which directly influence HOC sorption and binding are solubility and molecular weight. As previously discussed, the HOCs are relatively high in molecular weight and have very low solubilities. These properties tend to make them hydrophobic and lipophilic. The solubility of a compound has also been shown to have an inverse linear correlation to $K_{ow}$, bioconcentration factor, and sorption to organic carbon sorbents.

### Soil Properties

Soil properties and their influence on sorption of HOCs is a keen area of research. General soil properties which influence compound sorption are soil particle charge, ion exchange capacity, expanding lattice structures of clays, soil organic matter (SOM) content, pH and surface area.

Agronomists concerned with the efficacy and persistence of pesticides have investigated a variety of sorption properties of soil. Recently, environmental researchers have also turned their attention toward soil properties which influence the mobility and sorption of HOCs in soils. The soil properties investigated include soil texture or particle size, clay minerology, surface area, ion-exchange capacity, soil solution ratio (solids concentration), water saturation and percent soil organic matter (SOM).

Texture, Surface Area and Mineralogy. A considerable amount of variability of sorption of organic compounds to soils has been noted (Elabd, et al, 1986; Wood, et al, 1987; Gauthier, et al, 1987; Schrap and Opperhuizen, 1989). Overall, sorption of HOCs has been shown to be poorly correlated with whole soil texture or with individual soil size fractions (Jones, et al, 1989; Khan, et al, 1979; Means, et al, 1980 and 1982; Karickhoff, 1981). However, Nekedi-Kizza, et al (1983) found less sorption variation among the silt and clay sized fractions of a soil than for sand. Karickhoff, et al (1979) state that the differences in sorption to clay and silt sized fractions of soils are due to the differences in the organic carbon content of these materials.

Clay mineralogy affects ion exchange capacity and surface area. Clay mineralogy has also been shown to influence sorption of ionic organic compounds (Karickhoff and Brown, 1978). However, the research of Hassett, et al (1980) reported no correlation between clay minerology and sorption of HOCs.

Surface area is related to soil texture with silt and clay having greater total surface area than sand. Surface area was not shown to be well correlated to organic compound sorption in a study of the Borden aquifer by MacKay, et al (1986).

Exchange Capacity and Soil pH. Cation exchange capacity (CEC) and pH of a soil are important influences on ionic compound sorption (Karickhoff and Brown, 1978). However, for neutral compounds such as HOCs, variations in CEC and soil pH have not been shown to affect sorption (Means, et al, 1980 and 1982; Hassett, et al, 1980).

Moisture Content. Although the present study evaluates sorption of HOCs to saturated soils, the effects of soil moisture content on the sorption of organic vapors to unsaturated soils has recently been investigated. Chiou and Shoup (1985) and Chiou, et al (1988) have shown that as the relative humidity is increased the sorption of HOCs to soils is decreased, until at a relative humidity of approximately 90%, the sorption capacities of the organic compounds approaches those found in aqueous solutions (i.e., saturated conditions). Sorption in unsaturated soils has also been shown to be related to water content by Wood, et al (1987) and Lambert (1966).

Soil Organic Matter. Numerous researchers have shown soil organic matter (SOM) to be the most directly correlated and predominant soil property affecting the sorption of HOCs. Early researchers, such as Goring (1962) and later Lambert, et al (1965) and Lambert (1966, 1967, and 1968) established that soil organic matter is "the most representative index of soil sorption equilibria" (Lambert, 1967). Lambert also indicated that SOM behaves in a similar fashion to a water-immiscible organic solvent used in a solvent extraction procedure for isolating HOCs. Lambert suggested that HOCs should partition between water and SOM in a correlative fashion to HOCs partitioning between an organic solvent and water.

Karickhoff (1984) also stresses the importance of SOM content in the sorption of HOCs. Karickhoff states that for large, nonpolar organic compounds containing more than 10 carbon atoms, sorption is controlled by organic matter, and that sorption to the mineral fraction alone is "insignificant in natural sediments".

The partitioning of a HOC between water and SOM has been described by Hamaker and Thompson (1972) on a soil organic carbon basis using:

$$K_{OC} = \frac{K}{OC}$$

where,

$K_{OC}$ = equilibrium partition coefficient normalized on an organic carbon basis.

K = equilibrium partition coefficient between whole soil and water.

OC = percent organic carbon in the soil.

Then, Chiou, et al (1979) showed a relationship between $K_{OC}$ and solubility (S) for HOCs covering more than seven orders of magnitude in solubility and four orders of magnitude in $K_{OC}$ as follows:

$$\log K_{OC} = 3.80 - 0.557 \log S$$

where,

S = solubility in μmoles/l.

The discussion and equations above were cited to establish that $K_{oc}$ can be directly related to S. In addition, $K_{ow}$ has previously been shown to be directly related to S, also. For example, the relationship between $K_{oc}$ and $K_{ow}$ as given by Kenaga and Goring (1980) for 45 organic compounds is:

$$\log K_{oc} = 1.377 + 0.544 \log K_{ow}$$

Other pertinent relationships between $K_{ow}$, $K_{oc}$ and S as described by various researchers are compiled in Appendix A. Although the results of the researchers cited imply that the $K_{ow}$, $K_{oc}$ and S relationships are independent of SOM source, other research shows that there are slight variances in sorption from one soil organic to another for the same compound. Garbarini and Lion (1986) indicate that the type of organic and its oxygen content are important in sorption of TCE. Schrap and Opperhuizen (1989) suggest that all sorption studies use at least one reference sorbate so that variances in SOM sorption found by different researchers can be more appropriately compared. Gauthier, et al (1987) suggest that variances in $K_{oc}$ for pyrene are due to aromaticity differences in 14 organic matter samples investigated. However, despite the differences, the $K_{oc}$ values for an organic compound sorbed to various soils and sediments are generally found to be within a factor of two to ten (Gschwend and Wu, 1985; Roy and Griffin, 1985).

Other research has shown that the close relationships between $K_{ow}$, $K_{oc}$ and S break down for soils and sediments with very low OC. Banerjee, et al (1985) suggest that for SOM contents less than 0.2%, sorption is not controlled by OC. Southworth and Keller (1986) show that SOM influence is minimal at OC contents less than 0.1%, and MacKay, et al (1986) showed poor sorption correlations to Borden aquifer sand containing 0.018% OC.

Different fractions of SOM have been also investigated in an effort to identify HOC sorption variations with SOM fractions. Shin, et al (1970) removed sequential fractions of SOM using ether, alcohol, hot water, HCl, and $H_2O_2$ digestion. These researchers found that DDT sorption increased when lipoidal materials were removed; that sorption was greater as the organic matter humification increased; and that sorption to SOM dominates over sorption to the mineral fraction of the soil. Kozak, et al (1983) investigated the sorption of prometryn and metolachlor to a whole soil; to a humic extracted fraction of the soil (humic and fulvic acids); and to the humin and mineral fractions of the soil. These researchers showed that the preference for sorption to the various fractions was, in increasing order, mineral, humin, whole soils and humic extractables (humic and fulvic acids).

### Aqueous Properties Affecting Sorption and Binding

The sorption and binding of nonpolar, neutral HOCs are affected by several aqueous properties. These properties include solution pH and ionic strength, soil-solution ratio, microorganisms and macromolecules, cosolvents and dissolved organic matter.

Solution pH and Ionic Strength. Lowered solution pH has been shown by Tramonti, et al (1986) to increase lindane sorption. Increased ionic strength of solution has been shown by Karickhoff (1979) to have little effect on HOC sorption. However, Tramonti, et al (1986) and Traina, et al (1989) showed decreased sorption with increased ionic strength.

Soil-Solution Ratio. The concentration of solids or adsorbent in a soil solution (i.e. the soil-solution ratio) has also been investigated. Although O'Connor and Connolly (1980) showed effects of variances in sorption with different solids concentrations, Karickhoff, et al (1979) and Bowman and Sans (1985) convincingly showed that sorption was independent of solids concentration. Bowman and Sans (1985) suggested that previously reported solids concentration effects might be attributed to incomplete spinning down of solids in the centrifugation process and/or to experimental errors.

## Hydrophobic Sorption

Sorption can also be thought of in terms of the sorbate having a very low affinity for the solvent (Weber, 1972). HOCs are large, uncharged, nonpolar, low solubility molecules having low affinities for water (i.e, they have weak solute-solvent interactions). This disliking of water results in HOCs having an affinity for sorption at a solid-liquid interface. This type of sorption is commonly referred to as hydrophobic sorption. Hassett, et al (1980) also describes hydrophobic sorption as result of weak solute-solvent (i.e., solvophobic) interactions rather than being attributed to strong sorbate-solute interactions.

Hydrophobic sorption is not related to increases in enthalphies (Chiou, et al, 1979) as are ionic or polar compound sorption, but perhaps to increases in entropy as structured water shells surrounding organic solutes are destroyed (Horvath and Melander, 1978; Hamaker and Thompson, 1972). Hydrophobic sorption is highly correlated to SOM content and increases as the HOCs increase in molecular weight, molecular volume, and carbon atom content. Hydrophobic sorption decreases with increases in compound polarity and solubility.

Many researchers have described hydrophobic sorption as a partitioning of the solute between water and SOM (Chiou, et al, 1983; Gschwend and Wu, 1985; Karickhoff, 1984). Chiou, et al (1983) also showed that this type of sorption is noncompetitive for binary HOC solutes. Hydrophobic sorption to hydrophobic portions of SOM is also described by Khan (1978) as the primary mechanism of sorption for organochlorine insecticides, such as DDT, DDD, and Dieldrin. Khan (1978) states that water molecules would not compete with the nonpolar HOC molecules for sites on the hydrophobic portions of SOM and that the primary sites for sorption could be lipids.

### Van der Waal's Bonding

Another mechanism contributing to HOC sorption is van der Waal's-London bonds. These bonds are additive and result from short range dipole-dipole interactions established instantaneously by fluctuations in electron distributions in a molecule's electron orbitals. These interactions are weak and decrease in an inverse relationship to the sixth power as intermolecular distances increase (Jury, 1986). Although weak, the additive nature of these bonds is considered important in sorption of large molecules such as HOCs (Khan, 1978; Pussemier, et al, 1989).

### Intraorganic Matter Diffusion

Research has also included investigations of rate-controlled, reversible and non-equilibrium sorption. This has led to the notion that binding of HOCs to OM is actually a partitioning process into the OM, or intraparticle diffusion, which is rate controlled and partially reversible. Rate-controlled sorption of organic compounds, which has been described as a short initial phase of rapid uptake followed by a longer period of slow uptake, has been reported by Wu and Gschwend (1986), Khan (1973), Miller and Weber (1986), Rao, et al (1979), and Bouchard, et al (1988). Reversibility has been investigated by Karickhoff (1984), Bowman and Sans (1985), van Genuchten, et al (1977) and Wauchope and Myers (1985).

Recently, investigations by Brusseau and Rao (1989a), Nkedi-Kizza, et al (1989), Brusseau and Rao (1989b) and Brusseau, et al (1989) have led to the conclusion that observations of HOC rate-limiting and non-equilibrium sorption are due to HOC diffusion into the organic matter. This mechanism is termed intraorganic matter diffusion (IOMD). The IOMD approach is in agreement with the partition model as postulated by Chiou, et al (1983), and the rate-controlling aspects of the model could help explain reduced travel times of HOCs in aquifers and increased flushing times required for contaminant removal (Brusseau and Rao, 1989b).

### Other Mechanisms

Other types of binding mechanisms proposed for the nonpolar HOCs are charge transfer bonds, entropy generation and magnetic interactions (Jury, 1986; Khan, 1978; Hamaker and Thompson, 1972). These are considered minor mechanisms for HOC binding, however, when compared to hydrophobic bonding, van der Waal's-London bonds and IOMD binding.

## Organic Matter

### Description and Characterization

The importance of organic matter in controlling the fate of HOCs in the environment necessitates an understanding of humic and fulvic materials. Decayed organic matter can be classified as non-humic and humic organic substances. The non-humic organics have recognizable chemical and physical characteristics and include waxes, fats, amino acids, peptides, carbohydrates and proteins. The non-humic fraction tends to be readily attacked by microorganisms and thus non-humic components have relatively short half lives. The humic fraction has no readily defined physical and chemical characteristics, has longer half-lives, is chemically complex, has molecular weights up to several hundred thousand, and tends to be hydrophilic in character (Schnitzer, 1978).

The humic fraction can be further subdivided into three subgroups on an operationally-defined basis (Schnitzer, 1978). The portion of the humic fraction that is soluble in both acid and base is known as fulvic acid. The portion which is soluble in base but is insoluble in acid below a pH of two is called humic acid. The fraction which is neither soluble in acid or base is called humin. These distinctions are somewhat arbitrary and the nomenclature given to the humic and fulvic acids derive from weak acidic functional groups contained in these materials (Stewart, 1982).

Humic and fulvic acids are found throughout the environment in soils, sediments, surface waters, ground waters, and oceans. When found in soils and sediments, these organic materials are known as soil organic matter (SOM). Humic and fulvic materials found in aqueous environments are called dissolved organic matter (DOM). The characteristics of humic and fulvic acids are discussed below.

Fulvic acids (FA) have molecular weights between 1,000 and 30,000. They are described as open, flexible, linear polyelectrolytes composed of highly oxidized aromatic rings with a large number of side chains whose building blocks are benzene-carboxylic and phenolic acids held together by hydrogen bonds, van der Waal's bonds, and pi-bonding (Schnitzer, 1978; Stevenson, 1982). The flexible, open structure of FA can react to changes in pH and ionic strength which allows FA to trap organic and inorganic contaminants (Schnitzer, 1978). FA has a greater oxygen content than humic acid but lower carbon and nitrogen content. The number of oxygen-containing functional groups (such as carbonyl, carboxyl, hydroxyl and carboxylate) of FA is also greater. Also, FA has more aliphatic carbon and less aromatic carbon than HA (Steelink, 1977).

Humic acids (HA) can have much greater molecular weights than FA ranging from 10,000 to 100,000 or greater. HA, like FA, also has a flexible structure composed of aromatic rings and nitrogen in cyclic forms and in peptide chains (Stevenson, 1982). Proposed structures for HA and FA are shown on Figures 1 and 2, respectively.

The insoluble humin fraction is believed to be tightly bound to soil minerals. The humin fraction is composed of HA, FA, and nonsoluble plant and microbial residues.

## Genesis of Humics

The formation of humic substances is a process that involves the enzymatic degradation, metabolism, polymerization and condensation of plant and animal remains by

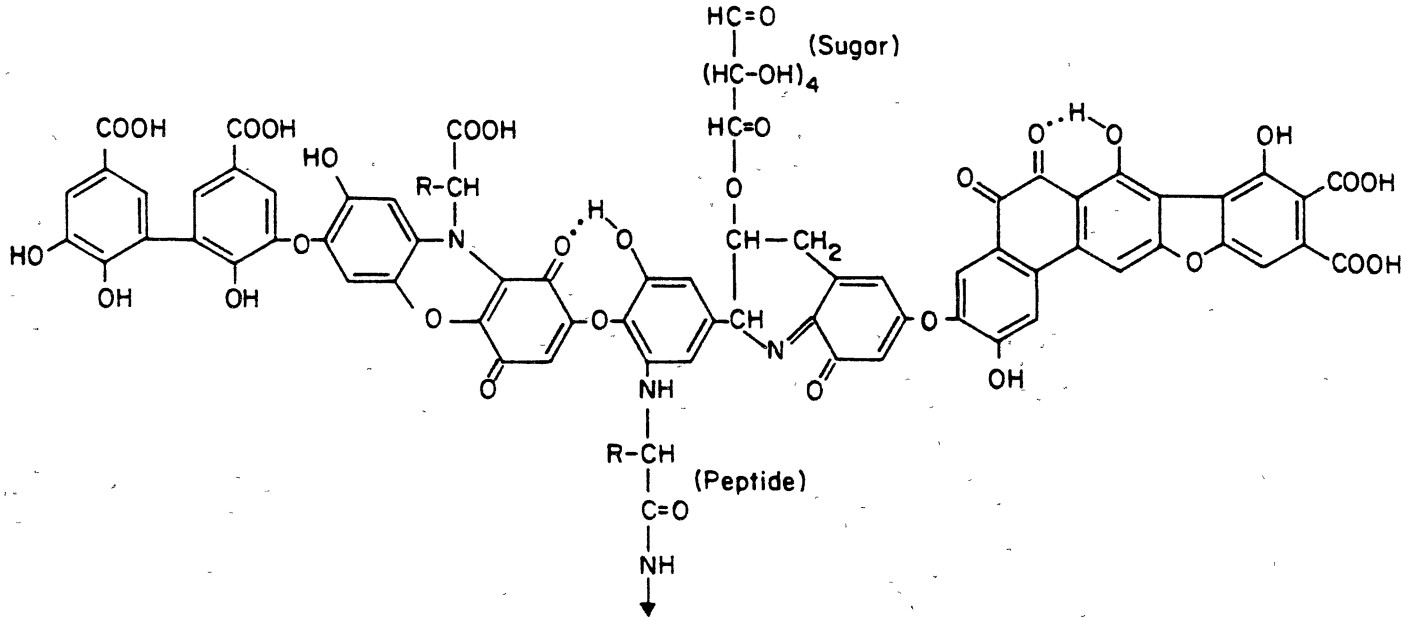

Figure 1. Proposed Partial Structure of Humic Acid (Stevenson, 1982).

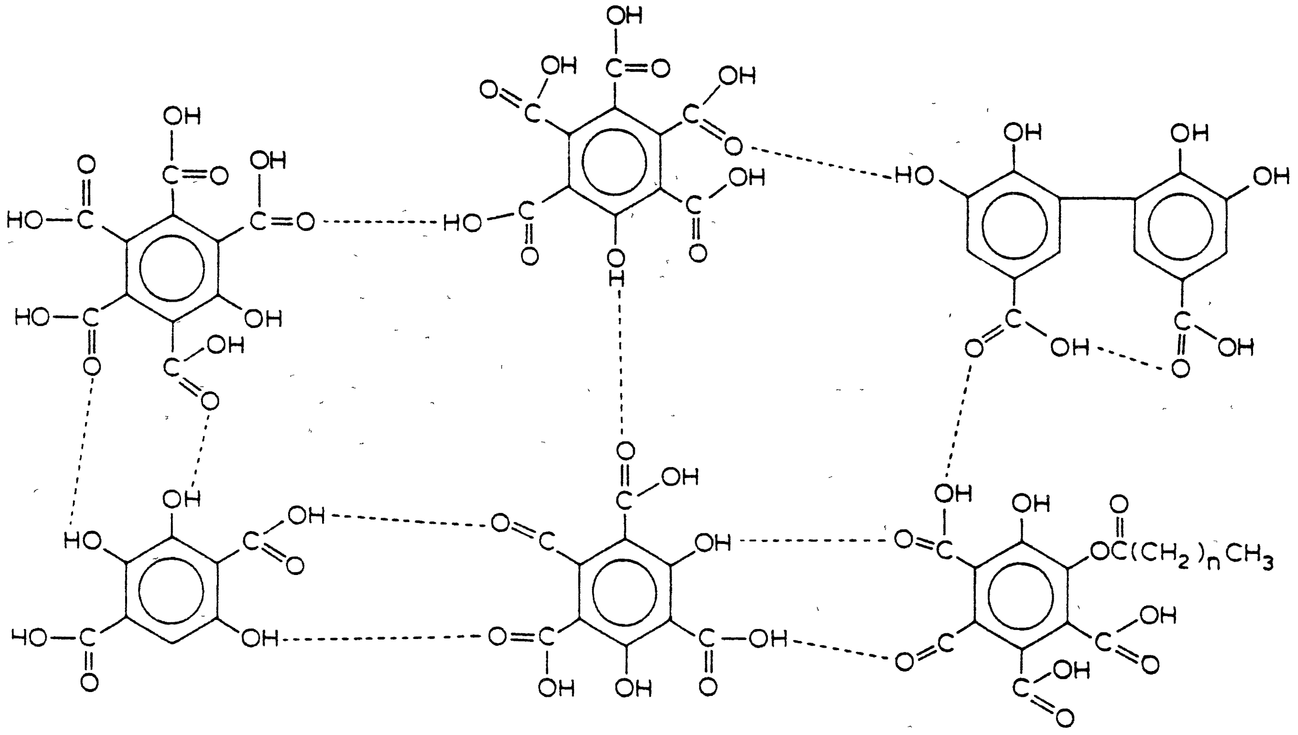

Figure 2. Proposed Partial Structure of Fulvic Acid (Schnitzer, 1978).

microorganisms (Stevenson, 1982). Low molecular weight compounds such as lignin and cellulose are used to start the process, which through condensation and polymerization reactions produces large, high molecular weight humic materials. Humic substances are typically considered very heterogeneous since the original source of the organic matter can vary as well as the reactions, processes, and intermediate products (Stevenson, 1982).

### Changes with Time and Depth

The organic matter in soils adjusts to changes in the environment and land use activity establishing new equilibrium conditions in a few years to tens of years. Although the non-humic soil fraction or soil biomass in the upper or A horizon of a soil can turn over every few years, the humin and humic fractions can have mean resident times greater than 1000 years. Fulvic acid is generally much less long lived with mean resident times in the 400-year to 500-year range (Stevenson, 1982).

The lower soil horizons, however, such as the B horizon and buried horizons, can have SOM resident times in the 700-year to 8400-year range compared to upper horizons in the 500-year range (Stevenson, 1982). Once leached to the lower soil horizons, the organic matter is apparently more isolated from degradative processes occurring in the upper horizons, resulting in longer residence times. The lower soil horizons also contain less organic matter than the upper horizon (Thurman, 1985).

In addition, the ratio of humic to fulvic acids generally increase with an increase in depth (Kononova, 1966). Stevenson (1985) suggests that the upper soils selectively retain the humic fraction while letting the fulvic fraction move downward preferentially in a chromatographic fashion resulting in the higher HA/FA ratios observed with depth.

### Retention of Organic Matter by Clays

HA and FA are typically found associated with the clay fraction of a soil (Stevenson, 1985). Organic matter can be retained by clay through several mechanisms.

First, insoluble polymeric complexes of HA and FA can be formed. Also, polymeric complexes of HA and FA can be bound together by divalent and trivalent cations such as $Ca^{+2}$, $Fe^{+3}$ and $Al^{+3}$. A schematic diagram of a clay-humate complex in soil is given as Figure 3. Binding can also be accomplished through ion exchange, hydrogen bonding, and van der Waal's bonding. Organic matter can also be held in interlayers of expanding clays, and bound by coordination and anion exchange to hydrous oxides (Stevenson, 1982).

However, the most likely mechanism of organic matter retention by clays, according to Stevenson (1985), is the formation of a clay-metal-humus complex. This occurs when the negative charge on the clay is neutralized by polyvalent metal cations bound to the humus. The acidic group on the humus is neutralized as well, thus linking the organic matter to the clay via a salt bridge. Although the charge on the clay is occluded from ion exchange with ionic species in solution, the bound organic matter can provide active sites for ion exchange as well as hydrophobic sites for hydrophobic sorption (Stevenson, 1982).

## Retention of Contaminants by Organic Matter

As previously discussed, organic matter has the ability to sorb or bind a variety of inorganic and organic compounds. The mechanisms of HOC binding have been addressed thus far mainly in terms of solute-solvent interactions and have been primarily attributed to hydrophobic bonding and van der Waal's bonding. However, the interactions between HOC solutes and organic matter as the sorbent are also important. These interactions are thought to depend primarily on the physical shape of the organic matter as determined by its chemical properties, such as charged functional groups, and the characteristics of the aqueous solution, such as pH and ionic strength.

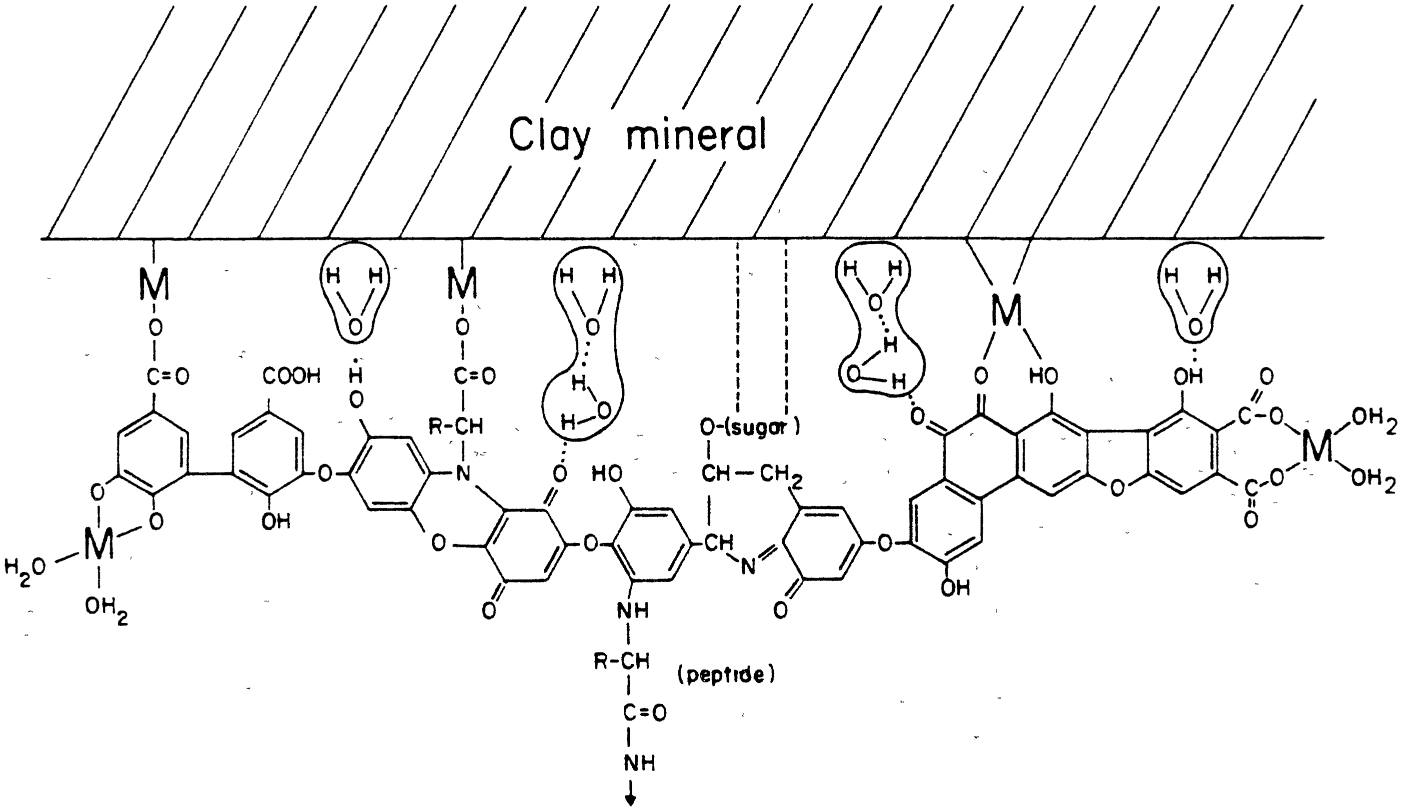

Figure 3. Proposed Schematic Diagram of a Soil Clay-Humate Complex. Polvalent Positively Charged Cations are Represented by M (Stevenson, 1985).

## Development of Hydrophobic Interiors

Humic and fulvic acids have been described by Khan and Schnitzer (1972) and Schnitzer (1978) as having cross-linked, open flexible structures with cavities capable of retaining HOCs in the internal voids of an organic structure analogous to a molecular sieve. This structure is affected by pH and ionic strength. Schnitzer (1978) shows dramatic photographs of HA and FA as solution pH is increased. At low pH values the organic molecules occur as elongated fibers. Then, as the pH is raised, the fibers mesh into a sponge-like structure, and then to a flattened, sheet-like structure at high pH. These reactions are attributed to the repulsion of carboxyl and hydroxyl functional groups as they become ionized at higher pH values. These repulsive electrostatic forces are greater than the attractive forces, such as van der Waal's bonding, pi bonding and hydrogen bonding, which dominate at lower pH values, causing the organic molecule to uncoil and flatten out into lamellae punctured by various sizes of voids (Schnitzer, 1978).

Ghosh and Schnitzer (1980) showed that at high pH and low ionic strength, HA and FA molecules uncoil and behave like flexible, linear colloids. However, at lowered pH and increased ionic strength, these materials began to coil, forming rigid spherocolloids and aggregations of spherocolloids. At high organic matter concentrations (>3500 mg/l), the HA and FA acted as spherocolloids at all pH and ionic strengths. Figure 4 summarizes these results. The effect of concentration was attributed to a lack of available space in the concentrated solution to allow for uncoiling. The pH effect was explained by electrostatic repulsion of ionized functional groups at higher pH values as described above. The effect of ionic strength could be attributed to repulsive forces of cations attached to the ion exchange sites of the organic functional groups on the humic molecules.

Thus, pH and dissolved ions can result in the formation of coiled, uncharged humic molecules with hydrophobic interiors. These hydrophobic portions of the humic molecules have the potential to bind HOCs.

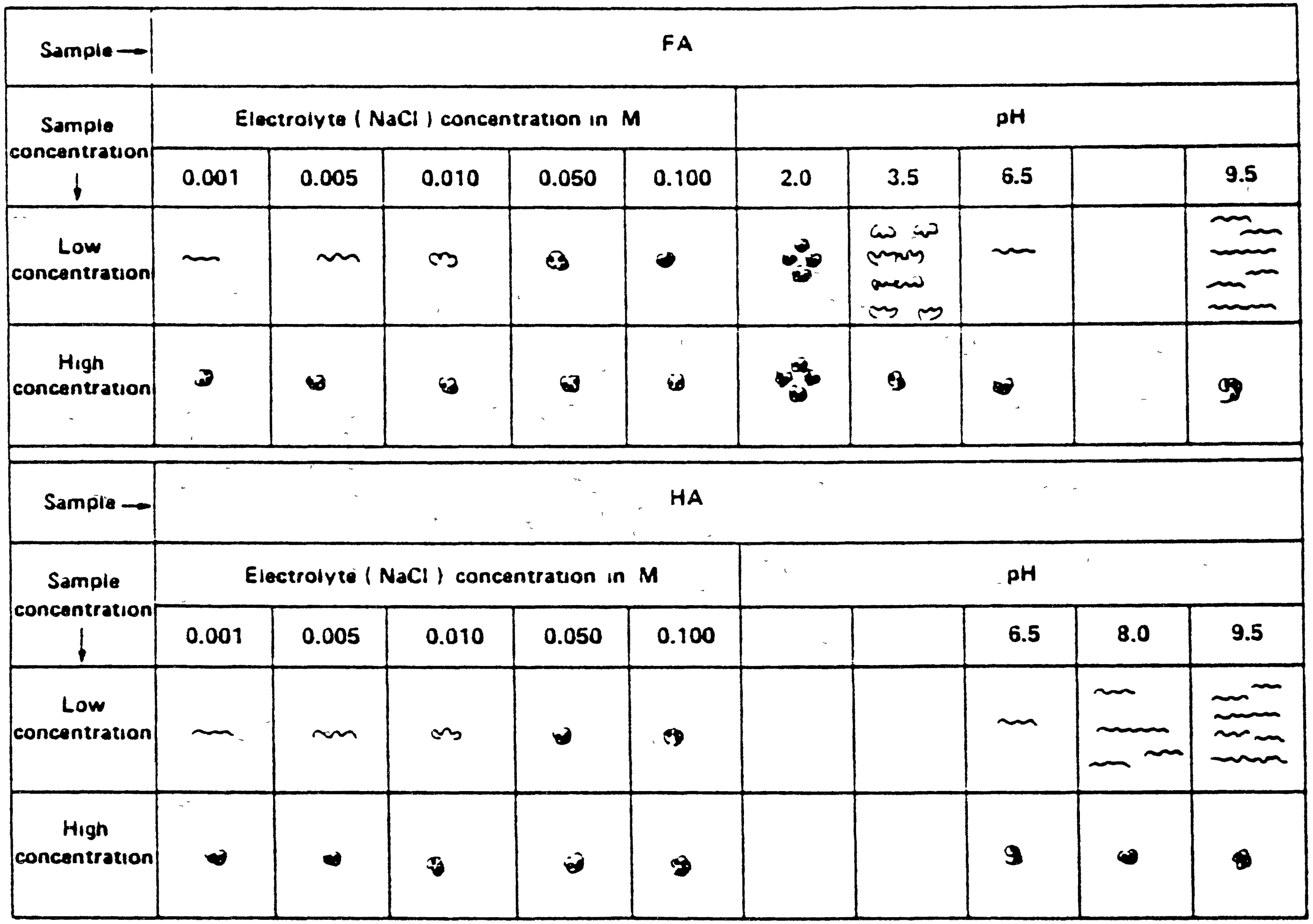

Figure 4. Schematic Diagram Depicting the Changes in Structure of Fulvic Acid (FA) and Humic Acid (HA) with Variations in Ionic Strength (NaCl), pH and Sample Concentration (i.e., Humate Concentration) in Solution (Ghosh and Schnitzer, 1980).

