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DISSERTATION

EVALUATION OF THE POLYMER THEORY APPLICABILITY IN DESCRIBING SORPTION OF 1,2-DICHLOROBENZENE ONTO A PEAT SOIL AND MODEL SORBENTS

Submitted by

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for the degree of Doctor of Philosophy

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY SAMSURI A. WAHID ENTITLED EVALUATION OF THE POLYMER THEORY APPLICABILITY IN DESCRIBING 1,2-DICHLOROBENZENE SORPTION ONTO A PEAT SOIL AND MODEL SORBENTS BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

EVALUATION OF THE POLYMER THEORY APPLICABILITY IN DESCRIBING 1,2-DICHLOROBENZENE SORPTION ONTO A PEAT SOIL AND MODEL SORBENTS

Sorption of hydrophobic organic compounds (HOCs) onto soil organic matter (OM) has been regarded as a partitioning process. Partitioning is characterized as having linear sorption isotherms, noncompetitive sorption, and no desorption hysterisis. However, many studies of HOC sorption onto soil OM have yielded results that are inconsistent with partitioning theory. An alternative that has received much attention is the "glassy versus rubbery polymer" theory.

According to the polymer theory, sorption occurs at two distinct regions of the soil OM, amorphous and condensed regions. The amorphous region is analogous to a rubbery polymer, and the condensed region is analogous to a glassy polymer. Diffusion of HOCs into the amorphous region is fast; with linear sorption isotherms and noncompetitive sorption. On the other hand, diffusion of HOCs onto the condensed region is slow with linear sorption isotherms and competitive sorption.

The present study was conducted to evaluate the applicability of this theory in describing 1,2-dichlorobenzene (DCB) sorption onto a Pahokee peat soil as well as two model sorbents, cellulose and poly-vinyl chloride (PVC). Results with these two sorbents were used to gain insight into the mechanism of DCB sorption onto soil OM. Cellulose (a rubbery polymer) was selected to model the amorphous regions and PVC (a glassy

polymer) to model the condensed regions. The Freundlich model was used to fit the sorption data, and Freundlich constants (K_f) and n coefficients of the sorption isotherms were compared. Experiments were designed to measure DCB sorption and desorption with respect to (1) equilibration time; (2) effect of naphthalene as a possible competitor for sorption sites; (3) effect of naphthalene equilibration time on its competition for sorption; and (4) effect of ionic strength.

The polymer theory could not adequately describe the sorption and desorption of DCB with the peat soil. The sorption isotherms were highly linear, but they were unaffected by equilibration time, which is inconsistent with the polymer theory. Except at an initial DCB concentration of 5 μg/mL, desorption of DCB from the peat soil did not vary significantly with equilibration time and initial DCB concentration, which could not be explained by the polymer theory. Pre-equilibration of the peat soil with naphthalene significantly increased DCB sorption, which is also not accounted for by the polymer theory. The lack of effect of ionic strength on DCB sorption by the peat soil suggests that diffusion, as proposed by the polymer theory, was not the dominant mechanism for the sorption process. However, the polymer theory was successful in predicting the effect of naphthalene equilibration time on naphthalene competition with DCB for sorption sites.

The polymer theory was unable to describe DCB sorption with cellulose as the sorption isotherms were concentration dependent and affected by equilibration time. The polymer theory was also unable to explain desorption of DCB from cellulose as affected by equilibration time and initial DCB concentration, the increase in DCB sorption by cellulose pre-equilibrated with naphthalene, and the effect of naphthalene equilibration time on DCB sorption.

The polymer theory was most successful in describing sorption and desorption of DCB with PVC. As predicted by the theory, DCB sorption onto PVC was nonlinear and time-dependent. The theory was also able to explain the effect of naphthalene equilibration time on its competition with DCB for sorption sites.

Both partitioning and diffusion mechanisms appear to have been important in HOC sorption onto Pahokee peat. The high linearity of sorption isotherms for DCB with Pahokee peat is consistent with the partitioning, which is also supported by the nonlinear sorption isotherms for DCB with cellulose. The diffusion mechanism of the polymer theory would explain the reduction in DCB sorption with longer naphthalene equilibration time.

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CHAPTER I

INTRODUCTION AND PROBLEM STATEMENT

Organic compounds can persist in soils and sediments for a long time even for chemicals that have high intrinsic rates of volatilization and biodegradation (Pignatello, 1990). It is generally believed that sorption of these compounds to soil OM is the main reason for their persistence. Sorption is the underlying mechanism that controls the fate of organic compounds in the environment (Senesi and Miano, 1995; Pignatello and Xing, 1996). Sorption refers to the reversible retention of solutes by sorbents without distinction to the processes involved (Chiou, 1989; Koskinen and Harper, 1990; Scow, 1993). Sorption can occur by physical adsorption on surfaces or by partitioning (dissolution) into a phase such as soil OM (Pignatello and Xing, 1996). Sorption may occur by van der Waals-London interactions, charge transfer (hydrogen bonding), ligand exchange, and ion-exchange reactions (Scow, 1993). Sorption of polar, ionic compounds is well understood because it can be explained by the functional groups of the compounds. In most cases, these functional groups govern the types of attraction between these compounds and the sorbents. However, sorption of nonpolar, nonionic, hydrophobic organic compounds (HOCs) is not well understood.

Sorption interactions of HOCs with soil OM have been widely investigated. HOCs include the aromatic compounds found naturally in petroleum products as well as chemicals produced commercially such as polychlorinated biphenyls and some

pesticides. Sorption controls movement, transport, bioavailability and biodegradation of the HOCs. Consequently, it is often included in modeling fate, transport, risk assessment, clean-up, and biodegradation of HOCs. Therefore, an understanding of the sorption process is crucial to the success of the models and their implementation for the remediation of polluted sites (Pignatello and Xing, 1996).

Studies have shown that OM of soils and sediments is the most important sorbent of the HOCs (Brusseau, 1989; Chiou, 1989; Grathwohl, 1990; Deschauer and Kogel-Knabler, 1992; Herbert et al., 1993; Kopinke et al., 1995; Govi et al., 1996; Luthy et al., 1997). The sequestration of HOCs to soil OM is not well understood (Weber et al., 1992). There are no direct observational data revealing the molecular scale at which HOCs sorb. Macroscopic observations are used to make inferences about the sorption mechanisms of HOCs. A more sophisticated understanding of the mechanisms at the microscale is needed, and this can be achieved by the synthesis of knowledge obtained from the study of simpler systems (Luthy et al., 1997).

Sorption of HOCs to soil OM was first regarded as a partitioning process because the observed sorption isotherms were shown to be linear (Karickhoff, 1981; Chiou, 1989; Rutherford and Chiou, 1992). However, in other studies the linearity of sorption isotherms of HOCs with soil OM as expected for partitioning did not occur (for examples Brusseau and Rao, 1989; Nkedi-Kizza et al., 1989; Farrel and Reinhard; 1994; Schrap et al., 1994; Huang et al., 1997). In recent years, researchers have applied the concept of rubbery and glassy polymers, borrowed from the field of polymer science, to soil OM. This concept was used to explain isotherm nonlinearity and other deviations from the partitioning assumptions (Carroll et al., 1994; Young and Weber, 1995, Pignatello and

Xing, 1996, Xing et al., 1996; Xing and Pignatello, 1997). However, there is very little research to validate the applicability of this concept to explain the mechanism of HOC sorption to OM. The objective of this study was to test the validity of the "rubbery" versus "glassy" concept as applied to the sorption on HOC onto soil OM.

RESEARCH OBJECTIVES

This study was conducted to test the applicability of the rubbery versus glassy polymer theory in describing 1,2-dichlorobenzene (DCB) sorption and desorption data with Pahokee peat, cellulose (a rubbery polymer) and poly-vinyl chloride (PVC) (a glassy polymer). Experiments were conducted to:

1. Determine the effect of equilibration time on DCB sorption.
2. Determine the effect of pre-treating (aging) the sorbents with naphthalene on the sorption of DCB.
3. Determine the effect of sorbate competition on DCB sorption.
4. Determine the effect of ionic strength on the sorption of DCB.
5. Make inferences about the mechanism(s) responsible for the sorption of HOCs based on data from the sorption studies described above.

HYPOTHESES

The general hypothesis of this study is that differences in sorption isotherms of HOCs with different sorbents can be used to make inferences about the mechanism(s) of the sorption process and the conformational structure of the sorbents. Based on this hypothesis, the following specific hypotheses will be tested:

1. Cellulose, which is a rubbery polymer, will exhibit linear sorption isotherms whereas PVC, which is a glassy polymer, will exhibit sorption isotherms similar to Pahokee peat.
2. Sorption affinities of DCB will increase with time for Pahokee peat and PVC but not with cellulose.
3. Desorption of DCB from PVC and Pahokee peat will be less than for cellulose.
4. DCB and naphthalene will exhibit competition for sorption sites on Pahokee peat and PVC, but not for cellulose.
5. Sorption of DCB to Pahokee peat and PVC will be greater for sorbents pre-treated with naphthalene for 1 d as compared to systems with these sorbents that have been previously treated with naphthalene for 100 d.
6. Sorption of DCB to Pahokee peat at a lower $CaCl_2$ concentration will be higher than at a higher concentration.

CHAPTER II

LITERATURE REVIEW

Definitions of terms

There are many definitions of the term sorption in the literature because researchers have defined sorption to fit the context of their studies. Therefore, the use of the term is sometimes confusing because there is no general agreement on its definition among researchers, including soil scientists. Chiou (1989) defined sorption broadly, as removal of solutes (sorbates) by sorbents without any reference to a specific mechanism. Hasset and Banwart (1989), and later the Soil Science Society of America (1997), defined sorption as the removal of an ion or molecule from solution by adsorption and absorption when the exact nature of the process is unknown. The term adsorption refers to retention of atoms, molecules, or ions on the surfaces of solids by chemical or physical binding (Chiou, 1989; Soil Science Society of America, 1997). Absorption is used to describe a process whereby a component is transferred from the bulk state of one phase into the bulk state of another phase (Hasset and Banwart, 1989). According to this definition, once a component is absorbed, it will become a part of the new phase. Consequently, all absorption processes are considered irreversible.

There is a major disadvantage to considering adsorption and absorption as the only processes contributing to sorption of HOCs onto soil OM. As pointed out by Hasset and Banwart (1989), sorption occurs when the free energy of sorption is negative.

Enthalpy and the entropy terms influence the free energy of sorption. Enthalpy is a function of the difference in the bonding strength between the surface of the sorbate and the sorbent. Entropy, on the other hand, is related to the increase or decrease in the order of the system upon sorption. The adsorption and absorption terms only include processes that influence the strength of the sorbate/sorbent bonds, i.e., the enthalpy term. The processes that can be listed under the absorption and adsorption terms are London-van der Waals, coulombic-electrostatic, charge transfer, π bonds, hydrogen bonding, ligand exchange, dipole-dipole or orientation energy, dipole-induced dipole, and chemisorption. Therefore, by including only the adsorption and absorption in defining the sorption, we leave out the contribution of forces related to the entropy. The main process in the entropy-related forces is partitioning, which is also known as dissolution. McBride (1994) defined partitioning, also termed hydrophobic forces, as the enhanced attraction between the sorbent and the sorbate in a solvent because the solvent-sorbate attractive interaction is weaker than the solvent-solvent attractive interaction. Partitioning is the driving force for sorption in soils if an organic sorbate has less affinity for water than water for itself (McBride, 1994). Organic compounds that are slightly polar or nonpolar (i.e., have almost zero dipole moment) have low affinity for water, and therefore, they are termed hydrophobic organic compounds (HOCs).

The term partitioning denotes the removal of organic chemicals from solution by which the sorbed organic chemical permeates into the network of an organic medium by forces common to solution such as van der Waals and hydrophobic forces (Chiou, 1989). Partitioning is analogous to the extraction of an organic compound from water into an organic phase. Water molecules are not attracted to large nonpolar molecules and

therefore cannot orient their polar OH bonds in ways that are compatible with the normal structure of liquid water (Sposito, 1989). As a result, the nonpolar organic compounds have low water solubility, and the disruption of the water structure is energetically unfavorable (McBride, 1994). Consequently, nonpolar organic compounds are forced out of the solution and will sorb to weakly hydrating surfaces such as soil OM. Repulsion of the nonpolar organic compounds from water molecules is the driving force for the sorption of the HOCs. Partitioning is distinguished from adsorption by retention of sorbate within the internal spaces or voids of the sorbent material, whereas with adsorption, the sorbate only occupies the surface of the adsorbate (Stevenson, 1994).

In this study, the term sorption will refer to all reversible processes involving the removal of organic chemicals from solution and will not include any irreversible process. Therefore, it will not include the formation of bound residues or chemisorption (specific binding) which are both irreversible processes. With the current concept of humic substances as macromolecular, gel-like, polymeric materials (Wershaw, 1993; Stevenson, 1994), it is difficult to picture sorption of nonionic organic chemicals to humic materials as just a surface phenomenon.

Partitioning of hydrophobic organic compounds by organic sorbents

Traditionally, sorption of nonionic organic chemicals such as the HOCs to soil OM has been treated as a partition phenomenon, especially at low concentrations (Chiou et al., 1979; Karickhoff et al., 1979; Karickhoff, 1981; Chiou, 1989; Rutherford and Chiou, 1992). Chiou et al. (1983) adapted the Flory-Huggins theory to analyze the sorption of nonionic organic compounds in soil by considering the major components of soil humus to be amorphous polymeric substances. The theory was developed to describe

the thermodynamics of dilute solutions of small solute molecules in large molecular weight polymers. They found that solute insolubility in water was the primary factor affecting the soil OM-water coefficients (K_{om}). Sorption of HOCs to OM sorbents is expected to be linear (concentration-independent) and noncompetitive. Noncompetitive means that the sorption of a HOC is not affected by other HOCs in the same solution, and consequently the HOCs do not compete for sorption sites. Arguments in support of partition mechanisms have been provided by Chiou (1989) as follows:

1. High linearity of the sorption isotherm;
2. Inverse linear relationship between sorption (partition) coefficient (K_{om} or K_{ow}) and solute water solubility (S_w);
3. Generally low exothermic heat from solutes in solvent-water and soil-water equilibria; and
4. Absence of sorptive competition between solutes as typical of adsorption on surfaces.

Rutherford and Chiou (1992) determined the sorption of benzene, trichloroethylene, and carbon tetrachloride at room temperature from aqueous solution and from vapor on two high-organic content soils. Solute sorption from water exhibited linear isotherms over a wide range of concentrations. They suggested that simple partitioning involving soil OM was the dominant process in the uptake of the solutes. In another study, Rutherford et al. (1992) determined sorption of benzene and carbon tetrachloride from water at room temperature on three high-organic content soils and cellulose, to evaluate the effect of sorbent polarity on the solute partition coefficients. The isotherms they reported were highly linear for both solutes on all the OM samples,

which is consistent with a simple partition model. Linear sorption isotherms also have been reported by Chiou and Kile (1994) for some HOCs including *n*-hexane, carbon tetrachloride, benzene, and trichloroethylene on high-organic content peat.

Limitations of the partitioning model

The simple partitioning mechanism concept assumes that soil OM acts as a solvent in which hydrophobic compounds partition. The concentration in the aqueous phase is related to the sorbed phase concentration by an equilibrium isotherm. A simple linear model is used to approximate sorption data:

$$C_s = K_D C_w \qquad (1)$$

where C_s is the mass of solute sorbed per unit mass of solid at equilibrium with a solution solute concentration (C_w), and K_D is the distribution coefficient. The equation is modified to include terms that include the organic carbon mass fraction (f_{oc}) and organic carbon-normalized partition coefficient (K_{oc}) to model sorption of non-polar organic compounds to organic sorbents because soil OM is the principal sorbent for organic compounds. The term K_D, K_{oc}, and f_{oc} are related by the following equation:

$$K_{oc} = K_D / f_{oc} \qquad (2)$$

Equation (1) only applies when there is a linear relationship between concentrations in the sorbed phase and the aqueous phase. However, many studies have shown that sorption between nonionic organic chemicals to soil OM exhibits nonlinear sorption and desorption behavior (Brusseau and Rao, 1989; Nkedi-Kizza et al., 1989; Farrell and Reinhard, 1994; Schrap et al., 1994; Spurlock and Biggar, 1994; McGinley et al., 1996; Aroca et al., 1996; Aochi and Farmer, 1997; Huang et al., 1997). The nonlinear

sorption and desorption relationship may result from biphasic sorption and desorption rates. The sorption and desorption usually proceeds with an initial "fast" rate followed with a subsequent "slow" rate. Spurlock and Biggar (1994) have pointed out that the abundance of data showing the nonlinearity of sorption and desorption isotherms indicates that isotherm linearity is not a prerequisite for partitioning. Nonlinear sorption can occur whenever chemical concentrations are high enough that the activity coefficient is not constant or sorption mechanisms other than simple hydrophobic sorption are operating (Brusseau and Rao, 1989). Given the abundance of data showing nonlinear sorption isotherms for nonionic chemicals and organic sorbents, we can conclude that the partitioning mechanism involves mechanisms other than simple hydrophobic partitioning between aqueous and organic phases.

In the literature, the terms partition and partitioning have been used to include both the simple hydrophobic mechanism and mechanisms other than surface sorption. One such mechanism is diffusion in internal voids or micropores, which will be discussed in more detail in a later section.

In addition to nonlinearity, several researchers have reported desorption isotherms that do not follow sorption isotherms, a condition known as hysteresis (Pignatello, 1990; Pignatello et al., 1993; Hunter et al., 1996; Aochi and Farmer, 1997; Huang and Weber, 1997). Kinetically, hysteresis means that sorption is faster than desorption (Pignatello, 1989; Brusseau and Rao, 1989; Pignatello, 1991). Hysteresis results from slow release of HOCs from sorption sites. The effect is more pronounced with longer equilibration time. Pignatello and Huang (1991) studied desorption of several pesticides from soils and sediment materials and found desorption occurred at two different rates. They termed the

fraction that desorbed at the faster rate as the fast fraction and the other fraction as the slow fraction. They also found that the slow fraction of some pesticides increased with contact time in the environment.

Aochi and Farmer (1997) studied sorption/desorption behavior of 1,2-dichloroethane and found two rates of sorption of 1,2-dichloroethane on humic surfaces. A study by Pignatello (1990) indicated that even compounds such as halogenated alkanes and alkenes, which are normally regarded as labile in the environment by their volatility and weak equilibrium sorption tendencies, can generate kinetically slow sorbed residues. He suggested that this behavior is probably typical of nonpolar organics. Xing and Pignatello (1997) summarized the following evidence, which suggests that the partition model is too simplistic to be used for describing the sorption of HOCs to OM sorbents:

1. Nonlinear isotherms, which suggest the concentration dependency of "dissolved" compounds inside an OM sorbent;
2. Competition in multisolute systems, implying site specificity or size/structure factors;
3. Concentration-dependent heat of sorption, indicating that the sorption potential is not constant; and
4. Evidence that OM sorbents possess an internal surface (de Jonge and Mittelmeijer-Hazeleger, 1996).