## Development of Micelles

Humic substances have also been described as having surfactant properties. Wershaw, et al (1969) showed that HA reduces surface tension of water and solubilizes DDT. Thurman (1985) describes humic molecules as having hydrophobic and hydrophilic ends. In the aqueous phase, Thurman suggests that these molecules could align themselves is such a way that the hydrophilic end is oriented toward water molecules and the hydrophobic (or lypophilic) end oriented with the hydrophobic portions of other humic molecules. These humic-derived surfactants are noted to cause foaming in streams (Thurman, 1985). Thurman also indicates that this foaming of the humic substances forms micelles which are "capable of dissolving oils and other hydrophobic constituents."

Wershaw (1986) presents a model for micelle formation by humic substances as a mechanism for the binding of HOCs. In this model, humic materials are thought of as amphiphiles which have hydrophilic and hydrophobic portions. The amphiphiles are bound together into aggregates through hydrogen bonding, pi bonding, and hydrophobic bonding. These aggregates are oriented in such a way as to form a structure having charged hydrophilic exterior surfaces and hydrophobic interiors in a fashion similar to membranes or micelles. Tanford (1980) describes self-aggregation of amphiphilic molecules into micelles or membranes as the orientation of polar portions of the molecules facing out toward the water. The hydrophobic tails of the amphiphilic molecules then join to form an internal, solvent-filled cavity capable of dissolving hydrocarbons and hydrophobic substances within them (Tanford, 1980).

Although less homogeneous than biological membranes, Wershaw (1986) indicates that humic micelles and membranes could react in a number of sorption and binding reactions. The exterior of the micelles would be negatively charged due to ionized carboxyl and hydroxyl functional groups. These would allow humus sorption to clays through cation exchange and clay-metal-humate reactions as well as allow sorption of ionic contaminants from solution. At the same time, the solvent-like interior of the micelle could allow incorporation of HOCs into the micelle.

### Partitioning into Hydrophobic Interiors and Micelles

The Wershaw micelle model is in agreement with and provides support for the mechanism described by Chiou, et al (1983) in which HOC binding is described as a liquid-liquid type of partitioning of the HOC from water into the soil humic matter. Chiou, et al (1986) also propose that HOCs are, in effect, partitioning into HA and FA micelles, resulting in apparent increased aqueous solubility.

Linking the Wershaw (1986) model of micelles with the pH-induced spherocolloid model of Ghosh and Schnitzer (1980) would provide additional mechanisms for the formation of hydrophobic interiors in HA and FA spherocolloid molecules or micelles. This in turn would allow partitioning of HOCs into the hydrophobic core of these molecules. Enhanced formation of hydrophobic interiors due to lowered solution pH would also help to explain the results of some researchers which indicate that nonionizable, nonpolar HOCs bind to a somewhat greater degree to humic materials at lowered pH than at higher pH values (Tramonti, et al, 1986). The partition model would also explain the lack of HOC bisolute competition described by Chiou, et al (1983) since specific binding sites would not be necessary if HOCs are indeed bound by partitioning into a nonpolar solvent such as the interior or cores of HA, FA or humin micelles, membranes or amphiphiles.

## Dissolved Organic Matter and Its Effects

Dissolved organic matter is present in almost all aquatic environments and is frequently referred to in terms of dissolved organic carbon (DOC). Dissolved organic carbon concentrations can range from 0.1 to 8 mg/l in ground water, from 0.5 to 1.2 mg/l in the ocean, from 0.1 to 15 mg/l in surface water and up to 50 mg/l in swamps (Choppin and Allard, 1985).

Dissolved organic matter has been shown to participate in a number of reactions. For instance, DOM has been shown by Schnitzer (1978) and Stevenson (1982) to have polyelectrolyte properties and can, depending on pH, affect the flocculation of clays in suspension (Thurman, 1985). Surfactant properties and HOC solubility enhancement properties as previously discussed are other DOM effects. DOM has also been shown to inhibit the bioavailability and toxicity of metals and organics to fish and other aquatic biota (McCarthy, 1989; Carlberg, et al, 1986; Zitko, et al, 1973).

In the purification of drinking water by activated carbon, Jain and Snoeyink (1973) and Snoeyink, et al (1977) have shown that DOM can reduce the sorption capacity and bed life of activated carbon columns for HOCs by preferentially adsorbing the larger DOM molecules over the smaller HOC molecules.

However, Koeleian and Curl (1989) showed no competition between HOC and DOM sorption to a natural kaolinite clay. Chiou, et al (1983) showed no competition between HOC bisolutes when bound to SOM. This implies that DOM which is generally hydrophilic in character should not be competitive with hydrophobic organic compounds in sorption to soils. In fact, if DOM was bound by a soil, HOCs would have an enhanced medium into which they could partition (Koeleian and Curl, 1989). Furthermore, Chiou, et al (1986) also showed no interference or competition in the solubility enhancement effects of DOM binding bisolutes in solution, and they concluded that this further strengthens the concept that DOM constitutes an organic solvent-like phase into which HOCs can partition.

## Facilitated Transport

Research has recently turned to enhanced or facilitated transport of contaminants in surface waters, ground waters and in soils. Several researchers have proposed that transport of HOCs is facilitated via colloids, cosolvents, macromolecules, microorganisms, sewage effluent and DOM. An overview of the literature pertaining to these transport media is provided in order to establish the concept and importance of facilitated transport which lead to consideration of DOM as a potential mechanism for facilitated transport.

### Colloids

Colloids are characterized as particles with a diameter in the range of 0.001 to 1.0 μm (Thurman, 1985). Colloids have been described by Lopez-Avila and Hites (1980), as the transport mechanism of numerous organic compounds found in a river downstream from the wastewater outfall of a chemical manufacturing plant. These researchers found that the compounds with the highest $K_{ow}$ were strongly bound to river colloids and were found transported the farthest distance downstream from the plant.

Means and Wijayaratne (1982 and 1984) showed that estuarine colloids bind organic compounds and that the sorption is correlated to the organic carbon content of the colloids. Wijayaratne and Means (1984) also indicate that herbicide sorption to organic estuarine colloids was 10 to 35 times greater than sorption to soil or sediment organic matter.

Soil particulate colloids have also been shown to transport through macropores in the soil (Pilgrim and Huff, 1983). McCarthy and Zachara (1989) suggest that mobile colloids in soil and ground water could be important transport mechanisms in contaminant migration and indicate that additional research in this area is needed.

## Cosolvents

The effect of cosolvents on HOC solubility has been previously discussed. A number of researchers have shown that in soils, HOC sorption and attenuation decrease in a semi-logarithmic fashion as the percent cosolvent in the solution increases (Fu and Luthy, 1986b and 1985; Woodburn, et al, 1989; Rao, et al, 1985; Nkedi-Kizza, et al, 1987; Walters and Guiseppi-Elie, 1988). This effect increases as the hydrophobicity of the compounds increase (Munz and Roberts, 1986).

## Macromolecules

Macromolecules have been shown by Enfield and Bengtsson (1988) and Harvey, et al (1989) to move faster than the average ground-water velocity and could be capable of transporting bound HOCs more rapidly and farther distances than expected. Macromolecules can move at a rate greater than the average ground-water velocity since, due to their size, their transport is limited to channels and the secondary pore structure of the porous matrix. Macromolecules are not able to move through the intergranular pore space (McCarthy and Zachara, 1989).

## Microorganisms

Microorganisms have been shown to bind HOCs (Bell and Tsezos, 1987; Karickhoff, 1984). Microorganisms have also been shown to be transported considerable distances in ground water (Smith, et al, 1985; Keswick, et al, 1982; Harvey, et al, 1989). Thus, there exists the potential for facilitated transport of HOCs via microorganisms.

## Municipal Sewage

Sewage effluent has not been investigated as a medium for transport facilitation, per se. However, Bouwer, et al (1984) showed trace organic compounds entering ground water beneath a sewage effluent rapid infiltration site. Tomson, et al (1981) showed greater movement than was expected of numerous trace organic compounds to ground water beneath the same site. Boyle and Fuller (1987) have shown facilitated transport of zinc through soils using municipal solid waste leachate. Hassett and Anderson (1979 and 1982) have investigated the effects of HOC interactions with the DOM associated with sewage effluents in rivers, and showed that DOM extracted from sewage and natural water reduced the sorption of HOCs to the particulate matter in sewage and rivers. Hassett and Anderson (1982) also indicated that river particulates are less effective at sorption than sewage particulates.

Sewage sludge can affect SOM, metal attenuation, and the potential for contaminant migration. Sewage sludge applied to land has been shown to affect the elemental content of soil humic acid beneath the sludge and the sorption of trace metals by the sludge (Senesi, et al, 1989). Dudley, et al (1987) have shown copper and nickel to be associated with the soluble organic components in sludge-amended soils.

## Dissolved Organic Matter

Facilitated transport of contaminants by dissolved organic matter such as HA and FA has been investigated by few researchers. The DOM can be considered a third component in a system containing soil or sediment and a HOC. Most of this research has been done on interactions of DOM with inorganic compounds. Very little research has been completed on enhanced transport of HOCs by DOM.

Investigations of DOM interactions with inorganic compounds include the work by Hering and Morel (1988) who showed that humic acid binds copper and calcium in a noncompetitive fashion. Allard, et al (1989) have shown that sorption of americium onto alumina in the presence of humic materials to be enhanced or decreased depending on the pH of the solution. Inskeep (1989) has shown that DOM inhibits the sorption of sulfate to amorphous iron oxide and kaolinite and he relates this effect to the quantity of oxygen-containing functional groups of the DOM.

Early observations in the sorption and transport of HOCs in the presence of DOM were reported by Ballard (1971). Ballard showed that DDT was leached through a forest soil after urea was added to the soil to raise the pH which consequently solubilized and dispersed the humic materials in the soil. The solution which leached through the soil was then collected and analyzed. DDT was found to be primarily associated with dissolved humic acid (91%) and to a lesser degree with fulvic acid (9%) in the leachate (Ballard, 1971). Also, Wershaw, et al (1969) showed that DDT can be solubilized by sodium humate and Poirrier, et al (1972) showed that coloring colloids in natural waters can bind DDT at high concentration and thus provide a transport mechanism. Landrum, et al (1984) evaluated the movement of HOCs through a Sep-Pac C-18 cartridge in the presence of dissolved Aldrich humic acid. The Sep-Pac was found to retain unbound HOCs while allowing humic-bound HOCs to pass through the column. Thus, DOM was found to facilitate HOC transport through the column (Landrum, et al, 1984).

### Previous HOC-Soil-DOM Investigations

Although numerous researchers have investigated the sorption of HOCs to SOM, or investigated the binding of HOCs to DOM, scant literature has been found in which all three components were intentionally investigated in the same system at the same time. A three-component system such as this would be expected in the environment. The following investigations by Caron, et al (1985) and West, et al (1984) are examples in which soil, HOC and DOM were all present simultaneously in the experiments.

Caron, et al (1985) investigated the effects of sorption of DDT and lindane to a river sediment in the presence and absence of humic acid in the aqueous phase. The HA used had previously been extracted from the same river sediment source and was added to batch shaker reactors at a concentration of 6.95 mg/l DOC. The batch samples contained either radiolabelled DDT or lindane and were equilibrated for 24 hours. In the absence of the DOC, lindane, which has a relatively high solubility compared to DDT, showed a lower partition coefficient to the sediment than did the much less soluble DDT, as would be expected. The dissolved HA showed no effect on lindane sorption or solubility enhancement as would also be expected by the work of Chiou, et al (1986) and Kile and Chiou (1989). However, DDT was affected by the DOC in solution which considerably lowered the amount of DDT sorbed to the sediment and increased the amount remaining in solution. This effect was attributed to binding of DDT to the DOC and thus the humic-bound DDT was then no longer able to be sorbed by the sediment (Caron, et al, 1985). These researchers concluded that DOC could have an important effect on the transport of HOCs in aqueous systems where sediment organic carbon content is low and the DOC concentration is relatively high.

West, et al (1984) investigated the transport of hexachlorobenzene (HCB) in a low-carbon soil column experiment in the presence and absence of a dissolved ground water humic material. Initial experiments showed that the HCB would bind strongly to the dissolved humic material. Later experiments showed that the humic material (9.0 mg/l DOC) by itself would move through the soil column in a conservative or non-adsorbing fashion. However, the HCB (20 µg/l influent concentration) by itself was severely retarded in the column, and maximum effluent concentrations never exceeded 0.05 µg/l. Then, when the humic material and HCB were mixed together in the feed solution prior to input to the soil column, the humic-bound portion of the HCB moved through the column relatively unimpeded, eluting at approximately the same time as the humic material at a concentration of 0.92 µg/l. It was concluded that the humic-bound portion of the HCB underwent mediated transport due to the DOC, while the freely dissolved portion of the HCB, which was not bound to the dissolved humic material, sorbed strongly to the soil.

## Present HOC-Soil-DOM Investigation

Although the authors discussed above show mediated transport in a three-component system (DOC, soil and HOC), the experimental conditions investigated were somewhat limited. For instance, in both cases only one soil was chosen for investigation. Also, at most two HOCs were compared in a single experiment (Caron, et al 1985). These compounds (DDT and lindane) which are at opposite extremes of the solubility range of HOCs. Chiou, et al (1986) has since shown no solubility enhancement effects on any of the compounds they tested (including lindane) which had an aqueous solubility greater than 1 mg/l. Kile and Chiou (1989) have further refined the concept of DOM solubility enhancement and state that for the solubility increase of an HOC to be significant the DOC concentration in solution must be at least two orders of magnitude greater than the solubility of the HOC in pure water. Finally, Caron, et al (1985) and West, et al (1984) performed their experiments at one pH and not over the range of environmental pH values. They also only investigated one dissolved organic matter each at a single DOC concentration in their three-component systems.

The purpose of the present study is to further investigate the potential of using DOM as a mediating factor for facilitating transport in three-component systems. The investigation extends previous research in several ways. First, an appropriate range of environmental solution pH conditions is incorporated. Also, three soils collected from various soil horizons and possessing differing soil properties and SOM contents were used. In addition, two different dissolved organic matter sources were employed. DOM concentrations covering the environmental range of DOC concentration found in ground waters and most surface waters were also investigated. Finally, three environmentally significant organochlorine HOCs were used. The HOCs were selected so that their solubilities would span an appropriate range in which enhanced solubility due to environmental concentrations of DOC could be effective.

# CHAPTER III

# MATERIALS AND METHODS

## Introduction

Experiments in this study were designed to observe the sorption of nonionic, hydrophobic organic compounds (HOCs) on three soils at three different pH values in the presence of increasing concentrations of dissolved organic matter (DOM) in solution. Experiments were conducted utilizing aqueous slurries of soil and water shaken in batch reactors. Various combinations of soil, DOM and HOCs were added to the batch reactors, shaken until equilibrium was attained and then centrifuged. Aliquots of the supernatant were then extracted with hexane and analyzed by gas chromatography. The batch experiments, procedures and materials used are described below in detail.

## Reagents

The reagents, and the HOC and DOM compounds used in this study are listed along with their sources in Table I. All reagents were used as received.

The HOCs used are common and persistent insecticides found throughout the environment and were selected for use as representatives of low solubility, nonionic hydrophobic solutes. These compounds were not only chosen due to their environmental significance and persistence, but also for their physical characteristics as listed in Table II. Among the physical characteristics desired of the model solutes selected were high molecular weight, nonionic compounds with a range of low solubilities and having relatively low vapor pressures, medium to high octanol-water partition coefficients ($K_{OW}$),

## TABLE I

## REAGENTS USED IN STUDY

| Reagent | Alternate Name(s) | CAS[a] Registry Number | Source | Purity or Grade |
|---|---|---|---|---|
| p,p' - DDT | 1,1,1-Trichloro-2,2-bis(4-chlorophenyl)-ethane<br>1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane | 50-29-3 | Aldrich | 99 + % |
| p,p' - DDD | TDE<br>1,1-Dichloro-2,2-bis(4-chlorophenyl)-ethane<br>2,2-Bis(4-chlorophenyl)-1,1-dichloroethane | 72-54-8 | Aldrich | 99 + % |
| Dieldrin | Octalox<br>1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endro-5,8-dimethanonaphthalene | 60-57-1 | Fisher | 99 + % |
| Humic Acid, Sodium Salt | Aldrich Humic Acid | — | Aldrich | Technical Grade |
| Fulvic Acid | International Humic Substances Society (IHSS) Standard Soil Fulvic Acid (1S102 F) | — | IHSS | Research Standard |
| Acetone | — | — | Fisher | 99.5% |
| Hexanes | — | — | Fisher | Certified Pesticide Residue Analysis |

[a] Chemical Abstracts Service

# TABLE II

## CHARACTERISTICS OF MODEL SOLUTES

| HOC | M.W.[a] | M.P.[a](°C) | V.P.[a](torr) | Solubility in Water at 25°C (ppb)[a,b] | Log $K_{ow}$ |
|---|---|---|---|---|---|
| p,p' - DDT | 354.49 | 107 - 109 | 7.3 x $10^{-7}$<br>(at 30°C) | 5.5 - 25 | 5.98 - 6.36[a,c] |
| p,p' - DDD | 320.05 | 109 - 112 | 10.2 x $10^{-7}$<br>(at 30°C) | 20 - 90 | 5.99 - 6.08[a] |
| Dieldrin | 380.95 | 175 - 176 | 1.8 x $10^{-7}$<br>(at 20°C) | 195-200 | ~5.15[c] |

[a] Callahan, et al, 1979.
[b] Biggar and Riggs, 1974.
[c] Henry, et al, 1989.

and a high potential for sorption to soils. These characteristics were considered desirable for the following reasons.

The nonionic nature of the compounds was selected to evaluate the sorption of uncharged nonpolar compounds (as opposed to polar or ionic compounds). The characteristic of low vapor pressure was desirable to minimize the potential for volatile losses during the experiments. The low solubility and medium to high octanol-water partition coefficients are characteristics of compounds with the propensity for sorption to soils and the potential to bind to DOM. A range in both solubility and $K_{ow}$ was chosen to evaluate the variation in sorption and binding with variation in these characteristics.

Other considerations for the selection of these compounds as model solutes were of a practical nature. These included favorable potential for using microextraction procedures on small sample volumes and the use of similar gas chromatography procedures for extract analysis.

## Soils

Soils selected for use in this study were native Oklahoma soils collected and provided by Dr. Brian Carter, Department of Agronomy, Oklahoma State University. The soils were chosen so that a variations in soil organic matter, texture and horizon could be evaluated. The Mullhall soils are described as fine-loamy, siliceous, thermic Udic Paleustolls and the Navina soils are fine-loamy mixed thermic Udic Argiustolls (Henley, et al, 1987).

The methods used to characterize the properties of the soils chosen for use are listed in Table III. The soils were received in an air-dried condition. They were then sieved through a 40 mesh sieve (0.425 mm openings) to remove rootlets and stored in air-tight containers until used.

## TABLE III

## METHODS USED TO ANALYZE SOILS USED IN STUDY

| Property / Characteristic | Method / Reference |
|---|---|
| Soil Name (type locality) | Carter / a |
| ID used in experiments | — |
| Soil Horizon | Carter / a |
| Depth Sampled (cm) | Carter / a |
| Land Use | Carter / a |
| Organic Matter (%) | Walkley-Black / b |
| Organic Carbon (%) | % Organic Matter ÷ 1.72 / a,c |
| Soil Class (Texture) | Carter / a |
| Sand (%) | Wet Sieve / b |
| Silt (%) | Wet Sieve / b |
| Clay (%) | Stoke's Law / b |
| Soil pH | 50:50 Soil:Water Solution / b |
| Water Content (%) | 103°C / b |
| CEC (meq/100 g) | $BaCl_2$ / b,c,d |
| AEC (meq/100 g) | $BaCl_2$ / b,c,d |
| Clay Mineralogy | XRD / a,b,c |

[a] Dr. Brian Carter, Dept. of Agronomy, OSU (1989).
[b] U.S.D.A., S.C.S (1987).
[c] Page, et al(1982).
[d] Gillman (1979).

## Batch Reactors

The batch reactors used in all sorption experiments consisted of 40 ml hypo vials. These vials are commonly used in the collection of water samples for volatile organic analyses. The vials used were obtained from Supelco, Inc. and are clear, borosilicate glass with dimensions of 29 x 81 mm. The vials were capped with open-top screw caps lined with Teflon-faced silicon septa. The vials were analytically cleaned as outlined in Appendix B prior to each use.

## Experimental Descriptions and Procedures

The experiments performed in this study fall under several general categories. These are soil characterization, preliminary tests, sorption isotherms and DOM experiments. Detailed explanations of these experiments and their procedures are given below.

### Soil Characterization

Soils were characterized following the methods of analysis previously listed in Table III. The reader is directed to the references listed in the table for detailed soil characterization procedures.

### Preliminary Tests

A variety of preliminary tests were necessary prior to performing the sorption isotherm and DOM experiments. These tests were run to establish soil-solution ratios, equilibrium times, DOM sorption potential and organic carbon contents.

Since preliminary test results of soil-solution and equilibrium time experiments were to be used in a qualitative rather than quantitative fashion, typically only single samples were run in these tests. However, duplicate samples were run on the DOM sorption screening experiments. Triplicate samples were run on all subsequent isotherm and DOM experiments.

### Soil-Solution Ratio Screenings

The soil-solution ratio screenings were performed to determine the amount of soil necessary to sorb 70% to 90% of the HOCs from solution after taking into account any losses, such as glassware sorption, found in the control vials. The 70% to 90% adsorption range was chosen so that a majority, but not all, of the HOC would be removed from solution by the soils when there was no DOM in solution. Thus, when DOM was added to the vials in subsequent DOM experiments, any decrease or increase in HOC concentration in solution, i.e., any difference in HOC sorbed to the soil due to the addition of the DOM, would be apparent.

First, for the soil-solution ratio screenings various masses of air-dried soils were weighed on a Mettler AE-160 model digital balance ( 0.0000 g digital display) and then added to the reactor vials. Although air-dried soil mass was used in weighing out soils in the experiments, results of the subsequent isotherm and DOM experiments were adjusted to reflect moisture-free soil mass. The masses of the various soils used in these screening trials are listed in Table IV.

Next, separate test solutions of the HOCs were prepared in distilled, deionized water. The water used in all experiments was purified prior to use by passing through a Gelman Sciences Water-I model deionizer fitted with a deionizer/activated-carbon filter cartridge. Distilled water was produced using a Barnstead A-1015 model electric distillation unit to supply water for use in the deionizer. A complete description of the preparation of the HOC test solutions and HOC gas chromatograph standards is given in Appendix B.

Then, the HOC solutions were pipetted into the reactor vials. The vials were securely capped and placed horizontally on a two-speed reciprocating shaker (Eberbach

# TABLE IV

## EXPERIMENTAL CONDITIONS FOR SOIL–SOLUTION RATIO SCREENING TRIALS

| Vial ID Prefix | g Soil[a] | g Soil[b] | g Soil[c] | Description |
|---|---|---|---|---|
| A | 0 | 0 | 0 | Blank Control Vials |
| MA | 0.05 | 0.15 | 0.10 | MA Soil Screening Vials |
| MA | 0.10 | 0.30 | 0.20 | MA Soil Screening Vials |
| MA | 0.25 | 0.60 | 0.40 | MA Soil Screening Vials |
| MA | 0.50 | 1.00 | 0.60 | MA Soil Screening Vials |
| MA | — | 2.00 | 1.00 | MA Soil Screening Vials |
| MA | — | — | 2.00 | MA Soil Screening Vials |
| MB | 0.05 | 0.15 | 0.10 | MB Soil Screening Vials |
| MB | 0.10 | 0.30 | 0.20 | MB Soil Screening Vials |
| MB | 0.25 | 0.60 | 0.40 | MB Soil Screening Vials |
| MB | 0.50 | 1.00 | 0.60 | MB Soil Screening Vials |
| MB | — | 2.00 | 1.00 | MB Soil Screening Vials |
| MB | — | — | 2.00 | MB Soil Screening Vials |
| NB | 0.05 | 0.15 | 0.10 | NB Soil Screening Vials |
| NB | 0.10 | 0.30 | 0.20 | NB Soil Screening Vials |
| NB | 0.25 | 0.60 | 0.40 | NB Soil Screening Vials |
| NB | 0.50 | 1.00 | 0.60 | NB Soil Screening Vials |
| NB | — | 2.00 | 1.00 | NB Soil Screening Vials |
| NB | — | — | 2.00 | NB Soil Screening Vials |

[a] Vials used for screening DDT (35 ml solution, 25 ppb.)
[b] Vials used for screening DDD (30 ml solution, 90 ppb.)
[c] Vials used for screening Dieldrin (30 ml solution, 90 ppb.)

Corp. model 6010). Although adverse reactions of the HOCs with light was not expected, the vials were covered with a black cloth as a precautionary measure. The vials were then shaken overnight at 180 oscillations per minute (low setting on shaker). Ambient laboratory temperatures were recorded to be 23°C ± 2°C for all experiments.

After shaking, the vials were centrifuged on an International Equipment Co. model Centra-7 centrifuge at 1200 rpm for one hour. The centrifuge speed and duration were determined using the following equation by Roy, et al (1987) for the spinning down of soil particles with a 0.1 μm radius and an average density of 2.65 g/cm (Freeze and Cherry, 1979).

$$t = \frac{3.71 \times 10^8}{(\mathrm{rpm})^2} \ln (R_b/R_t)$$

where,

$t$ = centrifuge time, minutes.

rpm = revolutions per minute.

$R_b$ = distance from the center of the centrifuge rotor to the bottom of the centrifuge tube (or reactor vial), cm.

$R_t$ = distance from the center of the centrifuge rotor to the top of the solution in the centrifuge tube (or reactor vial), cm.

In these experiments, the centrifuge speed was found to be limited to 1200 rpm to prevent vial breakage. Thus, the time needed to centrifuge the samples was determined to be one hour. Note that this procedure removes 0.1 μm diameter particles which is well within the colloid particle range of 0.001 to 1.0 μm (Thurman, 1985) and considerably less than the maximum diameter of 3.9 μm for clay particles (Freeze and Cherry, 1979).

After centrifuging, aliquots of the clear supernatant solutions were removed with a pipette for HOC extraction using a modified microextraction technique described in Keith (1981). This technique is advantageous since it allows relatively small sample aliquots (10 to 100 ml) to be extracted with 0.2 to 5 ml of solvent. The microextraction method was chosen for these experiments since the total sample volume was never more than 35 ml.

The extractions were performed by pipetting 5 to 8 ml of the DDT solutions or 2 to 4 ml of DDD or Dieldrin solutions into separate 12 ml screw-top test tubes. The amount of HOC solution extracted depended on the sensitivity of detection of the GC for the compounds and the initial concentration of the HOCs. Larger volumes of the solutions were needed as the experiments progressed because of decreasing sensitivity of the GC detector with age. Initial concentrations of DDT were 25 µg/l, and 90 µg/l for DDD and Dieldrin. Thus a larger DDT solution volume was needed for extraction than for DDD or Dieldrin.

Next, 2 ml of hexane was added to each test tube. Teflon tape was used to cover the test tube opening and then the screw cap was securely emplaced. The tubes were shaken horizontally on the reciprocating shaker at 280 oscillations per minute (high setting) for 10 minutes. After shaking, the solvent phase was allowed to separate from the water phase with the test tubes standing in a vertical position. The solvent phase was then withdrawn with 5.25-inch, disposable, borosilicate glass pipettes and transferred to 1.5-ml storage vials. The storage vials used were 12 x 35 mm in dimension with an open-top screw caps and Teflon-faced silicone septums (Wheaton Scientific). The sample extracts were then stored at less than 4°C until analyzed.

In addition to the supernatant samples collected from the reactor vials, duplicate samples of the initial HOC test solutions used to fill the reactor vials were collected before and after filling these vials. This was done to quantify the initial concentration of the solution used to fill the reactor vials and to account for potential losses through volatilization while filling the vials. The losses during filling of the vials was found to be nominal, and the extraction efficiency was found to be approximately 85% to 105%. All data gathered during the study were subsequently corrected using the extraction efficiencies generated for the individual experiments.

### Equilibrium Time Screenings

The screenings for equilibrium times were performed to determine how much shaking time was needed in order for the systems to reach equilibrium with respect to HOC sorption. Table V lists the experimental conditions for the equilibrium time screenings.

Shaking time for DDT from the equilibrium screening trials was established at 8 hours and at 24 hours for DDD and Dieldrin. These times allowed for equilibrium as well as a practical working working schedule for subsequent isotherm and DOM experiments.

### pH Adjustment Screenings

In order to achieve soil-solution pH values in the range of 4, 7 and 10 after 24 hours of shaking, additional screening tests were performed on the soils to determine the amount of hydrochloric acid or sodium hydroxide that was necessary to adjust the initial HOC test solutions. Also, additional screening tests showed that the acid and base had no apparent adverse effects, such as hydrolyis reactions, on the HOCs in the test solutions since the HOC concentrations remained constant throughout these screening tests. The hydrogen ion activity (pH) of solutions used in experiments was measured using a Fisher Accumet model 900 pH meter equipped with a Fisher model E-58 combination electrode probe.

### DOM Sorption Screenings

Finally, screening tests were run to evaluate whether the DOM used in the DOM experiments might sorb to the soils. In order to accomplish this goal a series of DOM sorption tests were performed. First, concentrated solutions of humic acid (HA) and fulvic acid (FA) were prepared so that the DOM could be added to the reactor vials in a volumetric fashion. The HA concentrate was prepared by placing 1.00 g of HA sodium salt in a 100 ml volumetric flask and filling with deionized water. This produced a 10,000 mg/l HA

# TABLE V

# EXPERIMENTAL CONDITIONS FOR EQUILIBRIUM TIME SCREENING TRIALS

| Vial ID Prefix | DDT[a] g Soil[d] | DDT[a] Hours Shaken | DDD[b] g Soil[d] | DDD[b] Hours Shaken | Dieldrin[c] g Soil[d] | Dieldrin[c] Hours Shaken | Description |
|---|---|---|---|---|---|---|---|
| A | 0 | 0 | 0 | 0 | 0 | 0 | Blank Control Vials |
| A | 0 | 1 | 0 | 1 | 0 | 1 | Blank Control Vials |
| A | 0 | 6 | 0 | 2 | 0 | 2 | Blank Control Vials |
| A | 0 | 12 | 0 | 4 | 0 | 7.75 | Blank Control Vials |
| A | 0 | 24 | 0 | 11 | 0 | 17.25 | Blank Control Vials |
| A | 0 | 48 | 0 | 18 | 0 | 24 | Blank Control Vials |
| A | — | — | 0 | 39 | 0 | 48.5 | Blank Control Vials |
| MA | 0.15 | 1 | 0.20 | 1 | 0.30 | 1 | MA Soil Screening Vials |
| MA | 0.15 | 6 | 0.20 | 2 | 0.30 | 2 | MA Soil Screening Vials |
| MA | 0.15 | 12 | 0.20 | 4 | 0.30 | 7.75 | MA Soil Screening Vials |
| MA | 0.15 | 24 | 0.20 | 11 | 0.30 | 17.25 | MA Soil Screening Vials |
| MA | 0.15 | 48 | 0.20 | 18 | 0.30 | 24 | MA Soil Screening Vials |
| MA | — | — | 0.20 | 39 | 0.30 | 48.5 | MA Soil Screening Vials |
| MB | 0.30 | 1 | 0.40 | 1 | 0.60 | 1 | MB Soil Screening Vials |
| MB | 0.30 | 6 | 0.40 | 2 | 0.60 | 2 | MB Soil Screening Vials |
| MB | 0.30 | 12 | 0.40 | 4 | 0.60 | 7.75 | MB Soil Screening Vials |
| MB | 0.30 | 24 | 0.40 | 11 | 0.60 | 17.25 | MB Soil Screening Vials |
| MB | 0.30 | 48 | 0.40 | 18 | 0.60 | 24 | MB Soil Screening Vials |
| MB | — | — | 0.40 | 39 | 0.60 | 48.5 | MB Soil Screening Vials |

TABLE V (Continued)

| | DDT[a] | | DDD[b] | | Dieldrin[c] | | |
|---|---|---|---|---|---|---|---|
| Vial ID Prefix | g Soil[d] | Hours Shaken | g Soil[d] | Hours Shaken | g Soil[d] | Hours Shaken | Description |
| NB | 0.30 | 1 | 0.40 | 1 | 0.60 | 1 | NB Soil Screening Vials |
| NB | 0.30 | 6 | 0.40 | 2 | 0.60 | 2 | NB Soil Screening Vials |
| NB | 0.30 | 12 | 0.40 | 4 | 0.60 | 7.75 | NB Soil Screening Vials |
| NB | 0.30 | 24 | 0.40 | 11 | 0.60 | 17.25 | NB Soil Screening Vials |
| NB | 0.30 | 48 | 0.40 | 18 | 0.60 | 24 | NB Soil Screening Vials |
| NB | — | — | 0.40 | 39 | 0.60 | 48.5 | NB Soil Screening Vials |

[a] DDT: 35 ml solution, 25 ppb.

[b] DDD: 30 ml solution, 90 ppb.

[c] Dieldrin: 30 ml solution, 90 ppb.

[d] The g soil used was determined in previous soil-solution ratio screening trials to sorb 60-80% of the particular HOC in solution.

stock concentrate. Then, FA concentrate was prepared by placing 0.10 g of FA in a 10 ml volumetric flask and filling with 0.1 N sodium hydroxide solution. The basic solution was used to ensure complete dissolution of the FA as recommended by the supplier (MacCarthy, 1989). This produced a 10,000 mg/l FA stock concentrate. These DOM stock concentrates were used in all subsequent experiments involving dissolved organic matter.

The DOM sorption screening tests were first run using HA as the DOM source. The experimental conditions for the HA sorption screeing tests are listed in Table VI. The concentrated HA solution was added in various amounts to reactor vials using a microliter syringe. The HA solution was then allowed to air dry. This was done so that premature potential reactions could be avoided when the soil was added to the vials next. Then, the reactor vials were filled with distilled, deionized water, shaken for 24 hours and centrifuged as previously described. It should be noted that the dried organic matter was immediately resolubilized upon addition of the water.

The supernatant was analyzed for DOM concentration using UV adsorbance at 254 ηm. This is a wavelength for measuring DOM concentration in solution employed by previous researchers for investigations of humic and fulvic acids (DeHaan, 1983; West, et al, 1984). The UV analyses were perfromed using a Spectronic 1201 spectrophotometer manufactured by Milton Roy Co. The spectrophotometer was calibrated using humic and fulvic acid standard solutions prepared in the same range as the test solutions using the concentrated stock solutions previously described.

No HA sorption was noted for any of the soils and the screening trials were then repeated with a FA solution. However, due to the limited quantities of MA and MB soil and the extremely limited and very expensive supply of the FA only the NB soil was tested with the FA as a DOM source. Again, no sorption was detected. The experimental conditions for the FA sorption screening trials are listed in Table VII.

## TABLE VI

## EXPERIMENTAL CONDITIONS FOR HA SORPTION SCREENING TRIALS

| Vial ID Prefix | µl of 10,000 mg/l HA stock concentrate added[a] | = | mg/l HA added[b] | = | mg/l HA OC added | g Soil | Description |
|---|---|---|---|---|---|---|---|
| HA | 0 | | 0 | | 0 | 0 | Blank Control Vials |
| HA | 0.75 | | 0.25 | | 0.042 | 0 | HA Vials |
| HA | 1.50 | | 0.50 | | 0.083 | 0 | HA Vials |
| HA | 3.00 | | 1.00 | | 0.166 | 0 | HA Vials |
| HA | 7.50 | | 2.50 | | 0.415 | 0 | HA Vials |
| HA | 15.00 | | 5.00 | | 0.830 | 0 | HA Vials |
| HA | 30.00 | | 10.00 | | 1.660 | 0 | HA Vials |
| HA | 75.00 | | 25.00 | | 4.150 | 0 | HA Vials |
| HA | 150.00 | | 50.00 | | 8.300 | 0 | HA Vials |
| HA | 225.00 | | 75.00 | | 12.450 | 0 | HA Vials |
| MA, MB or NB | 0 | | 0 | | 0 | 0.30 | MA, MB or NB Soil Control Vials |
| MA, MB or NB | 0.75 | | 0.25 | | 0.042 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 1.50 | | 0.50 | | 0.083 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 3.00 | | 1.00 | | 0.166 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 7.50 | | 2.50 | | 0.415 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 15.00 | | 5.00 | | 0.830 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 30.00 | | 10.00 | | 1.660 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 75.00 | | 25.00 | | 4.150 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 150.00 | | 50.00 | | 8.300 | 0.30 | MA, MB or NB Soil Test Vials |
| MA, MB or NB | 225.00 | | 75.00 | | 12.450 | 0.30 | MA, MB or NB Soil Test Vials |

[a] HA is 16.6% organic carbon.

[b] 30 ml of distilled, deionized water added to each reactor vial.

## TABLE VII

## EXPERIMENTAL CONDITIONS FOR FA SORPTION SCREENING TRIALS

| Vial ID Prefix | µl of 10,000 mg/l FA stock concentrate added[a] | = | mg/l FA added[b] | = | mg/l FA OC added | g Soil | Description |
|---|---|---|---|---|---|---|---|
| FA | 0 | | 0 | | 0 | 0 | Blank Control Vials |
| NB | 0 | | 0 | | 0 | 0.30 | NB Soil Control Vials |
| NB | 0.25 | | 0.083 | | 0.042 | 0.30 | NB Soil Test Vials |
| NB | 0.50 | | 0.167 | | 0.084 | 0.30 | NB Soil Test Vials |
| NB | 1.00 | | 0.333 | | 0.167 | 0.30 | NB Soil Test Vials |
| NB | 2.50 | | 0.833 | | 0.417 | 0.30 | NB Soil Test Vials |
| NB | 5.00 | | 1.67 | | 0.835 | 0.30 | NB Soil Test Vials |
| NB | 10.00 | | 3.33 | | 1.665 | 0.30 | NB Soil Test Vials |
| NB | 25.00 | | 8.33 | | 4.165 | 0.30 | NB Soil Test Vials |
| NB | 50.00 | | 16.67 | | 8.335 | 0.30 | NB Soil Test Vials |
| NB | 75.00 | | 25.00 | | 12.500 | 0.30 | NB Soil Test Vials |

[a] FA is 50% organic carbon.

[b] 30 ml of distilled, deionized water added to each reactor vial.

## DOC Determination

As can be seen from Tables VI and VII the DOM for HA and FA were added to reactor vials on an approximately equal organic carbon basis. Although the stock concentrates for each of the DOMs was 10,000 mg/l the organic carbon content was different for each material. The IHSS FA is a reference standard and was reported by the supplier as having 50% organic carbon (MacCarthy, 1989) and almost no ash content (0.79%). The HA sodium salt as supplied by Aldrich Chemical Co. on the other hand is a technical grade reagent and has been noted to have considerable ash content ranging up to approximately 60% (Carter and Suffet, 1982). Carter and Suffet (1982) found the organic matter (OM) content of the Aldrich HA used in their experiments to be about 40%.

In order to better quantify the organic matter content of the Aldrich HA salt used in the present experiments a loss-on-ignition screening trial was performed at 400°C for 24 hours on several samples following the procedures outlined by Ball (1964), Davies (1974), and Page, et al (1982). This resulted in an organic matter content of approximately 31% in the Aldrich HA. Page, et al (1982) recommends dividing the OM content by a factor of 1.72 to 2.00 to convert OM to organic carbon (OC). An average conversion value of 1.87 was used to yield approximately 16.6% OC in the Aldrich HA used in these experiments.

Thus, the value of 16.6% OC was used as the OC of the HA in all subsequent experiments and calculations. This allowed organic carbon to be added to all HA and FA experiments on an approximately equal carbon basis.

## Sorption Isotherm Tests

Isotherm tests were performed on the soils without DOM addition to provide adsorption constants for the HOCs. Constant soil masses were added to the reactor vials and HOC solutions covering a range of concentrations were then added to the vials. Isotherm tests were run in triplicate and experimental conditions are given in Table VIII.

# TABLE VIII

## EXPERIMENTAL CONDITIONS FOR SORPTION ISOTHERM TESTS

| | DDT | | DDD | | Dieldrin | | |
|---|---|---|---|---|---|---|---|
| Vial ID Prefix | Conc. (mg/l)[a] | g Soil | Conc. (mg/l)[b] | g Soil | Conc. (mg/l)[b] | g Soil | Description |
| I | 5 | 0 | 10 | 0 | 10 | 0 | Blank Isotherm Control Vials |
| I | 10 | 0 | 30 | 0 | 30 | 0 | Blank Isotherm Control Vials |
| I | 15 | 0 | 50 | 0 | 50 | 0 | Blank Isotherm Control Vials |
| I | 20 | 0 | 70 | 0 | 70 | 0 | Blank Isotherm Control Vials |
| I | 25 | 0 | 90 | 0 | 90 | 0 | Blank Isotherm Control Vials |
| MA | 5 | 0.15 | 10 | 0.20 | 10 | 0.30 | MA Soil Test Vials |
| MA | 10 | 0.15 | 30 | 0.20 | 30 | 0.30 | MA Soil Test Vials |
| MA | 15 | 0.15 | 50 | 0.20 | 50 | 0.30 | MA Soil Test Vials |
| MA | 20 | 0.15 | 70 | 0.20 | 70 | 0.30 | MA Soil Test Vials |
| MA | 25 | 0.15 | 90 | 0.20 | 90 | 0.30 | MA Soil Test Vials |
| MB or NB | 5 | 0.30 | 10 | 0.40 | 10 | 0.60 | MB and NB Soil Test Vials |
| MB or NB | 10 | 0.30 | 30 | 0.40 | 30 | 0.60 | MB and NB Soil Test Vials |
| MB or NB | 15 | 0.30 | 50 | 0.40 | 50 | 0.60 | MB and NB Soil Test Vials |
| MB or NB | 20 | 0.30 | 70 | 0.40 | 70 | 0.60 | MB and NB Soil Test Vials |
| MB or NB | 25 | 0.30 | 90 | 0.40 | 90 | 0.60 | MB and NB Soil Test Vials |

[a] 35 ml solution.

[b] 30 ml solution.

All experimental procedures for shaking, centrifuging and extraction are as previously described.

## DOM Experiments

The focus of this study was the DOM experiments. In order to evaluate the effect of DOM on the sorption of HOCs to soils, the following experiments were performed. Each HOC at a set concentration was run with each soil at an approximate pH of 4, 7 and 10. In addition, DOM (HA or FA) was added to different reactor vials in increasing amounts up to an organic carbon concentration of about 12.5 mg/l (approximately 75 mg/l HA or 25 mg/l FA). The details of the experimental conditions are presented in Tables IX to XI which show the amount of soil and water added to each vial as well as the DOM and HOC concentrations used. All experimental procedures regarding reactor vial preparation, addition and drying of HA or FA concentrates, weighing and addition of soils, addition of HOC solution, shaking, centrifuging, and extracting HOCs were as described in previous sections of this chapter. All DOM experiments were performed in triplicate.

Batch reactor vials were divided into various classes for the DOM experiments based on their experimental function. These classes are described below.

Soil Test Reactor Vials: These vials contained water, an HOC, a soil and either HA or FA as DOM. These vials were intended to show the effects of sorption of HOCs to soils in the presence of DOM.

Soil Control Reactor Vials: These vials contained water, an HOC and a soil. The soil control vials provided a measure of the sorption of the HOCs in the absence of DOM.

HA and FA Reactor Vials: These vials contained water, a HOC and either HA or FA. These vials were intended to indicated the effect of DOM on the HOCs in the absence of soil.

# TABLE IX

## EXPERIMENTAL CONDITIONS FOR DDT[a] DOM EXPERIMENTS CONDUCTED AT pHs 4, 7 AND 10

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | mg/l HA = added[c] | mg/l HA OC = added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | mg/l FA = added[c] | mg/l FA OC = added | Description |
|---|---|---|---|---|---|---|---|---|
| HA or FA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | Blank Control Vials |
| HA or FA | 0 | 17.5 | 5.0 | 0.83 | 5.5 | 1.57 | 0.875 | HA or FA Vials |
| HA or FA | 0 | 35.0 | 10.0 | 1.66 | 11.0 | 3.14 | 1.570 | HA or FA Vials |
| HA or FA | 0 | 87.5 | 25.0 | 4.15 | 27.5 | 7.86 | 3.930 | HA or FA Vials |
| HA or FA | 0 | 175.0 | 50.0 | 8.30 | 55.0 | 15.71 | 7.855 | HA or FA Vials |
| HA or FA | 0 | 262.5 | 75.0 | 12.45 | 82.5 | 23.57 | 11.785 | HA or FA Vials |
| MA | 0.15 | 0 | 0 | 0 | 0 | 0 | 0 | MA Soil Control Vials |
| MA | 0.15 | 17.5 | 5.0 | 0.83 | 5.5 | 1.57 | 0.785 | MA Soil Test Vials |
| MA | 0.15 | 35.0 | 10.0 | 1.66 | 11.0 | 3.14 | 1.570 | MA Soil Test Vials |
| MA | 0.15 | 87.5 | 25.0 | 4.15 | 27.5 | 7.86 | 3.930 | MA Soil Test Vials |
| MA | 0.15 | 175.0 | 50.0 | 8.30 | 55.0 | 15.71 | 7.855 | MA Soil Test Vials |
| MA | 0.15 | 262.5 | 75.0 | 12.45 | 82.5 | 23.57 | 11.785 | MA Soil Test Vials |

TABLE IX (Continued)

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | = mg/l HA added[c] | = mg/l HA OC added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | = mg/l FA added[c] | = mg/l FA OC added | Description |
|---|---|---|---|---|---|---|---|---|
| MB or NB | 0.30 | 0 | 0 | 0 | 0 | 0 | 0 | MB or NB Soil Control Vials |
| MB or NB | 0.30 | 17.5 | 5.0 | 0.83 | 5.5 | 1.57 | 0.785 | MB or NB Soil Test Vials |
| MB or NB | 0.30 | 35.0 | 10.0 | 1.66 | 11.0 | 3.14 | 1.570 | MB or NB Soil Test Vials |
| MB or NB | 0.30 | 87.5 | 25.0 | 4.15 | 27.5 | 7.86 | 3.930 | MB or NB Soil Test Vials |
| MB or NB | 0.30 | 175.0 | 50.0 | 8.30 | 55.0 | 15.71 | 7.855 | MB or NB Soil Test Vials |
| MB or NB | 0.30 | 262.5 | 75.0 | 12.45 | 82.5 | 23.57 | 11.785 | MB or NB Soil Test Vials |

[a] Initial DDT concentration in reactor vials was 25 ppb.

[b] HA is 16.6% OC.

[c] 35 ml of DDT solution added to each vial.

[d] FA is 50% OC.

## TABLE X

## EXPERIMENTAL CONDITIONS FOR DDD[a] DOM EXPERIMENTS CONDUCTED AT pHs 4, 7 AND 10

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | = mg/l HA added[c] | = mg/l HA OC added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | = mg/l FA added[c] | = mg/l FA OC added | Description |
|---|---|---|---|---|---|---|---|---|
| HA or FA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | Blank Control Vials |
| HA or FA | 0 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | HA or FA Vials |
| HA or FA | 0 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | HA or FA Vials |
| HA or FA | 0 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | HA or FA Vials |
| HA or FA | 0 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | HA or FA Vials |
| HA or FA | 0 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | HA or FA Vials |
| MA | 0.20 | 0 | 0 | 0 | 0 | 0 | 0 | MA Soil Control Vials |
| MA | 0.20 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | MA Soil Test Vials |
| MA | 0.20 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | MA Soil Test Vials |
| MA | 0.20 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | MA Soil Test Vials |
| MA | 0.20 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | MA Soil Test Vials |
| MA | 0.20 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | MA Soil Test Vials |

TABLE X (Continued)

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | = mg/l HA added[c] | = mg/l HA OC added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | = mg/l FA added[c] | = mg/l FA OC added | Description |
|---|---|---|---|---|---|---|---|---|
| MB or NB | 0.40 | 0 | 0 | 0 | 0 | 0 | 0 | MB or NB Soil Control Vials |
| MB or NB | 0.40 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | MB or NB Soil Test Vials |
| MB or NB | 0.40 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | MB or NB Soil Test Vials |
| MB or NB | 0.40 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | MB or NB Soil Test Vials |
| MB or NB | 0.40 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | MB or NB Soil Test Vials |
| MB or NB | 0.40 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | MB or NB Soil Test Vials |

[a] Initial DDD concentration in reactor vials was 90 ppb.
[b] HA is 16.6% OC.
[c] 30 ml of DDD solution added to each vial.
[d] FA is 50% OC.

# TABLE XI

# EXPERIMENTAL CONDITIONS FOR DIELDRIN[a] DOM EXPERIMENTS CONDUCTED AT PHS 4,7 AND 10

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | = mg/l HA added[c] | = mg/l HA OC added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | = mg/l FA added[c] | = mg/l FA OC added | Description |
|---|---|---|---|---|---|---|---|---|
| HA or FA | 0 | 0 | 0 | 0 | 0 | 0 | 0 | Blank Control Vials |
| HA or FA | 0 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | HA or FA Vials |
| HA or FA | 0 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | HA or FA Vials |
| HA or FA | 0 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | HA or FA Vials |
| HA or FA | 0 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | HA or FA Vials |
| HA or FA | 0 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | HA or FA Vials |
| MA | 0.30 | 0 | 0 | 0 | 0 | 0 | 0 | MA Soil Control Vials |
| MA | 0.30 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | MA Soil Test Vials |
| MA | 0.30 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | MA Soil Test Vials |
| MA | 0.30 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | MA Soil Test Vials |
| MA | 0.30 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | MA Soil Test Vials |
| MA | 0.30 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | MA Soil Test Vials |

TABLE XI (Continued)

| Vial ID Prefix | g Soil | ml of 10,000 mg/l HA stock concentrate added to vial[b] | = mg/l HA added[c] | = mg/l HA OC added | ml of 10,000 mg/l FA stock concentrate added to vial[d] | = mg/l FA added[c] | = mg/l FA OC added | Description |
|---|---|---|---|---|---|---|---|---|
| MB or NB | 0.60 | 0 | 0 | 0 | 0 | 0 | 0 | MB or NB Soil Control Vials |
| MB or NB | 0.60 | 15.0 | 5.0 | 0.83 | 5.0 | 1.67 | 0.835 | MB or NB Soil Test Vials |
| MB or NB | 0.60 | 30.0 | 10.0 | 1.66 | 9.5 | 3.17 | 1.585 | MB or NB Soil Test Vials |
| MB or NB | 0.60 | 75.0 | 25.0 | 4.15 | 23.5 | 7.83 | 3.915 | MB or NB Soil Test Vials |
| MB or NB | 0.60 | 150.0 | 50.0 | 8.30 | 47.0 | 15.67 | 7.835 | MB or NB Soil Test Vials |
| MB or NB | 0.60 | 225.0 | 75.0 | 12.45 | 70.5 | 23.50 | 11.750 | MB or NB Soil Test Vials |

[a] Initial Dieldrin concentration in reactor vials was 90 ppb.
[b] HA is 16.6% OC.
[c] 30 ml of Dieldrin solution added to each vial.
[d] FA is 50% OC.

Blank Control Reactor Vials: These vials contained water and a HOC only. These vials were intended to indicate the losses of HOCs due to the combined potential effects of volatilization and glassware sorption in the absence of DOM and soil.

The terms soil test vials, soil control vials, HA or FA vials, and blank control vials will be used hereafter as shorthand descriptors of the reactor vials and their contents as outlined above.

## Analysis of HOCs in Sample Extracts

The amount of HOCs sorbed to the various soils was determined by difference in the liquid phase after taking control losses into account. The HOC sample extracts were analyzed following chromatographic conditions suggested in Method 608 for organochlorine pesticide analyses (Federal Register, 1984). A Perkin-Elmer Sigma 2000 model gas chromatograph equipped with a nickel$^{63}$ electron-capture detector was utilized. A Supelco, Inc. glass column (6 feet in length with 2 mm inner diameter and 0.25 - inch outer diameter) packed with three percent SP-2100 on 100/120 Supelcoport support was employed for compound separation. The carrier gas (supplied by Big Three Industries, Grand Prarie, Texas) was 95% argon and 5% methane (on a mole percent basis) flowing at a rate of 60 ml per minute. The injector temperature was 290°C, the detector temperature was 350°C, and the oven temperature was maintained isothermally at 240°C. A Perkin-Elmer LCI-100 integrator was used to produce chromatograms and to calculate elution times and peak areas. The gas chromatograph was calibrated with standard curves at least once a day using HOC standard solutions prepared as described in Appendix B.

# CHAPTER IV

# RESULTS AND DISCUSSION

## Soil Characterization

The results of the analyses conducted to characterize the three soils used in the experiments are tabulated in Table XII. Review of Table XII provides a variety of observations and correlations regarding the various soil properties. The first observation is that the soil organic carbon content (SOC) decreases with the depth of sampling (i.e., soil horizon depth). This observation is in agreement with that of Thurman (1985) regarding decreased SOC with soil depth. A plot of SOC versus maximum depth of collection is shown on Figure 5. The organic carbon (OC) percentages of the MB and NB soils are noted to be similar. However, they are less than the MA soil OC content.

Soil texture was another property selected for evaluation of similarities and differences of HOC sorption. The MA and NB soils have a similar clay content while the MA and MB soils have similar silt contents. The sand content varies among the soils.

The soil pH results show that all of these soils are acidic. Addition of 0.1 N hydrochloric acid directly to the soils showed no reaction, confirming acidic soils lacking carbonates (Carter, 1989). This result is typical of acidic soils in central Oklahoma.

The water content of the air-dried soils varied. There appeared to be no correlation between water content and other properties among the soils.

The exchange capacities of the soils can be correlated to clay and silt content, and to clay mineralogy. That is, the soils with the greater clay and silt fractions, and larger vermiculite and smectite contents tend to also have greater CEC and AEC (Carter, 1989).

## TABLE XII

## PROPERTIES, CHARACTERISTICS AND METHODS USED TO ANALYZE SOILS USED IN STUDY

| | Soils | | | |
|---|---|---|---|---|
| Property / Characteristic | MA | MB | NB | Method / Reference |
| Soil Name (type locality) | Mulhall | Mulhall | Navina | Carter / a |
| ID used in experiments | MA | MB | NB | — |
| Soil Horizon | A | Bt2 | BA | Carter / a |
| Depth Sampled (cm) | 0-16 | 43-66 | 35-45 | Carter / a |
| Land Use | Pasture | Pasture | Fallow/Wheat | Carter / a |
| Organic Matter (%) | 1.76 | 1.43 | 1.52 | Walkley-Black / b |
| Organic Carbon (%) | 1.023 | 0.831 | 0.884 | % Organic Matter ÷ 1.72 / a,c |
| Soil Class (texture) | Sandy Loam | Clay Loam | Loam | Carter / a |
| Sand (%) | 58.2 | 35.4 | 42.5 | Wet Sieve / b |
| Silt (%) | 28.6 | 31.8 | 43.2 | Wet Sieve / b |
| Clay (%) | 13.2 | 32.8 | 14.2 | Stoke's Law / b |
| Soil pH | 6.0 | 5.8 | 5.1 | 50:50 Soil:Water Solution / b |
| Water Content (% by weight) | 0.645 | 2.378 | 1.114 | 103°C / b |
| CEC (meq/100 g) | 8.45 | 10.55 | 4.75 | $BaCl_2$ / b,c,d |
| CEC (meq/100 g) | 10.20 | 20.90 | 11.40 | Ammonium Acetate / e |
| AEC (meq/100 g) | 0.05 | 0.19 | 0.06 | $BaCl_2$ / b,c,d |

TABLE XII (Continued)

| Property / Characteristic | Soils MA | MB | NB | Method / Reference |
|---|---|---|---|---|
| Clay Mineralogy[†]: | | | | XRD / a,b,c |
| Quartz | *** | *** | *** | |
| Kaolinite | *** | *** | ** | |
| Illite | *** | ** | ** | |
| Hydrated Interlayer Vermiculite (HIV) | trace | none | none | |
| Smectite/HIV | none | * | * | |

[a] Dr. Brian Carter, Dept. of Agronomy, OSU (1989).
[b] U.S.D.A , S.C.S. (1987).
[c] Page, et al(1982).
[d] Gillman (1979).
[e] Chapman (1965).
[†] The * symbol in the X-Ray Diffraction (XRD) interpertation represents a relative or qualitative abundance of clay minerals present in the sample.

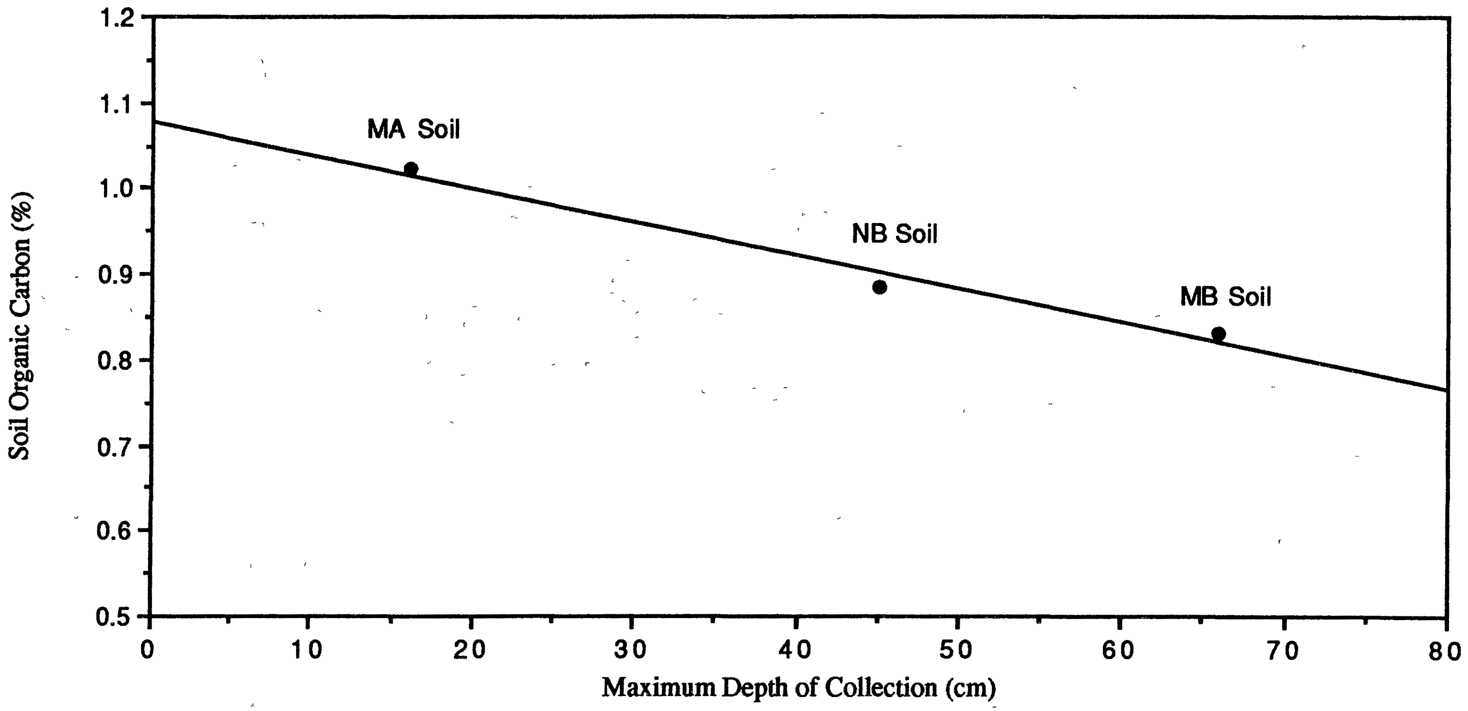

Figure 5. Plot of Soil Oganic Carbon Content Versus Soil Depth.

The cation exchange capacity (CEC) and anion exchange capacity (AEC) were found to be the greatest for the MB soil followed by NB and MA. Overall, exchange capacity values are somewhat low due to the minor quantities of vermiculite and smectite clay minerals present in the samples. Comparison of the ammonium acetate and barium chloride CEC results shows that the ammonium acetate method yielded slightly greater exchange capacities than the barium chloride method. Although chosen because it allows for a concurrent determination of CEC and AEC, the barium chloride method has been shown to typically yield minor to noticeably lower exchange capacities compared to other methods (Gillman, 1979; Page, 1972; Carter, 1989).

The clay mineralogies of the soils used in this study are similar. The clay mineralogies are dominated by quartz, kalonite and illite with minor or trace amounts of vermiculite and smectite.

## Preliminary Tests

### Soil-Solution Ratio Screenings

The soil-solution ratio screenings allowed the amount of each soil needed to sorb approximately 70 to 90% of each HOC (after control losses were taken into account) to be determined. The MB and NB soils sorbed HOCs less than the MA soil probably as the result of their lower soil organic matter contents. Thus, in order to sorb an appropriate amount of a compound, more soil was required per vial for the MB and NB soils than for the MA soils for a given HOC.

The least soluble HOCs were sorbed more readily than the more soluble HOCs. Therefore, less soil was required for the DDT tests than for DDD or Dieldrin tests. In addition, the DDT test solution concentration of 25 μg/l was less than the 90 μg/l solution concentration used for the DDD and Dieldrin experiments. The DDT and DDD stock solutions were made at their maximum reported solubilities to enhance their analytical detection potential. The Dieldrin was more easily detected, however, and was arbitrarily added at the same concentration as the DDD. The greater solution concentrations of DDD and Dieldrin also necessitated greater amounts of soil to be used in the DDD and Dieldrin tests. The amount of each soil found to sorb 70 to 90% of the model HOCs is listed in Table XIII.

## Equilibrium Time Screenings

The screening tests for the equilibrium times were performed to establish shaking times for the batch reactors. The experimental conditions for these tests are outlined in Table V of the preceding chapter.

The sorption of all HOCs was very rapid with the majority of the uptake occurring within the first few hours of shaking. The uptake rate then tailed off and diminished to a minor uptake rate. This sorption behavior is typical of organic compound uptake as described by Wu and Gschwend (1986), Khan (1973), Miller and Weber (1986), Rao, et al (1979), and Bouchard, et al (1988). Figure 6 is a typical equilibrium-time uptake-curve for the present study where the percent compound remaining in solution versus time is shown.

Roy, et al (1987) indicate that equilibrium in batch adsorption studies is achieved when there is no more than a 5% change in solution concentration in any subsequent 24-hour period. DDT, being more hydrophobic than DDD or Dieldrin, reached the equilibrium conditions suggested by Roy, et al (1987) slightly faster than the latter two compounds. Actual shaking times for the experiments were based on a practical working schedule after equilibrium was achieved. Thus, the equilibrium time for DDT was established at 8 hours, and the equilibrium time established for DDD and Dieldrin was 24 hours.