Compounds that are sequestered by the sorbents and slowly desorbed are termed "aged- compounds" and should not be confused with bound residues. Bound residues are those residual fractions that can only be extracted by procedures that will appreciably alter the nature of those residues; these molecules are changed in some manner and are

usually converted to the original compound by vigorous hydrolysis. In contrast, aged compounds can be extracted from soil by organic solvents often under vigorous conditions (Alexander, 1995). Increased contact time between organic chemicals and organic sorbents leads to stronger sorption (Huang and Weber, 1997) and greater resistance to desorption (Pignatello et al., 1993).

Another assumption of equation (1) is that the system in which sorption or desorption processes take place is in equilibrium at the time the data were taken. Most sorption and desorption studies are conducted using a short equilibration time, usually less than a week. Sorption data from various studies suggest that in some cases, equilibrium is only achieved after a long equilibration period (Brusseau, 1989; Nkedi-Kizza et al., 1989; Brusseau et al., 1991; Pedit and Miller, 1996; Pignatello and Xing, 1996; Weber and Huang, 1996; Xing and Pignatello, 1996). Sorption that occurs slowly, rate-limited, and highly time-dependent is termed nonequilibrium sorption.

In this study, the term nonequilibrium sorption/desorption will be used to include the nonlinear isotherm, hysteresis, and slow sorption/desorption conditions. Recent review articles have contained discussions of several processes that may be responsible for the nonlinear and nonequilibrium sorption and desorption of organic compounds (Pignatello and Xing, 1996; Luthy et al., 1997). We use kinetic data to make inferences about the possible mechanisms responsible for the nonequilibrium sorption/desorption.

Models of humus structure

Humic substances are collectively called humus. They consist of a physically and chemically heterogeneous mixture of relatively high molecular weight organic

compounds of mixed aliphatic and aromatic nature. Humus is formed by synthesis reactions (humification) during the decay process and transformations of biomolecules that originate from dead or living organisms and microbial activity (Stevenson, 1982). It may be pictured as a three-dimensional network of randomly oriented polymer chains and as having a relatively open, flexible structure perforated by voids (Schnitzer, 1978). Humus is not a true polymer because it does not have repeating units. Humus substances can be fractionated into several components based on their solubilities in acid and base. The most widely studied fractions of humus are humic and fulvic acids. The humic acid fraction is extracted using a mild alkali and then precipitated in dilute acid. The fulvic acid fraction, on the other hand, is soluble in both dilute alkali and dilute acid. Although humic and fulvic acids share some structural features, significant differences exist. Fulvic acids have lower molecular weights and higher O to C ratios as compared to humic acids.

Ghosh and Schnitzer (1980) indicated that both humic and fulvic acids behave like rigid "spherocolloids" at high sample concentrations, low pH, and high amount of neutral electrolytes. The humic and fulvic acids, however, are flexible linear colloids under conditions of low sample concentrations, low ionic strength, but not too low pH. The molecular shapes and conformational structures of humic substances under different conditions are discussed conceptually by Swift (1989). On the other hand, Chen and Schnitzer (1989) provided scanning electron micrographs of various humic fractions under varying conditions and found that low sample concentrations, neutral pH, and low ionic strength, the humus components exist like flexible linear colloids.

Maurice and Namjesnik-Dejanovic (1999) used nanometer-scale atomic force microscopy (AFM) to view physical shapes and forms of humic substances sorbed to the basal-plane surface of mica. The images showed neither spherical nor open linear structures of humic substances as predicted by Gosh and Schnitzer (1980) but rather ring structures. They argued that many polymeric materials have ring structures, which may assume rod-like aggregates when the two ends bend or join together. Joining of both ends of the rodlike polymeric aggregates eliminates the energetically unfavorable regions.

Wershaw (1993) proposed a different model for humus. According to this model, humus is viewed as having separate hydrophobic and hydrophilic parts (amphophile), and given the right environment, the humus molecules can form pseudomicelles. Humus is also viewed as consisting of ordered aggregates of amphipiles composed mainly of relatively unaltered plant polymer segments attached to carboxylic acid groups. These aggregates arrange themselves in such a way that the hydrophobic parts of the molecules are in the interiors, and the hydrophilic parts of the molecules make up the exterior surfaces. Ordered aggregates of humus in soils and sediments exist as bilayer membranes coating mineral grains and as micelles in solution. The hydrophobic interior regions of the humic membrane and the micelles are envisioned to possess some freedom of motion, i.e., to be liquid-like. The exterior, on the other hand, is highly charged.

Specific sorption

Specific sorption and molecular diffusion are the potential causes of slow sorption in soil (Pignatello and Xing, 1996). Specific sorption, which is also known as

chemisorption, is a process whereby sorptive bonds are formed between the sorbate and the sorbent. The formation or breaking of these bonds requires high energies of activation. Although specific sorption (chemisorption) has been shown to be an important mechanism for sorption of certain organic chemicals to organic materials, a study by Brusseau et al. (1991) showed that the mechanism is not important for sorption of HOCs. They designed experiments to identify the process responsible for the nonequilibrium sorption of HOCs by soils and river sediments. Results from the experiments were compared to data obtained from systems wherein rate-limited sorption was known to be caused by specific sorbate/sorbent interactions. They concluded that specific sorbate-sorbent interactions did not contribute to rate-limited sorption of HOC by natural sorbents.

Diffusion mechanisms

Based on the structures proposed for humus, there are two possible diffusion mechanisms for the sequestration (entrapment) of HOCs in soil OM. The first is diffusion of the HOCs into the micropores or the structural voids of the humus, a mechanism termed intraorganic matter diffusion (IOMD). The second is diffusion into the hydrophobic interior of the pseudomicelle structure of the humus. Both mechanisms have been suggested by as being responsible for the sequestration of HOCs by OM. However, the former is more extensively studied and is generally assumed to be the mechanism responsible for nonequilibrium sorption and desorption conditions. Chang et al. (1997) studied the sorption kinetics for the volatile organic compounds toluene, *n*-hexane, and acetone when in contact with dry, pressed humic acid disks by monitoring

the weight change of the sorbent with a microbalance. They found that the time scale for these compounds to penetrate the humic acid disks was approximately several seconds estimated by the observed diffusivity. They concluded that it was unlikely that diffusion through the humic acid disks was the rate limiting slow process. However, the humic acid disks were not humidified. As a result, there was a lack of hydrophobic repulsion forces. It may not be appropriate to extrapolate their results to aqueous systems where sorbates partition and travel through more tortuous path in the humic acid structure. Also, humic acid swells in an aqueous system, creating more micropores in its structure.

Humus structure in relation to sorption

Engebretson and Wandruszka (1994) investigated structure of five dissolved humic acids by monitoring the fluorescence behavior of a pyrene probe added to the solutions. In a humic acid solution of low ionic strength, hydrophobic domains are loosely constructed and relatively accessible by both the solvent and solvent-borne quenchers. An HOC associated with such regions is subject to normal diffusive motion that brings it into frequent contact with quenchers located along the periphery of the cavity. At high ionic strength, hydrophobic colloids are formed. Temperature has the same effect as ionic strength on the humic acid microorganization. But these authors warned that their observations are not universally applicable to all humic acids because of differences in humus aromaticity and aliphatic contents. Engebretson et al. (1996) measured association indices of humic acid with nonpolar compounds based on the fluorescence anisotropy of a diphenyloxazole probe. The variations of the indices provided support for the formation of humic pseudomicelles that can sequester

hydrophobic species from the solution environment. The structure of humic acid in solution depended on its molecular size and tendency to expand.

Chien et al. (1997) also suggested the applicability of pseudomicellar theory to explain the sorption of HOCs to humic substances. They examined the effects of hydrophilic and hydrophobic paramagnetic probes on the nuclear magnetic relaxation of atrazine in 10% humic acid solution. They found that a hydrophobic neutral paramagnetic probe caused rapid paramagnetic relaxation in atrazine solubilized by the humic acid solution, while no paramagnetic relaxation was induced by a hydrophilic paramagnetic probe. Atrazine that was solubilized by the humic acid solutions occupied a hydrophobic domain, which was only accessible to neutral hydrophobic molecules. Therefore, their study confirmed the existence of a hydrophobic domain of organic substances.

Intraorganic matter diffusion theory

The mechanism wherein HOCs are sequestered into micropores or structural voids of OM is termed intraorganic matter diffusion (IOMD), sometimes called a "hole-filling" mechanism. Based on studies of the surface area of three soil OM samples using CO_2 and N_2 gas adsorption, de Jonge and Mittelmeijer-Hazeleger (1996) reported that soil OM is a microporous material with a high surface area. Their study also suggested that the microporous structure is not strongly affected by hydration of the samples. They proposed "configurational diffusion" as the primary transport mechanism of nonionic organic contaminants in soil OM micropores based on the pore dimensions. Numerous other authors have also suggested that HOCs compounds are sequestered in the

micropores or structural voids of the humus materials (Nkedi-Kizza, 1989; Brusseau et al., 1991; Schlautman and Morgan, 1993; Hu and Brusseau, 1995; Weber and Huang, 1996; Xing et al., 1996; Aochi and Farmer, 1997). Sorbing materials are subject to diffusive constraints throughout the entire time course of sorption and desorption because of the porous nature of sorbing particles.

Support for IOMD is as follows:

1. Biphasic sorption and desorption isotherms are observed between HOCs and soil OM (Schrap et al., 1994; Aochi and Farmer, 1997).
2. Desorption of organic compounds occurs slowly depending on their time in the environment (Alexander, 1995; Loehr and Weber, 1996).
3. Organic cosolvents increase the rates of sorption and desorption because they cause the soil OM to swell (Brusseau et al., 1991; Xing et al., 1996).
4. Competitive sorption occurs between solute pairs (Xing and Pignatello, 1997).
5. Higher temperatures increase the linearity of sorption and desorption isotherm because organic polymers swell as temperature increases (Carroll et al., 1994; Young and Weber, 1995; Xing and Pignatello, 1997; Lebouf and Weber, 1997).
6. Sorption capacity of organic compounds depends on the dimensional structure of organic sorbents (Young and Weber, 1995; Chin et al., 1997; Iglesias-Jimenez et al., 1997; Xing and Pignatello, 1997).
7. Size and structure of organic compounds influence their sorption to OM sorbents (Hu et al., 1995; Chiou et al., 1998).

8. Model substrates (e.g., cellulose, lignin, and chitin) give a linear correlation between polarity index (PI), which is total O content plus total N content divided by total C content, and sorption but no correlation between sorption and PI for OM sorbents (Stuer-Lauridsen and Pedersen, 1997).
9. For soil treated to remove OM, symmetrical breakthrough curves are found for all displaced solutes (Nkedi-Kizza et al., 1989).
10. Gas sorption on dry OM sorbents reveals internal micropores sites accessible only by diffusion of the gas through the solid phase (de Jonge and Mittelmeijer-Hazeleger, 1996).

Factors affecting intraorganic matter diffusion of HOCs

Although there is much evidence pointing to IOMD as the mechanism causing nonequilibrium sorption and desorption phenomena, the process is poorly understood. IOMD depends on several factors; some are well characterized, while most of them are not. Some of the factors that have been investigated are as follows:

1. Polarity index (PI) (as previously defined), size, and structure of the HOCs (Rutherford et al., 1992; Chiou and Kile, 1994; Hu et al., 1995; Maxin and Kogel-Knabner, 1995; Pignatello and Xing, 1996; Torrents at al., 1997; Xing and Pignatello, 1997; Chiou et al., 1998);
2. PI, aromaticity (condensation), molecular weight and structure of the OM sorbents (Gratwohl, 1990; Chen et al., 1996; Chin et al., 1997; Huang and Weber, 1997; Iglesias-Jimenez et al., 1997; Torrents et al., 1997; Xing, 1997; Xing and Pignatello, 1997);

3. Hydration status of the OM sorbent (Graber and Borisover, 1998);
4. Temperature (Young and Weber, 1995; Xing and Pignatello, 1997; Lebouf and Weber, 1997);
5. The presence of organic cosolutes (Rao et al., 1985; Brusseau et al., 1991; Xing et al., 1996; Onken and Traina, 1997);
6. pH of the system (Schlautman and Morgan, 1993); and
7. Ionic strength (Schlautman and Morgan, 1993; Spurlock and Biggar, 1994).

There is no general consensus, however, on how each of the factors affects the diffusion of the sorbates into the sorbents.

The effect of cosolutes

The effect of cosolutes (i.e., other chemicals that are present with the principal solute in the solution mixture) on the sorption of HOCs to soil OM is one of the factors most extensively studied. Cosolutes can increase or decrease the solubility of the sorbate due to increased or decreased in hydrophobicity. If the hydrophobicity of a sorbate is reduced, the sorbate will be less favorable competing with the cosolute in sorption (Rao et al., 1985). However, the effect of cosolutes also depends on the amount of OM in the system. Onken and Traina (1997) studied the effect of a cosolute on the sorption of various nonionic organic solutes to humic acid-mineral complexes. They found that the presence of anthracene cosorbate with pyrene or naphthalene increased sorption. However, sorption enhancement diminished as the fraction of organic carbon (f_{oc}) increased. They argued that the addition of cosolutes to low f_{oc} systems aids transition from adsorption/condensation-type interactions to a partitioning-type interaction. They

also suggested that the presence of a cosolute did not effect sorption where partitioning was already the primary process. If partitioning were not occurring, the addition of cosolute reduced the surface excess of the solute by competing for adsorption sites. This competition occurred until surface organic carbon increased to a sufficient concentration to promote partitioning. An additional consideration is that cosolutes may change the conformation of the OM matrix, as the result of changes in solvent polarity (Ghosh and Schnitzer, 1980; Brusseau et al., 1991).

McGinley et al. (1993) studied sorption of the HOCs tetrachloroethylene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene onto four subsurface soils to determine the competitive effects of cosolutes. They found that the uptake of the individual HOCs from aqueous solution by the soils was reduced in the presence of the other HOCs. Because their soils were derived from sedimentary rocks, they concluded that sorption occurred by surface reactions rather than by partitioning to organic matrices. The same group then studied competitive sorption between tetrachloroethylene and 1,2,4-dichlorobenzene onto two subsurface soils (McGinley et al., 1996). With one soil, sorption isotherms of individual HOCs were nonlinear, while for the other soil the isotherms were more linear. They found that sorption of the HOCs in a binary solute system was competitive for the soil that exhibited nonlinear sorption isotherms for individual HOCs. Sorption of the HOCs in a binary solute system was additive for the soil that exhibited more linear sorption isotherms for individual HOCs. The suggested that the isotherm nonlinearity and competitive sorption occurred because a greater fraction of the sorption occurred on or within tightly ordered or condensed organic matrices rather than within more amorphous OM. The results of these two studies by the

McGinley et al. are in accordance with the polymer theory of soil OM structure, which will be discussed later in the chapter.

The effects of cosolutes on HOC sorption onto rubber and glassy polymers were studied by Xing et al. (1996). They measured the sorption of atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triaznie), prometon (2,4-*bis*-(isopropylamino)-6-methoxy-5-triazine), cyanazine (2-((4-choloro-6-ethylamino)-1,3,5-triazin-2-YL-)amino-2-methyl propanenitrile), 2-choloro-4,6-dimethoxy-s-triazine, 5-chloro-1,3,-dimethoxybenzene, and trichloroethylene onto rubbery polymers (polyethylene, cellulose, and chitin) and glassy polymer (poly(2,5-diphenyl-*p*-phenylene oxide) as a single solute or as a mixture of solutes. They found no competition between the solutes for sorption onto the rubbery polymers which is consistent with ideal partition sorption (Henry's Law). Atrazine was found to compete with its analogs for sorption sites on the glassy polymer, but weak or no competition was observed for atrazine and trichloroethylene. They concluded that sorption onto the rubbery polymers occurred through partitioning while sorption onto the glassy polymer was by both partitioning and hole filling.

Xing and Pignatello (1996) studied the competitive sorption between 1,3-dichlorobenzene or 1,4-dichlorobenzene and natural aromatic acids in soil OM and found that the acids suppressed the sorption of the HOCs. Since they used peat soil which is almost mineral free (93% OM), they concluded that competition occurred in the soil OM phase. They also concluded that the soil OM has two distinct domains onto which HOCs can sorb. Sorption occurred by partitioning (dissolution) in one domain while hole-filling mechanisms took place in the other domain. They argued that competition took place

only in the hole-filling domain since sorption in the partitioning (dissolution) regions, in theory, is not competitive.

Based on the results from previous studies, there were three effects of cosolutes on HOC sorption. There may be no effect of cosolute on HOC sorption, because partitioning is already the primary sorption mechanism (Onken and Traina, 1997). Other theories suggest that the absence of an effect may be because the HOC is sorbed onto the amorphous regions of the sorbents (McGinley at al., 1996). Researchers attribute an increase in sorption by sorbent in the presence of cosolute to an increase in sorbent hydrophobicity (Brusseau, 1991; Onken and Traina, 1997). Cosolute has also been shown to cause a reduction in sorption of HOCs. McGinley et al. (1993) postulated that competition occurred because sorption occurred by surface reactions onto soil fragments other than the OM. Recently, sorption competitiveness was attributed to sorption into condensed and glassy regions of the sorbents as suggested by the polymer theory (McGinley et al., 1996; Xing and Pignatello, 1996; Xing et al., 1996; Xing and Pignatello, 1998).

The effect of ionic strength

The presence of a cosolute can also increase the ionic strength of the system. High diffusant concentrations can cause swelling of organic polymers. Organic cosolutes have been reported to cause swelling and softening of OM (Brusseau et al., 1991). Carter and Suffet (1982) studied the binding of DDT (2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane) to dissolved humic materials and found that binding was increased by an increase in ionic strength at fixed pH. No effect of increasing ionic strength was

observed on the binding of naphthalene to water-soluble organic carbon (Traina et al., 1989). Schlautman and Morgan (1993) measured the binding of several polyaromatic hydrocarbons (pyrene, anthracene, and perylene) to a well-characterized humic material (Suwannee River humic and fulvic acids), and they reported a decrease in binding with increasing ionic strength. This could result from swelling of the OM polymers, which would facilitate diffusion in and out of the humic material polymers. At high ionic strength, specific interactions were found to contribute proportionally less, relative to hydrophobic and van der Waal's forces (Spurlock and Biggar, 1994). Therefore, partitioning and diffusion-like mechanisms are more likely to occur at high ionic strength.

Another plausible reason for the increase in sorption at lower ionic strength can be explained by the changes in humic substance structure at different ionic strengths. The conformational structure of humic substances has been shown to change in relation to ionic strength, pH, and cation valency (Gosh and Schnitzer, 1980; Engerbretson and Wandruszka, 1994; Maurice and Namjesnik-Dejanovic, 1999). If sorption occurs by diffusion and hole-filling rather than by partitioning, then the conformational structure of the sorbent is important. Organic matter adopts a more compact structure at high ionic strength (Gosh and Schnitzer, 1980); therefore, fewer pores are available for diffusion by HOC into the sorbent. As a result, less sorption is expected to occur at high ionic strength.