# TABLE XIII

# RESULTS OF SOIL-SOLUTION RATIO SCREENING

| | Grams of Soil Necessary to Sorb 70 to 90% of HOC | | |
|---|---|---|---|
| HOC | MA | MB | NB |
| DDT | 0.15 | 0.30 | 0.30 |
| DDD | 0.20 | 0.40 | 0.40 |
| Dieldrin | 0.30 | 0.60 | 0.60 |

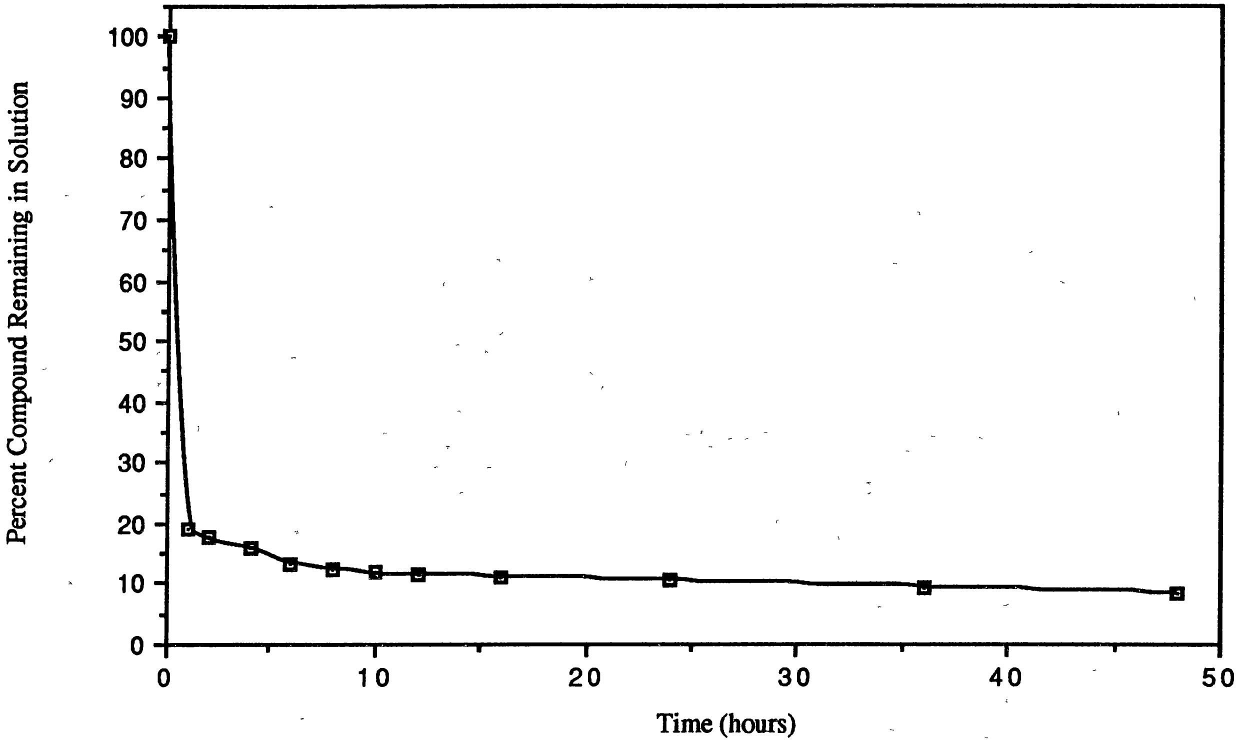

Figure 6. Typical Equilibrium-Time Uptake-Curve Showing Percent Compound Remaining in Solution Versus Time.

### DOM Sorption Screenings

Screening tests were performed to indicate possible sorption of HA or FA to the soils. These tests are described in Tables VI and VII of Chapter III.

UV spectrophotometry at 254 nm showed that the DOM concentration in the control reactor vials (soil and water at pH 4, 7, and 10) of the DOM sorption screening tests increased slightly at all pH values. This increase was probably due to minor solubilization of fulvic and/or humic material from the naturally-occurring organic matter present in the soils. The average increase of DOM in solution for all the soils over the entire pH range used was approximately 4%. The increase of DOM in solution was considered minor.

Since the DOM concentration in solution increased at all pH values in the control vials, it was decided to run the DOM sorption tests (DOM added to vials) at neutral pH only. This was done to conserve the limited supplies of soils and DOM.

UV spectrophotometry showed no decrease in DOM in solution over the entire concentration range of DOM added to the soil test vials and control reactor vials. Thus, no sorption of either HA or FA to the soils was apparent in these tests. In addition, an increase in DOM concentration was observed in the control vials which supports the conclusion that no HA or FA was sorbed by the soils.

## Sorption Isotherm Tests

Isotherm tests were performed on the soils in the absence of DOM at neutral pH in order to establish HOC adsorption constants. The experimental conditions for these tests are described in the previous chapter. During the isotherm tests, a loss of the HOCs from solution in the control reactor vials (no soil) was observed for all compounds used. Since the vapor pressures of the compounds are very low, the losses were considered to be due to hydrophobic sorption to glassware. The losses in the controls varied depending on the initial HOC concentration, and ranged from 39% to 75% for DDT, 13% to 62% for DDD, and 15% to 31% for Dieldrin. As a result, the total sorption observed in the vials containing soil had the control losses subtracted in order to determine the actual sorption to the soils. The isotherm data collected for the HOCs and soils used in this study are tabulated in Appendix C.

## Langmuir Isotherms

Adsorption isotherm data are often described graphically using Langmuir or Freundlich isotherm plots (Montgomery, 1985). The Langmuir isotherm relates the mass of solute sorbed per mass of adsorbent (q) to the equilibrium concentration of the solute in solution (C). The Langmuir isotherm is depicted graphically as an arithmetic plot of q versus C. Langmuir isotherms for the adsorption data given in Appenidx C are shown on Figures 7 to 9. These isotherms were based on the micrograms of the HOCs sorbed per gram of soil organic carbon (SOC).

As can be seen on Figures 7 and 8, the isotherm plots for DDT and DDD show normal or L-type Langmuir curves (Hounslow, 1983). The L-type curves are typically linear near the origin. Then, as adsorption sites become filled and the solute concentration is increased the curve becomes convex. When all adsorption sites are filled, the sorption capacity of the sorbent is exceeded and the curve becomes horizontal (Montgomery, 1985). The data points for DDT and DDD on Figures 7 and 8 follow the typical L-type Langmuir curve but appear to decrease slightly after the maximum sorption capacity is reached. However, this decrease was only about 10% at most. The decrease was considered relatively minor and may have been due to laboratory error. Additional data points could not be generated in order to confirm the possible decrease in sorption with increasing solute concentration since the reported solubility limits of the compounds had been reached at the fifth data point.

Figure 9 shows the Langmuir plot for the Dieldrin isotherm data. These data plot in a linear fashion for all of the soils tested. There is no apparent curvature of these isotherm

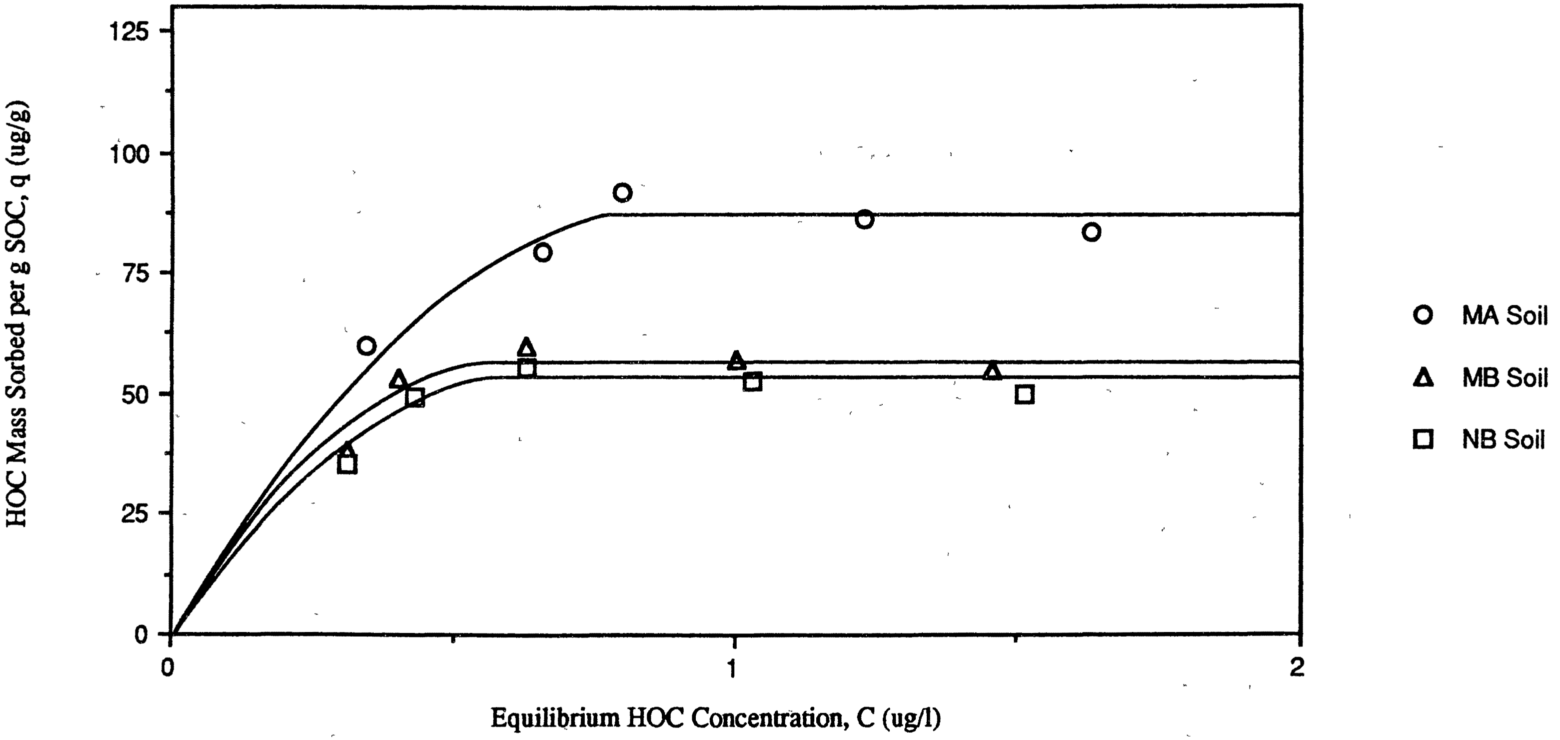

Figure 7. Langmuir Isotherm Plot of q Versus C for DDT for all Soils.

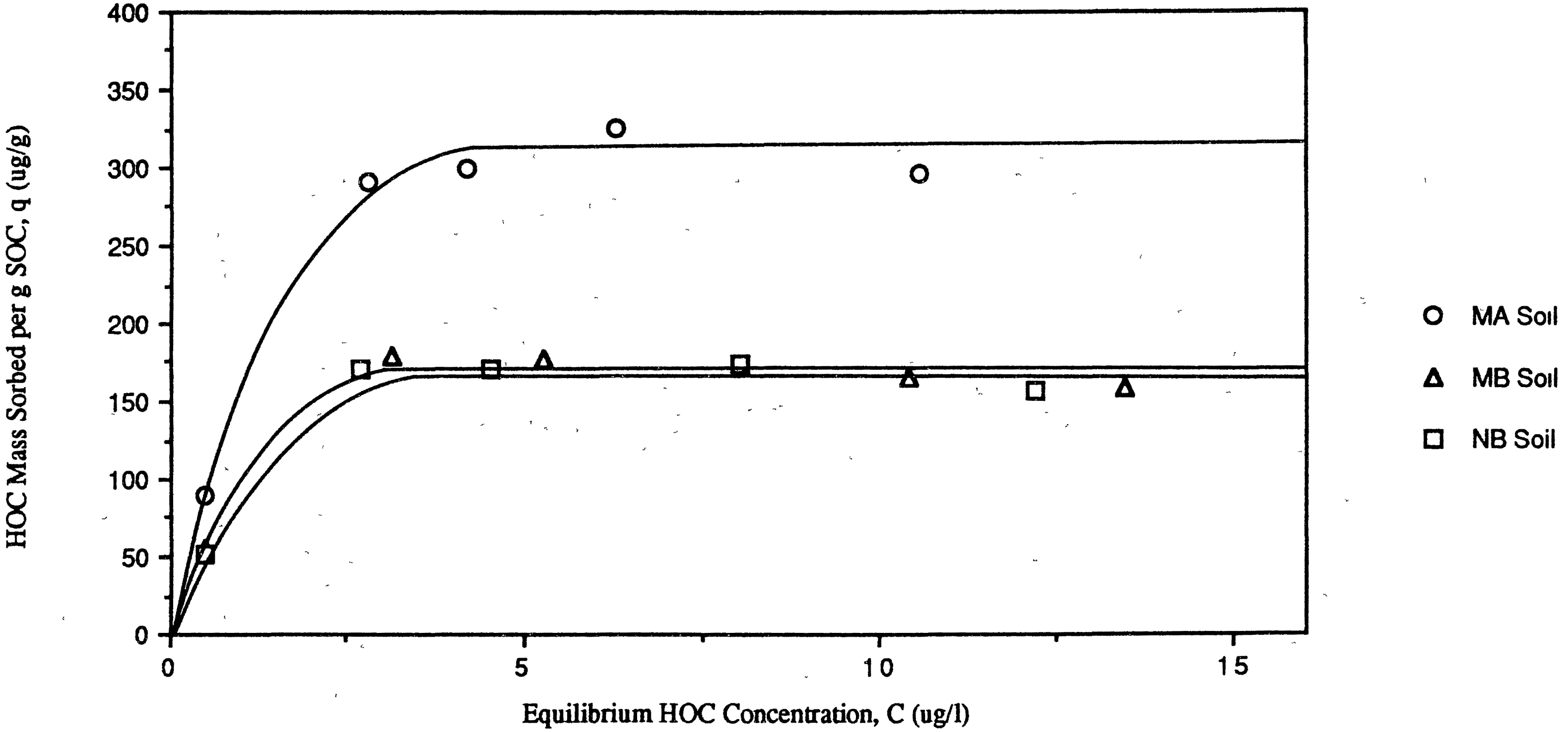

Figure 8. Langmuir Isotherm Plot of q Versus C for DDD for all Soils.

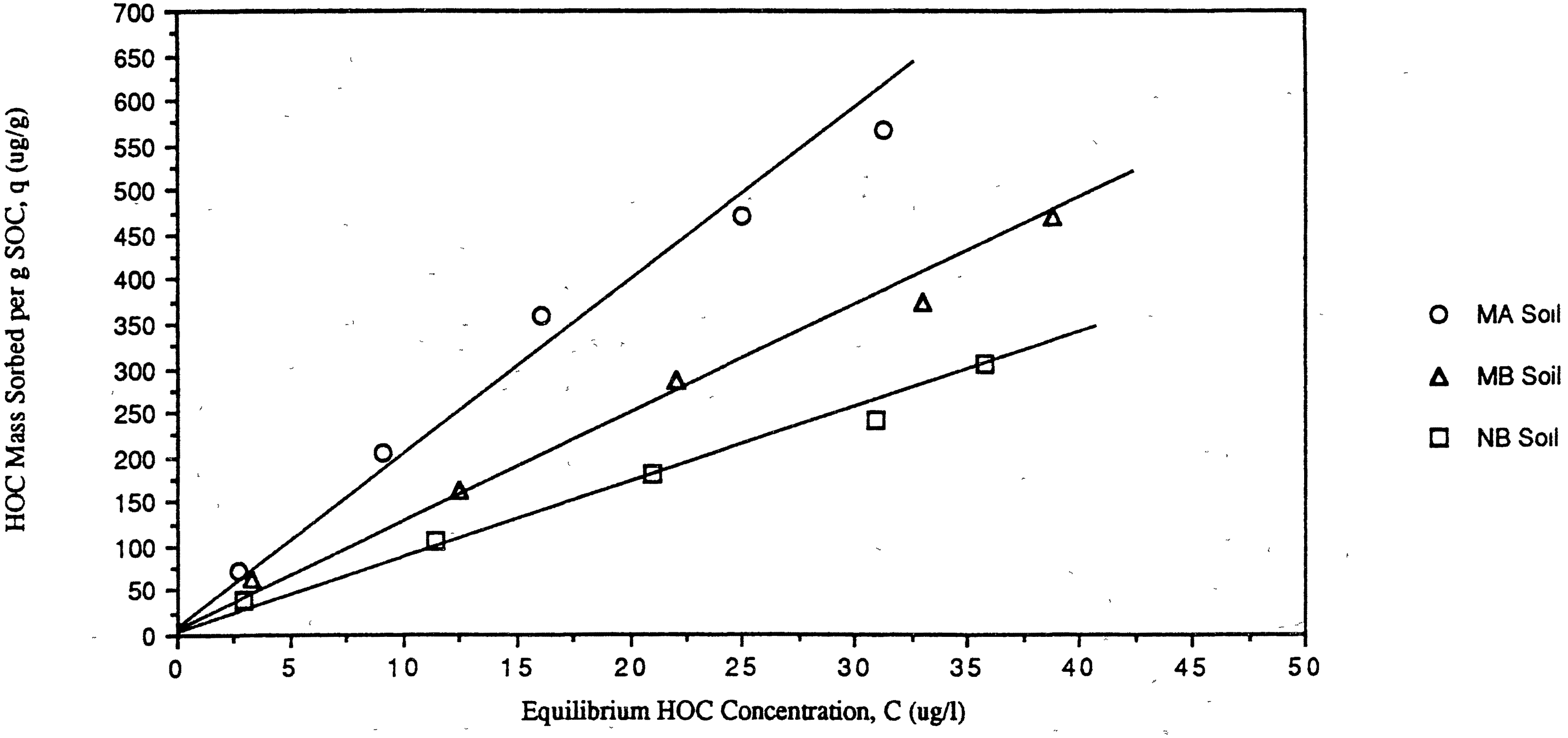

Figure 9. Langmuir Isotherm Plot of q Versus C for Dieldrin for all Soils.

lines since the sorption capacity of the soils was not exceeded, as appeared to be the case for the DDT and DDD isotherms. This may be due to the fact that Dieldrin is more soluble than DDT or DDD and did not sorb sufficiently to exceed the sorption capacity of the soils. Figure 9 is also a L-type Langmuir curve. The data in this case simply plot in the linear portion of the L-type curve and do not extend into the convex or horizontal portion of the L-type curve.

Inspection of Figures 7 to 9 shows that for a given HOC, the isotherm data plots for the MB and NB soils are below the MA soil isotherm plots. This difference may be explained by the variability of soil organic matter of different soils. Soil organic matter (SOM) has been previously discussed in the literature review as being diverse in origin and composition from one source to another. The partitioning of organic compounds to SOM has also been shown to vary due to differences in SOM composition (Garbarini and Lion, 1986; Gauthier, et al, 1987). The isotherm results for the three soils and compounds used in the present study are an example of this variability. In addition, as previously described in the literature review, Gschwend and Wu (1985) and Roy and Griffin (1987) point out that this variability may be as great as an order of magnitude in partitioning for the sorption of an organic compound to a variety of different soils. Finally, the isotherm data for the MB and NB soils plot near each other for DDT and DDD but show more variability for Dieldrin. This result may be due to differing interactions between the different HOCs and the organic matter of the various soils.

## Freundlich Isotherms

The Freundlich adsorption isotherm is an empirically-derived relationship between the mass of solute sorbed per mass of adsorbent (q) and the equilibrium concentration of the solute in solution (C). The Freundlich isotherm is often used by researchers to describe the sorption of compounds to soils. The Freundlich isotherm is a log-log plot of q versus C. The q and C parameters are related by the following expression.

$$q = KC^{1/n}$$

where,

$q$ = µg of solute sorbed per g of sorbent.

$C$ = µg of solute remaining in solution per ml (or g at dilute solutions) of water at equilibrium.

$K$ = intercept at log 1 concentration (i.e., at 0). K is the Freundlich distribution or partition coefficient between the solute sorbed and the solute remaining in solution, and gives a rough measure of the sorption capacity of the sorbent (Weber, 1972). When the sorbent is represented by soil organic carbon, K becomes $K_{SOC}$.

$n$ = slope of the line.

Figures 10 to 12 show the Freundlich isotherm data plots for the HOCs sorbed to the three soils. These isotherms were based on the micrograms of HOC sorbed per gram of soil organic carbon (SOC). The isotherms for DDT and DDD show a linear increase in sorption (q) as the equilibrium concentration (C) increases. This linearity continues up to the point that the soils become saturated with these compounds. At saturation, the isotherm lines become horizontal as was also noted for the Langmuir isotherm plots. The linear portion of the Freundlich isotherm plots can be used up to the saturation point to calculate the isotherm constants, K and n, described in the Freundlich equation. Figure 12 shows that the Dieldrin isotherm data are linear throughout since the sorption capacities of the soils were not exceeded.

The Freundlich partition coefficients to soil organic carbon ($K_{SOC}$), slopes (n), and coefficients of determination ($r^2$) of the isotherms are given in Table XIV for sorption of the HOCs to the SOC mass of the three soils. The slope (n) is a change in mass sorbed to a gram of SOC per change in the equilibrium concentration of the HOC. The slope can be considered a rough measure of how intensly a compound sorbs to a sorbent (Weber, 1972). The adsorption intensity is an indicator of the energy of sorption (Freundlich,

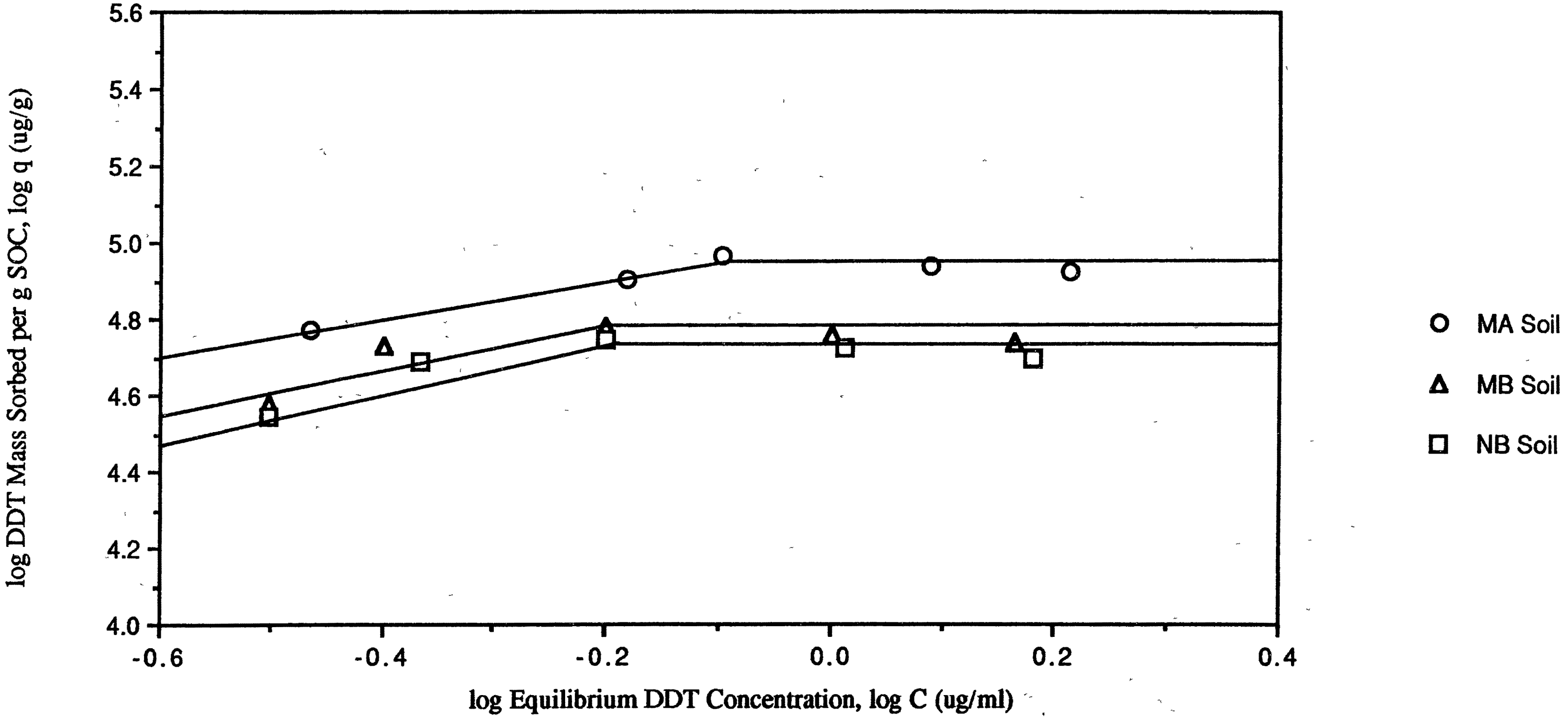

Figure 10. Freundlich Isotherm Plot of q Versus C for DDT for all Soils.

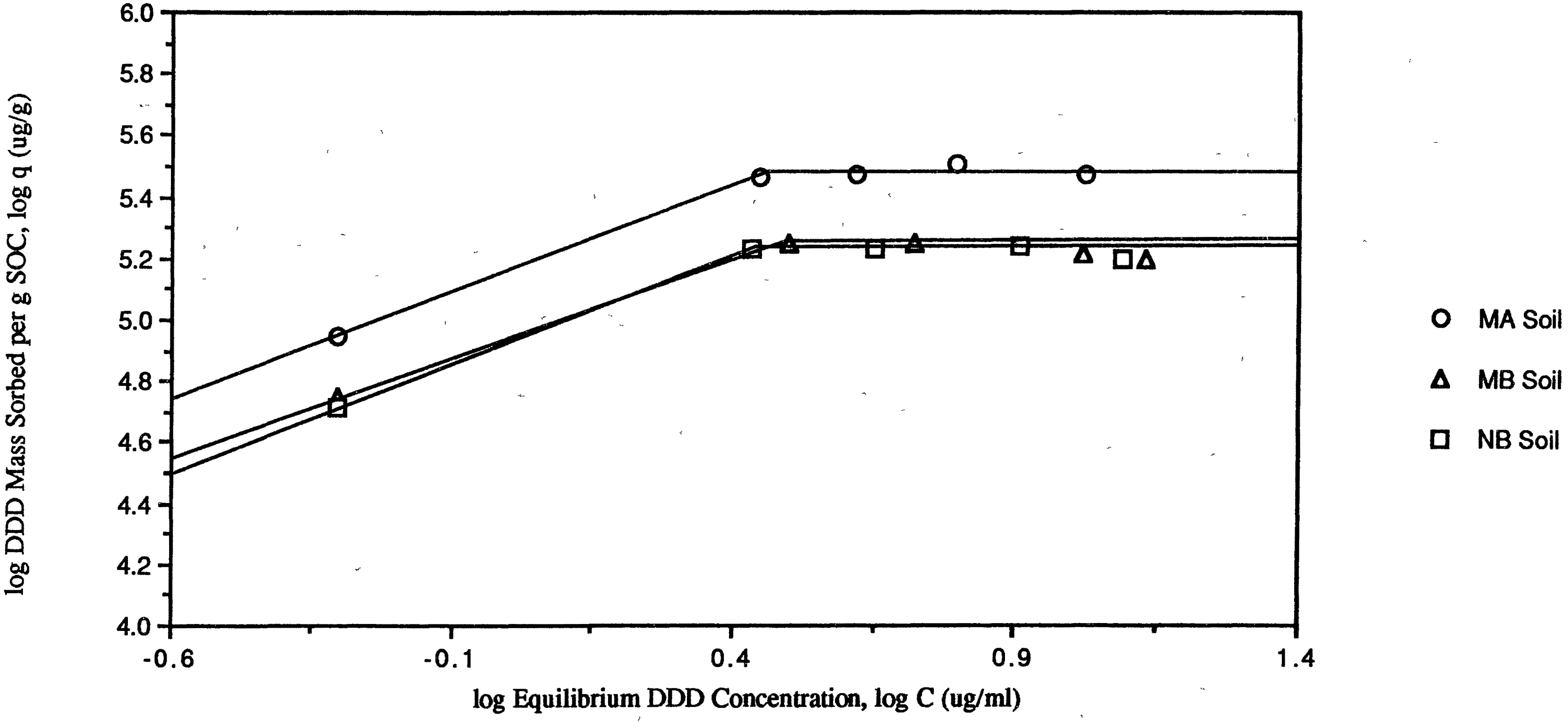

Figure 11. Freundlich Isotherm Plot of q Versus C for DDD for all Soils.

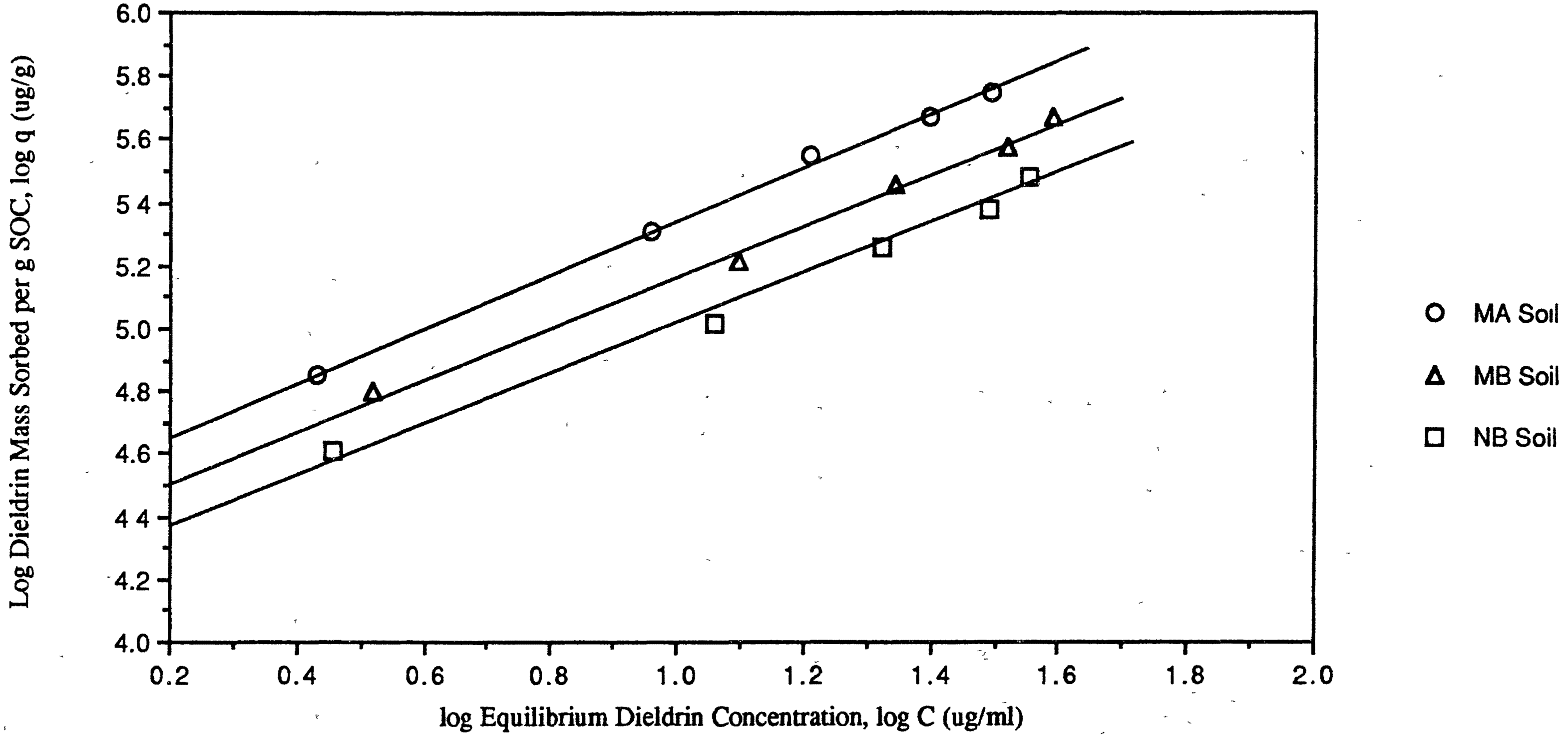

Figure 12. Freundlich Isotherm Plot of q Versus C for Dieldrin for all Soils.

## TABLE XIV

## FREUNDLICH ISOTHERM COEFFICIENTS FOR HOC SORPTION TO SOILS

| Compound and Soil | Solubility (μg/l) | log $K_{ow}$ | Freundlich log $K_{soc}$ reported[a] | Freundlich log $K_{soc}$ this study | n | $r^2$ |
|---|---|---|---|---|---|---|
| DDT | 5.5-25 | 5.98-6.36 | 5.12-5.55 | | | |
| MA | | | | 5.00 | 0.49 | 0.99 |
| MB | | | | 4.92 | 0.61 | 0.81 |
| NB | | | | 4.88 | 0.66 | 1.00 |
| DDD | 20-90 | 5.99-6.08 | — | | | |
| MA | | | | 5.16 | 0.69 | (b) |
| MB | | | | 4.94 | 0.64 | (b) |
| NB | | | | 4.93 | 0.71 | (b) |
| Dieldrin | 195-200 | ~5.15 | ~4.1 | | | |
| MA | | | | 4.50 | 0.85 | 1.00 |
| MB | | | | 4.36 | 0.81 | 0.99 |
| NB | | | | 4.23 | 0.80 | 0.99 |

[a] Soil organic carbon partition values ($K_{soc}$) from previously reported investigations (Henry, et al, 1989; Hamaker and Thompson, 1972).

[b] Not determined due to limited data.

1926) and is independent of the partition coefficient. Thus, one compound may lose more energy when adsorbed (i.e., have a greater n value) than another and still have a lower sorption capacity to a particular sorbent than a compound with a smaller n value. Table XIV shows that the slope is greatest for Dieldrin and least for DDT. The coefficient of determination ($r^2$) shows good overall correlations between q and C for DDT and Dieldrin. The $r^2$ value for DDD was not determined since the number of data points on the sloping portion of the isotherm plot were limited.