Jones and Tiller (1999) studied the effect of pH, ionic strength, and cations in solution on the binding of phenanthrene by a soil humic acid using fluorescence quenching technique. The phenanthrene binding coefficient with the dissolved soil

humic decreased with increasing ionic strength. However, they offered an opposite explanation from what other researches have offered as to why binding coefficients of the HOC decreased with increasing ionic strength. They argued that at high ionic strength values, the soil humic acid retains a more compact configuration by screening the effects of repulsive forces. They also argued that the lower electrolyte concentrations allow an expanded humic conformation, exposing more sites that have affinity for the HOC. On the other hand, some researches have proposed that high ionic strength might cause polymers to swell, which allows HOCs to diffuse in and out of the polymeric materials more easily. Regardless of the explanation, the results of Jones and Tiller (1999) are consistent with the results from other studies, showing that sorption coefficients of HOCs decreased as the ionic strength increased.

Recent concepts explaining sorption of HOCs to soil OM

Recently, several researchers have attempted to explain the bimodal and slow sorption/desorption of organic compounds by borrowing from the field of polymer science, the concept of "soft and rubbery" versus "hard and glassy" to describe the structure of soil OM (Carroll et al., 1994; Young and Weber, 1995; McGinley et al., 1996; Pignatello and Xing, 1996; Xing et al., 1996; Xing and Pignatello, 1997). The glassy and rubbery phases of polymers refer to their segmental chain motion which confers their specific volume (Seymour, 1992). The transition between the two phases occurs sharply at a certain temperature range, referred to as a glass transition temperature (T_g). Other physical changes that accompany segmental chain motion at T_g are stiffness, refractive index, dielectric properties, gas permeability, X-ray adsorption, and heat

capacity. Polymers adopt a glassy phase at temperature below the T_g and an amorphous phase at temperature above the T_g (Boenig, 1973). In the glassy regions, i.e. below T_g, the segments of polymer chains are frozen and in fixed positions. In other words the structure of the polymer is crystalline-like rendering very little or no diffusional motion (Boenig, 1973). In the amorphous state, chains are less crystalline, less ordered, and have high degree of diffusional motion (Boenig, 1973; Seymour, 1992).

The rubbery and glassy polymer concept as outlined by Luthy et al. (1997) is as follows:

1) The structure of a rubbery polymer is amorphous and expanded, while the glassy polymer is condensed.
2) Sorption of solute to a rubbery polymer is rapid but slow to a glassy polymer.
3) Sorption isotherms for rubbery polymers are linear but nonlinear for glassy polymers.
4) Desorption from rubbery polymers does not show hysterisis, while hysterisis is observed for desorption from glassy polymers.
5) No competition between solutes will be observed for sorption to rubbery polymers, while with glassy polymers competition should be observed.

According to this concept, a soil OM macromolecule is viewed as having two separate phases where HOC sorption can take place. The first phase is made up of hard, condensed organic material analogous to the glassy state of synthetic polymers. The sorption processes that take place at this site would probably be both linear partitioning and IOMD. The diffusion of solute into this form of the OM would be slow, and sorption and desorption data would exhibit nonlinear, hysteresis, and competition between solutes

for sorption. The second phase is made up of soft, amorphous organic material analogous to the rubbery state of synthetic polymers. Sorption and desorption for this phase would be described by linear isotherms, rapid diffusion, no hysteresis and no competition for sorption (Luthy et al., 1997). The effects of several factors on the IOMD process, such as those mentioned in the previous section of this review, can be more easily explained by this new macromolecule concept.

The two-phase polymer concept was first proposed by Carroll et al. (1994) to explain the biphasic desorption characteristic of polychlorinated biphenyls (PCBs) from Hudson River sediments. They observed both a rapidly desorbing labile component (desorbed from the sediment in 24 h) and a more slowly desorbing resistant component (desorbed in 170 h). The fraction of the more resistant components was a function of PCB concentration and total organic carbon in the sediment, independent of inorganic particle size. There was no effect on PCBs desorption by milling the sediment, but heat treatment enhanced the desorption rate and significantly decreased the resistant fraction. From these observations they proposed that the labile and resistant fractions arose from different diffusional rates of PCBs associated with two structurally distinct phases of the sediment OM. One was conceptualized as a swollen phase and the other as a condensed phase. The swollen and condensed phases were later termed by other authors as rubbery and glassy, respectively.

Xing et al. (1996) studied competitive sorption on natural and model sorbents between atrazine, a polar organic compound, and cosolutes, including nonpolar hydrophobic compounds. The cosolutes used in the study included several *s*-triazine analogs, a substituted benzene analog (5-chloro-1,3-dimethoxy-benzene), and

trichloroethene. The sorbents were a mineral soil (3% OM), a peat soil (93% OM), soil humic acid particles (99% OM), "rubbery" polymers (polyethylene, cellulose, and chitin), a "glassy" polymer (poly[2,6-diphenyl-*p*-phenyleneoxide]), and a mesoporous silica gel. The isotherms for single solutes on the rubbery polymers were linear and no competition between solutes for sorption sites was observed in multi-solute systems, which is consistent with ideal partition sorption. Other sorbents showed nonlinear isotherms and significant competition between atrazine and its analogs but no competition between atrazine and trichloroethene. The results also indicated that like a glassy polymer, soil OM is a dual-mode sorbent. Sorption appeared to occur by both simple partitioning and hole-filling mechanisms. When combined with data from previous studies, the authors concluded that dual-mode sorption by soil OM is applicable to both polar and nonpolar compounds.

Dual-mode sorption in which partitioning and hole-filling mechanisms occur concurrently as in glassy polymers is further supported in a study by the same group (Xing and Pignatello, 1997). They studied the sorption of chlorobenzene, 1,2-dichlorobenzene, and 1,3-dichlorobenzene from water to high organic soils, humic acid particles, native peat, humin, and poly(vinyl chloride). Sorption of the HOCs was nonlinear and competitive and affected by temperature and cosolute addition on all sorbents. These results are in accord with the proposed dual-mode sorption. Sorption of the HOCs to peat soil and its components was progressively nonlinear and competitive following the order of humic acid, native peat, and humin. They suggested that this order reflected the increasing "glassy" characteristics (high rigidity and condensation) of the OM. The authors conceptualized soil OM as an amalgam of rubbery and glassy phases,

with each phase having a dissolution (partitioning) domain. But unlike the rubbery phase, the glassy phase also contains holes in which IOMD processes can take place. The holes are nanometer-size voids or cavities within the soil OM and are bounded by macromolecules. Normally, water or small natural organic molecules fill the holes. Sorption specificity is conferred by the number, size, steric, and electronic characteristics of the holes.

Young and Weber (1995) have presented additional support for the rubbery and condensed phases model of soil OM. They calculated isosteric heats of phenanthrene sorption to three natural soil materials having organic carbon with varying degrees of diagenetic alteration. The isotherms of the sorption were measured at different temperatures. As solid-phase loading increased, the isotherms became highly linear, and the process became less exothermic. These observations are expected if a classical surface adsorption reaction is used to explain the results. However, the isosteric heat values calculated using a pure supercooled solute standard state were less exothermic than expected for a surface adsorption process at the highest sorption capacity. This can only be explained by a model that envisions the OM as a macromolecule that is gradually transformed by a diagenetic processes from a loose amorphous structure to more condensed and ultimately highly microcrystalline structure like that of anthracite coal.

Weber and Huang (1996) measured and characterized the rates of sorption of phenanthrene to soils and sediments by examining the time dependence of solute phase distribution relationships (PDRs) in completely mixed batch reactors. They conducted the experiments using a range of concentrations to obtain a time series of nonequilibrium PDRs for each sorbent-sorbate system over reaction periods ranging from 1 min to 14

days. They found that the nonequilibrium PDRs were increasingly nonlinear as the reaction time increased. They postulated a three-domain particle-scale model to explain the sorption behavior and functional relationships underlying the time dependence of the PDRs. Their model contained three discrete soil components on which sorption can take place. The soil components are exposed inorganic surfaces along with amorphous and condensed OM. Huang and Weber (1997) further examined the sorption and desorption of penanthrene with ten natural sorbents of different geological ages and OM composition. They found that the sorption affinities of these materials to phenanthrene and the degree of isotherm nonlinearity and hysterisis were inversely correlated with the O/C atomic ratios of the OM. The more physically condensed and chemically reduced soil OM matrices exhibited greater solute affinity, sorption isotherms that were more nonlinear, and more pronounced hysteresis.

Model sorbents

Cellulose was used in the present study as an amorphous polymer sorbent. Cellulose is made up of glucose repeating units joined by 1,4-β-acetal linkage of D-glucose. Cellulose is largely a linear polymer, and very polar. However, it is insoluble in water. This is because of the strong intermolecular hydrogen bonds, with a small amount of cross-linking (Seymour, 1992). The capacity of cellulose molecules to retain water depends on the accessibility of the hydroxyl groups, the packing density of the molecules, and on the intermolecular forces. Cellulose with lower degree of crystallinity and weaker intermolecular forces should be more hydrophilic than more densely packed fibers. In addition, less crystalline molecules should be more accessible to penetration of other

molecules. The success of organic molecules in penetrating cellulose molecules depends on their abilities to displace water molecules in the cellulose structure. Because the chemical properties of the cellulose molecules are governed by hydrogen bonds, molecules that can form hydrogen bonds with cellulose can penetrate easier. Nitikin (1962) provided details about the physical and the chemical properties of cellulose. There is no hydrophobic domain in the cellulose molecules.

PVC has been used as a model for glassy polymers. PVC is made up of ethylene monomers with a chlorine atom attached to each alternate carbon molecule. Similar to cellulose, PVC is strongly polar. The molecules are attracted to each other by a strong dipole-dipole interactions, which result from electrostatic interaction between a chlorine atom in one molecule and a hydrogen atom in another (Seymour, 1992). Only polar molecules can form surface interactions with PVC. As the forces that bind the PVC molecules together are stronger than the hydrogen bonds that bind the cellulose molecules, diffusion into the PVC structure is much more difficult than diffusion into cellulose. Partitioning into PVC can be ruled out as a mechanism for HOC sorption since hydrophobic regions do not exist in PVC. Sorption will be through diffusion, as was the case with cellulose, but the process will be affected by concentration of the sorbate and equilibration time because the PVC structure is condensed and rigid.

The use of sorption isotherm to determine sorption mechanisms

In most sorption and desorption studies, we are interested in the relationship between the amount of a particular chemical in association with the sorbent. To obtain such relationship, we have to know:

1. The initial amount or concentration of the chemical of interest in the solution;
2. The amount of sorbent in the solution;
3. The volume of the solution; and
4. The amount or concentration of the chemical remaining in the solution after an equilibration period.

The relationship between the total chemical concentration in association with the sorbent can be defined by the term C_s, which is based on the quantity of chemical sorbed per amount of sorbent. The total chemical concentration in the solution will be defined by the term C_w. The relationship between the two terms is commonly referred as a sorption isotherm. The term isotherm indicates that the sorption data are obtained at constant temperature. The sorption isotherm data are usually plotted as an XY plot where C_s is plotted on the Y-axis and C_w on the X-axis.

Depending on which mechanism is dominating, the isotherm may exhibit different shapes. The are several equations that can be used to fit the experimentally determined sorption data. The most commonly used equation is the Freundlich isotherm, which was described earlier (equation 1). The Freundlich equation takes the form of

$$C_s = K_f C_w^n \qquad (3)$$

The term K_f is the Freundlich coefficient, and n is the exponential order in C_w, which is also a measure of nonlinearity involved. The Freundlich equation is used extensively to

describe sorption because of its simplicity and general utility (Green and Karickhoff, 1990) as compared to other equations, which may be better in describing sorption in some cases but are more complicated and lack generality.

There are three possible shapes of isotherms that are observed from experimentally determined sorption isotherms data fitted to the Freundlich isotherm (Fig. 1). The first type ($n < 1$) reflects the situation in which sorption decreases at higher sorbate concentrations. This can occur when the binding mechanism is site specific. As the specific binding sites become filled, the remaining sites are less attractive to the sorbate. The second type ($n > 1$) is the opposite of the first case. In this case, binding increases as the concentration of sorbate increases. This situation may occur in situation where earlier bindings alter the surfaces of the sorbent and this alteration favors further sorption. The last type ($n = 1$) is observed when the affinities of the sorbent for the sorbate remain constant regardless of the concentration of the sorbate. This is called a linear isotherm, and theoretically this shape will be observed when partitioning is the dominant mechanism. It is important to note that sorption isotherms often are linear at a very narrow range of low sorbate concentrations.

Sorption data can be fitted into a linear equation if the Freundlich isotherm terms are log-transformed:

$$\log C_s = \log K_f + n \log C_w \qquad (4)$$

A plot of log C_s against log C_w is a straight line, with the slope of the line being the n term and log K_f is the intercept on the Y-axis. The values of the K_f and the n terms can be easily determined from plots of the log transformed sorption data. A detail discussion on sorption isotherms can be found in Chapter 11 of Schwarzenbach et al. (1993).

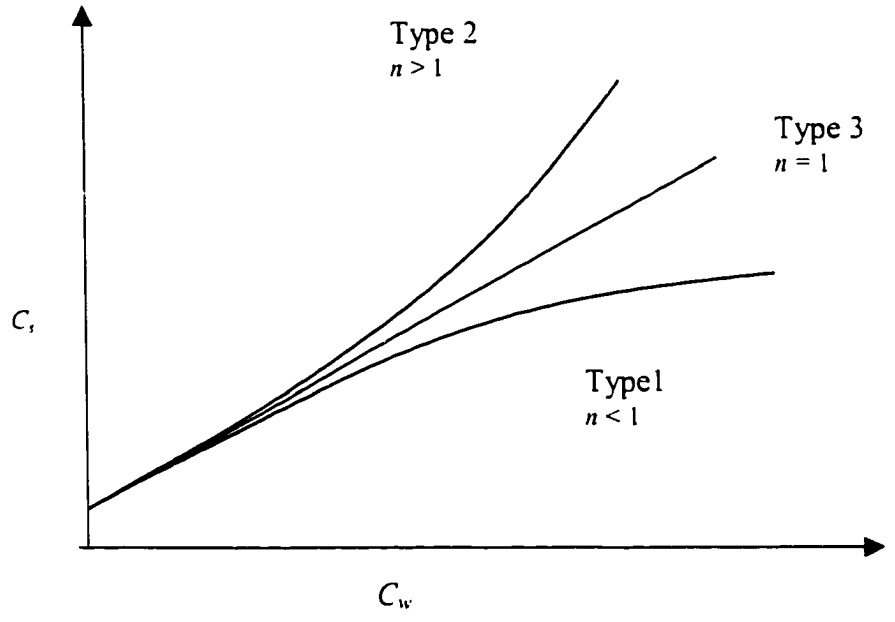

Fig. 1. Three types of possible relationship between C_s and C_w which can be fitted to the Freundlich model (Equation 3).

When the term n equals unity, the Freundlich constant becomes a partition constant, and its value is a function of the ratio of C_s and C_w. This is the case when sorption is purely governed by the partitioning mechanism. Another case in which the n term can equal unity is when the equilibrium solute concentration is very low.

The inclusion of the word equilibrium applied to the Cs and C_w terms is a misnomer because most often sorption data are not obtained at equilibrium but rather after an equilibration period that is convenient for the researcher. Therefore, the Freundlich constant is not a truly equilibrium constant but rather a kinetic expression relating the sorbed concentration to the aqueous concentration at any given time. The Freundlich equation also indicates that when n is unity, the Freundlich constant is independent of the solute and sorbate concentrations. This is not always the case because partition coefficients (K_f is a partition coefficient when n is unity) are affected by the amount of adsorbing solids (O'Connor and Connolly, 1980). These researchers observed a decrease in the partition coefficient (the ratio of C_s to C_w) as the sorbent concentration was increased. However, a study by Bowman and Sans (1985) of the sorption of the pesticides chlorpyrifos ((O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate), heptachlor (heptachloro tetrahydro 4,7-methanoindene), lindane (1,2,3,4,5,6-hexachloro cyclohexane), methoxychlor (1,1'-(2,2,2-trichloro ethylidene *bis* (4-methoxy))-benzene), parathion (diethyl 4-nitrophenyl thionophosphate), and picloram (4-amino-3,5,6-trichloro picolinic acid) to a Bondhead sandy loam (3.9% OM) and a Morris illite (< 2 μm fraction), sorbent concentrations did not affect the sorption coefficients.

A value of n of less or more than unity suggests that mechanisms other than partitioning are responsible for sorption. The departure of the n term from unity has been

used by many researchers to indicate that mechanisms other than partitioning were responsible for sorption of HOCs. An increase in Freundlich coefficients with equilibration time occurs when sorption increases as a function of time. Variability in the *n* and K_f terms with time has been used to gain insight into sorption mechanisms (Xing et al., 1996; Xing and Pignatello, 1997; Xing and Pignatello, 1998; Xia and Ball, 1999). For example, Xing and Pignatello (1996) examined the *n* and K_f terms as a function of time to understand the nature of soil OM as a sorbent of organic pollutants. They claimed that their study was the first to show direct experimental evidence that isotherms were variable with time. They used 1,3-dicholorbenzene (relatively hydrophobic), 2,4-dichlorophenol (both hydrophobic and polar surface area), and metolachlor (2-chloro-*N*-[2-ethyl-6-methylphenyl]-*N*-[2-methoxy-1-methylethyl] acetamide) as sorbates. A mineral soil containing approximately 3% OM, a peat soil that consisted 93% OM, and PVC (as a model for soil OM) were used as sorbents. For 1,3-dichlorobenzene sorption to peat soil, the K_f values increased, and the *n* term values decreased as contact time was increased from 1 to 30 d. The sorption of 1,3-dichlorobenzene to PVC was slow, and the isotherms were nonlinear but identical for different equilibration times. In all cases of sorption, they found that *n* was less than unity and decreased as sorption increased. They concluded from the isotherms that sorption could be separated into a fast fraction (amount sorbed after 1 d) and a "slow" fraction (amount sorbed thereafter) and that soil OM has both partition and adsorption domains analogous to the dual-mode sorption model of glassy polymers.

Further research needed

The arguments provided so far for IOMD are inconclusive. Linear sorption isotherms for HOCs to OM sorbents have been reported by several researchers (Karickhoff, 1981; Chiou, 1989; Rutherford and Chiou, 1992; Rutherford et al., 1992; Chiou and Kile, 1994), which is not consistent with the IOMD theory. The linearity of the sorption data suggests that sorption only involves simple partitioning and not a dual-mode sorption, which includes both simple partitioning and hole-filling mechanisms.

This review on sorption of HOCs to OM sorbents has revealed that more studies are needed to understand sorption and desorption mechanisms. Until microscopic spectroscopy is available to look at the mechanisms directly, we have to rely on sorption and desorption data to make inferences about the mechanisms involved. Results from several studies using a variety of HOCs and sorbents suggest that the concept of rubbery and glassy phases of soil OM structure can adequately describe to the sorption involving HOCs. Although this concept looks promising in explaining the dual-mode of HOCs sorption to soil OM, its validity has not been extensively tested. Graber and Borisover (1998) attempted to challenger the concept by using data from several other studies, which may or may not be related to the concept. For example, the concept of rubbery and glassy polymers is applicable to the description of sorption of HOCs to soil with high OM content, but not to mineral soils with very low OM because the mechanisms involved between these two types of soils may be fundamentally different. Therefore, comparison of isotherm data should only be made when sorption experiments are carried out under similar conditions, especially with regard to the sorbates and the sorbents used. Otherwise, comparison of results from unrelated studies can result in gross

misinterpretations of the results. There are several issues about the rubbery versus glassy polymer concept that need to be addressed. All studies suggesting the usefulness of the concept are based on sorption isotherm data. If the concept is valid, it should apply to both sorption and desorption by a variety of sorbents.

RESEARCH GOALS

The present study was undertaken to test the rubbery versus glassy polymer concept by using both sorption and desorption data. DCB sorption onto Pahokee peat, cellulose powder, and PVC will be measured. Sorption and desorption data at several equilibration times will be used to test the concept. DCB sorption in competition with naphthalene will also be measured. The results from this study should be useful in extending our knowledge of HOC sorption and desorption processes in general, and on the rubbery versus glassy polymer concept in particular.

DCB is selected as a sorbate in this study because it is a common soil and water pollutant (Mackay et al., 1992; Prager, 1995; Montgomery, 1996). It is regarded as hydrophobic or apolar, as reflected by its low water solubility constant and high octanol-water partition coefficient (log K_{ow}). DCB belongs to the chlorobenzene group, for which the sorption characteristics have been extensively studied (Xing and Pignatello, 1996; 1997; and 1998). Naphthalene is more hydrophobic than DCB and should compete more favorably for sorption sites. Pahokee peat is used as a representative sorbent for soil OM because it is a well characterized material that has been used in several sorption studies (Xing et al., 1996; Xing and Pignatello, 1997). Cellulose powder is chosen because it has an amorphous structure and has been reported to behave as a rubbery

polymer (Xing et al., 1996). PVC is chosen because it has the characteristics of a glassy polymer, and these have been well documented in the literature (Xing and Pignatello, 1997).

CHAPTER III

MATERIALS AND METHODS

Materials

The hydrophobic organic compounds used in this study were 1,2-dichlorobenzene (DCB) and naphthalene. Their physical and chemical properties are listed in Table 1. Pahokee peat, poly-vinyl chloride (PVC), and cellulose were used as sorbents. The chemical and physical properties of the sorbents are listed in Table 2.

The DCB, naphthalene, cellulose powder, and PVC were purchased from Aldrich Chemical Co. (Milwaukee, WI). The purities of DCB and naphthalene were 99%. Hexane of 95% nanograde purity and methanol of spectranalyzed grade were purchased from Mallinckrodt Baker, Inc., Paris, KY and Fischer Scientific, Fair Lawn, NJ, respectively. The Pahokee peat was purchased from The International Humic Substance Society (IHSS) (Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN). The Pahokee peat contained 44% C, 6.9% ash, and 1.7% SiO_2 on a dry weight basis (IHSS).

Methods

General methodology for sorption studies

Sorption studies were carried out in an aqueous solution of 0.01 M $CaCl_2$ containing 200 μg/mL of mercuric chloride ($HgCl_2$) at a concentration of 200 μg/mL as

Table 1. The physical and chemical properties of the sorbates.

Chemical name	Log K_{ow}	Vapor pressure (Pa at 25°C)	Solubility
1,2-Dichlorobenzene	3.38[1]	200[2]	147 mg/L in water at 25°C [2] miscible in alcohol[3]
Naphthalene	3.37[4]	11[5]	30 mg/L 25°C[4] 66.2 g/L in methanol at 23°C

[1] Prager, J. C. (1995)
[2] Mackay, D. et al. (1992)
[3] Montgomery, J. H. (1996)
[4] USEPA (1992)
[5] CRC (1999)

Table 2. The physical and chemical properties of the sorbents.

Name	Wet glass transition temperature T_g (°C)	N_2 BET surface area[1] (m^2/g)	Average particle diameter (mm)
Pahokee peat	43[1]	0.90[2]	-
PVC	85[3]	0.363[3]	0.11[3]
Cellulose	- 45[4]	2.4[5]	20[5]

[1]Data for humic acid taken from Leboeuf and Weber (1998)
[2]Xing and Pignatello (1997)
[3] Xing and Pignatello (1996)
[4] Leboeuf and Weber (1998)
[5] Xing et al. (1996)

bioinhibitor unless mentioned otherwise. Wolf et al. (1989) showed that $HgCl_2$ was an effective bioinhibitor, equivalent to three times autoclaving, without changing the chemical and physical properties of the soils used in their adsorption studies. The $CaCl_2$ solution was buffered following the method of Burgos et al. (1996). The buffer solution was prepared by adding 50 mL of 0.1M potassium phthalate to a solution of 22.6 mL of 0.1M NaOH in 100 mL double-distilled water. The buffer solution was added to the $CaCl_2$ solution at 5% (v/v). DCB and naphthalene solutions were prepared by first dissolving the chemicals in methanol and then quantitatively adding them to the $CaCl_2$ solution using a microsyringe. In all experiments, the final methanol concentration in each vial was kept constant at 0.1% (v/v) to avoid cosolvency effects on sorption (Rao et al., 1990; Xing et al., 1996). Sorbents (0.05 g) were suspended in a vial containing 10 mL of $CaCl_2$ solution. This sorbent to solution ratio should result in 20 - 80% sorption of DCB from the solution based on the results of Bowman and Sans (1985) and Xing and Pignatello (1996). The suspensions were prepared in 12-mL vials with Teflon-lined caps. The vials were shaken for 1 min by hand and then placed on a rotary shaker. The shaking process was continued for the next 24 h. The vials that required equilibration time for more than 24 h were stored in the dark at room temperature. The vials were shaken manually by hand for about 30 sec every 2 days for the rest of the equilibration period to resuspend the sorbent in the solution.

At the end of each equilibration period, contents of each vial were centrifuged at 2000 X g for 20 min and extracted. In each case, 2 mL of the supernatant was transferred to a 4-mL vial containing 2 mL of hexane. The vial was placed horizontally on an end-over-end shaker and shaken for 24 h. After 24 h, the amount of DCB in the hexane

extract was analyzed with a Hewlett Packard Model 5890 Series II Plus gas chromatography using a 0.32 mm X 30 m HP-5 capillary column (Hewlett-Packard Company, San Fernando, CA). The stationary phase of this capillary column is a crosslinked 5 % phenyl methyl siloxane, and the film thickness is 0.25 μm. A flame ionization detector (FID) was used in the analysis. The mobile phase was helium gas and the flow rate was set at 2 mL/min. The injection volume was 2 μL. The analyses were done with temperature programming. The initial oven temperature was set at 70 °C for 4 min. The temperature was then increased at a rate of 15 °C/min to a final temperature of 160 °C. The total time for each analysis was 7 min. Under these parameters, the DCB peak came out at around 6.7 min. For each set of samples analyzed on the gas chromatograph, a standard curve was prepared from the responses of at least four known concentrations of DCB in hexane.

In each set of experiments, DCB was added at four concentrations (5, 10, 25 and 50 μg/mL), using triplicates for each treatment. Three vials without any sorbent containing 50 μg/mL DCB solution were included in each set of experiments to determine the recovery rate of the extraction procedure. The amount of DCB adsorbed was calculated using mass balance. The amount of DCB sorbed equals the amount added minus the amount remaining in solution after the equilibration period.

Experiment 1. The effects of equilibration time on the sorption and desorption of DCB with Pahokee peat, PVC, and cellulose.

Sorption experiments were conducted by adding 10 mL of 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ solution containing DCB at 5, 10, 25 or 50 μg/mL into 12-mL vials

containing 0.05 g of Pahokee peat, PVC, or cellulose. Triplicate samples were prepared for each DCB concentration. Triplicate vials without any sorbent spiked with 50 μg/mL 1,2-diclorobenzene in 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ solution were also included in each set of experiment to determine the loss of 1,2-dicholorobenzene from the vials during the equilibration. The vials were then shaken for 24 h, after which time the vials were removed from the shaker, and depending on treatment, the vials were either centrifuged or placed in the dark at room temperature to undergo further equilibration. After each equilibration time, the vials were centrifuged at 2000 X g for 20 min. Then 2 mL of the supernatant was transferred from the vials to 4-mL vials (Teflon lined screw caps) containing 2 mL of hexane. The vials were tightly capped, placed in a holding rack, and shaken for 24 h. The concentrations of DCB in the organic phase (top layer) were determined using the procedure described in the general methodology section.

Desorption experiments were conducted with solutions from the vials used in the sorption studies. To each vial 10 mL of 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ was added. The vials were placed in a holding rack and shaken. After 24 h, the vials were centrifuged at 2000 X g for 20 min. Then 2 mL of supernatant was removed from each vials and added to a 4-mL vial (Teflon lined screw cap) containing 2 mL of hexane. The extraction of DCB and the determination of its concentration in the extract were as described in the sorption experiments.

Experiment 2. The effect of naphthalene pretreatment on DCB sorption to Pahokee peat, PVC, and cellulose

An experiment was designed to determine the effect of naphthalene on the sorption of on DCB to Pahokee peat, PVC, and cellulose. DCB was added to 0.01 M

$CaCl_2$ + 200 μg/mL $HgCl_2$ solution containing Pahokee peat, PVC, or cellulose with or without naphthalene. The concentrations of DCB were 5, 10, 25, or 50 μg/mL. In experiments with naphthalene, 10 mL of solution containing 25 μg/mL naphthalene in 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ was added to the containing 0.05 g of Pahokee peat, PVC, or cellulose. The vials were equilibrated for 1 d and then centrifuged for 200 X g for 20 min. The supernatant was removed, and 10 mL of 1,2-dicholorobenzene in 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ solution was added. After an equilibration period of 15 d, the vials were centrifuged at 2000 X g for 20 min. Then, 2 mL of the supernatant was transferred to a 4-mL vial containing 2 mL of hexane. The vials were placed on a holding rack and shaken on a table shaker. After 24 h, the amount of DCB remaining in solution was measured by using the gas chromatographic method described earlier. For samples without naphthalene, the procedure was similar including an equilibration time of 15 d.

Experiment 3. The effect of length of sorbent pretreatment with naphthalene on DCB sorption.

A second set of experiments was designed to study the effect of aging naphthalene with Pahokee peat, PVC, and cellulose at two times (1 and 100 d) on the sorption of DCB. This experiment was carried out by pretreating 0.05 g of Pahokee peat, PVC, and cellulose with naphthalene (10 mL of 25 μg/mL) in 12-mL screw cap vials. The naphthalene was prepared in 0.01 M $CaCl_2$ + 200 μg/mL $HgCl_2$ solution from a methanol solution. The final concentration of methanol in each vial was 0.1% (v/v). Triplicate samples were used for each treatment. Triplicate samples without sorbent were also included as controls. After the pretreatments, the vials were centrifuged at 2000 X g

and the supernatant in the vials was removed. Then, 10 mL of a solution of 0.01M $CaCl_2$ + $HgCl_2$ containing DCB at concentrations of 5,10, 25, or 50 μg/mL was added to each vial. The check samples were spiked with 50 μg/mL DCB. The vials were placed on a holding rack and shaken for 24 h on a table shaker. The vials then were stored in the dark at room temperature. The vials were shaken manually by hand every 2 d to resuspend the sorbent in the solution. After 15 d, the vials were centrifuged at 2000 X g for 20 min. Then, 2 mL of supernatant was transferred to a 4-mL vial and tightly capped. The vials were shaken for 24 h to extract the DCB from the aqueous phase into the hexane. After shaking, the concentration of DCB in the hexane was determined by gas chromatography using methods described previously.

Experiment 4. The effect of ionic strength on the sorption of DCB to PVC, cellulose, and Pahokee peat

To determine the effect of ionic strength on the sorption of DCB to the PVC, cellulose, and Pahokee peat another set of experiments were conducted. The experiments were conducted using two $CaCl_2$ concentrations (0.01M and 0.0001M) with a $HgCl_2$ concentration of 200 μg/mL. The equilibration time was 1 d. DCB was present at concentrations of 5,10, 25, or 50 μg/mL. After each equilibration time, the solution concentrations of DCB were determined using the procedure described for previous experiments.

Analysis of data

Sorption isotherm data were plotted using the values of DCB sorbed/g of sorbent (C_s) versus solution concentrations of DCB (C_w) or their log-transformed values. Plots of

the untransformed data were used to describe the sorption isotherm qualitatively, while plots of the log-transformed data were used to give quantitative interpretations. Freundlich coefficients for sorption isotherms (K_f) were determined from the intercepts of the log-transformed plots, while the coefficient of C_w (n) was given by the slope of the regression line.

SAS statistical software (SAS System, 1998) was used for all statistical analysis. General Linear Model procedure (proc glm) was used to determine the statistical significant of the K_f and n values of each isotherm, and also mean values. The SAS code used to determine the statistical significant of K_f and n is shown in Appendix I, while the SAS code to determine the statistical significant of the desorption data is shown in Appendix II. A confidence level of 95% (p value < 0.05) was used to determine the statistical significant of the sorption data.

CHAPTER IV

RESULTS AND DISCUSSION

The effects of equilibration time on DCB sorption and desorption with PVC, cellulose, and Pahokee peat

Sorption

Experiments were conducted to determine the effect of equilibration time on the sorption of DCB onto the Pahokee peat and model sorbents. Cellulose is considered a rubbery polymer with an expandable structure, while PVC is considered a glassy polymer with a more condensed structure. It has been reported (Carrol et al., 1994; Xing and Pignatello, 1996; Xing et al., 1996; Xing and Pignatello, 1997) that the sorption isotherms of DCB with cellulose would be linear with time, while sorption isotherms for PVC would be affected by the equilibration time. Soil OM has been considered to have both amorphous and condensed regions exhibiting both partitioning and diffusion (hole filling) characteristics (Carroll et al., 1994; Leboeuf and Weber, 1997). Therefore, the effect of equilibration time on DCB sorption by the Pahokee peat should be intermediate between that found with PVC and cellulose.

The sorption isotherms for PVC showed that DCB sorption increased with equilibration time (Fig. 2 and 3). This is reflected by sharp increases in the K_f values (Table 3). The differences in the K_f values were statistically significant at the 95% confidence level ($p < 0.05$). Xing and Pignatello (1996) also observed this pattern of

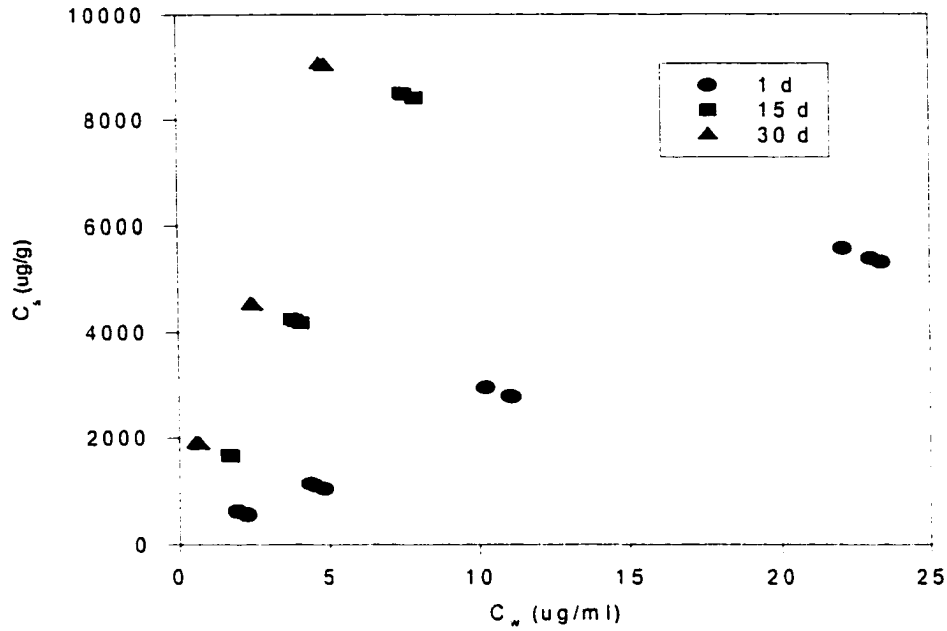

Fig. 2. Sorption isotherms of DCB onto PVC at three equilibration times.

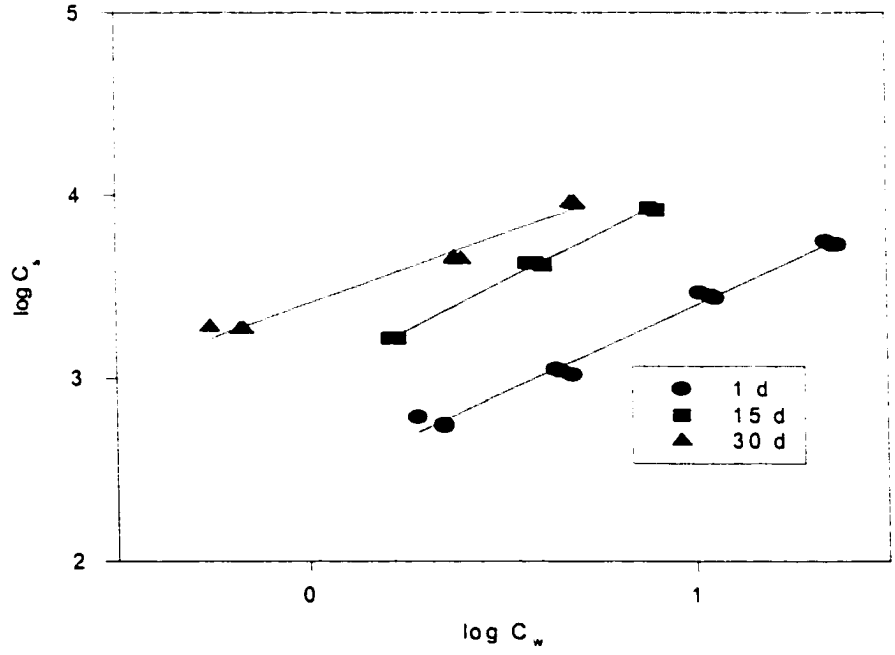

Fig. 3. Sorption isotherms of DCB onto PVC at three equilibration times (log-transformed data).

Table 3. The values of K_f, n, and R^2 for DCB sorption isotherms with each sorbent at three equilibration times.

Sorbent	Equilibration time (d)	K_f (mL/g)	n	R^2
PVC	1	274.73[†a]	0.96[a]	0.99
	15	972.52[b]	1.07[b]	1.00
	30	2586[c]	0.74[c]	0.98
Cellulose	1	4.79[a]	1.60[a]	0.94
	15	1.24[a]	2.15[b]	0.90
	30	28.78[b]	1.17[c]	0.96
Pahokee peat	1	252.9[a]	0.98[ab]	0.98
	15	180.4[b]	1.07[b]	0.99
	30	326.7[a]	0.90[a]	0.95

[†] Values with the same letter under a column for each sorbent indicate that they are not statistically significant at the 95% confidence level.

sorption of 1,3-dichlorobenzene onto PVC. However, the K_f values for their sorption isotherms were lower than those measured in this study. Perhaps the position of chlorine atoms influences the sorption process. Also, the water-to-solid ratio used in their study was 140, while in this study the ratio was 200. The octanol/water partition coefficients for both compounds are the same, which suggests partitioning mechanism alone cannot explain the differences in the K_f values. The increases in the K_f values with equilibration time observed for DCB sorption onto PVC in this experiment are consistent with the hypothesis that sorption is time-dependent for HOC diffusion into a glassy polymer.