Table XIV also shows the Freundlich $K_{soc}$ values determined for the HOCs used in this study, and for DDT and Dieldrin as reported by previous researchers for sorption to other soils (Henry, et al, 1989; Hamaker and Thompson, 1972). The results of the present study indicate that the $K_{soc}$ value for DDT is slightly lower, and that the $K_{soc}$ value for Dieldrin is slightly higher than the results for the previous studies using different soils. The differences in the $K_{soc}$ values are, however, within an order of magnitude of each other as found by Roy and Griffin (1987) for partition variability to different soils, and are probably due to differences in SOM composition as previously discussed.

The log $K_{soc}$ values shown in Table XIV can be used to compare sorption results with various system properties. For example, $K_{soc}$ is well correlated with $K_{ow}$, and inversely related to compound solubility (S) as previously pointed out by Karickhoff, et al (1979) and Chiou, et al (1979). In addition, $K_{ow}$ is also well correlated to S as shown by Chiou, et al (1977). These researchers, along with Banerjee, et al (1982), Chiou and Schmedding (1982), Isnard and Lambert (1989), Kenaga and Goring (1980), and Means, et al (1980), show that although relationships between $K_{soc}$, $K_{ow}$ and S can vary somewhat, they tend to be within general agreement of each other for a large number of organic compounds and different soil types.

Chiou, et al (1979) showed that $K_{soc}$ is related to S using the equation log $K_{soc}$ = 3.80 - 0.557 log S using numerous organic compounds and soils. A bivariate plot of log $K_{soc}$ for all three soils used in the present study versus log S is shown on Figure 13. This

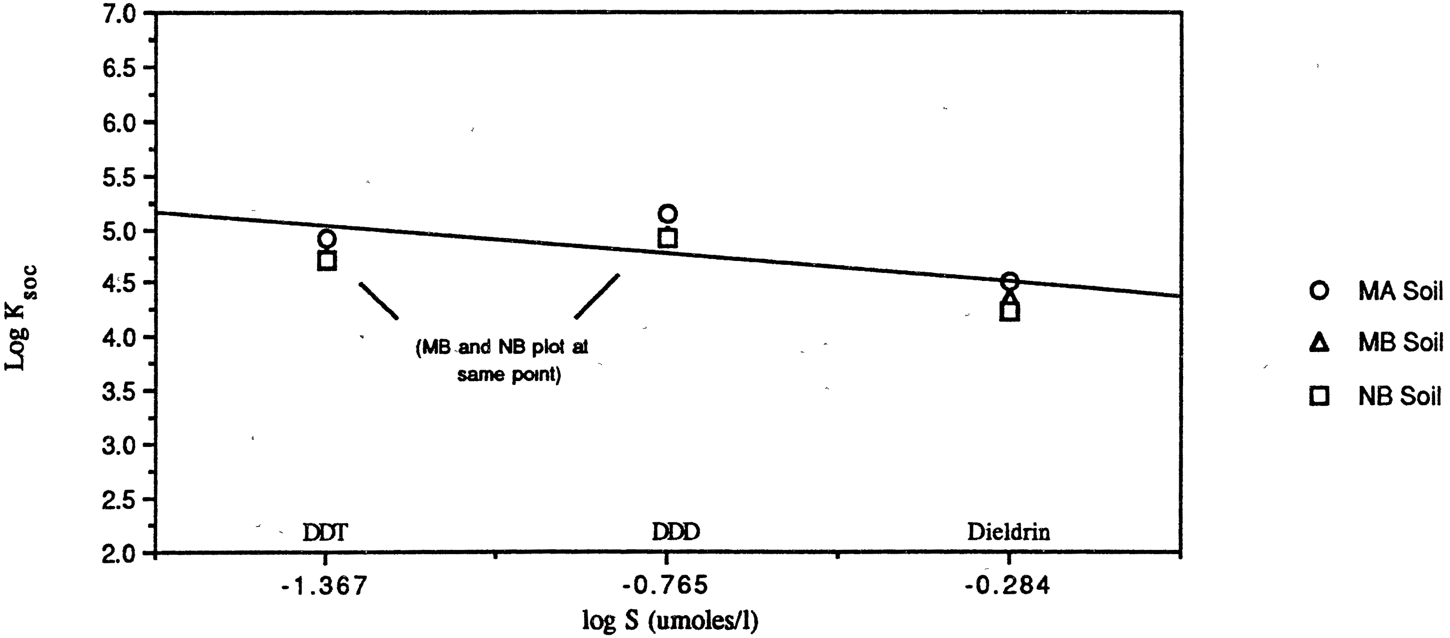

Figure 13. Plot of log Solubility Versus log Ksoc for Compounds and Soils Used in This Study.

plot can be described using a single line drawn through the data for all three soils. The resulting equation is log $K_{soc}$ = 4.367 - 0.499 log S (with $r^2 = 0.533$).

Next, relating $K_{soc}$ to $K_{ow}$, Kenaga and Goring (1980) found that log $K_{soc}$ = 1.377 + 0.544 log $K_{ow}$ for sorption of 45 organic compounds to a variety of soils. The $K_{ow}$ and $K_{soc}$ data for the present study are plotted on Figure 14 and yield the relationship log $K_{soc}$ = 1.180 + 0.620 log $K_{ow}$ (with $r^2 = 0.860$). The differences in the S, $K_{ow}$ and $K_{soc}$ relationships developed in the present study and those found for previous researchers are probably due to the limited number of HOCs and soils being tested in this study.

$K_{soc}$ is also well correlated with the percentage soil organic carbon content as demonstrated by Hamaker and Thompson (1972). In addition, $K_{soc}$ is well correlated with soil sample depth (i.e., soil horizon). Bivariate plots of $K_{soc}$ versus soil organic carbon content, and $K_{soc}$ versus soil depth are shown on Figures 15 and 16, respectively, for the soils used in this study. As can be seen by Figure 15, log $K_{soc}$ increases as the percent organic carbon increases. Figure 16 shows that log $K_{soc}$ decreases with a decrease in soil depth.

As previously noted, the $K_{soc}$ values for a particular HOC have been shown to be similar for the MB and NB soils. These two soils also consistently have lower $K_{soc}$ values than the MA soil. However, the $K_{soc}$ values found for all of the soils were reported with respect to the organic carbon content of the soils. That is, q in the Freundlich equation represents the HOC mass sorbed per mass SOC on an equal organic carbon basis for all of the soils. Thus, on an equal carbon basis, the difference between the $K_{soc}$ values observed for the A-horizon and B-horizon soils, and the similarity of the $K_{soc}$ values for the two B-horizon soils used in these experiments, may be due to differences in the soil organic matter composition with depth. For instance, the fulvic acid percentage of soil organic matter has been noted to increase with depth (Kononova, 1966; Stevenson, 1985). Fulvic acids have also been shown to bind HOCs to a lesser degree than humic acids (Chiou, et al, 1986). Although not measured in the soils used in this study, differences in the fulvic-humic ratio

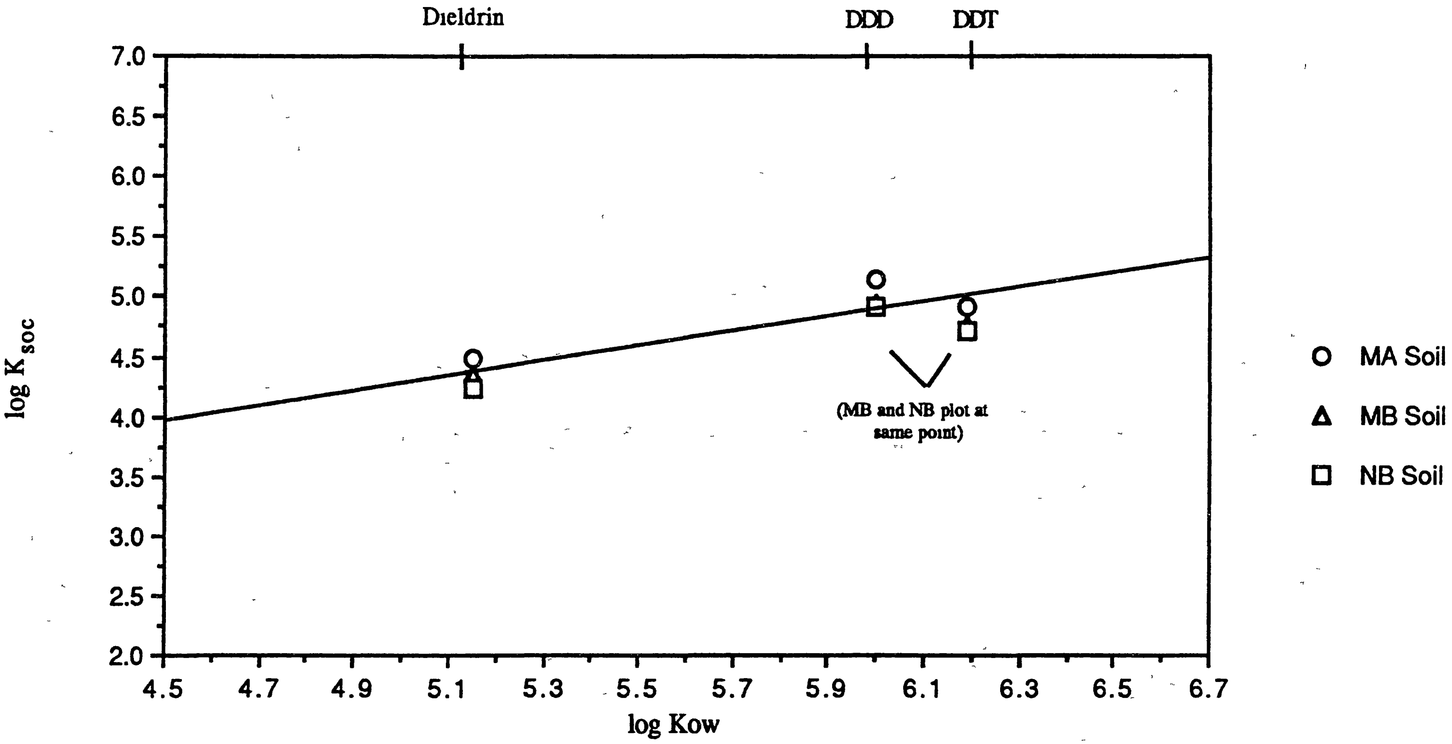

Figure 14. Plot of log Ksoc Versus log Kow for Compounds and Soils Used in This Study.

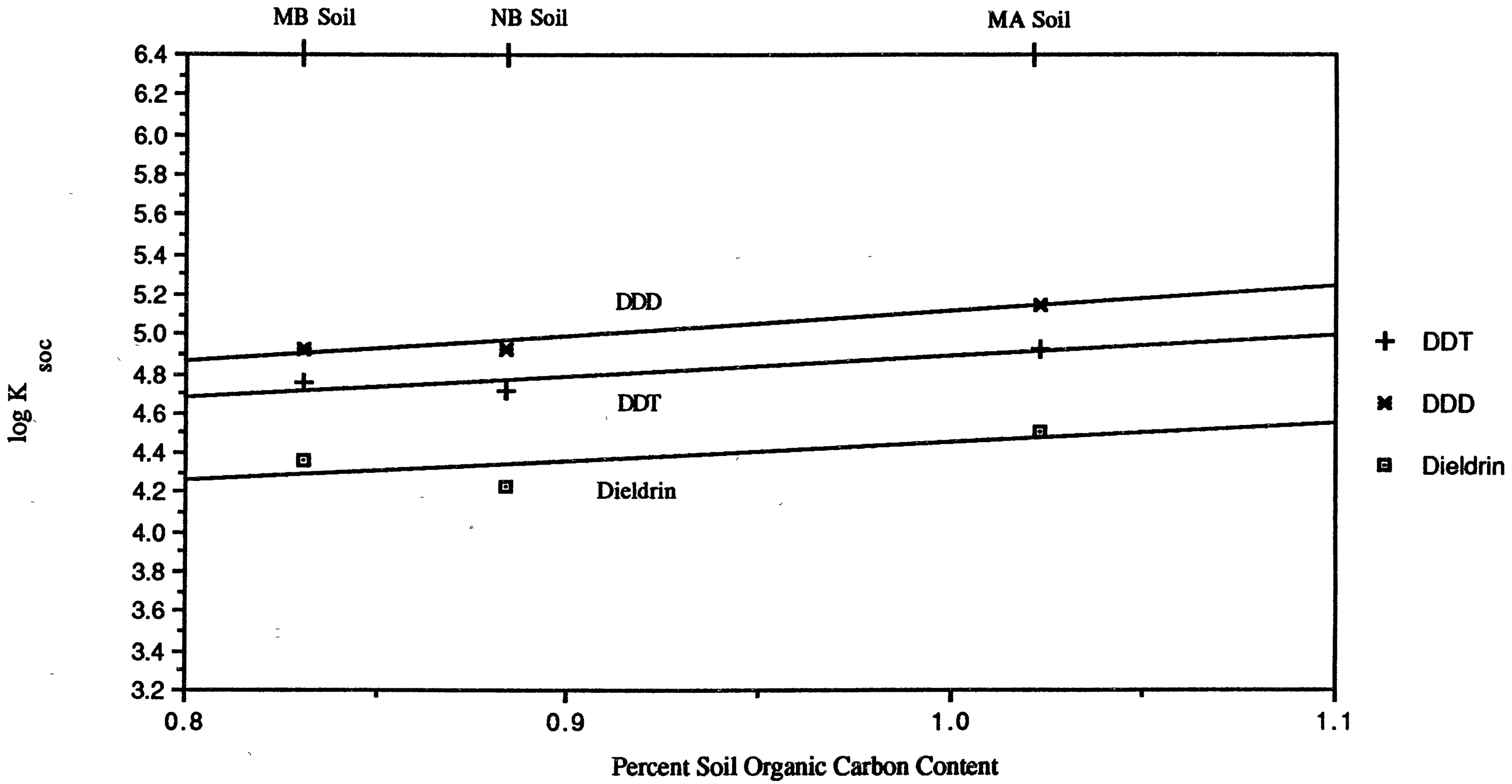

Figure 15. Plot of log Ksoc Versus Soil Organic Carbon Content for the Compounds and Soils Used in This Study.

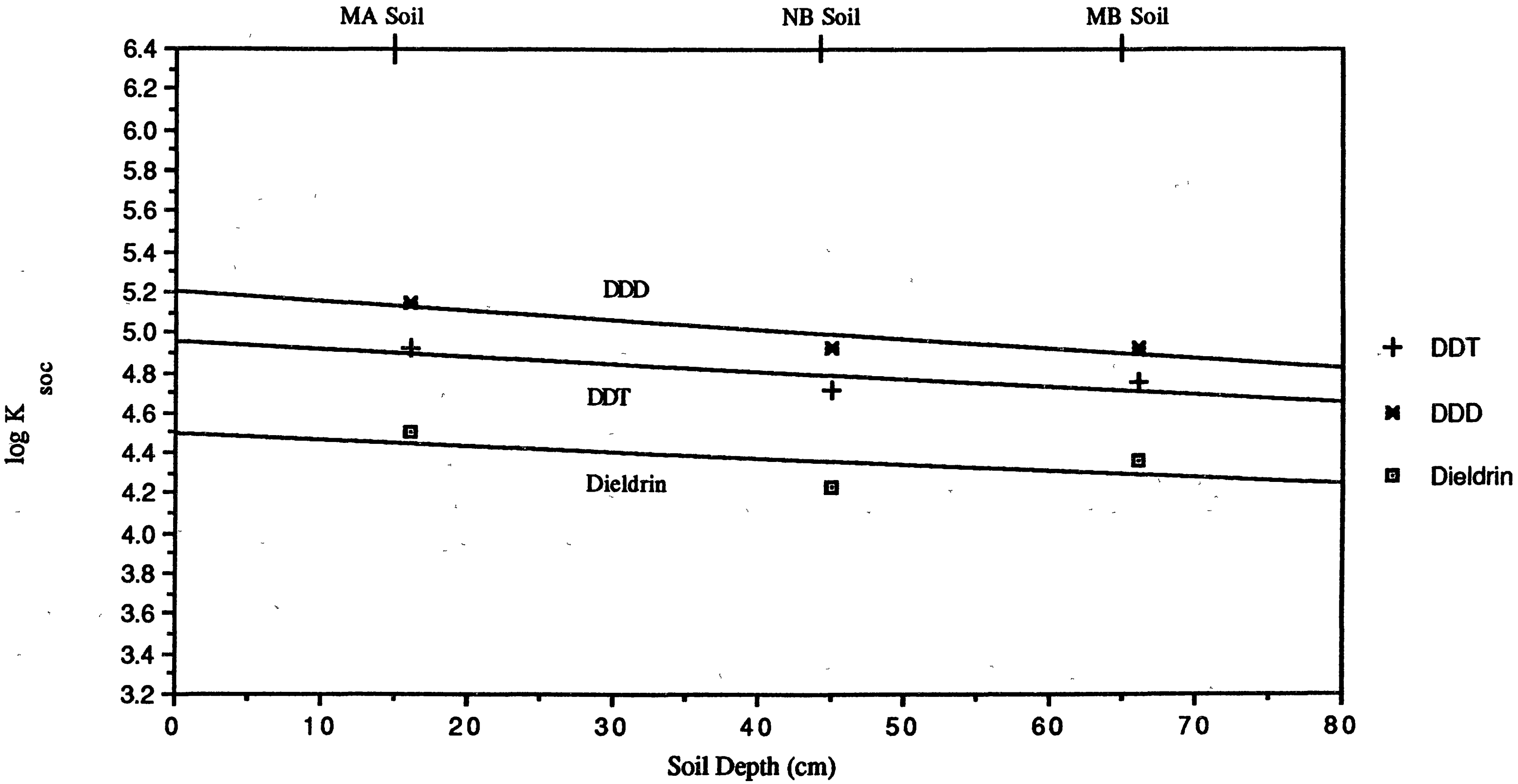

Figure 16. Plot of log Ksoc Versus Soil Depth for the Compounds and Soils Used in This Study.

may account for the observed differences in $K_{SOC}$ values for the A-horizon and B-horizon soils.

The $K_{SOC}$ values found for this study are poorly correlated with all other soil properties given in Table XII. This conclusion is in agreement with the observations of Karickhoff, et al (1979), Karickhoff (1981), Means, et al (1980 and 1982), and Hassett, et al (1980) who indicate that soil organic matter is the most important determinant for sorption of HOCs.

## Dissolved Organic Matter Experiments

The DOM experiments consisted of a series of tests in which the effects of DOM on the sorption of HOCs to soil were evaluated over a range of solution pH values. The soil test reactor vials contained a constant mass of soil, a HOC and increasing concentrations of a DOM in solution at a pH of 4, 7 or 10. It should be noted that the organic carbon fraction of DOM is known as dissolved organic carbon (DOC), and that the organic matter used in the experiments was added on a DOC content basis for consistency.

As with the isotherm tests, the control reactor vials used in the DOM experiments showed noticeable losses. These losses were attributed to glassware sorption. The losses were variable depending on the system pH, the HOC used, and the concentration of DOM in the vial. The average loss for DDT ranged from 31% for the vials containing the maximum DOM concentration used to 62% for the vials containing no DOM in solution. Similarly, the losses found for DDD ranged from 33% to 67%, and 21% to 23% for Dieldrin. The sorption in the soil test reactor vials was corrected using the appropriate controls, as was done in the isotherm tests, so that sorption to the soils would not be overestimated. The losses for the control vials are tabulated in Appendix C.

The results of the DOM experiments were also adjusted so that evaluation of sorption to the three soils could made on an equal soil organic carbon basis. The mass of a

HOC sorbed (C') can be found by subtracting the equilibrium mass of the HOC in solution (C) from the initial mass of the compound added to the vial ($C_O$).

Next, the mass sorbed was normalized with respect to the initial mass by dividing C' by $C_O$. Then, $C'/C_O$ was divided by the mass of soil organic carbon (i.e., the sorbent) in the soil test vial. This procedure provides a way for sorption to the different soils to be evaluated on an equal soil organic carbon basis. Thus, sorption to the SOC is represented as $C'/C_O$ per μg SOC.

Next, the equilibrium mass of compound remaining in solution (C) was also normalized by dividing by the initial mass ($C_O$). Then, $C/C_O$ was divided by the μg of solution in the vial. A dilute solution of HOC is assumed, therefore, one milliliter of solution equals approximately one gram of mass. The equilibrium mass is thus represented as $C/C_O$ per μg of solution.

Finally, $C'/C_O$ per μg SOC was divided by $C/C_O$ per μg of solution to yield a distribution coefficient ($K'_{soc}$). The distribution coefficient, $K'_{soc}$, represents the partition between the mass of compound sorbed and the mass of compound in solution at equilibrium. This relationship can be written as the following equation:

$$K'_{soc} = \frac{C'/C_O \text{ per } \mu g \text{ SOC}}{C/C_O \text{ per } \mu g \text{ solution}}$$

It should be noted that the $K'_{soc}$ values represent single-point distribution coefficients at equilibrium for the DOM experimental results, and should not be confused with the Freundlich $K_{soc}$ values, which represent the approximate sorption capacity of the sorbents described in the isotherm results. The $K'_{soc}$ data for the DOM experiments are compiled in Appendix C.

## DDT Experiments

### Humic Acid

The soil test reactor vials contained DDT at a concentration of 25 μg/l and HA ranging in concentration from 0 to 12.45 mg/l as dissolved organic carbon (DOC) at a solution pH of 4, 7 or 10. The effects of HA added to the vials are shown on Figures 17 to 19. These figures show that HA affects the partition of DDT differently depending on the soil used, the pH of the solution, and the concentration of the HA.

Review of Figures 17 to 19 also shows that, in general, as the DOC concentration increases, the $K'_{SOC}$ values at first increase to a maximum and then begin to decrease. This observation may be explained as follows. At 0 mg/l HA concentration the sorption to the glassware in the control vials was usually at its maximum. Then, as HA was added, the glassware sorption in the control vials decreased rapidly due to DDT binding to the DOC in solution. Chiou, et al (1986) showed that DDT solubility increases as the DOC concentration increases. Thus, the DOC also appeared to increase the solubility of DDT and reduced sorption to the glassware in the present study. Then in the soil test reactor vials, as DOC was added, the glassware sorption of DDT was inhibited by the HA as in the controls. Since more of the DDT was made available in solution by the HA, a greater amount of the DDT could be sorbed by the soil. Thus, the greatest partition to the soil occurs at low concentrations of DOC due to a redistribution of the DDT by the HA. However, at greater concentrations of HA the DOC appears to outcompete the soil for binding of the available DDT in solution. This results in a lower partition coefficient ($K'_{SOC}$). Therefore, at DOC concentrations above approximately 2 to 4 mg/l of Aldrich HA, DDT sorption is reduced and could potentially be made available for transport.

However, at pH 10 and 0 mg/l DOC, the MB and NB soils were noted to be at their maximum $K'_{SOC}$ value as shown on Figure 17. Additional DOC at low concentrations did not initially increase the partition coefficient as found for the other examples, but steadily

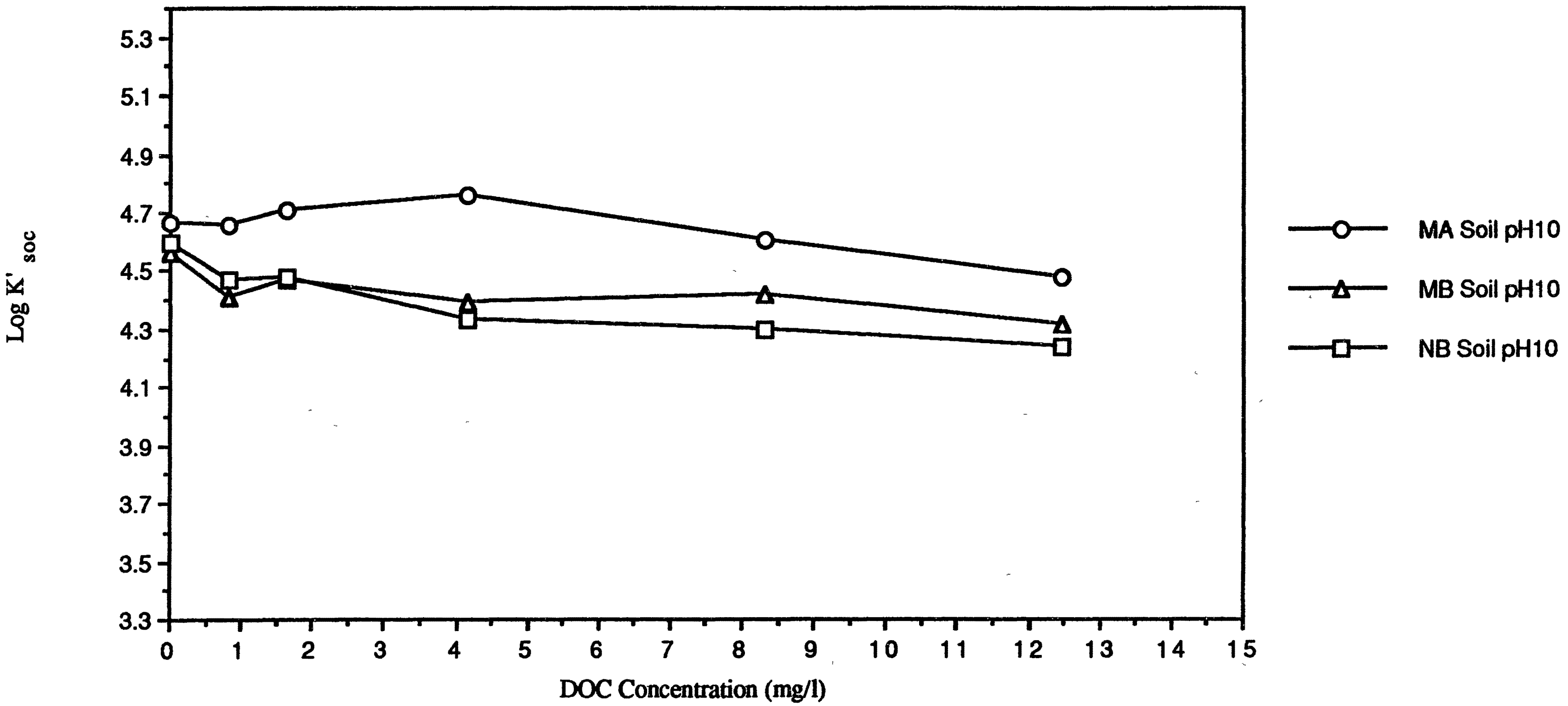

Figure 17. Log K'soc Versus DOC Concentration for DDT in the Presence of HA at pH 10.

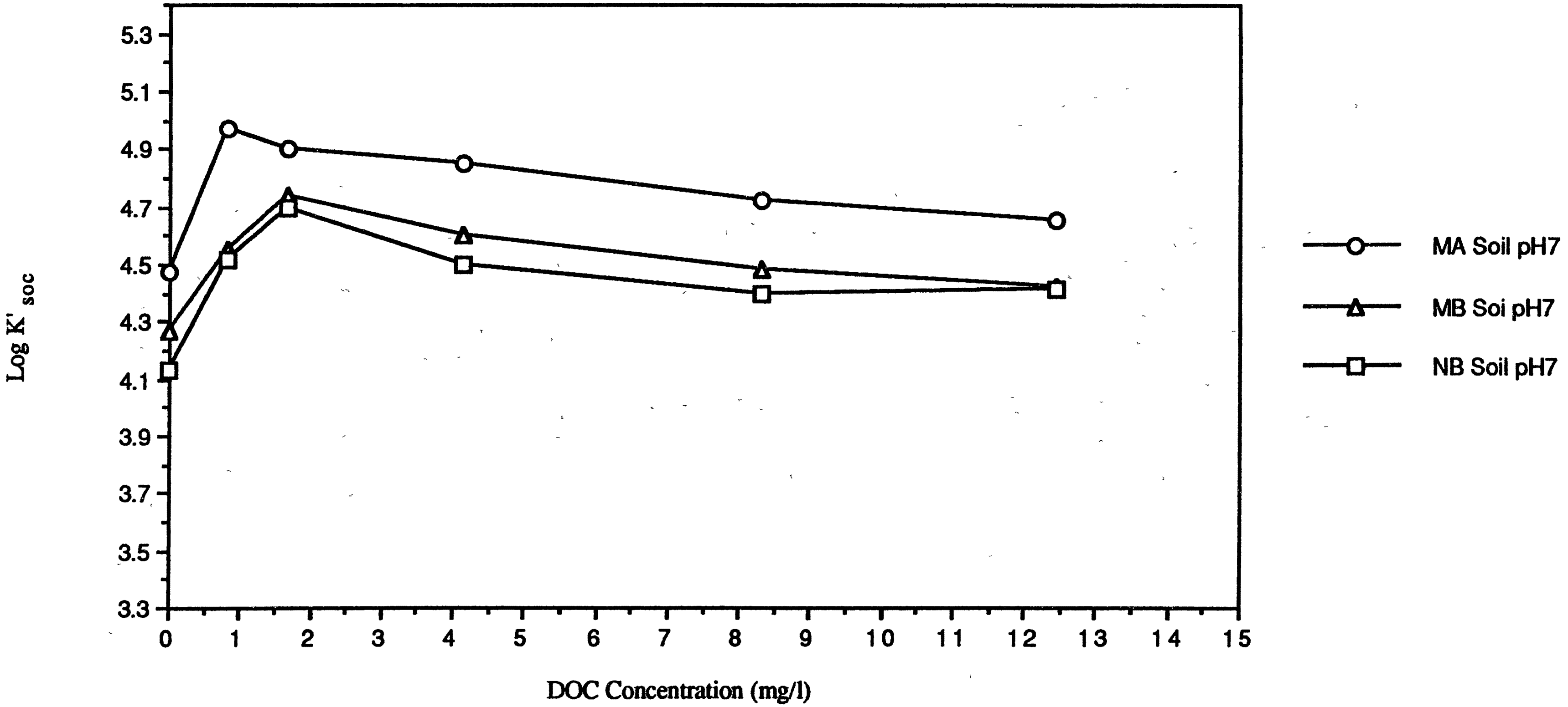

Figure 18. Log K'soc Versus DOC Concentration for DDT in the Presence of HA at pH 7.

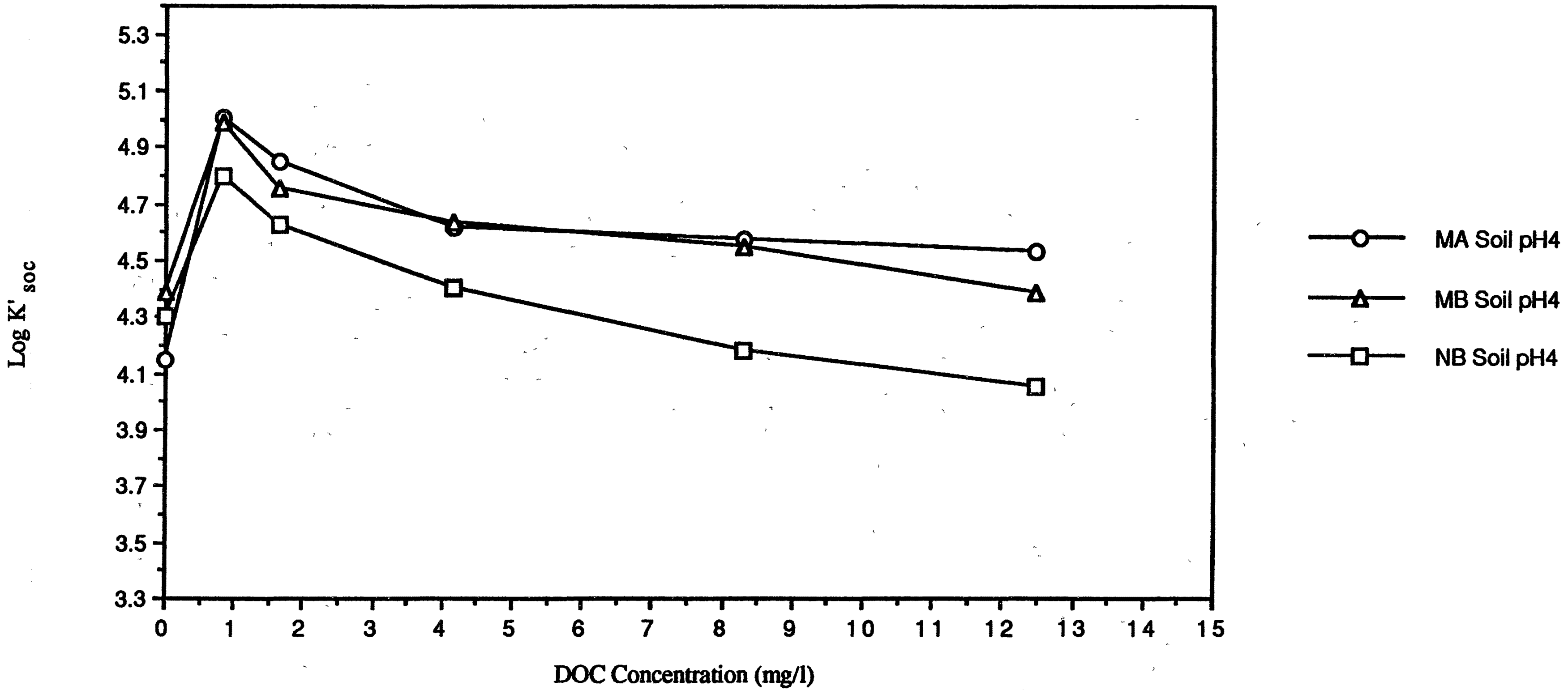

Figure 19. Log K'soc Versus DOC Concentration for DDT in the Presence of HA at pH 4.

decreased the $K'_{soc}$ as the DOC concentration was increased. Apparently, at pH 10 the MB and NB soils exhibit maximum sorption at 0 mg/l DOC and redistribution of DDT by increasing concentrations of DOC results in more of the DDT being bound in solution.

The effect of pH on the ability of HA to decrease the $K'_{soc}$ of DDT to the soils can be evaluated by observing the maximum and minimum $K'_{soc}$ values for each soil at the different pH values. The difference between the maximum and minimum $K'_{soc}$ values is greatest at pH 4 and least at pH 10 for all soils. This may be due to changes in the humic molecules in solution as the pH is lowered. The spherocolloid model of Ghosh and Schnitzer (1980) and the observations of Schnitzer (1978) showed that lowered solution pH resulted in a coiling of the humic molecules in solution. This coiling in turn could lead to an increase in the formation of hydrophobic interiors of the humic molecules as discussed in the literature review. Therefore, a greater binding of DDT to the DOM in solution could take place at lower pH values resulting in larger decreases in $K'_{soc}$ than at higher pH values. Thus, at pH 4 the HA in solution appears to be more effective in competing with the soil for binding of DDT than at higher pH values.

Figures 17 to 19 also show that, in general, the MA soil has a greater partition coefficient than the MB or NB soils, as was previously shown in the isotherm tests. In addition, Figures 17 and 18 show that the MB and NB partition coefficients are plotted relatively close together as found in the isotherm tests. At pH 4, however, Figure 19 shows that the plot of the MB soil results are closer to those of the MA soil than to the NB soil. The lower pH apparently slightly enhances the ability of the SOM of the MB soil to bind DDT. The greater adsorption to the MB soil at the lower pH value can possibly be explained by the variability of SOM composition from soil to soil and the potential for slightly differing reactions for these soils as the pH is changed.

## Fulvic Acid

The soil reactor vials for the FA tests contained 25 µg/l DDT and FA ranging from 0 to 11.79 mg/l as DOC at solution pHs of 4, 7 and 10. It should be noted that although every attempt possible was made to add the FA to the vials in precisely the same concentrations as the HA concentrations, the actual FA concentrations were slightly different than the HA concentrations. The effects of FA on sorption of DDT at the three pH values investigated are shown on Figures 20 to 22.

The effect of FA in solution shows no definitive trends for the $K'_{SOC}$ values, and appears to have little if any effect on inhibiting DDT sorption to SOC. Chiou, et al (1986) showed that dissolved FAs had much less effect on solubility enhancement of DDT when compared to dissolved HAs. Little or no effect of FA in solution was observed in the present study on the sorption of DDT to the SOC since the sorption potential of the soil organic carbon appears to be much greater than the binding potential of the FA in solution.

The $K'_{SOC}$ data plotted on Figures 20 to 22 are almost horizontal and show relatively little variability. The difference between the maximum and minimum $K'_{SOC}$ value for any line shown on these figures averages 2.5% ± 0.78%. This is considerably lower than the variability shown for the HA tests which averaged a maximum difference in $K'_{SOC}$ values of 10.6% ± 4.0%. Therefore, FA appears to have little effect on DDT partitioning in these experiments. Although the $K'_{SOC}$ values might appear to be increasing slightly for the MA and NB soils at pH 4 and for the NB soil at pH 7, the increases are minor and are within the variability shown in this experiment.

As with the HA experiments previously described, the partition of DDT to the MA soil was greater than partition to the MB or NB soils for all pH values. Also, the soils generally plotted near each other, except for the MA soil at pH 7 which showed a slight initial increase in $K'_{SOC}$ as the DOC concentration increased. This increase then leveled off at a point approximately 3% greater than its initial $K'_{SOC}$ value throughout the maximum

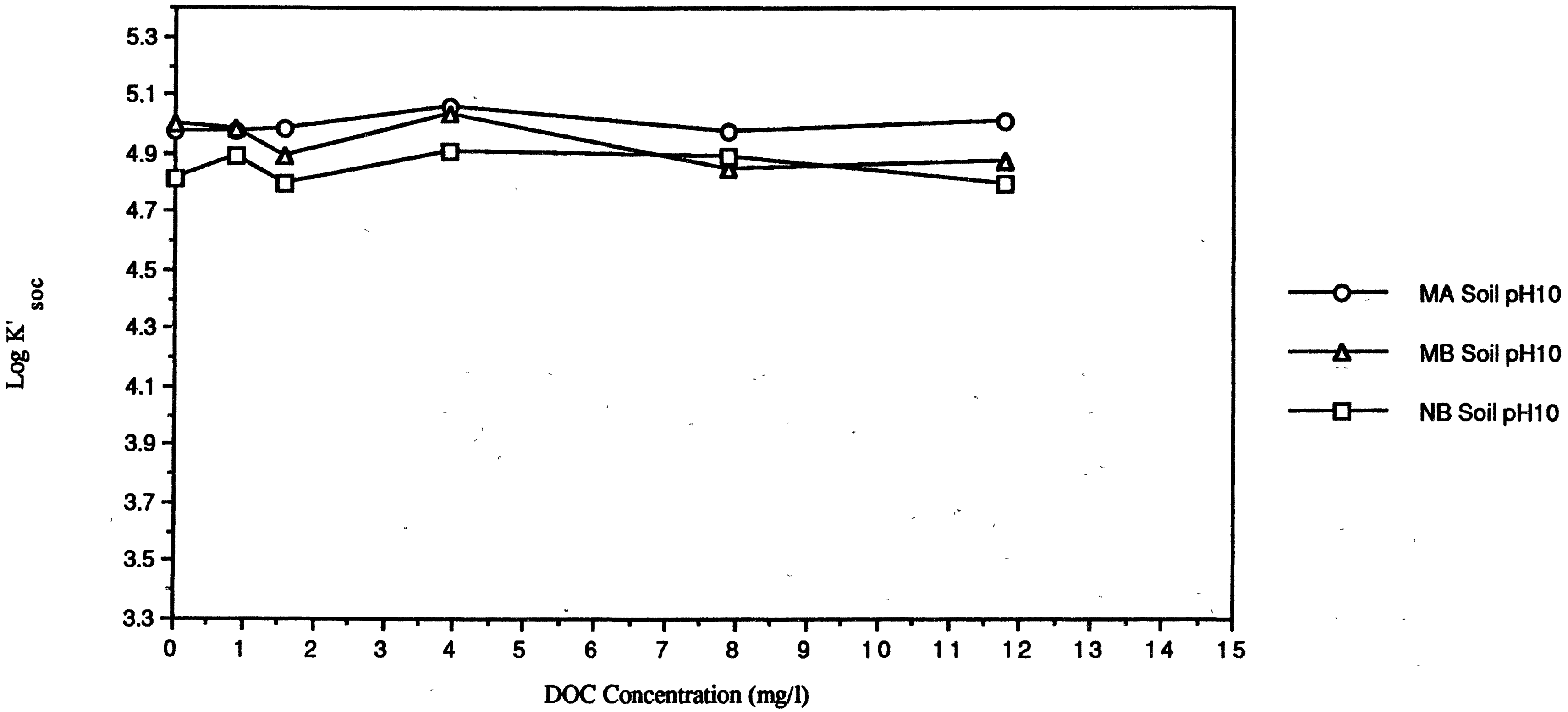

Figure 20. Log K'soc Versus DOC Concentration for DDT in the Presence of FA at pH 10.

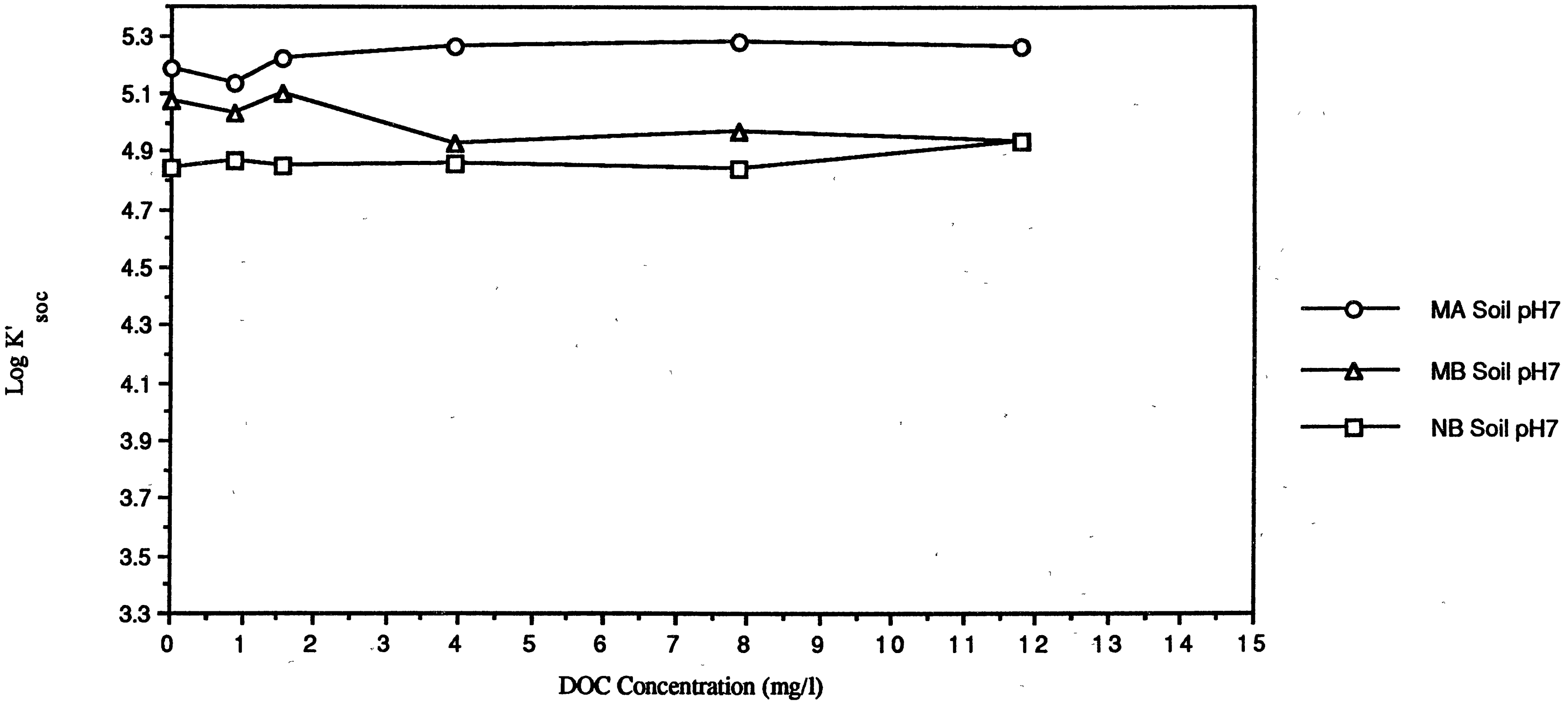

Figure 21. Log K'soc Versus DOC Concentration for DDT in the Presence of FA at pH 7.

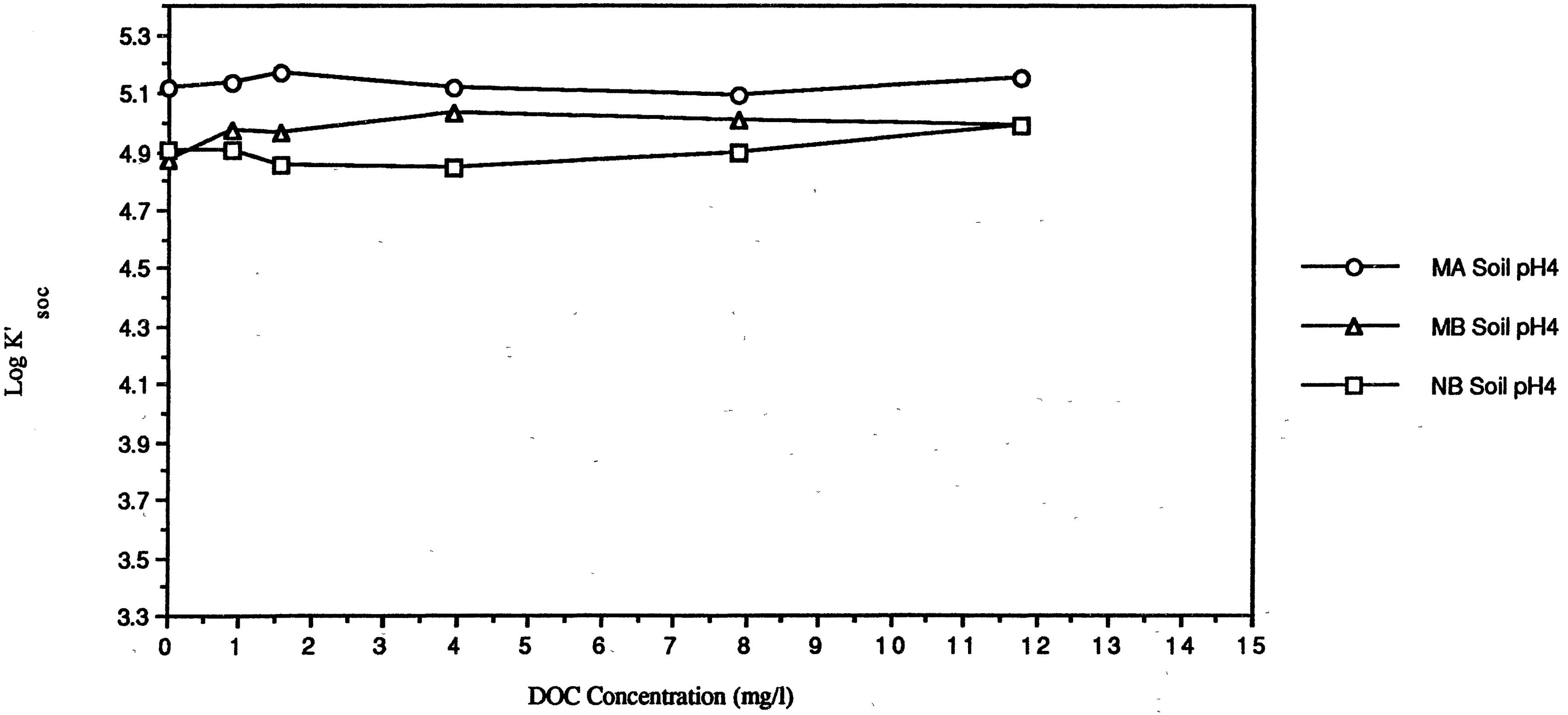

Figure 22. Log K'soc Versus DOC Concentration for DDT in the Presence of FA at pH 4.

DOC concentration added. The overall greater $K'_{soc}$ values for the MA soil at pH 7 may be due to variability in soil organic matter composition and variable interactions as previously discussed.

## DDD Experiments

### Humic Acid

The soil reactors for the DDD experiments contained 90 µg/l DDD and HA ranging from 0 to 12.45 mg/l as the DOC, and a solution pH of 4, 7 or 10. The results of DOM in solution on the sorption of DDD to the three soils is shown on Figures 23 to 25.

Review of Figures 23 to 25 shows that as the DOC concentration is increased, the partition coefficient for DDD at first increases to a maximum and then decreases as the HA continues to be added at greater concentrations. This is similar to the effects observed for DDT in the presence of HA. The initially-low concentrations of DOC apparently reduces the sorption of DDD on the glassware and thus allows greater sorption to take place on the soil. Then as the HA concentration continues to be increased, the DOC in solution outcompetes the soil for binding DDD and the $K'_{soc}$ values decrease. Thus, at DOC concentrations above approximately 2 mg/l of Aldrich HA, sorption of DDD is reduced and its transport could potentially be facilitated by the humic material in solution.

The effect of pH on the ability of the HA to decrease the partition coefficient can be evaluated by observing the maximum drop in $K'_{soc}$ values as the DOC concentration is increased. The maximum decrease in $K'_{soc}$ values observed for all of the soils is at pH 4 and least at pH 10. The DOC is more effective at binding DDD in solution at the lower pH value possibly due to the coiling of the humic molecules as previously discussed in light of the Ghosh and Schnitzer (1980) research.

Finally, Figures 23 to 25 show that the $K'_{soc}$ values for the MA soil are consistently greater than the $K'_{soc}$ values for the MB and NB soils. Also, the plots of the

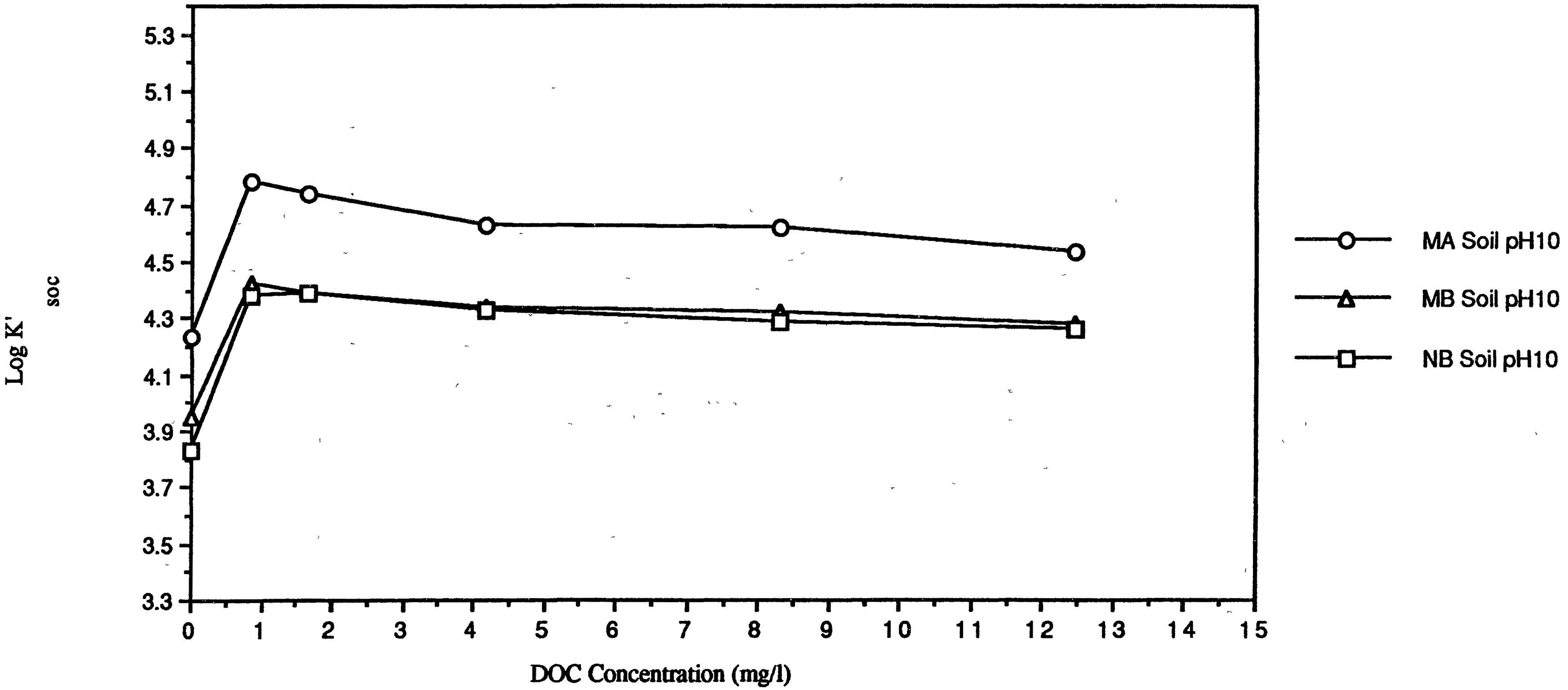

Figure 23. Log K'soc Versus DOC Concentration for DDD in the Presence of HA at pH 10.

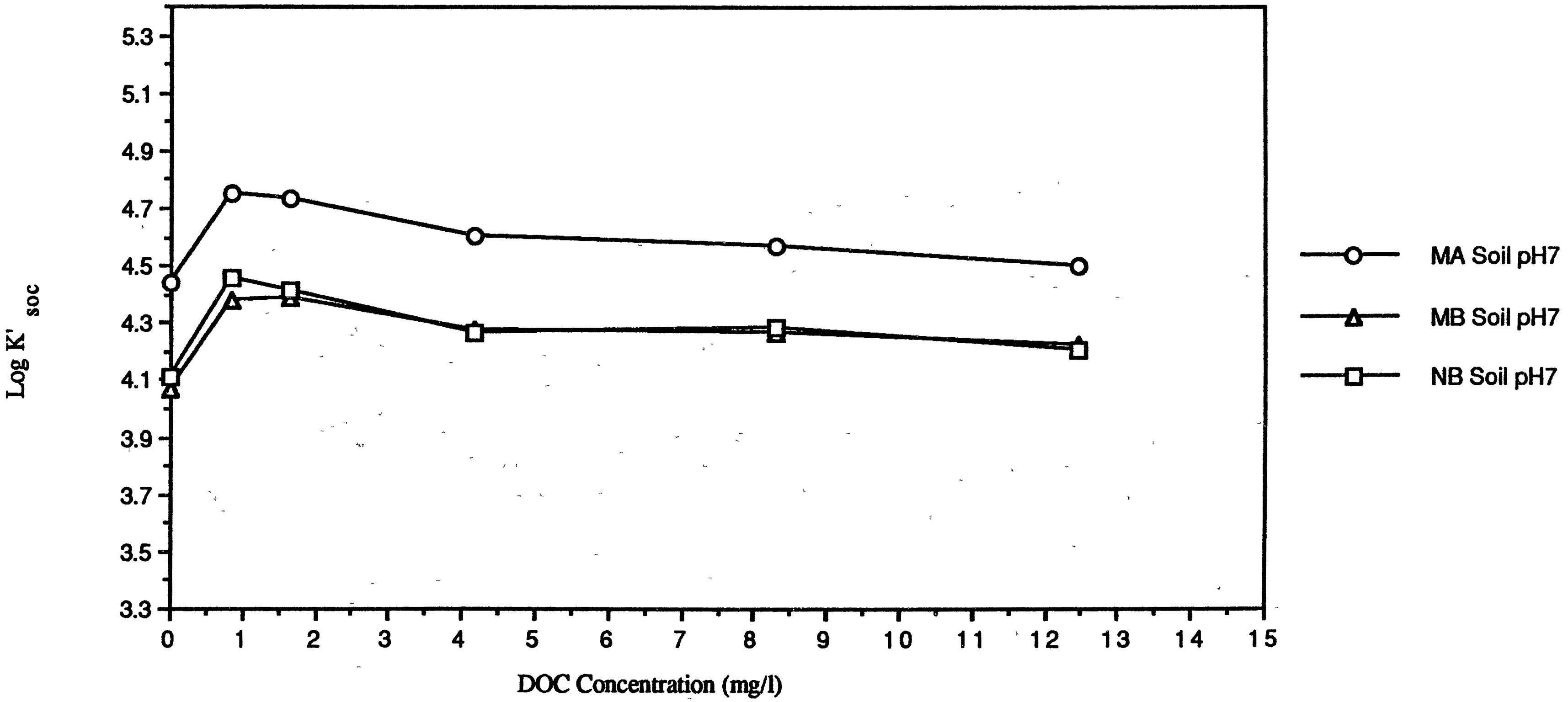

Figure 24. Log K'soc Versus DOC Concentration for DDD in the Presence of HA at pH 7.

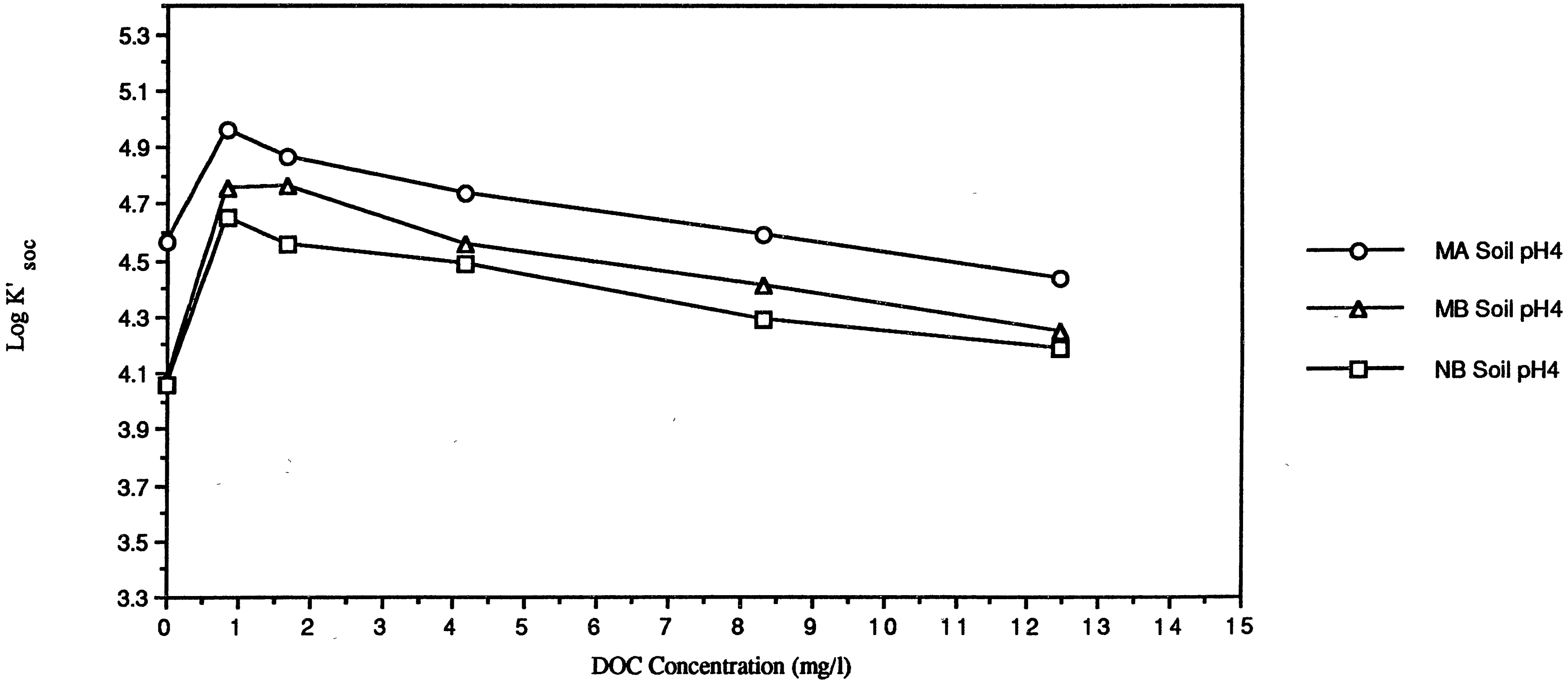

Figure 25. Log K'soc Versus DOC Concentration for DDD in the Presence of HA at pH 4.

MB and NB soil data are relatively close to each other except at pH 4 where the MB soil data are slightly greater than the NB soil data. These differences show the variability of different soil organic matter to bind HOCs under changing conditions. Since all SOM has different origins and composition, variable reactions under changing conditions would seem reasonable. In addition, the variability is relatively small and well within the order of magnitude of partitioning variation as described by Roy and Griffin (1987) for sorption of organic compounds to various soils.

### Fulvic Acid

The FA experiments were conducted under the same conditions as those for the HA experiments described above. However, the FA concentration ranged from 0 to 11.75 mg/l as DOC. The results of these tests are shown on Figures 26 to 28.

As with the DDT experiments, the effects of FA on the sorption of DDD were not as pronounced as the effects of HA. As can be seen on Figures 26 to 28, the initial concentrations of FA appeared to redistribute the DDD and allow for greater sorption to the soil. However, the effects after this initial redistribution were slightly different at the three different solution pH values tested. At pH 10 the partition coefficient decreased slightly with an increase in DOC concentration. At pH 7 the $K'_{soc}$ values also decreased slightly as more DOC was added. At pH 4 the $K'_{soc}$ increased slightly as DOC was added. This result may be due to FA being more effective at redistributing the DDD at pH 4. However, the increase was only about 2.5% and is considered minor.

Overall, the effects of FA on DDD partitioning are moderate when compared to the HA experiments. The maximum change between any $K'_{soc}$ value for any plot shown on Figures 26 to 28 averaged 4.56% ± 1.12%. This is considerably less than the change for the plots of the HA experiments with DDD which showed an average maximum change for the $K'_{soc}$ values of 10.55% ± 2.83%.

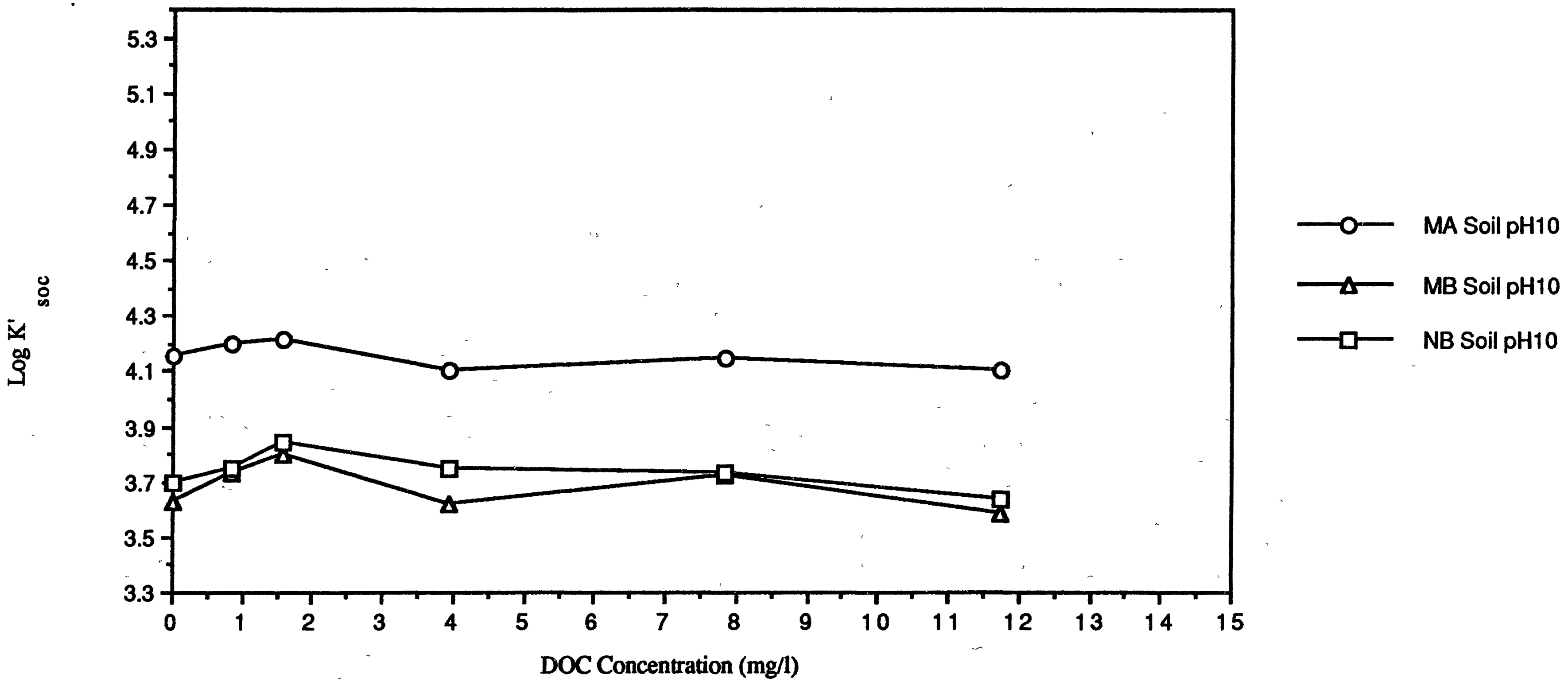

Figure 26. Log K'soc Versus DOC Concentration for DDD in the Presence of FA at pH 10.