For DCB sorption to PVC, there was no general pattern for the changes in the values of C_w exponent n, although the values indicated that the isotherms were not linear. The highest n value (1.07) was observed at 15 d, while the lowest was at 30 d (0.74). The values were significantly different at the 95% confidence level. The n value for the 1-d equilibration time (0.96) was the closest to unity, which is expected for an ideal partitioning mechanism. Nonlinear sorption results from sorption onto sites that have different energy distributions. Xing and Pignatello (1996) reported an n value (0.879) for 1,3-dichlorobenzene sorption with PVC for 1 and 30 d of equilibration. Because the HOC sorption isotherms were not linear, Xing and Pignatello (1996) argued that nonlinearity is not an artifact due to insufficient contact time. Therefore, the nonlinearity phenomenon relates to the mechanism of sorption rather than the kinetics of sorption.

It was hypothesized that sorption onto cellulose would not be affected by equilibration time because cellulose is a rubbery polymer, which has an expandable and flexible structure. Therefore, sorption of HOCs onto cellulose would yield linear isotherms, similar to a pure partitioning mechanism (Xing and Pignatello, 1996). The

sorption isotherms in this study (Fig. 4 and 5) did not support this hypothesis. Both the K_f and n values were affected by equilibration time (Table 3), suggesting that sorption was far from a partitioning-like mechanism. The K_f values for 1- and 15-d equilibration times were not significantly different, while the K_f value for 30 d was significantly different from these two. Sorption increased with equilibration time at lower initial DCB concentrations (5, 10, and 25 μg/mL), while at higher initial concentration (50 μg/mL), sorption decreased with equilibration time. The values of n were greater than unity for all equilibration times, indicating that sorption was greater at higher concentrations of DCB at these times.

The DCB sorption isotherms for Pahokee peat are shown in Fig. 6 and 7. Sorption of DCB onto the Pahokee peat was the closest to a true partitioning process. The K_f values between 1- and 30-d sorption were not significantly different (Table 3), indicating that equilibration time beyond 1 d did not affect the sorption processes. It also suggests that sorption was almost instantaneous which is expected of the partitioning process. The n values for the three-equilibration times were close to unity, as for ideal partitioning. In many previous studies, the pattern of sorption of HOCs onto soil OM was dual mode, involving both the partitioning and hole-filling mechanisms. However, Deitsch et al. (1998) reported linear sorption of 1,2-dichlorobenzene onto three organobentonites and peat soil. As in table 3, the K_f values for DCB sorption onto the Pahokee peat for 1- and 30-d equilibration were 253 and 327 mL/g, respectively. These values are similar to those reported by Xing and Pignatello (1996) for 1,3-dichlorobenzene sorption onto Pahokee peat after 1- and 30-d equilibration (252 and 321 mL/g, respectively). However, Xing and Pignatello (1996) did not report the statistical

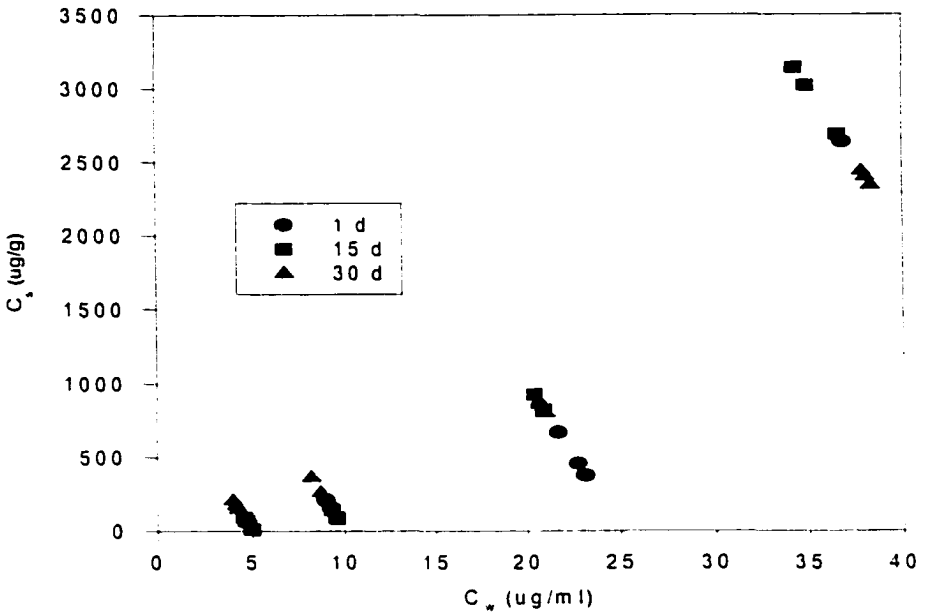

Fig. 4. Sorption isotherms of DCB onto cellulose at three equilibration times.

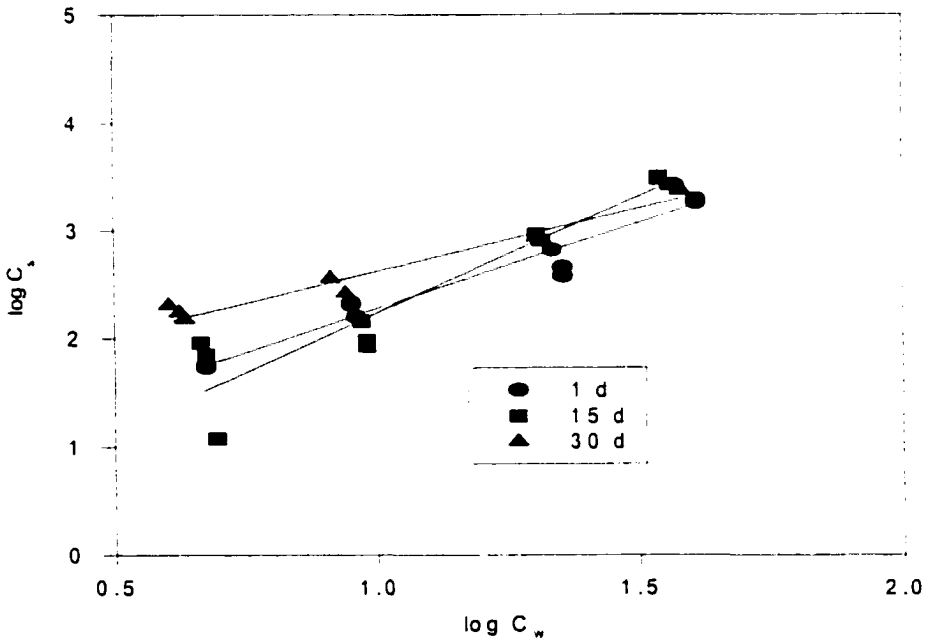

Fig. 5. Sorption isotherms of DCB onto cellulose at three equilibration times (log-transformed data).

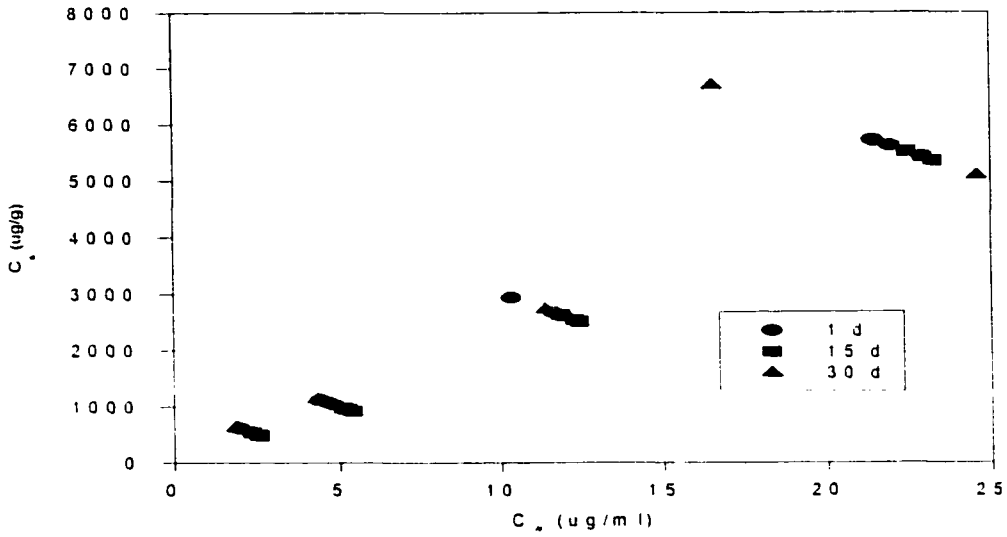

Fig. 6. Sorption isotherms of DCB onto Pahokee peat at three equilibration times.

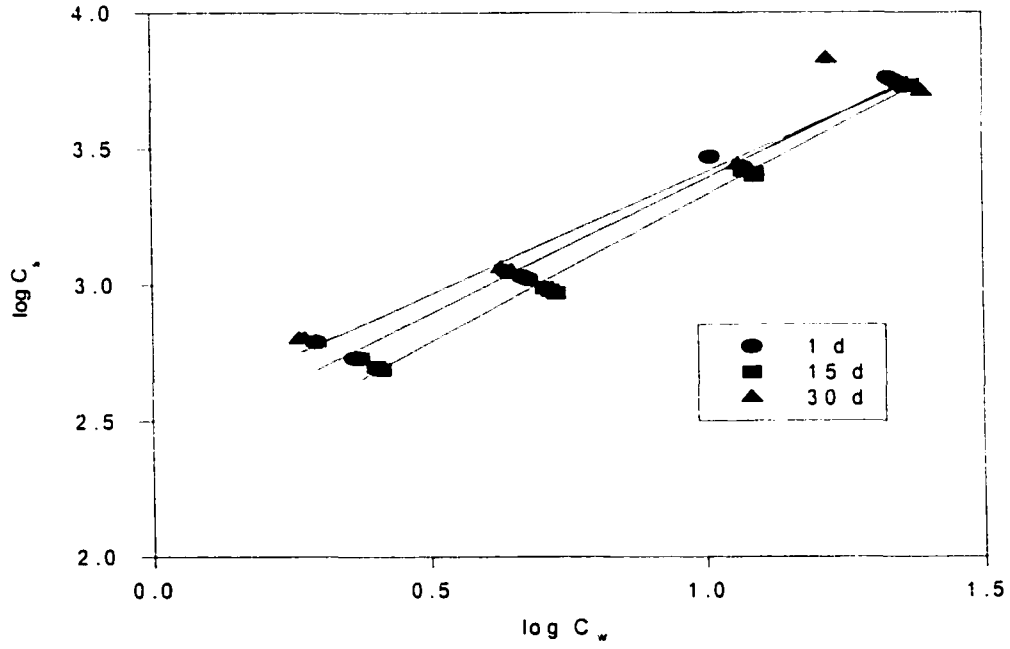

Fig. 7. Sorption isotherms of DCB onto Pahokee peat at three equilibration times (log-transformed data).

significant of their K_f values. Xing and Pignatello (1996) found that the *n* value for 30-d sorption was significantly lower (99% confidence level) than the *n* value for 1 d. In the present study, the *n* value at 30 d was also lower than that for 1 d, but the values are not significantly different.

The results of this study of sorption of DCB onto PVC, cellulose and Pahokee peat showed that the glassy versus rubbery polymer theory was applicable to explaining the sorption of DCB onto the PVC, but it failed to explain the sorption of DCB onto the other sorbents.

Desorption

A desorption study was conducted to determine the effect of equilibration time on the amount of DCB desorbed from the sorbents after initial sorption. This study was conducted to test the applicability of the glassy versus rubbery polymer theory to desorption processes. Desorption from the glassy polymer (PVC) and Pahokee peat should be slower than from the rubbery polymer (cellulose). In addition, equilibration time should affect desorption of DCB from PVC and Pahokee peat but not from cellulose.

The amounts of DCB desorbed from PVC equilibrated with four DCB concentrations are shown in Table 4. DCB desorbed from PVC equilibrated with 5 μg DCB/mL was less than the detection limit of the methods. However, for PVC equilibrated with DCB concentrations of 25 and 50 μg/mL, less DCB was desorbed with the longer DCB equilibration. The longer the period of equilibration, the slower the desorption. This could be explained by the time for diffusion from deeper holes in the

Table 4. The percentage of DCB desorbed from PVC after three equilibration times with varying DCB initial concentrations.

Initial DCB concentrations (μg/mL)	Equilibration times with DCB (d)	Amount sorbed (μg) (mean ± std. error)	Amount desorbed (μg) (mean ± std. error)	% Desorbed (mean ± std. error)
5	1	28.84 ± 1.08	BDL[5]	BDL
	15	50.00 ± 0.00	BDL	BDL
	30	50.00 ± 0.00	BDL	BDL
10	1	54.46 ± 1.35	11.62 ± 1.75	21.40 ± 3.4[†a]
	15	83.28 ± 0.17	5.33 ± 2.67	6.42 ± 3.21[a]
	30	93.76 ± 0.38	BDL	BDL[b]
25	1	142.1 ± 2.87	22.34 ± 1.34	15.73 ± 0.94[a]
	15	211.1 ± 0.95	18.56 ± 0.66	8.79 ± 0.29[b]
	30	225.7 ± 0.32	14.45 ± 0.33	6.40 ± 0.14[c]
50	1	271.8 ± 3.86	37.02 ± 0.32	13.63 ± 0.27[a]
	15	423.3 ± 1.34	34.86 ± 0.97	8.24 ± 0.24[b]
	30	451.4 ± 0.60	26.48 ± 0.71	5.87 ± 0.16[c]

[†] Values with the same letter under the column at each initial DCB concentration indicate that they are not statistically significant at the 95% confidence level.

[5]Indicates the value was below detection level of the method

PVC structure as would be expected for a glassy polymer. Sorption of DCB onto the PVC may have occurred by diffusion into holes in the PVC structure. Initially, DCB molecules filled holes near to the surfaces; with increased equilibration time, the DCB molecules penetrated into deeper holes. Desorption of DCB from the holes nearer to the surface would be more rapid, while desorption from holes in the inner structure would occur more slowly.

The amounts of DCB desorbed from the cellulose previously equilibrated for 1, 15, and 30 d with four concentrations of DCB are shown in Table 5. There was no detectable amount of DCB desorbed from the cellulose equilibrated with DCB concentrations of 5 and 10 μg/mL for any of the equilibration periods. The amounts of DCB desorbed from the cellulose previously equilibrated for 1 d were significantly greater than that for 30 d when DCB equilibration concentrations were 25 and 50 μg/mL. For each of these concentrations, there was no significant difference between the percentages of DCB desorbed from the cellulose previously equilibrated at 15 or 30 d. Thus, with cellulose, both sorption and desorption were affected by equilibration time. Consequently, neither the sorption nor the desorption data are consistent with results expected from the rubbery polymer model.

The amounts of DCB desorbed from the Pahokee peat previously equilibrated for 1, 15, and 30 d with four initial concentrations of DCB are shown in Table 6. At a concentration of 5 μg/mL, 42.87% of DCB was desorbed after 1 d, while no detectable amount was desorbed after 15 or 30 d. With peat samples previously equilibrated with 10 μg/mL, there were no significant differences in amounts of DCB desorbed for the equilibration times. For samples equilibrated with 25 μg/mL of DCB, there was a

Table 5. The percentage of DCB desorbed from cellulose after three equilibration times with varying DCB initial concentrations.

Initial DCB concentrations (μg/mL)	Equilibration times with DCB (d)	Amount sorbed (μg) (mean ± std. Error)	Amount desorbed (μg) (mean ± std. error)	% Desorbed (mean ± std. error)
5	1	2.76 ± 0.04	BDL[ξ]	BDL
	15	2.91 ± 1.20	BDL	BDL
	30	8.83 ± 0.81	BDL	BDL
10	1	9.63 ± 0.88	BDL	BDL
	15	5.39 ± 0.90	BDL	BDL
	30	14.83 ± 1.74	BDL	BDL
25	1	25.00 ± 4.86	9.13 ± 1.57	38.45 ± 9.48[†a]
	15	42.80 ± 1.75	2.78 ± 2.78	6.77 ± 6.77[b]
	30	42.27 ± 1.16	BDL	BDL[b]
50	1	106.4 ± 12.79	13.08 ± 1.83	12.99 ± 2.94[a]
	15	147.4 ± 6.81	5.14 ± 2.58	3.61 ± 1.81[b]
	30	119.5 ± 1.37	6.76 ± 0.15	5.66 ± 0.10[b]

[†] Values with the same letter under the column at each initial DCB concentration indicate that they are not statistically significant at the 95% confidence level.

[ξ]Indicates the value was below detection level of the method

Table 6. The percentage of DCB desorbed from Pahokee peat after three equilibration times with varying DCB initial concentrations.

Initial DCB concentrations (μg/mL)	Equilibration times with DCB (d)	Amount sorbed (μg) (mean ± std. error)	Amount desorbed (μg) (mean ± std. error)	% Desorbed (mean ± std. error)
5	1	28.17 ± 1.22	11.88 ± 1.84	42.87 ± 8.06[†a]
	15	25.41 ± 0.72	BDL[ξ]	BDL[b]
	30	31.19 ± 0.30	BDL	BDL[b]
10	1	53.89 ± 1.23	19.70 ± 1.60	36.71 ± 3.67[a]
	15	47.69 ± 0.77	17.81 ± 0.82	37.33 ± 1.39[a]
	30	55.73 ± 0.60	0.00	32.52 ± 2.04[a]
25	1	135.6 ± 5.98	38.43 ± 0.90	28.42 ± 1.18[a]
	15	128.1 ± 1.77	39.41 ± 1.08	30.76 ± 0.44[ab]
	30	131.6 ± 2.29	44.05 ± 1.75	33.45 ± 0.74[b]
50	1	279.2 ± 4.39	66.65 ± 0.82	23.89 ± 0.50[a]
	15	271.3 ± 2.35	73.13 ± 1.70	26.96 ± 0.75[a]
	30	290.9 ± 23.51	72.11 ± 7.25	25.47 ± 4.26[a]

[†] Values with the same letter under the column at each initial DCB concentration indicate that they are not statistically significant at the 95% confidence level.

[ξ] Indicates the value was below detection level of the method

significant difference between 1 and 30 d but not between 1 and 15 d. At the concentration of 50 μg/mL, there were no significant differences in the amounts desorbed. For Pahokee peat, equilibration time did not affect the percentage of DCB desorbed except at the lowest DCB concentration. This is consistent with the sorption data, which also showed the lack of effect of equilibration time. Therefore, the sorption and desorption data for DCB and Pahokee peat can be explained by a simple partitioning mechanism.

The effect of cosolute on DCB sorption

Researchers have studied the sorption isotherms of HOCs in systems containing more than one solute, to better understand mechanisms responsible for sorption. Chiou et al. (1983) argued that sorption of nonionic compounds from water onto soil is primarily a partitioning process, based on the linear sorption isotherms of binary nonionic compounds. They further argued that the linearity of sorption isotherms in a binary system indicates that there is no competitive effect between the two solutes. However, other researchers have reported a reduction or an increase in sorption of HOCs in the presence of a cosolute. Pignatello (1991) observed a reduction in ethylene dibromide sorption to soils in the presence of trichloroethylene as a cosolute. Brusseau (1991) and Onken and Traina (1997) reported that sorption of HOCs onto soil and aquifer materials was enhanced in the presence of other cosolutes. Xing et al. (1996) found that sorption of atrazine in the presence of a cosolute was reduced with a glassy polymer (poly(2,6-diphenyl-*p*-phenylene oxide)) but not with rubbery polymers (polyethylene, cellulose, and chitin).

In this part of the study, the sorption of DCB onto PVC, cellulose, and Pahokee peat without any cosolute was compared to that with the three sorbents that were previously equilibrated with naphthalene for 1 d. Sorption of naphthalene onto these sorbents should be similar to that of DCB sorption because both compounds are hydrophobic. However, the K_{ow} of naphthalene is higher than that of DCB. DCB sorption onto the naphthalene-treated sorbents could be unaffected, reduced, or increased as compared to the sorbents in the absence of naphthalene. If DCB sorption is unaffected, this would suggest that sorption is by partitioning. A reduction in DCB sorption would suggest that diffusion and hole filling are the mechanisms responsible for the sorption. Brusseau (1991) and Onken and Traina (1997) both postulated an increase in sorption of HOC in the presence of a cosolute because the cosolute increased the effective fractional organic carbon (f_{oc}) of the sorbents and therefore increased the hydrophobic environment of the sorbents. They speculated that the presence of cosolutes aids the transition from adsorption/condensation type surface interactions to an interaction similar to partitioning. Onken and Traina (1997) also postulated that there would be no effect of cosolute if partitioning were the primary mechanism for sorption. The polymer theory would predict a reduction in DCB sorption in the presence of naphthalene with PVC and Pahokee peat but not with cellulose.

DCB sorption isotherms for PVC previously equilibrated with naphthalene for 1 d and for PVC without naphthalene are shown in Fig. 8 and 9. DCB sorption was higher when the sorbent had been previously equilibrated with naphthalene as indicated by the higher K_f value. The K_f values for DCB sorption onto the sorbent with and without naphthalene pretreatment are 2430 and 972.5 mL/g, respectively (Table 7). The values

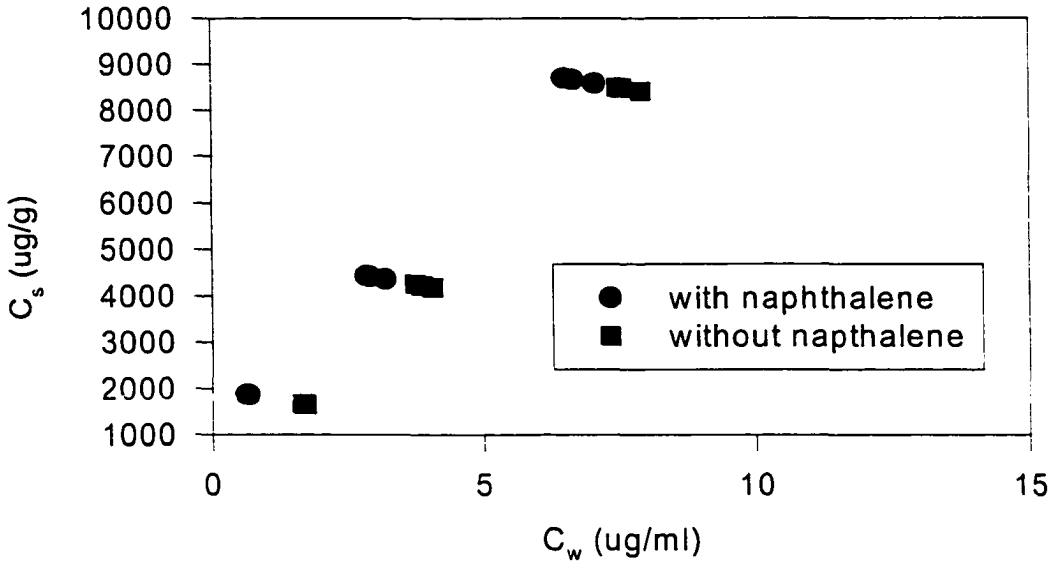

Fig. 8. 15-d sorption isotherms of DCB onto PVC with and without initial 1-d equilibration with naphthalene.

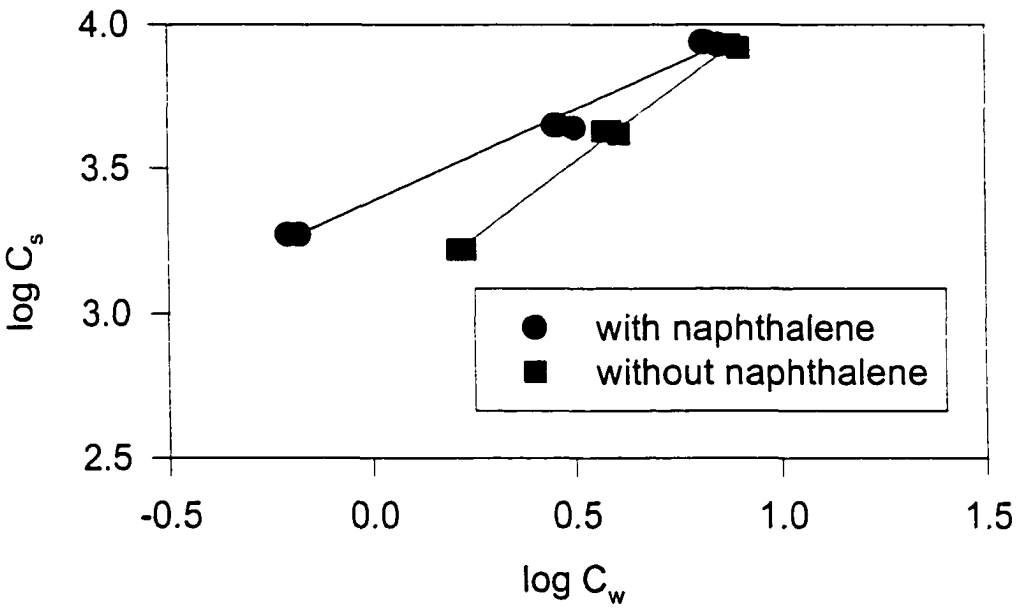

Fig. 9. 15-d sorption isotherms of DCB onto PVC with and without initial 1-d equilibration with naphthalene (log-transformed data).

Table 7. The values of K_f, n, and R^2 for DCB sorption isotherms with the sorbents with and without naphthalene pretreatment.

Sorbent	Treatment	K_f (mL/g)	n	R^2
PVC	With naphthalene	2430[a†]	0.63[a]	0.99
	Without naphthalene	972.5[b]	1.07[b]	1.00
Cellulose	With naphthalene	65.81[a]	0.86[a]	0.91
	Without naphthalene	1.24[b]	2.15[b]	0.90
Pahokee peat	With naphthalene	400.2[a]	0.75[a]	0.98
	Without naphthalene	180.4[b]	1.07[b]	0.99

† Values with the same letter under a column for each sorbent indicate that they are not statistically significant at the 95% confidence level.

are significantly different at the 95% confidence level. The sorption data are not consistent with the glassy versus rubbery polymer theory or the partitioning theory. Based on the polymer theory, the DCB sorption onto PVC previously equilibrated with naphthalene would be less than sorption onto PVC without naphthalene treatment. However, the sorption data showed the opposite. A possible explanation is that equilibration with naphthalene created a hydrophobic environment in the PVC structure that facilitated diffusion. In other words, initial sorption of the cosolute increased the hydrophobicity of the surface of the sorbent interior environment, which would facilitate DCB penetration because of the increased entropy of the system, regardless of the mechanisms involved.

The *n* values for the DCB sorption isotherms for PVC that was equilibrated with naphthalene and for the sorbent that did not receive naphthalene are 0.63 and 1.07, respectively. They are significantly different at the 95% confidence level. These values indicate that sorption onto the PVC that previously received naphthalene is concentration dependent, which is the characteristic of a system having diffusion and hole-filling mechanisms as the primary mechanisms of sorption.

The DCB sorption isotherms for cellulose with and without naphthalene are shown in Fig. 10 and 11. Similar to the pattern observed with PVC, DCB sorption was higher with the sorbent previously equilibrated with naphthalene. The K_f values for DCB sorption isotherms for cellulose with and without pretreatment with naphthalene are 65.81 and 1.24 mL/g, respectively (Table 7). The values are significantly different at the 95% confidence level. The isotherms suggest that neither the partitioning nor the polymer theories alone could explain the difference in the DCB sorption for treated and

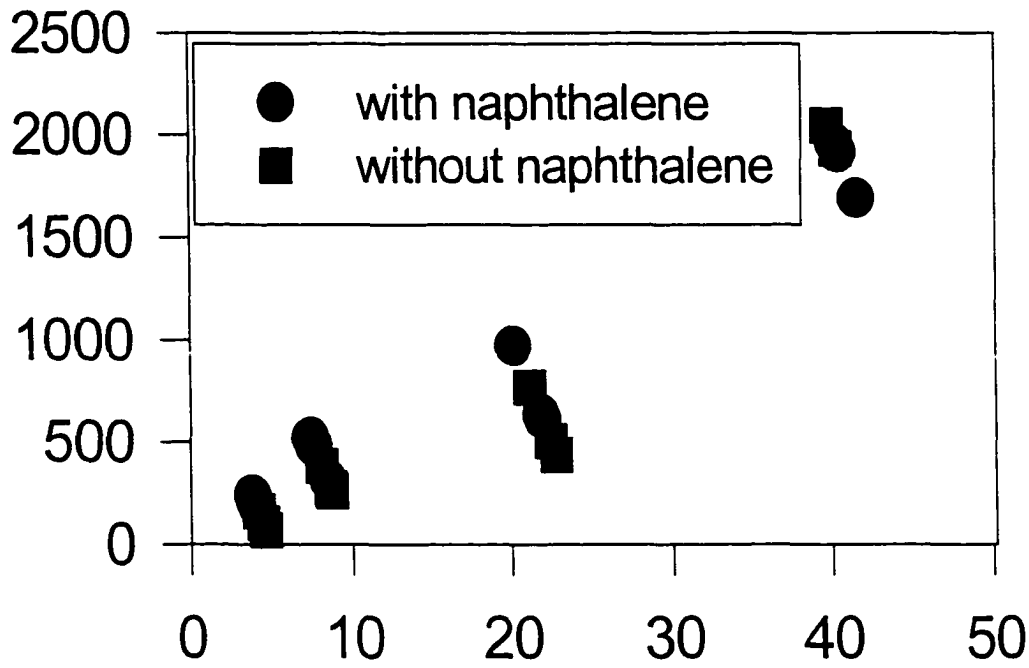

Fig. 10. 15-d sorption isotherms of DCB onto cellulose with and without initial 1-d equilibration with naphthalene.

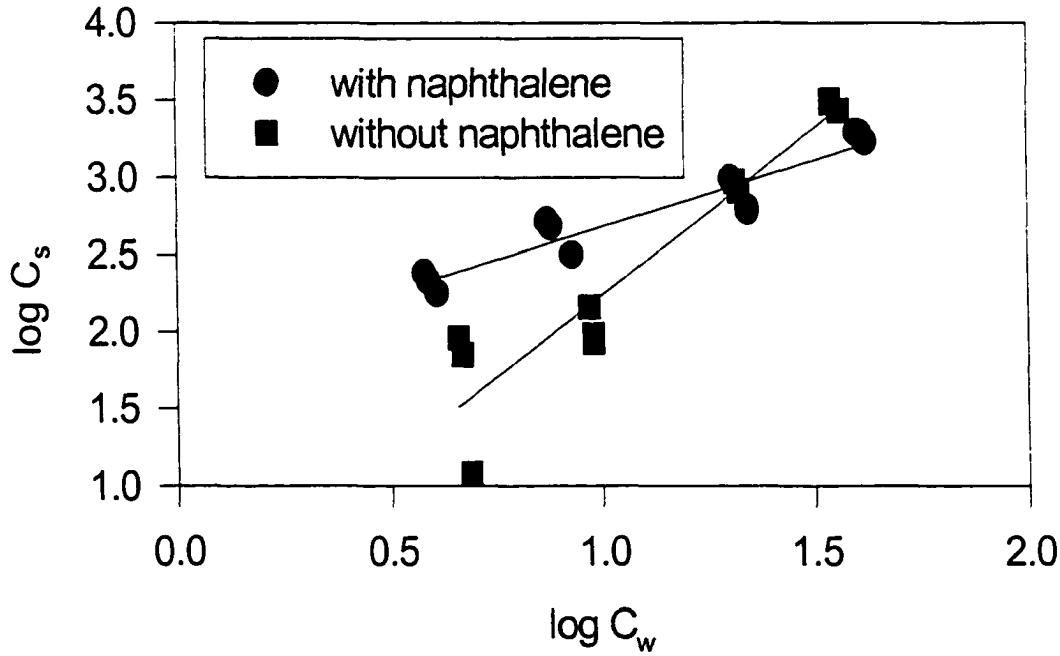

Fig. 11. 15-d sorption isotherms of DCB onto cellulose with and without initial 1-d equilibration with naphthalene (log-transformed data).

untreated cellulose. If DCB sorption is purely by partitioning, then the K_f values should be the same for both systems. The polymer theory also predicts the same outcome because sorption onto a rubbery polymer should not be affected by the presence of a cosolute.

Differences in the *n* values for the sorption isotherms of DCB with cellulose showed the same pattern as those observed for the PVC. A decrease in the *n* value was observed when cellulose was previously equilibrated with naphthalene. Based on the results of the previous experiment, DCB sorption in this experiment should also be governed by diffusion and hole filling. However, it was unlikely that these mechanisms were site specific. If they were, DCB sorption would be decreased by the naphthalene pretreatment.

DCB sorption isotherms for Pahokee peat with and without previous equilibration with naphthalene are shown in Fig. 12 and 13. DCB sorption onto the sorbent previously equilibrated with naphthalene was higher. The K_f values for the DCB sorption for pretreated and untreated Pahokee peat were 400.2 and 180.4, respectively (Table 7). The values were different at the 95% confidence level. Again, the partitioning and the polymer theories alone cannot explain the differences in the observed DCB sorption. Partitioning theory predicts no effect, while the polymer theory predicts a reduction in DCB sorption onto the pretreated Pahokee peat. The larger K_f value when naphthalene was present shows that naphthalene facilitated sorption of DCB. This can only be explained by postulating that the cosolute increased the hydrophobicity of the sorbent internal structure, hence increasing the effective f_{oc} (Brusseau, 1991; Onken and Traina, 1997). However, the DCB sorption pattern was different from that found with PVC and

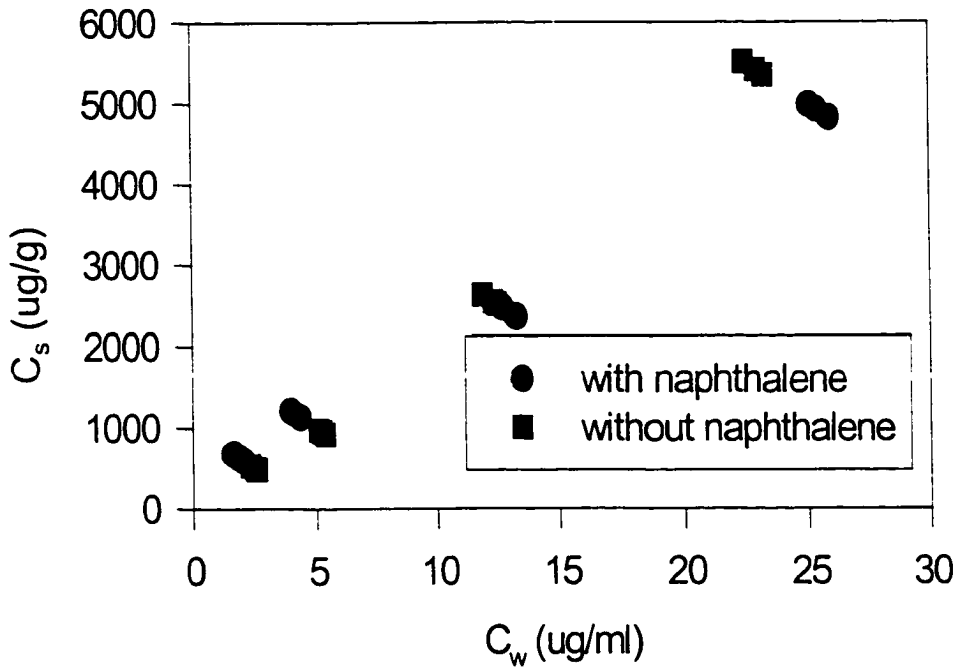

Fig. 12. 15-d sorption isotherms of DCB onto Pahokee peat with and without initial 1-d equilibration with naphthalene.

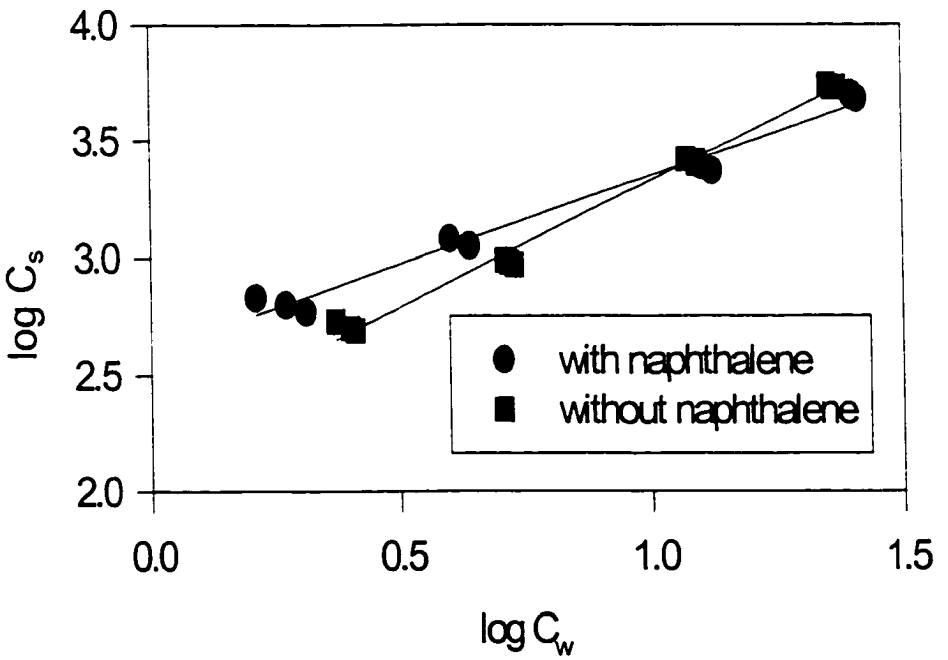

Fig. 13. 15-d sorption isotherms of DCB onto Pahokee peat with and without initial 1-d equilibration with naphthalene (log-transformed data).

cellulose. At higher initial DCB concentrations (25 and 50 μg/mL), the effect of sorbent pretreatment on DCB sorption was reversed. Thus, at higher concentrations of DCB, naphthalene did not facilitate the sorption of DCB onto the Pahokee peat. The data also show that initial sorption of DCB onto Pahokee peat was fast, which would occur if the internal environment of the peat became more hydrophobic.