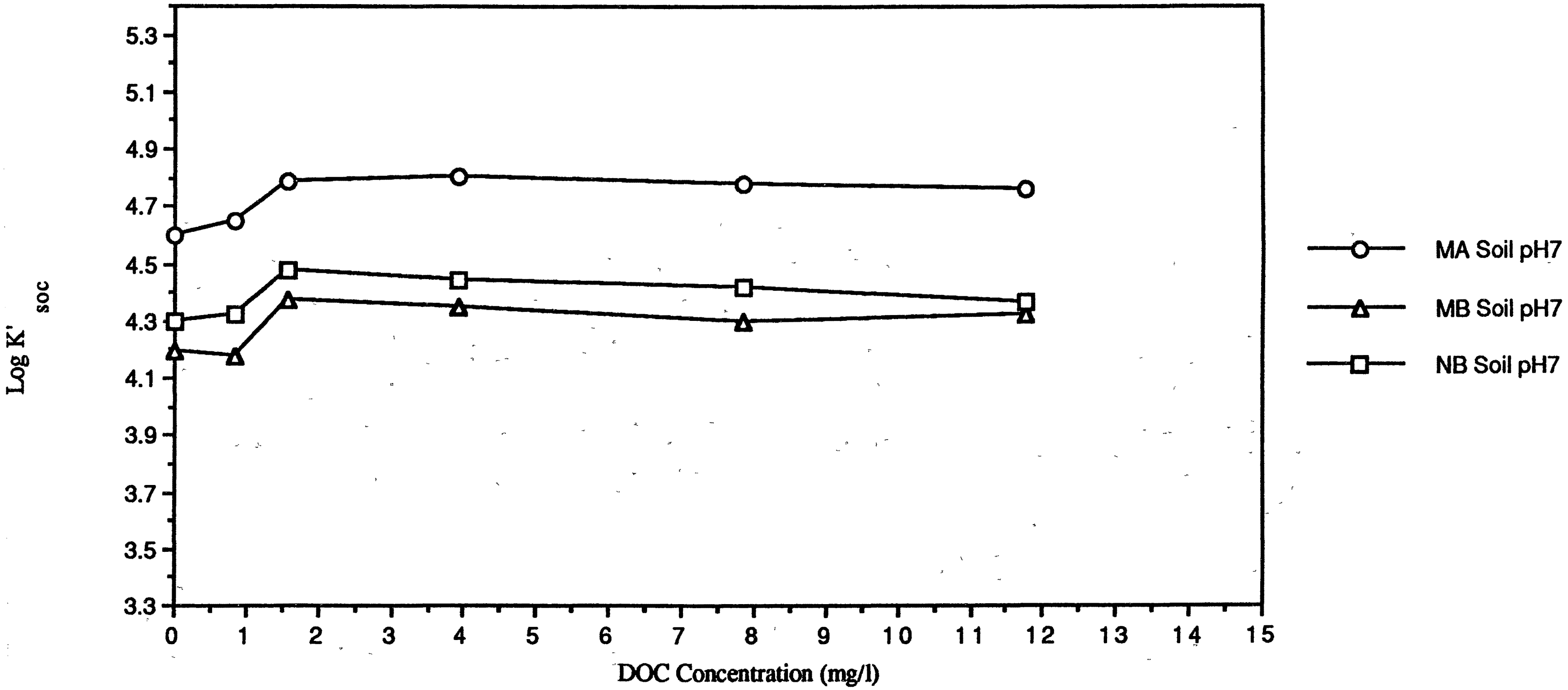

Figure 27. Log K'soc Versus DOC Concentration for DDD in the Presence of FA at pH 7.

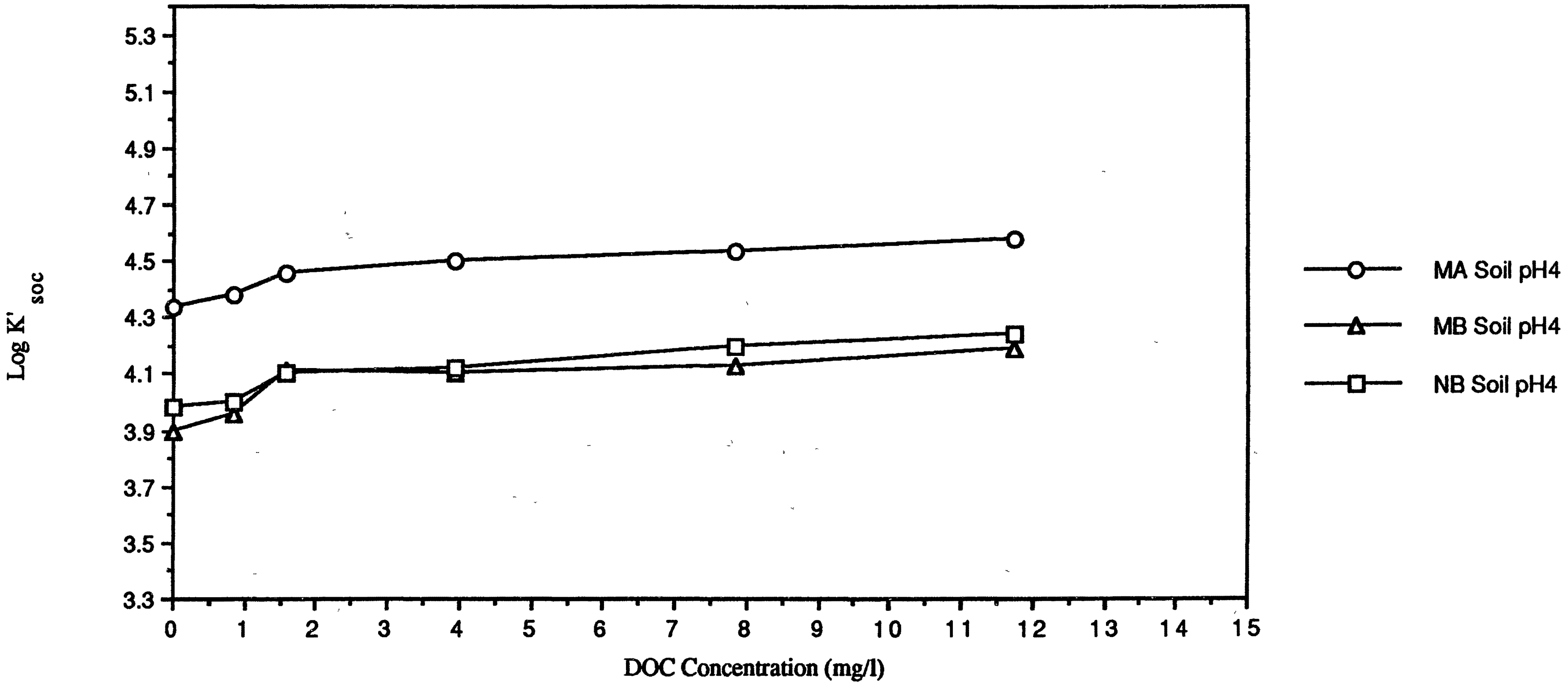

Figure 28. Log K'soc Versus DOC Concentration for DDD in the Presence of FA at pH 4.

Finally, the MA soil $K'_{soc}$ values for the FA experiment with DDD were consistently greater than the MB and NB soil values. The MB and NB soil data results were relatively close to each other for all pH values. The variability of the partition coefficients for the three soils is considered to be due to differences in soil organic matter composition as discussed previously.

## Dieldrin Experiments

### Humic Acid

The Dieldrin experimental vials contained 90 µg/l Dieldrin. The HA concentration ranged from 0 to 12.45 mg/l as DOC, and the solution pH was either 4, 7 or 10. The results of HA in solution on the sorption of Dieldrin to the three soils are shown on Figures 29 to 31.

The partition of Dieldrin to the three soils is less than the partition of DDD or DDT to the same soils. These results fit the conceptual models of Karickhoff, et al (1979) and Chiou, et al (1986) where more soluble HOCs, such as Dieldrin, are sorbed by SOM and bound by DOM to a lesser degree than less soluble HOCs, such as DDD or DDT. The effect of HA on Dieldrin partition coefficients is also much less than the effect of HA on DDT and DDD partitioning. The average maximum change in $K'_{soc}$ values for the plots shown on Figures 29 to 31 was 4.94% ± 1.85%. This is considerably lower than the maximum average change in $K'_{soc}$ values found using HA with DDT and DDD (10.60% ± 4.03% and 10.55% ± 2.83%, respectively).

However, Figures 29 to 31 do show some trends as HA was added to the vials. The Dieldrin was redistributed between the glassware and the soil by the HA at lower humic concentrations of approximately 2 to 4 mg/l DOC. This redistribution of the HOC is similar to, but not as pronounced as, that observed for DDT and DDD. The HA apparently is more effective at binding DDT and DDD than at binding Dieldrin as discussed

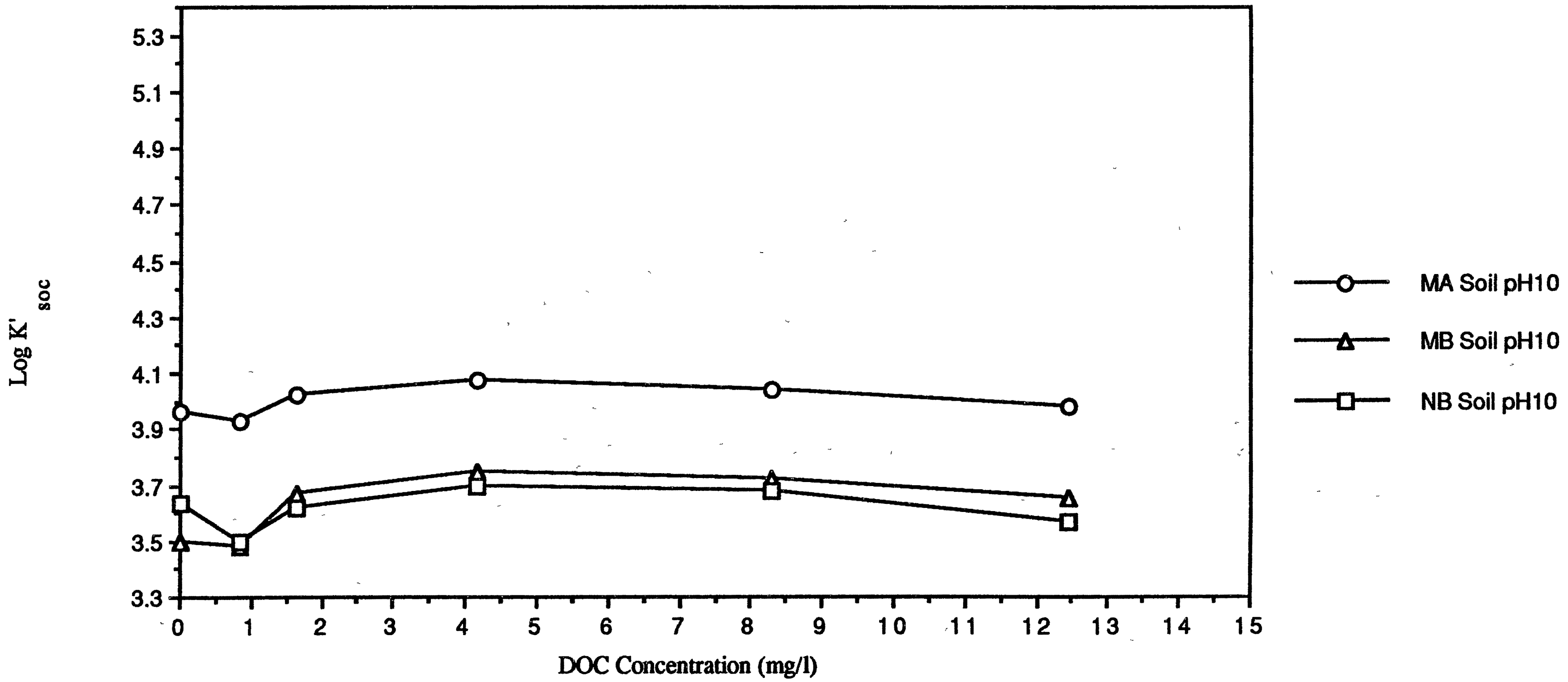

Figure 29. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of HA at pH 10.

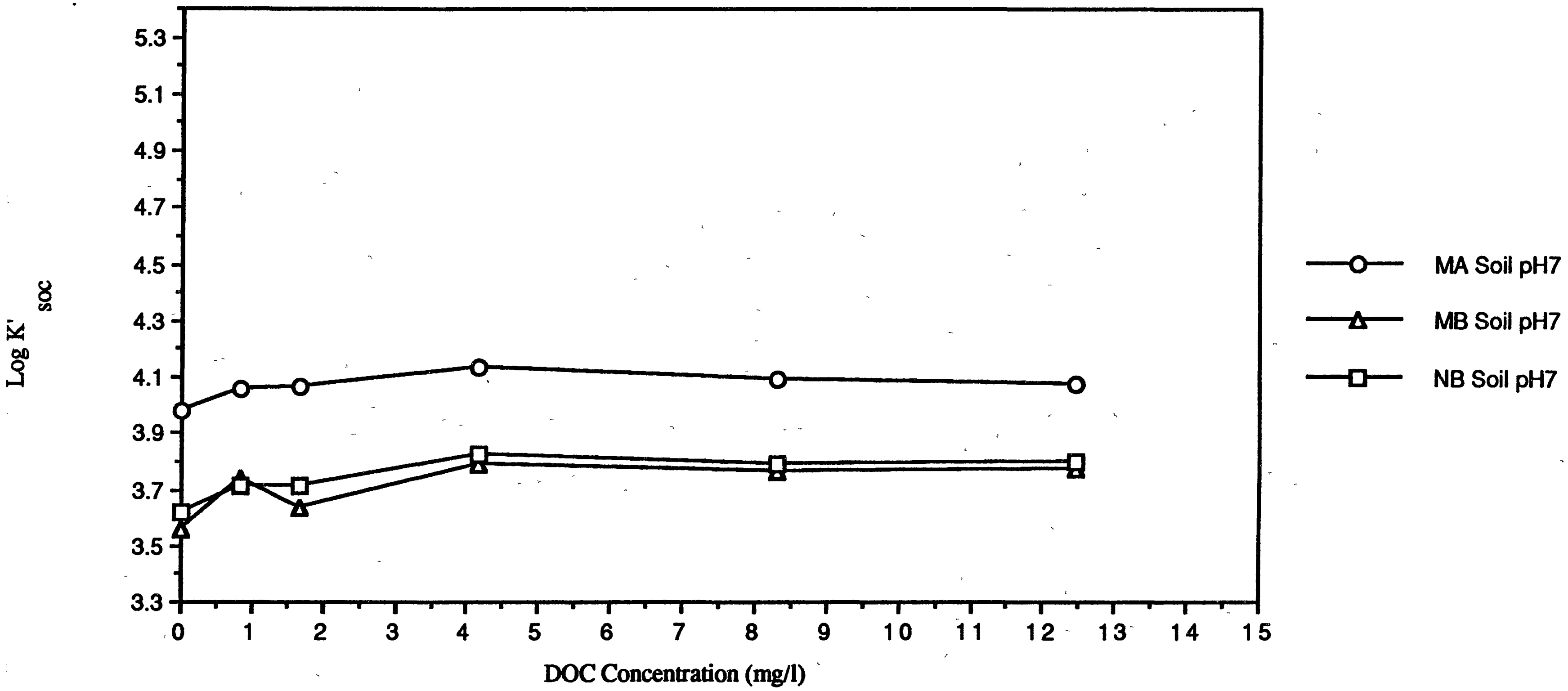

Figure 30. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of HA at pH 7.

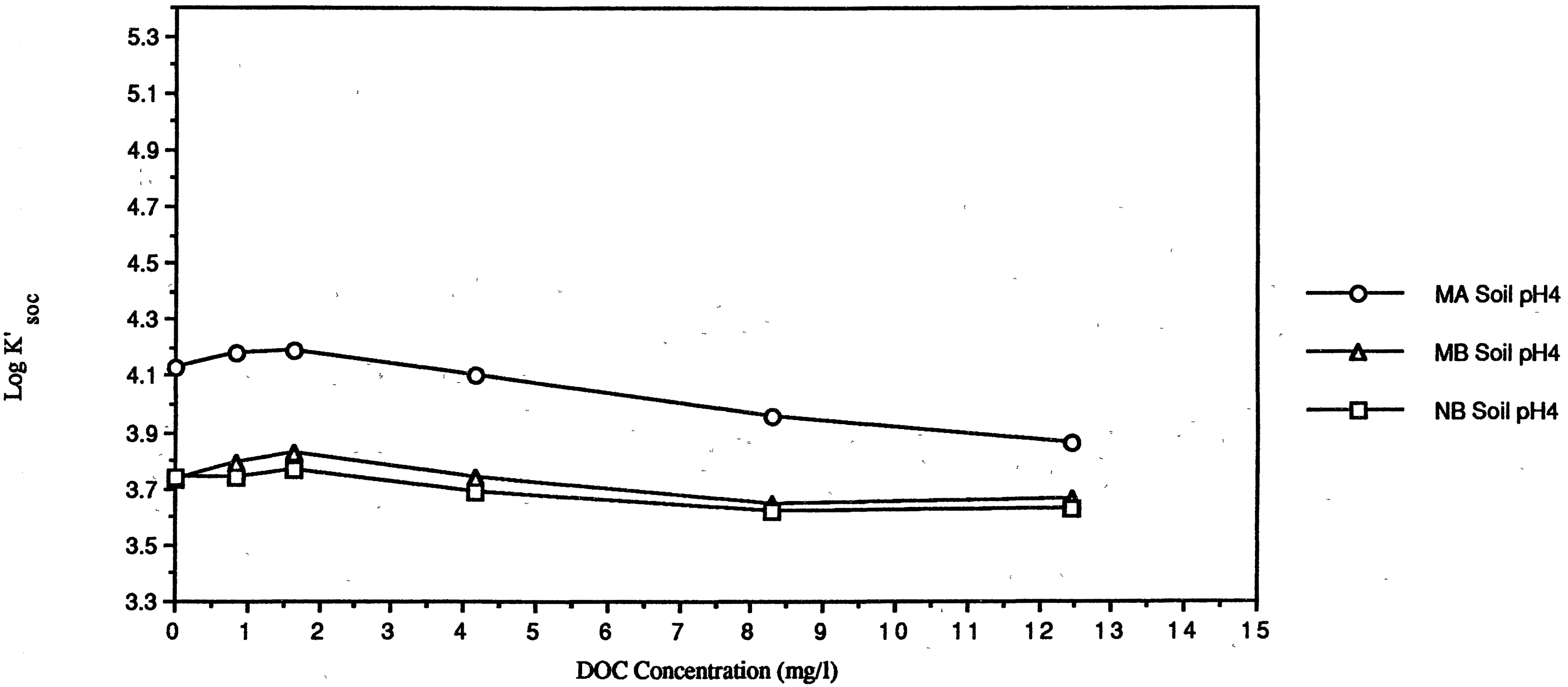

Figure 31. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of HA at pH 4.

previously. After the initial redistribution of the Dieldrin, the addition of increasing amounts of HA caused a slight to moderate decrease in the $K'_{soc}$ values. These effects are greatest for the pH 4 experiments. Increased coiling of the HA molecules in solution at the lower pH might be responsible for more Dieldrin remaining in solution resulting in the greater drop in $K'_{soc}$ values observed. As with previous results, the $K'_{soc}$ values found for the MA soil were greater than those found for the MB and NB soils. Also, the MB and NB soil $K'_{soc}$ values were noted to be similar.

### Fulvic Acid

The FA experiments were performed in the same fashion as the HA experiments described above. The FA in the vials ranged in concentration from 0 to 11.75 µg/l as DOC. The results of these experiments are shown on Figures 32 to 34.

Review of Figures 32 to 34 shows that FA does not affect the partitioning of Dieldrin to any of the soils tested. The average maximum change in $K'_{soc}$ values for the plots shown in these figures is 1.76% ± 0.77%. This is the lowest change observed for any of the experiments and indicates that FA in solution does not effect Dieldrin partitioning. Chiou, et al (1986) found that FA increased the solubility of HOCs much less than HA, and that the effect of FA on HOC solubility diminished as the $K_{ow}$ of the HOCs used decreased. Dieldrin has a lower $K_{ow}$ than DDT or DDD, and thus the observation of the present study that FA has no effect on Dieldrin partitioning is reasonable. In other words, the FA in solution cannot compete with the soil organic matter for binding of Dieldrin.

The $K'_{soc}$ values were found to be greater in all instances for the MA soil than for the MB and NB soils. Also, the plots of the MB and NB soil data were generally near each other. However, at pH 10 the MB soil data were observed to be slightly greater than the NB soil data. Finally, the $K'_{soc}$ value for the MA soil at pH 7 for the maximum DOC concentration was the only point which showed a noticeable increase or decrease of all the

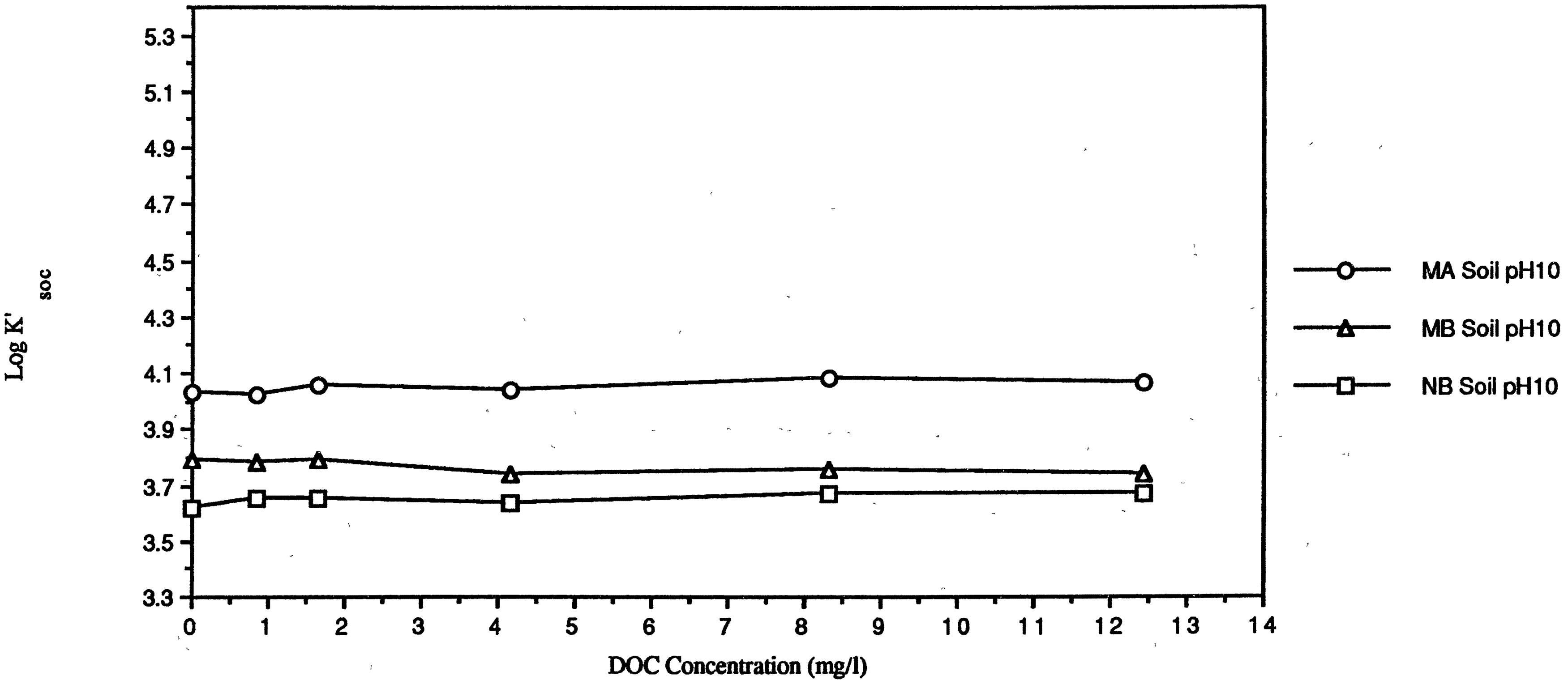

Figure 32. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of FA at pH 10.

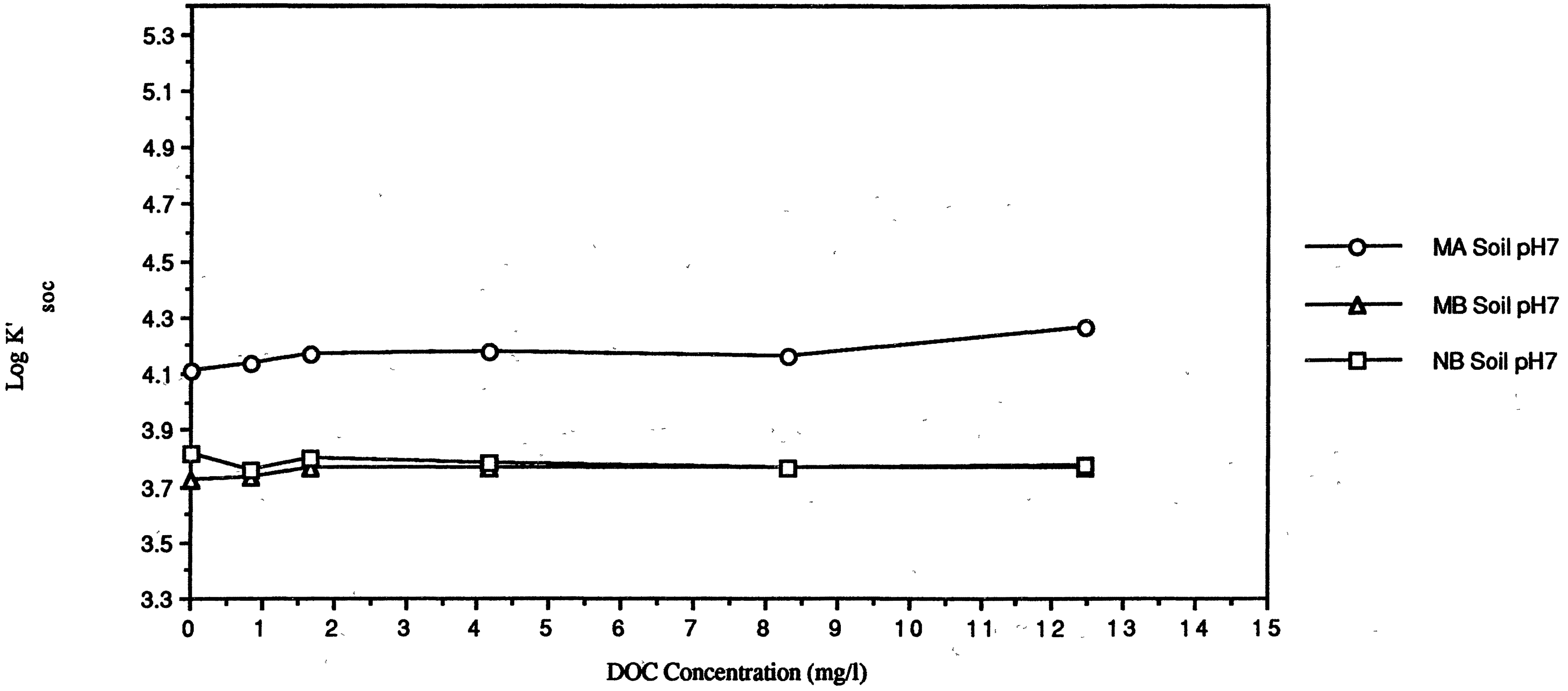

Figure 33. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of FA at pH 7.

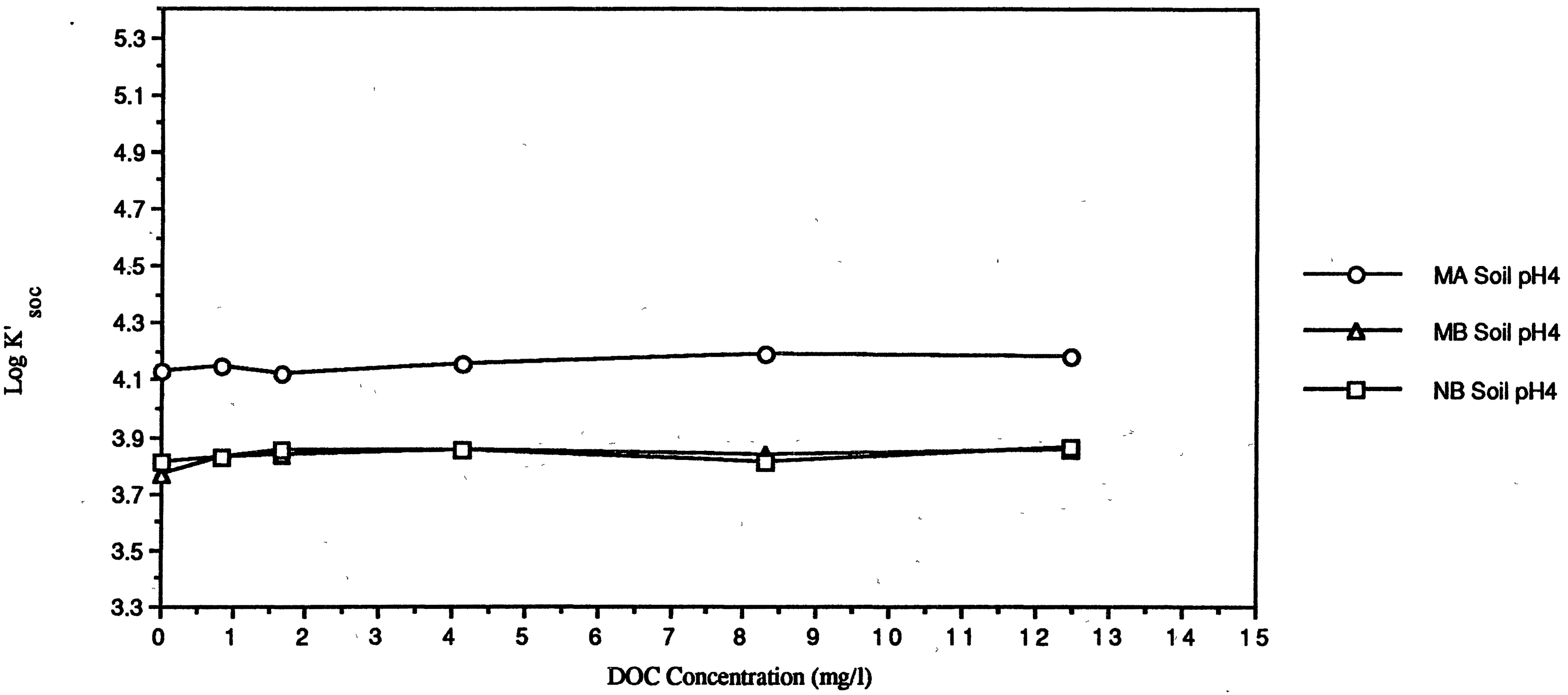

Figure 34. Log K'soc Versus DOC Concentration for Dieldrin in the Presence of FA at pH 4.

plots observed for this FA experiment. This point is thought to be an aberration since all of the other points on this line, as well as all of the other graphs in this FA experiment, show almost no variation and plot nearly horizontally.

## Summary of Isotherm Experimental Results

The results of the isotherm tests have been summarized in Table XIV. Soil organic carbon was found to be the dominant factor in sorption of the three HOCs to the three soils investigated. The Freundlich log $K_{SOC}$ values were found to be well correlated with solubility and octanol-water partition coefficients. Also, the Freundlich $K_{SOC}$ values were similar to previously-reported values for sorption of DDT and Dieldrin to other soils.

The Freundlich $K_{SOC}$ values for the present study were noted to vary slightly among the soil types with the MA soil always having greater log $K_{SOC}$ values than the MB or NB soils. The sorption results for the MB and NB soils were often similar. Since the Freundlich $K_{SOC}$ values were calculated on an equal soil organic carbon basis, the differences in sorption between the soils is considered attributable to changes in the organic matter sorption potential of the individual soils (Garbarini and Lion, 1986; Gauthier, et al, 1987). The Freundlich $K_{SOC}$ values were shown to decrease with the soil collection depth. Previous investigations have shown that changes in soil organic matter with depth generally include a higher percentage of fulvic acid comprising the total soil organic matter (Kononova, 1966; Stevenson, 1985). Fulvic acid has also been shown to sorb HOCs less than humic acid (Chiou, et al, 1986). Therefore, the differences in sorption to the various soils might be attributable to differences in soil organic composition with depth.