The differences in the *n* values were similar to those observed for the DCB sorption isotherms with PVC and cellulose. The *n* value for the sorption isotherm for Pahokee peat previously equilibrated with naphthalene was 400.2, while the value for isotherm onto Pahokee peat without naphthalene pre-equilibration was 180.38 (Table 7). The *n* values were different at the 95% confidence level. The lowering of the *n* value for the sorption isotherm for sorbent previously equilibrated with naphthalene is consistent with diffusion and hole filling.

There are two generalizations that can be made from these sorption data. First, regardless of the sorbent type, DCB sorption was increased in systems with sorbents previously equilibrated with naphthalene. Secondly, the *n* values decreased for sorbents pre-treated with naphthalene. This can best explained by partitioning of the naphthalene into the internal structure of the sorbents, increasing the hydrophobicity of the sorbent away from the aqueous phase. The partitioning process would not be site-specific, otherwise the 1-d equilibration would be insufficient for the naphthalene to fill the sorption sites (as shown by the increasing DCB sorption onto all the sorbents with equilibration time). In the present study, the cosolute (naphthalene) and the sorbate (DCB) were added sequentially. If the sorption of the HOCs were by diffusion (according to the polymer theory), then pretreatment with naphthalene would have

reduced the sorption of DCB onto PVC and Pahokee peat. It appears that partitioning was the mechanism controlling sorption when the sorbents were pretreated with naphthalene for 1 d, and diffusion was the primary mechanism that controlled sorption at 15-d equilibration because partitioning is fast and entropy driven, while diffusion is time-dependent.

The effect of naphthalene equilibration time on DCB sorption

The objective of this part of study was to determine the effect of naphthalene equilibration time on DCB sorption onto PVC, cellulose, and Pahokee peat. DCB sorption onto PVC was hypothesized to be affected by equilibration time, while sorption onto cellulose would not be affected by equilibration time. PVC, cellulose, Pahokee peat were equilibrated with naphthalene (25 μg/mL) for 1 and 100 d, at which times the naphthalene in the solution phase was removed. The sorbents were then equilibrated for 15 d with DCB (concentrations of 5, 10, 25, or 50 μg/mL).

It was hypothesized that sorption of DCB onto PVC equilibrated with naphthalene for 100 d would be less than that measured for PVC equilibrated for 1 d if naphthalene entered the inner structure and occupied sorption sites, rendering fewer sites available for sorption by DCB. However, the amounts of sorbed DCB onto cellulose previously equilibrated with naphthalene for the two time periods would not be significantly different because sorption of naphthalene onto the cellulose should be independent of equilibration time. For Pahokee peat, the results would be closer to those of PVC because it has both condensed and amorphous regions. Pahokee peat equilibrated for

100 d with naphthalene would have fewer sorption sites for DCB as compared to Pahokee peat equilibrated with naphthalene for just 1 d.

The sorption isotherms for DCB and PVC pretreated with naphthalene for 1 or 100 d are shown in Fig. 14 and 15. The isotherms clearly indicate that sorption onto PVC equilibrated with naphthalene for 1d was higher than the sorption for PVC equilibrated for 100 d, as seen in Table 8. The K_f value for 100 d (2430 mL/g) was about two times higher than the K_f value for 1 d equilibration (1222 mL/g). The values were significantly different at the 95% confidence level. The differences in the DCB sorption isotherms for PVC previously equilibrated with naphthalene followed the predicted patterns. For PVC, less DCB was sorbed with the longer equilibration time with naphthalene. The *n* value was also higher (concave-up) for the 100-d sample. Overall, the sorption isotherm data for DCB with PVC appeared to follow the glassy versus polymer theory. DCB sorption onto the PVC follows seems to result from a dual mode mechanism, involving both diffusion and hole filling, as predicted by the polymer theory.

Sorption isotherms for DCB onto cellulose previously equilibrated with naphthalene for 1 and 100 d are shown in Fig. 16 and 17. The isotherms show that at DCB concentrations of 5, 10, and 25 μg/mL, sorption onto cellulose equilibrated with naphthalene for 100 d was lower than sorption to cellulose equilibrated with naphthalene for 1 d. However, the trend was reversed at a DCB concentration of 50 μg/mL. The K_f values showed a decrease as the equilibration time of cellulose with naphthalene increased (Table 8). The K_f values for the DCB sorption onto the cellulose previously equilibrated with naphthalene for 1 and 100 d were 65.81 and 18.10 mL/g, respectively. The values were significantly different at the 95% confidence level. The *n* values for the

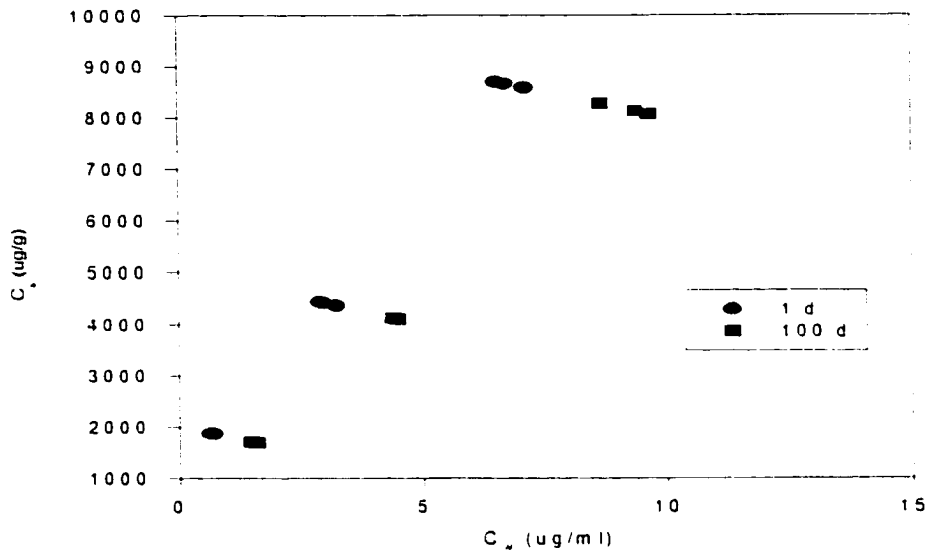

Fig. 14. The 15-d sorption isotherms for DCB and PVC previously equilibrated with naphthalene for 1 and 100 d.

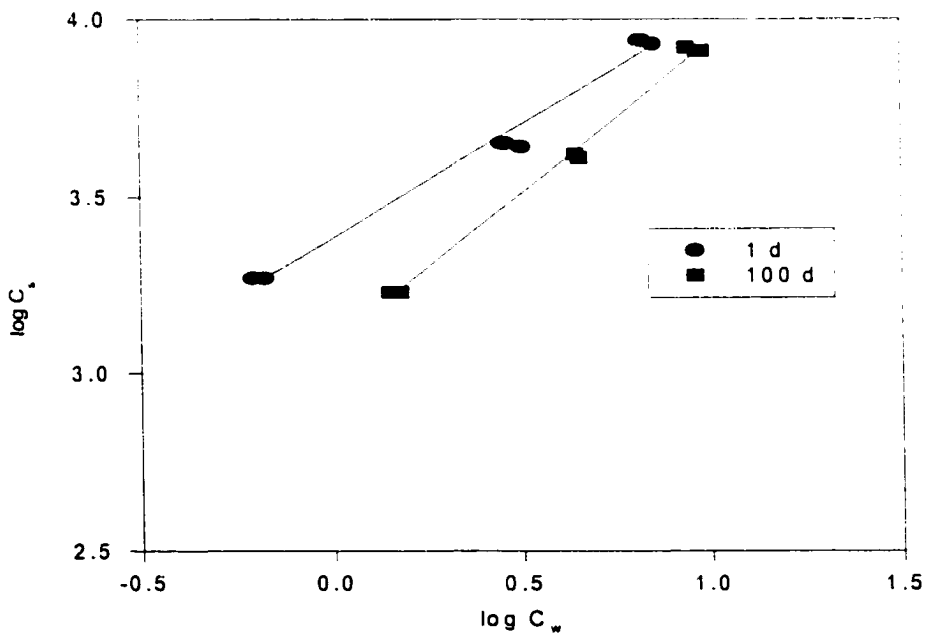

Fig. 15. The 15-d sorption isotherms for DCB and PVC previously equilibrated with naphthalene for 1 and 100 d (log-transformed data).

Table 8. The values of K_f, n, and R^2 for DCB sorption isotherms on the sorbents previously equilibrated with naphthalene for 1 or 100 d.

Sorbent	Equilibration time (d)	K_f (mL/g)	n	R^2
PVC	1	2430[†a]	0.63[a]	0.99
	100	1222[b]	0.85[b]	1.00
Cellulose	1	65.81[a]	0.86[a]	0.90
	100	18.10[b]	1.22[b]	0.90
Pahokee peat	1	400.2[a]	0.75[a]	0.98
	100	247.9[b]	0.87[b]	0.98

[†] Values with the same letter under the column for each sorbent indicate that they are not statistically significant at the 95% confidence level.

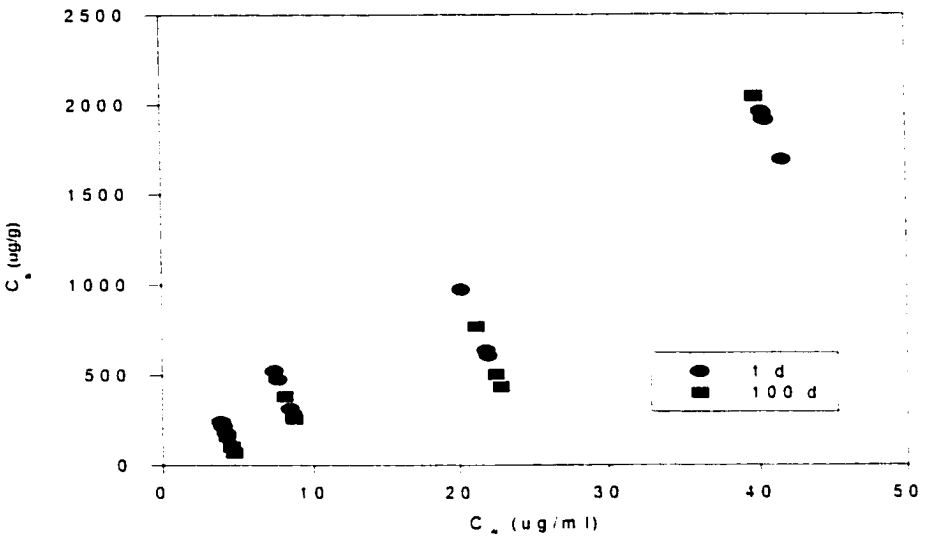

Fig. 16. The 15-d sorption isotherms for DCB and cellulose previously equilibrated with naphthalene for 1 and 100 d.

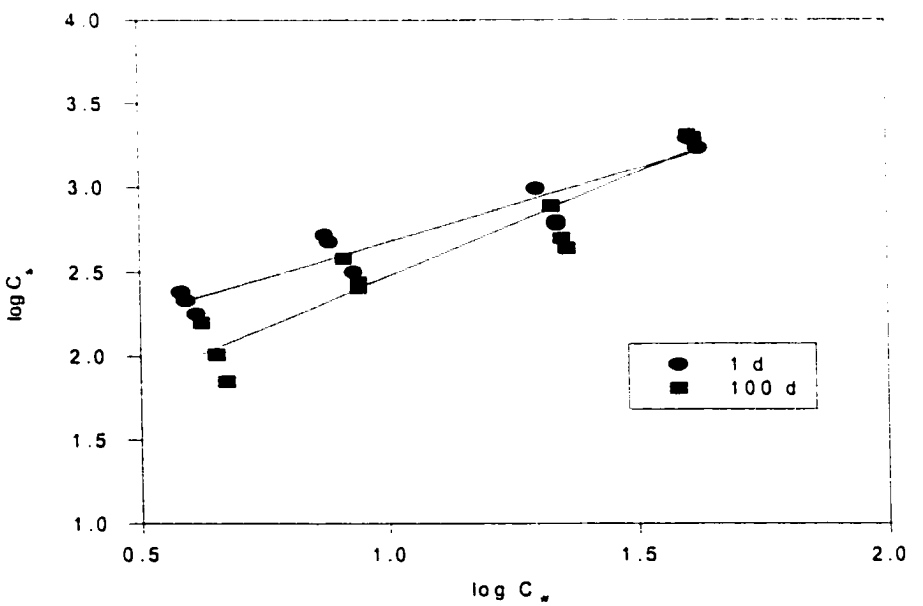

Fig. 17. The 15-d sorption isotherms for DCB and cellulose previously equilibrated with naphthalene for 1 and 100 d (log-transformed data).

cellulose sorption isotherms showed a pattern similar to the isotherms for the PVC. As the equilibration time with naphthalene increased, the *n* value also increased (concave-up). DCB sorption on cellulose previously equilibrated with naphthalene was not linear with respect to concentration and was affected by equilibration time. In other words, sorption did not follow the glassy versus rubbery polymer theory, which predicts no effect of equilibration time on HOC sorption onto cellulose.

The isotherms for DCB sorption onto Pahokee peat previously equilibrated with naphthalene for 1 and 100 d are shown in Fig. 18 and 19. The results indicate that DCB sorption was also affected by the equilibration time with naphthalene. The longer the equilibration of the peat with the naphthalene, the smaller the amount of DCB sorbed. The K_f values for DCB sorption isotherms with Pahokee peat previously equilibrated with naphthalene for 1 and 100 d were 400.2 and 247.9 mL/g, respectively (Table 8). The values are significantly different at the 95% confidence level. The *n* values for the DCB sorption isotherms increased from 0.75 to 0.87 as the naphthalene equilibration increased from 1 to 100 d. This pattern of increasing *n* values with increasing sorbent contact time with naphthalene was similar to the pattern shown by PVC and cellulose.

In an earlier part of this study, sorption of DCB onto Pahokee peat was found to fit more closely the partitioning mechanism, with nearly linear sorption isotherms and no significant effect of equilibration time on sorption. If this also applies to naphthalene, there should be no effect of naphthalene equilibration time on DCB sorption. However, the sorption data have shown that this is not the case. The results suggest that the sorption of naphthalene onto the Pahokee peat was by diffusion and hole filling mechanisms.

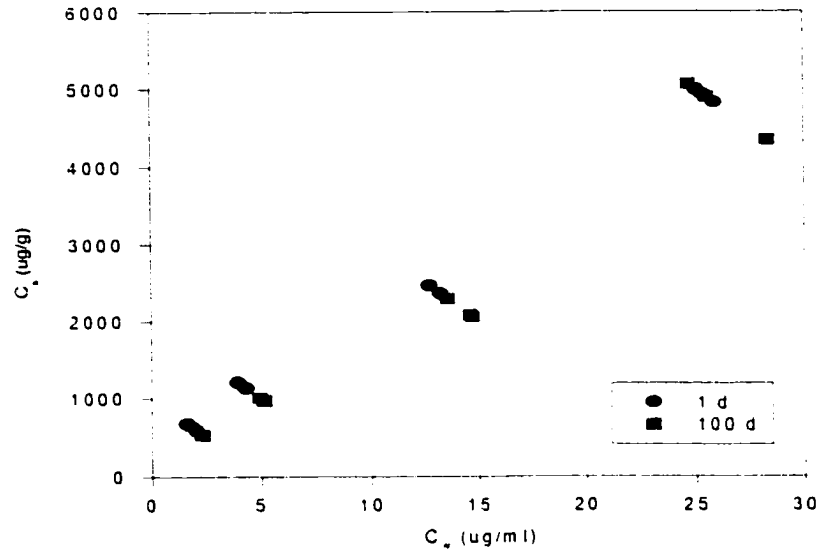

Fig. 18. The 15-d sorption isotherms for DCB and Pahokee peat previously equilibrated with naphthalene for 1 and 100 d.

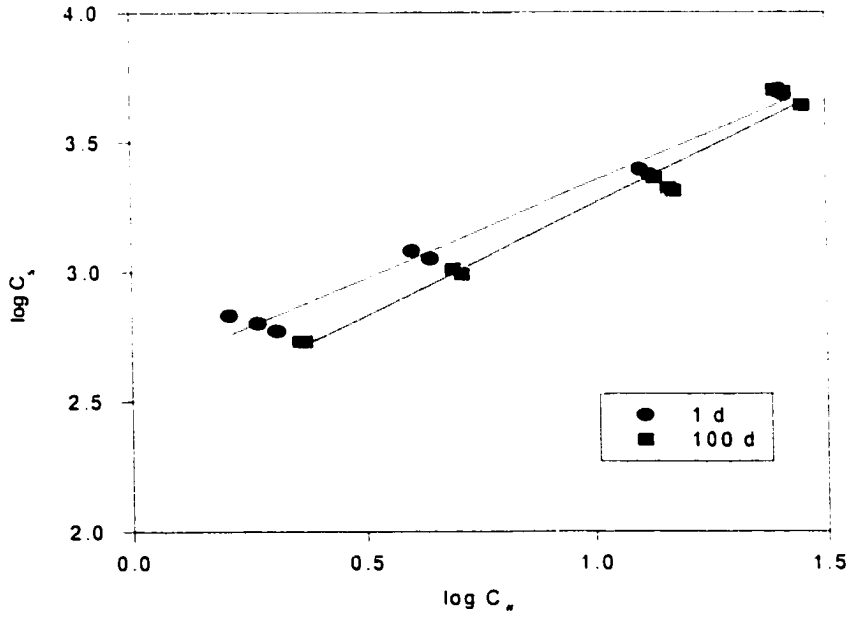

Fig. 19. The 15-d sorption isotherms for DCB and Pahokee peat previously equilibrated with naphthalene for 1 and 100 d (log-transformed data).

Two generalizations can be made with respect to the results from this part of the study. First, sorption of DCB was less in sorbent previously equilibrated with naphthalene for 100 d as compared to sorption for 1-d equilibration, regardless of the sorbent type. Secondly, the *n* values for the sorption isotherms increased with the longer naphthalene equilibration time with all three sorbents. The likely reason for the decreases in sorption of DCB onto sorbents equilibrated with naphthalene for the longer time period is that the sorption sites became less available to DCB.

The effect of ionic strength on DCB sorption

Sorption of DCB onto PVC, cellulose and Pahokee peat in the presence of two different concentrations of $CaCl_2$ was compared. Decreases in HOC sorption at higher ionic strength have been attributed to the compaction of humus (Traina et al., 1989; Schlautmann and Morgan, 1993). Based on the polymer theory, there should be no effect of ionic strength on DCB sorption onto cellulose because sorption should be by a partitioning-like mechanism rather than diffusion. Sorption of HOCs onto PVC should be increased by lowering the ionic strength because the PVC structure will be less compact, allowing opportunity for the HOCs to diffuse. The effect of ionic strength on DCB sorption onto Pahokee peat is expected to be similar to that found with PVC if the peat contains both condensed and amorphous regions.