Finally, the sorption of the three HOCs followed the order of DDT $\simeq$ DDD > Dieldrin. This is also the order the $K_{OW}$ values for these compounds, and in an inverse order of their solubilities.

## Summary of DOM Experimental Results

Results of the sorption of the three HOCs to the three soils in the presence of HA and FA at three different solution pH values have been shown in Figures 17 to 34. Review of these figures shows that pH influences the sorption of the HOCs. In general, as the pH is lowered, the partition to the soils in the presence of HA or FA in solution is decreased slightly. This effect is most likely due to increased coiling of the humic molecules in solution at lower pH values (Ghosh and Schnitzer, 1980; Schnitzer, 1978), and the resulting potential for the formation of hydrophobic interiors as the molecules coil. These hydrophobic interiors might then allow greater partitioning of the HOCs to the DOM.

The choice of HOC used also influenced the effect that dissolved organic carbon in solution had on the partition of a particular HOC. DDT and DDD showed the most noticeable changes in $K'_{soc}$ values while Dieldrin showed very little effect. Sorption and binding of HOCs by humic and fulvic acids is decreased as the solubility of the HOC used is increased (Karickhoff, et al, 1979; Chiou, et al, 1986). Since DDT and DDD have lower solubilities than Dieldrin, it seems reasonable that DDT and DDD showed more pronounced effects due to DOC in solution than did Dieldrin.

The type and concentration of dissolved organic matter in solution was also very important in determining the effect of HOC partitioning between the soils and the solution. The Aldrich humic acid showed much more pronounced effects than did the IHSS fulvic acid. Fulvic acids have been shown in previous research to bind and sorb HOCs to a lesser degree than humic acids (Chiou, et al, 1986). The results of the present study are in agreement with this observation. The concentration of the DOC was also found to be important. In general, the decrease in the partition to the soil was found to be greater as the DOC concentration increased. Thus, dissolved organic matter may provide a mechanism which could facilitate transport of HOCs in the environment.

Finally, the soil type also influenced the degree of partitioning. As was found for the isotherm tests, the MA soil generally sorbed greater amounts of the HOCs than did the

MB and NB soils. These differences were within an order of magnitude as typically found by previous researchers for the sorption of organic compounds to various soils (Gschwend and Wu, 1985; Roy and Griffin, 1987). Variability of partitioning is considered due to differences in individual soil organic matter composition (Gorbarini and Lion, 1986; Gauthier, et al, 1987).

The present study was performed to investigate the effect of DOM on the sorption of HOCs at different solution pH values in a three-component system (HOC-soil-DOM). The significance of this research is that the DOC in the experiments was used at concentrations found naturally in the environment (Thurman, 1985) and was shown to inhibit the sorption of HOCs over an environmental range of solution pH values. In addition, the HOCs used had solubilities in an appropriate range at which naturally-occuring concentrations of DOC might act as sorption inhibitors. That is, the HOC solubilities were at least two orders of magnitude less than the DOC concentration used (Kile and Chiou, 1989). In the past, research has focused on two-component systems containing either HOCs and soil, or HOCs and DOM. Having all three components in the system simultaneously is much more realistic, however.

The works of Caron, et al (1985) and West, et al (1984), as previously discussed in the literature review, did incorporate three-component systems. However, the research in each case was limited to one DOM source at a single concentration. In addition, the studies were conducted at one pH value. Also, although between these two studies, a total of three different organic compounds were chosen for investigation, only two of the compounds were in the appropriate solubility range as described by Kile and Chiou (1989) in which naturally-occuring concentrations of DOM might potentially inhibit sorption.

Thus, the present study is an expanded and much more realistic evaluation of sorption of HOCs in the presence of DOM. The results of this study indicate that DOM can have an effect on HOC sorption such that less sorption occurs than would have been predicted by simply using the $K_{ow}$ - $K_{soc}$ relationships developed by previous investigators in the absence of DOM. The influence of DOM could allow HOCs, which are known to be highly sorptive, and thus thought immobile, to be transported along with the DOM through soils to the ground water, through ground-water systems, and in surface waters. This facilitated transport could be significant and allow mobilization of HOCs much farther than previously expected. This transport mechanism may help explain the occurrence of highly sorptive organic compounds observed in surface-water and ground-water systems far from their sources.

Although built on related research performed over many years, the concept of facilitated transport has been developed and investigated primarily in the 1980s. Experiments in three-component systems have been reported infrequently, however. The current study supports and expands upon this previous research, and provides results which environmental scientists can use to better understand and predict the fate of HOCs in aqueous systems containing both dissolved organic matter and soil or sediment.

# CHAPTER V

# CONCLUSIONS

The results of this study verified or confirmed the results of previous research as well as providing additional results and conclusions for three-component (HOC-soil-DOM) systems. The verifications and conclusions drawn from this study are presented below.

- Confirmation was made that the sorption of hydrophobic organic compounds varies with different soils.
- The percentage of soil organic carbon in the soil was verified as the dominant soil factor controlling sorption of hydrophobic organic compounds.
- Soil organic carbon content decrease with depth was confirmed.
- The organic carbon of lower soil horizons appears to sorb hydrophobic organic compounds to a lesser degree than upper soil horizons.
- It was confirmed that hydrophobic organic compounds with lower solubilities or higher octanol-water partition coefficients sorb to soils to a greater extent than those compounds with higher solubilities or lower octanol-water partition coefficients.
- That the sorption of hydrophobic organic compounds to soil organic matter can be estimated using pre-existing knowledge of the compound's solubility and octanol-water partition coefficient was corroborated.
- Dissolved organic matter in solution was shown to bind hydrophobic organic compounds in solution and inhibit the sorption of these compounds to soils.
- The type of dissolved organic matter in solution was shown to determine the degree of inhibition of hydrophobic organic compound sorption to soils.

- Inhibition of hydrophobic organic compound sorption to soils was shown to increase as the dissolved organic matter concentration in solution increased.
- Slightly greater inhibition of sorption by dissolved organic matter was shown to take place at lower solution pH values than at higher pH values.
- Humic acid was shown to inhibit sorption of hydrophobic organic compounds to soils to a greater extent than fulvic acid.
- Inhibition of hydrophobic organic compound sorption by dissolved organic matter could mediate or facilitate the transport of these compounds in soils, ground waters and surface waters resulting in faster travel times and greater transport distances than would have been expected without the dissolved organic matter.
- The dissolved organic matter content of natural systems should be incorporated into models which are used to predict the fate and transport of hydrophobic organic compounds in the environment.

# CHAPTER VI

# RECOMMENDATIONS FOR FUTURE WORK

The potential for dissolved organic matter to bind HOCs in solution and thus inhibit the sorption of hydrophobic organic compounds to soils has been demonstrated. Binding of these compounds has the potential to influence their fate and transport. Therefore, the following recommendations for future work are made.

- Use radiolabelled compounds in future sorption investigations and measure the activity in the soil at equilibrium in order to accurately quantify the mass of a target compound sorbed.
- Pre-equilibrate the hydrophobic organic compound with the dissolved organic matter in solution to evaluate any potential effects on sorption during subsequent exposure to soil.
- Use dialysis tubing to separate the truly bound hydrophobic organic compound component from that which simply dissolved in solution.
- Use at least one reference target compound, soil and dissolved organic matter source so that comparison of results with other researchers can be accomplished.
- Use fulvic and humic acid derived from the same soil that is to be used as the sorbent in order to evaluate the effects of similar organic matter sources on the inhibition of hydrophobic organic compound sorption.
- Expand the number of soils, dissolved organic matter sources and compounds tested in order to develop a larger data base with which to draw conclusions and refine correlations.
- Use soil columns and field experiments in addition to batch studies in order to scale up the investigation and to calculate retardation coefficients.

- Investigate the effects of municipal sewage effluent as a dissolved organic matter source and its potential for facilitating transport of hydrophobic organic compounds.
- Investigate the potential for dissolved organic matter to mediate the desorption of hydrophobic compounds bound to soils using batch and/or column studies.
- Reevalute existing models regarding the fate and transport of hydrophobic organic compounds in order to include the potential for dissolved organic matter to inhibit sorption and facilitate transport of these compounds.

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# APPENDIXES

# APPENDIX A

# PERTINENT RELATIONSHIPS BETWEEN OCTANOL-WATER PARTITION COEFFICIENTS, SOLUBILITY AND SOIL ORGANIC CARBON PARTITION COEFFICIENTS

## TABLE XV

## RELATIONSHIPS BETWEEN $K_{ow}$, S, AND $K_{oc}$ AS DESCRIBED BY VARIOUS RESEARCHERS

| Researcher(s) | Relationship | Comments |
|---|---|---|
| Banerjee, et al (1982) | $\log K_{ow} = 5.2 - 0.68 \log S$<br>$\log K_{ow} = 6.5 - 0.89 \log S - 0.015\ (mp)$ | S = aqueous solubility (μmoles/l)<br>mp = melting point of compound |
| Chiou and Schmedding (1982) | $\log K_{ow} = -0.862 \log S + 0.710$ | S is in moles/l; used 36 HOCs covering 6 orders of magnitude of solubility |
| Isnard and Lambert (1989) | $\log K_{ow} = 3.15 - 0.72 \log S - 0.018 (\log S)^2$ | S is in mmoles/l; used 300 $K_{ow}$ and S values reported in literature |
| Karickhoff, et al (1979) | $\log K_{oc} = -0.54 \log S + 0.44$ | S is mole fraction solubility; used HOCs with solubilities ranging from 1 ppb to 1,000 ppm |
| Karickhoff (1981) | $\log K_{oc} = -0.197 - 0.594 \log S$ | Redefinition of the equation above to account for the crystal energy of the compound |
| Kenaga and Goring (1980) | $\log K_{oc} = 3.64 - 0.55 \log S$ | S is in mg/l; used 106 organic compounds |
| Page, et al (1982) | SOC = 0.58 (SOM) | SOC = soil organic carbon content,<br>SOM = soil organic matter content |
| Chiou, et al (1979) | $\log K_{som} = 4.040 - 0.557 \log S$ | S is in μmoles/l; used HOCs covering more than 7 orders of magnitude in solubility and 4 orders of magnitude in $K_{oc}$ |
| Means, et al (1980) | $\log K_{oc} = 4.070 - 0.82 \log S$ | S is in mg/ml |

TABLE XV (Continued)

| Researcher(s) | Relationship | Comments |
|---|---|---|
| Karickhoff, et al (1979) | $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ | S is mole fraction solubility; used HOCs with solubilities ranging from 1 ppb to 1,000 ppm |
| Karickhoff (1981) | $\log K_{soc} = 0.989 \log K_{ow} - 0.346$ | Redefinition of the equation above to account for the crystal energy of the compound |
| Briggs (1981) | $\log K_{om} = 0.52 \log K_{ow} + 0.78$ | $K_{om}$ = partition on an organic matter basis (see Page, et al, 1982 for OM-OC conversion) |
| Schwarzenbach and Westall (1981) | $\log K = 0.72 \log K_{ow} + \log SOC + 0.49$ | Showed that this relationship holds for sorption to soils with an OC content greater than 0.1% |

# APPENDIX B

# LABORATORY APPARATUS CLEANING PROCEDURE, AND PREPARATION OF HOC TEST SOLUTIONS AND GAS CHROMATOGRAPHY STANDARDS

## Laboratory Apparatus Cleaning Procedure

All laboratory apparatus coming in direct contact with samples or HOCs were composed of glass, stainless steel or Teflon. This was done to avoid potential phthalate ester contamination which is commonly associated with plastic product use. All equipment was thoroughly cleaned prior to each use by the following procedure.

- Hot water rinse.
- Warm water washing in Micro brand surfactant using a scrub brush.
- Thorough tap water rinse.
- Distilled water rinse.
- Deionized water rinse.
- Oven drying.
- Hexane rinse.
- Oven drying.

This procedure proved effective and neither cross-contamination with HOCs or phthalate ester interference was encountered.

## Preparation of HOC Test Solutions and Gas Chromatography Standards

Test solutions of the HOCs (DDT, DDD and Dieldrin) were prepared by adding known volumes of an initial pesticide stock concentrate to one liter of deionized water. The initial pesticide stock solution concentrates were prepared by weighing 1.0 mg of DDT or 5.0 mg of DDD or Dieldrin and placing in separate 10 ml volumetric flasks. The flasks were then filled with acetone to dissolve the pesticide. The stock solution concentrates were then used to prepare test solutions in water for use in the batch tests as well as for preparing standard solutions in hexane for use as gas chromatography standards. Steps for pesticide solution preparation are given in Table XVI.

## TABLE XVI

## HOC TEST SOLUTION PREPARATION

| Step | Solution Type | Description |
|---|---|---|
| DDT Solutions | | |
| 1 | Stock Concentrate | Weigh 1.0 mg DDT and place in 10 ml volumetric flask. Fill with acetone. Yields 100,000 µg/l stock concentrate solution. Store in 1.5 ml storage vials at 4°C. |
| 2 | Test Solution | Put 250 µl of the 100,000 µg/l stock concentrate in 1000 ml of deionized water. Stir and use immediately. Yields 25 µg/l test solution. |
| 3 | GC Standard | Put 25 µl of stock concentrate in 10 ml volumetric flask. Fill with hexane. Yields 250 µg/l GC standard solution. Store at 4°C in 1.5 ml vials. |
| 4 | GC Standard | Put 2 ml of the 250 µg/l GC standard in 10 ml of hexane. Yields 50 µg/l standard solution. Store as above. |
| 5 | GC Standard | Put 2 ml of the 50 µg/l GC standard in 10 ml of hexane. Yields 10 µg/l GC standard solution. Store as above. |
| DDD and Dieldrin Solutions | | |
| 1 | Stock Concentrate | Weigh 5.0 mg DDD or Dieldrin and place in seperate 10 ml volumetric flask. Fill with acetone. Yields 500,000 µg/l stock concentrate solution. Store at 4°C in 1.5 ml vials. |
| 2 | Test Solution | Put 180 µl of the 500,000 µg/l stock concentrate in 1000 ml of deionized water. Stir and use immediately. Yields 90 µg/l test solution. |
| 3 | GC Standard | Put 5 µl of stock concentrate in 10 ml volumetric flask. Fill with hexane. Yields 250 µg/l GC standard solution. Store at 4°C in 1.5 ml vials. |
| 4 | GC Standard | Put 2 ml of the 250 µg/l GC standard in 10 ml of hexane. Yields 50 µg/l standard solution. Store as above. |
| 5 | GC Standard | Put 2 ml of the 50 µg/l GC standard in 10 ml of hexane. Yields 10 mµg/l GC standard. Store as above. |

# APPENDIX C

# DATA TABLES FOR SORPTION ISOTHERM TESTS AND DOM EXPERIMENTS

## TABLE XVII

## SORPTION ISOTHERM RESULTS FOR DDT

| Sorbent as Soil Organic Carbon, m (mg/l) | Initial DDT Concentration, $C_0$ (µg/l) | Equilibrium DDT Concentration, C (µg/l) | Change in Compound Concentration, x (µg/l) | Mass Sorbed, (q = x/m) q (µg/g) |
|---|---|---|---|---|
| <u>MA Soil</u> | | | | |
| 43.43 | 5.0 | 0.343 | 4.657 | 107.23 |
| 43.43 | 10.0 | 0.657 | 9.343 | 215.13 |
| 43.43 | 15.0 | 0.800 | 14.200 | 326.96 |
| 43.43 | 20.0 | 1.229 | 18.771 | 432.21 |
| 43.43 | 25.0 | 1.629 | 23.371 | 538.13 |
| <u>MB Soil</u> | | | | |
| 69.43 | 5.0 | ~0.314[a] | 4.686 | 67.49 |
| 69.43 | 10.0 | 0.400 | 9.600 | 138.27 |
| 69.43 | 15.0 | 0.629 | 14.371 | 206.99 |
| 69.43 | 20.0 | 1.000 | 19.000 | 273.66 |
| 69.43 | 25.0 | 1.457 | 23.543 | 339.09 |
| <u>NB Soil</u> | | | | |
| 74.86 | 5.0 | ~0.314[a] | 4.686 | 62.59 |
| 74.86 | 10.0 | 0.429 | 9.571 | 127.85 |
| 74.86 | 15.0 | 0.629 | 14.371 | 191.97 |
| 74.86 | 20.0 | 1.029 | 18.971 | 253.42 |
| 74.86 | 25.0 | 1.514 | 23.486 | 313.73 |

[a] Near Detection limit.

## TABLE XVIII

## SORPTION ISOTHERM RESULTS FOR DDD

| Sorbent as Soil Organic Carbon, m (mg/l) | Initial DDD Concentration, $C_o$ (µg/l) | Equilibrium DDD Concentration, C (µg/l) | Change in Compound Concentration, x (µg/l) | Mass Sorbed, (q = x/m) q (µg/g) |
|---|---|---|---|---|
| <u>MA Soil</u> | | | | |
| 67.67 | 6.533 | ~0.500[a] | 6.033 | 89.153 |
| 67.67 | 22.567 | 2.800 | 19.767 | 292.109 |
| 67.67 | 24.433 | 4.167 | 20.266 | 299.483 |
| 67.67 | 28.267 | 6.267 | 22.000 | 325.107 |
| 67.67 | 30.600 | 10.567 | 20.033 | 296.040 |
| <u>MB Soil</u> | | | | |
| 108.33 | 6.533 | ~0.500[a] | 6.033 | 55.691 |
| 108.33 | 22.567 | 3.133 | 19.434 | 179.396 |
| 108.33 | 24.433 | 5.267 | 19.166 | 176.922 |
| 108.33 | 28.267 | 10.400 | 17.867 | 164.931 |
| 108.33 | 30.600 | 13.467 | 17.133 | 158.156 |
| <u>NB Soil</u> | | | | |
| 116.67 | 6.533 | 0.500 | 6.033 | 51.710 |
| 116.67 | 22.567 | 2.700 | 19.867 | 170.284 |
| 116.67 | 24.433 | 4.500 | 19.933 | 170.849 |
| 116.67 | 28.267 | 8.033 | 20.234 | 173.429 |
| 116.67 | 30.600 | 12.200 | 18.400 | 157.710 |

[a] Near Detection limit.

## TABLE XIX

## SORPTION ISOTHERM RESULTS FOR DIELDRIN

| Sorbent as Soil Organic Carbon, m (mg/l) | Initial Dieldrin Concentration, $C_0$ (µg/l) | Equilibrium Dieldrin Concentration, C (µg/l) | Change in Compound Concentration, x (µg/l) | Mass Sorbed, (q = x/m) q (µg/g) |
|---|---|---|---|---|
| <u>MA Soil</u> | | | | |
| 101.67 | 9.967 | 2.700 | 7.267 | 71.476 |
| 101.67 | 29.767 | 9.033 | 20.734 | 203.934 |
| 101.67 | 52.467 | 16.100 | 36.367 | 357.696 |
| 101.67 | 72.867 | 25.000 | 47.867 | 470.808 |
| 101.67 | 88.983 | 31.267 | 57.716 | 567.680 |
| <u>MB Soil</u> | | | | |
| 162.33 | 9.967 | 3.300 | 6.667 | 62.758 |
| 162.33 | 29.767 | 12.433 | 17.334 | 163.170 |
| 162.33 | 52.467 | 22.000 | 30.467 | 286.794 |
| 162.33 | 72.867 | 33.000 | 39.867 | 375.279 |
| 162.33 | 88.983 | 38.867 | 50.116 | 471.755 |
| <u>NB Soil</u> | | | | |
| 174.67 | 9.967 | 2.867 | 7.100 | 40.648 |
| 174.67 | 29.767 | 11.433 | 18.334 | 104.964 |
| 174.67 | 52.467 | 20.967 | 31.500 | 180.340 |
| 174.67 | 72.867 | 30.867 | 42.000 | 240.453 |
| 174.67 | 88.983 | 35.800 | 53.183 | 304.477 |

# TABLE XX

# $C'/C_0$ TO GLASSWARE IN THE CONTROL REACTOR VIALS IN THE PRESENCE OF HUMIC ACID

| | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| HOC<br>and pH | 0<br>0 | 29.05<br>0.83 | 58.10<br>1.66 | 145.25<br>4.15 | 290.50<br>8.30 | 435.75<br>12.45 |
| DDT | | | | | | |
| pH 10 | 0.480 | 0.432 | 0.277 | 0.185 | 0.022 | 0.000 |
| pH 7 | 0.791 | 0.498 | 0.111 | 0.111 | 0.060 | 0.056 |
| pH 4 | 0.863 | 0.421 | 0.370 | 0.336 | 0.361 | 0.394 |
| DDD | | | | | | |
| pH 10 | 0.694 | 0.310 | 0.218 | 0.174 | 0.132 | 0.101 |
| pH 7 | 0.625 | 0.314 | 0.192 | 0.158 | 0.087 | 0.097 |
| pH 4 | 0.720 | 0.148 | 0.152 | 0.113 | 0.143 | 0.181 |
| Dieldrin | | | | | | |
| pH 10 | 0.293 | 0.264 | 0.384 | 0.463 | 0.426 | 0.345 |
| pH 7 | 0.342 | 0.421 | 0.427 | 0.512 | 0.473 | 0.464 |
| pH 4 | 0.361 | 0.406 | 0.436 | 0.368 | 0.301 | 0.308 |

[a] Upper value is total DOC in vial in μg. Lower value is DOC concentration in mg/l.

# TABLE XXI

## $C'/C_0$ TO GLASSWARE IN THE CONTROL REACTOR VIALS IN THE PRESENCE OF FULVIC ACID

| | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| HOC<br>and pH | 0<br>0 | 29.05<br>0.79 | 58.10<br>1.57 | 145.25<br>3.93 | 290.50<br>7.86 | 435.75<br>11.79 |
| DDT | | | | | | |
| pH 10 | 0.467 | 0.448 | 0.463 | 0.349 | 0.389 | 0.405 |
| pH 7 | 0.536 | 0.563 | 0.487 | 0.487 | 0.472 | 0.476 |
| pH 4 | 0.604 | 0.546 | 0.540 | 0.590 | 0.556 | 0.543 |
| DDD | | | | | | |
| pH 10 | 0.719 | 0.701 | 0.695 | 0.722 | 0.716 | 0.716 |
| pH 7 | 0.522 | 0.477 | 0.292 | 0.307 | 0.304 | 0.321 |
| pH 4 | 0.725 | 0.719 | 0.669 | 0.656 | 0.617 | 0.580 |
| Dieldrin | | | | | | |
| pH 10 | 0.084 | 0.080 | 0.055 | 0.074 | 0.050 | 0.060 |
| pH 7 | 0.107 | 0.102 | 0.083 | 0.073 | 0.080 | 0.064 |
| pH 4 | 0.157 | 0.135 | 0.120 | 0.125 | 0.104 | 0.092 |

[a] Upper value is total DOC in vial in µg. Lower value is DOC concentration in mg/l.

# TABLE XXII

## LOG $K'_{soc}$ FOR DDT IN THE PRESENCE OF HUMIC ACID

| Soil<br>and pH | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| | 0<br>0 | 29.05<br>0.83 | 58.10<br>1.66 | 145.25<br>4.15 | 290.50<br>8.30 | 435.75<br>12.45 |
| MA Soil | | | | | | |
| pH 10 | 4.668 | 4.661 | 4.707 | 4.757 | 4.605 | 4.481 |
| pH 7 | 4.475 | 4.972 | 4.905 | 4.848 | 4.719 | 4.650 |
| pH 4 | 4.149 | 5.002 | 4.849 | 4.624 | 4.577 | 4.537 |
| MB Soil | | | | | | |
| pH 10 | 4.563 | 4.413 | 4.468 | 4.389 | 4.422 | 4.320 |
| pH 7 | 4.271 | 4.549 | 4.736 | 4.603 | 4.487 | 4.422 |
| pH 4 | 4.385 | 4.986 | 4.756 | 4.639 | 4.548 | 4.387 |
| NB Soil | | | | | | |
| pH 10 | 4.594 | 4.466 | 4.476 | 4.335 | 4.295 | 4.241 |
| pH 7 | 4.130 | 4.521 | 4.697 | 4.500 | 4.400 | 4.410 |
| pH 4 | 4.299 | 4.800 | 4.627 | 4.402 | 4.184 | 4.051 |

[a]Upper value is total DOC in vial in µg. Lower value is DOC concentration in mg/l.

## TABLE XXIII

## LOG $K'_{soc}$ FOR DDT IN THE PRESENCE OF FULVIC ACID

| | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| Soil<br>and pH | 0<br>0 | 27.54<br>0.88 | 55.09<br>1.57 | 137.72<br>3.93 | 275.44<br>7.86 | 413.16<br>11.79 |
| <u>MA Soil</u> | | | | | | |
| pH 10 | 4.972 | 4.976 | 4.982 | 5.059 | 4.978 | 5.011 |
| pH 7 | 5.182 | 5.136 | 5.216 | 5.265 | 5.279 | 5.259 |
| pH 4 | 5.120 | 5.132 | 5.169 | 5.119 | 5.089 | 5.150 |
| <u>MB Soil</u> | | | | | | |
| pH 10 | 5.001 | 4.982 | 4.890 | 5.037 | 4.851 | 4.869 |
| pH 7 | 5.076 | 5.028 | 5.097 | 4.932 | 4.974 | 4.936 |
| pH 4 | 4.873 | 4.976 | 4.966 | 5.036 | 5.008 | 4.987 |
| <u>NB Soil</u> | | | | | | |
| pH 10 | 4.812 | 4.890 | 4.793 | 4.909 | 4.894 | 4.799 |
| pH 7 | 4.847 | 4.868 | 4.853 | 4.859 | 4.843 | 4.938 |
| pH 4 | 4.909 | 4.903 | 4.850 | 4.843 | 4.899 | 4.989 |

[a] Upper value is total DOC in vial in μg. Lower value is DOC concentration in mg/l.

# TABLE XXIV

## LOG $K'_{soc}$ FOR DDD IN THE PRESENCE OF HUMIC ACID

| Soil<br>and pH | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| | 0<br>0 | 24.90<br>0.83 | 49.80<br>1.66 | 124.50<br>4.15 | 249.00<br>8.30 | 373.50<br>12.45 |
| <u>MA Soil</u> | | | | | | |
| pH 10 | 4.238 | 4.780 | 4.736 | 4.626 | 4.623 | 4.532 |
| pH 7 | 4.445 | 4.749 | 4.731 | 4.602 | 4.567 | 4.497 |
| pH 4 | 4.568 | 4.963 | 4.869 | 4.734 | 4.587 | 4.433 |
| <u>MB Soil</u> | | | | | | |
| pH 10 | 3.948 | 4.424 | 4.389 | 4.340 | 4.320 | 4.276 |
| pH 7 | 4.070 | 4.379 | 4.392 | 4.277 | 4.265 | 4.222 |
| pH 4 | 4.076 | 4.755 | 4.761 | 4.556 | 4.409 | 4.250 |
| <u>NB Soil</u> | | | | | | |
| pH 10 | 3.830 | 4.379 | 4.391 | 4.326 | 4.285 | 4.264 |
| pH 7 | 4.109 | 4.457 | 4.416 | 4.264 | 4.287 | 4.204 |
| pH 4 | 4.058 | 4.654 | 4.557 | 4.486 | 4.292 | 4.189 |

[a] Upper value is total DOC in vial in µg. Lower value is DOC concentration in mg/l.

# TABLE XXV

## LOG $K'_{soc}$ FOR DDD IN THE PRESENCE OF FULVIC ACID

| Soil and pH | DOC in Vials[a]<br>0<br>0 | <br>25.04<br>0.84 | <br>47.58<br>1.59 | <br>117.69<br>3.92 | <br>235.38<br>7.84 | <br>353.06<br>11.75 |
|---|---|---|---|---|---|---|
| MA Soil | | | | | | |
| pH 10 | 4.154 | 4.202 | 4.218 | 4.107 | 4.145 | 4.102 |
| pH 7 | 4.602 | 4.654 | 4.789 | 4.810 | 4.780 | 4.763 |
| pH 4 | 4.339 | 4.381 | 4.461 | 4.497 | 4.537 | 4.583 |
| MB Soil | | | | | | |
| pH 10 | 3.631 | 3.730 | 3.801 | 3.616 | 3.720 | 3.581 |
| pH 7 | 4.199 | 4.180 | 4.376 | 4.348 | 4.300 | 4.326 |
| pH 4 | 3.899 | 3.956 | 4.111 | 4.108 | 4.133 | 4.189 |
| NB Soil | | | | | | |
| pH 10 | 3.695 | 3.747 | 3.844 | 3.749 | 3.734 | 3.641 |
| pH 7 | 4.298 | 4.325 | 4.478 | 4.442 | 4.417 | 4.363 |
| pH 4 | 3.980 | 3.998 | 4.106 | 4.123 | 4.197 | 4.243 |

[a] Upper value is total DOC in vial in μg. Lower value is DOC concentration in mg/l.

## TABLE XXVI

## LOG $K'_{SOC}$ FOR DIELDRIN IN THE PRESENCE OF HUMIC ACID

| Soil and pH | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| | 0<br>0 | 29.05<br>0.83 | 58.10<br>1.66 | 145.25<br>4.15 | 290.50<br>8.30 | 435.75<br>12.45 |
| <u>MA Soil</u> | | | | | | |
| pH 10 | 3.960 | 3.930 | 4.021 | 4.072 | 4.043 | 3.978 |
| pH 7 | 3.982 | 4.058 | 4.062 | 4.136 | 4.096 | 4.078 |
| pH 4 | 4.132 | 4.179 | 4.193 | 4.100 | 3.961 | 3.860 |
| <u>MB Soil</u> | | | | | | |
| pH 10 | 3.502 | 3.479 | 3.671 | 3.744 | 3.723 | 3.649 |
| pH 7 | 3.557 | 3.735 | 3.633 | 3.790 | 3.765 | 3.776 |
| pH 4 | 3.732 | 3.790 | 3.823 | 3.741 | 3.650 | 3.664 |
| <u>NB Soil</u> | | | | | | |
| pH 10 | 3.635 | 3.502 | 3.615 | 3.696 | 3.681 | 3.567 |
| pH 7 | 3.617 | 3.712 | 3.717 | 3.827 | 3.789 | 3.798 |
| pH 4 | 3.739 | 3.743 | 3.764 | 3.693 | 3.616 | 3.632 |

[a] Upper value is total DOC in vial in µg. Lower value is DOC concentration in mg/l.

## TABLE XXVII

## LOG $K'_{SOC}$ FOR DIELDRIN IN THE PRESENCE OF FULVIC ACID

| | DOC in Vials[a] | | | | | |
|---|---|---|---|---|---|---|
| Soil and pH | 0 | 29.05 | 58.10 | 145.25 | 290.50 | 435.75 |
| | 0 | 0.83 | 1.66 | 4.15 | 8.30 | 12.45 |
| MA Soil | | | | | | |
| pH 10 | 4.031 | 4.027 | 4.058 | 4.043 | 4.079 | 4.067 |
| pH 7 | 4.113 | 4.131 | 4.169 | 4.180 | 4.159 | 4.267 |
| pH 4 | 4.133 | 4.148 | 4.122 | 4.154 | 4.192 | 4.181 |
| MB Soil | | | | | | |
| pH 10 | 3.793 | 3.784 | 3.789 | 3.737 | 3.753 | 3.743 |
| pH 7 | 3.724 | 3.727 | 3.766 | 3.766 | 3.767 | 3.762 |
| pH 4 | 3.768 | 3.824 | 3.837 | 3.856 | 3.836 | 3.853 |
| NB Soil | | | | | | |
| pH 10 | 3.620 | 3.655 | 3.657 | 3.637 | 3.669 | 3.669 |
| pH 7 | 3.819 | 3.754 | 3.797 | 3.779 | 3.767 | 3.771 |
| pH 4 | 3.806 | 3.829 | 3.855 | 3.852 | 3.812 | 3.862 |

[a] Upper value is total DOC in vial in µg. Lower value is DOC concentration in mg/l.

# VITA

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Candidate for the Degree of

Doctor of Science

Thesis: THE SORPTION OF HYDROPHOBIC ORGANIC COMPOUNDS IN THE PRESENCE OF ENVIRONMENTAL CONCENTRATIONS OF DISSOLVED HUMIC AND FULVIC ACIDS AT VARIABLE pH VALUES

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