DCB sorption isotherms (1-d equilibration) for PVC at two different $CaCl_2$ concentrations are shown in Fig. 20 and 21. There were no significant differences in sorption (95% confidence level) at initial DCB concentrations up to 25 μg/mL. However, at 50 μg/mL, sorption of DCB was much higher for the lower ionic strength as compared

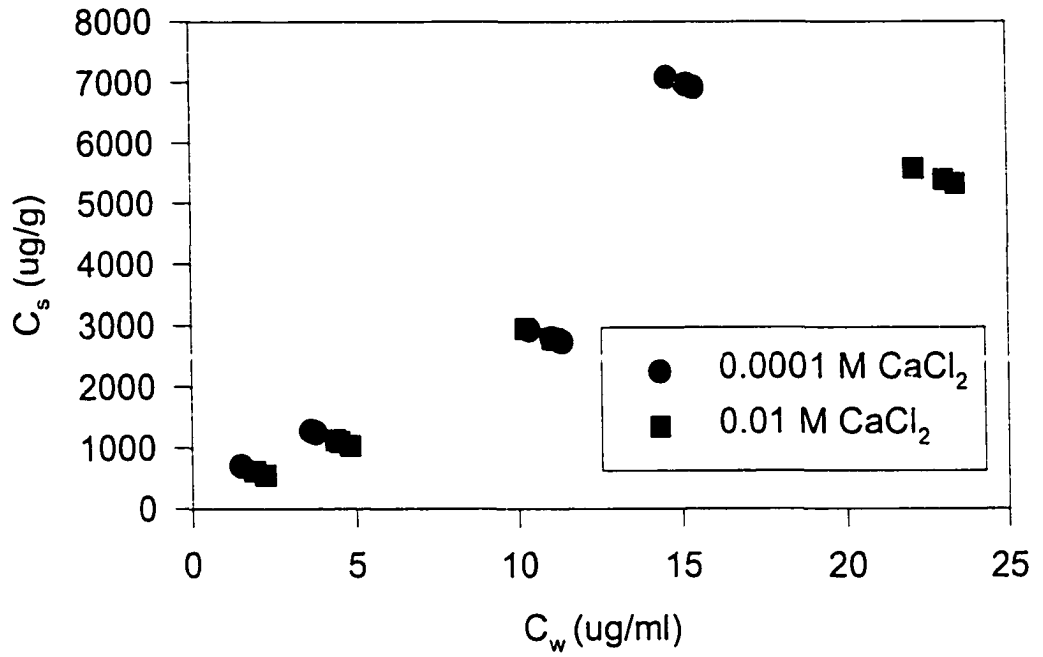

Fig. 20. DCB sorption isotherms (1-d) equilibrated onto PVC at two $CaCl_2$ concentrations.

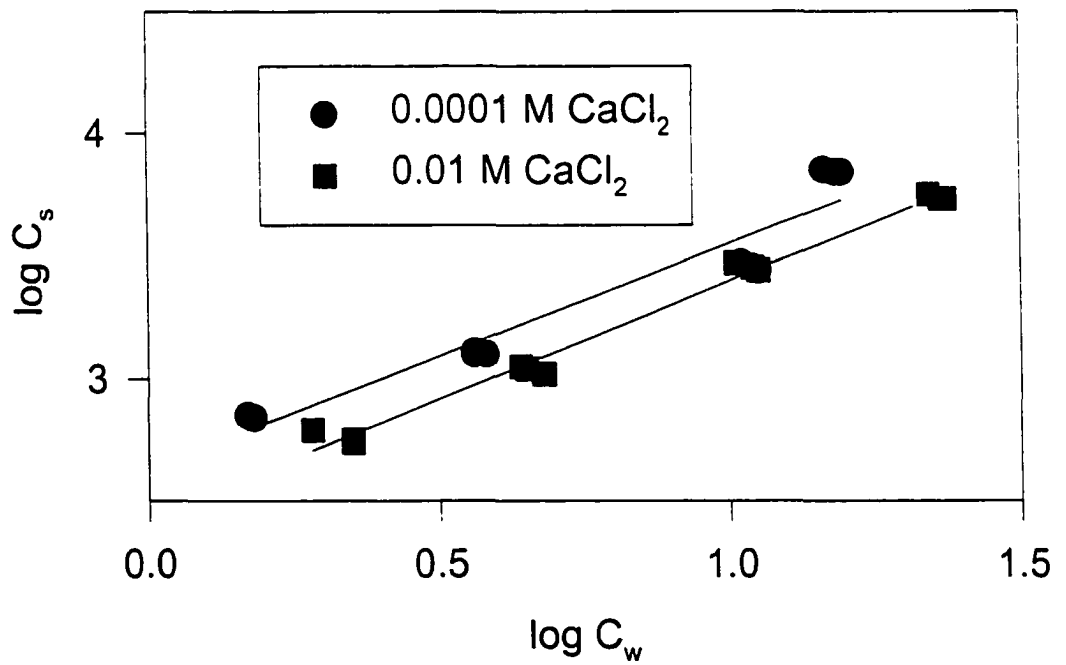

Fig. 21. DCB sorption isotherms (1-d) equilibrated onto PVC at two $CaCl_2$ concentrations (log-transformed data).

to the higher one. The K_f values for the 1-d sorption isotherms with PVC at 0.01 and 0.0001 M $CaCl_2$ were 275 and 434 mL/g, respectively (Table 9). The K_f value for the sorption isotherm at the lower ionic strength was significantly higher than the value for the system of higher ionic strength (95% confidence level). These results are in accordance with sorption of a HOC onto a glassy polymer for which sorption is by diffusion and hole filling. It is interesting to note that nearly equal amounts of DCB were sorbed at the lower range of concentrations, possibly because sorption was by partitioning, as suggested by many reported studies. The reason for the unexpected linearity of sorption data at low concentration ranges of DCB is unclear. The large difference in sorption at high DCB concentration may indicate that sorption at higher concentrations is dictated by diffusion. Therefore, at higher concentrations, sorption would be affected by the concentration gradient of the solute and by the accessibility of the sorbent to the solute molecules. On the other hand, sorption of HOC at lower concentrations is governed by the partitioning mechanism, which is independent of solute concentration gradient.

The *n* values for DCB sorption isotherms for PVC with 0.01 and 0.0001 M $CaCl_2$ were 0.91 and 0.96, respectively (Table 9), which were not significantly different at the 95% confidence level. The sorption experiments were only conducted at four initial DCB concentrations, making it difficult to see a pattern for the isotherm lines. Since, as was pointed out earlier, the value of *n* does not indicate the extent of sorption at any particular point in the isotherm, the values only represent the overall pattern of isotherm lines with increasing initial concentrations. Therefore, it is important to look at the isotherm plot from both the untransformed and the log-transformed data.

Table 9. The values of K_f, n, and R^2 for the DCB sorption isotherms in relation to two $CaCl_2$ concentrations.

Sorbent	$CaCl_2$ concentration	K_f (mL/g)	n	R^2
PVC	0.0001 M	433.8[a†]	0.91[a]	0.93
	0.01 M	274.7[b]	0.96[a]	0.99
Cellulose	0.0001 M	20.46[a]	1.36[a]	0.74
	0.01 M	4.79[a]	1.60[a]	0.94
Pahokee peat	0.0001 M	286.6[a]	0.89[a]	0.90
	0.01 M	252.9[a]	0.98[a]	0.98

† Values with the same letter under a column for each sorbent indicate that they are not statistically significant at the 95% confidence level.

Sorption isotherms for DCB with cellulose at the two $CaCl_2$ concentrations are shown in Fig. 22 and 23. Sorption at the initial DCB concentration of 25 μg/mL was not significantly different (95% confidence level) between the two $CaCl_2$ concentrations, but at 50 μg/mL, higher DCB sorption was observed. The results are similar to the sorption isotherms observed for PVC.

The *n* values for the sorption isotherms at 0.01 and 0.0001 M $CaCl_2$ were 1.36 and 1.60, respectively (Table 9), and they are not significantly different at the 95% confidence level. The values were higher than unity (concave up), suggesting diffusion and hole-filling were the mechanisms controlling DCB sorption. The concave-up pattern of the sorption isotherms suggests that the initial sorption of the DCB facilitated further sorption.

The DCB sorption isotherms (1-d equilibration) for the Pahokee peat equilibrated with $CaCl_2$ are shown in Fig. 24 and 25. The isotherm plots of the untransformed data did not indicate differences for DCB sorption with varying DCB concentrations. The K_f values of the sorption isotherms for systems with 0.01 and 0.0001 M $CaCl_2$ were 286.2 and 252.9, respectively (Table 9), which were not significantly different at the 95% confidence level. DCB sorption onto the Pahokee peat was not affected by the equilibration time, which suggests that partitioning was the most likely mechanism controlling the sorption. Unlike the sorption isotherms for cellulose, the isotherms for Pahokee peat did not show significant differences over the entire range of initial DCB concentrations. The *n* values for sorption isotherms for the systems at 0.01 and 0.0001 M $CaCl_2$ were 0.89 and 0.98, respectively (Table 9), which were not significantly different at 95% confidence level. The *n* values at 0.01 M $CaCl_2$ were closer to unity, suggesting

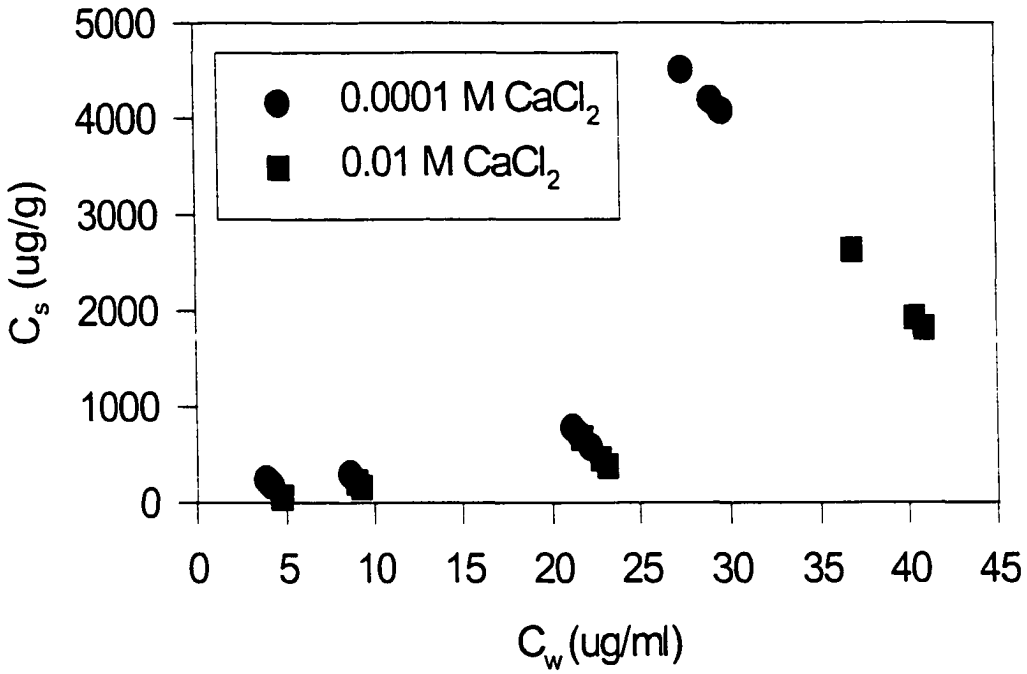

Fig. 22. DCB sorption isotherms (1-d) equilibrated onto cellulose at two $CaCl_2$ concentrations.

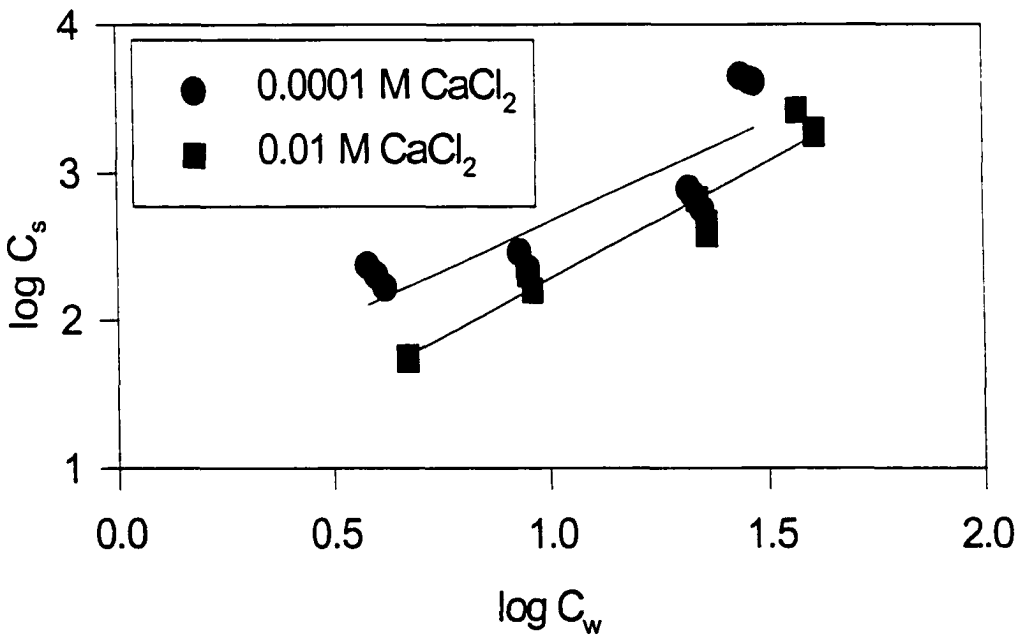

Fig. 23. DCB sorption isotherms 91-d) equilibrated onto cellulose at two ionic $CaCl_2$ concentrations (log-transformed data).

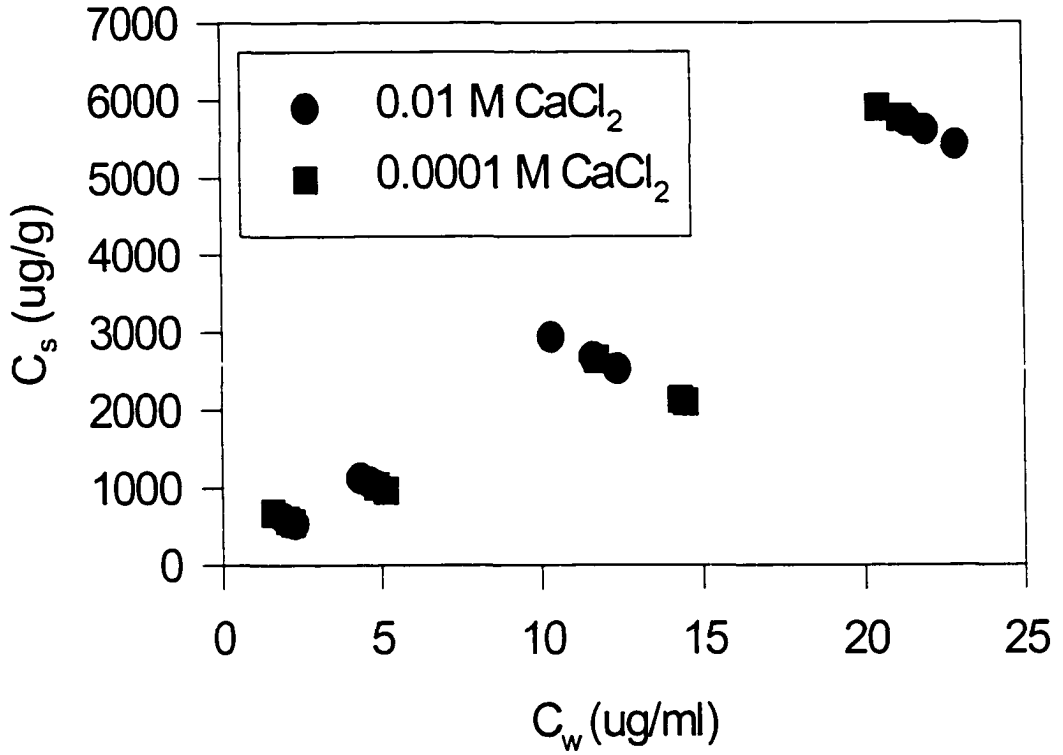

Fig. 24. DCB sorption isotherms (1-d) equilibrated onto Pahokee peat at two $CaCl_2$ concentrations.

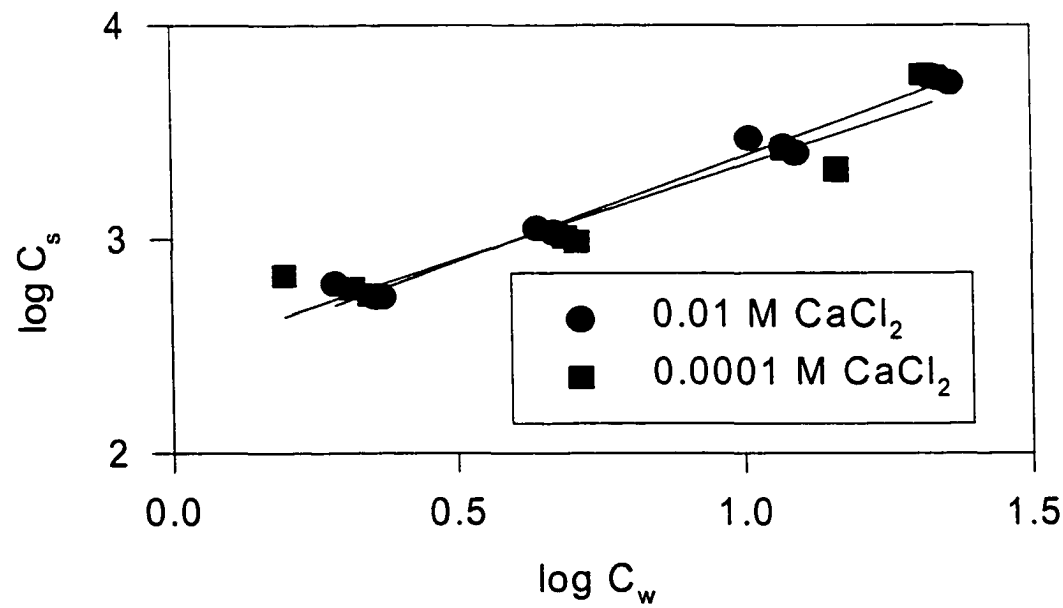

Fig. 25. DCB sorption isotherms (1-d) onto Pahokee peat at two $CaCl_2$ concentrations (log-transformed data).

that at lower ionic strength, diffusion and hole filling mechanism were also involved in the sorption processes.

CHAPTER V

GENERAL DISCUSSION

Models describing HOC sorption onto soil OM

Several models have been developed to explain the sorption of HOCs onto soil OM. Debates on which model is best to describe the process are continuing. Due to the hydrophobic nature of the HOCs, partitioning (dissolution) has been proposed as the mechanism governing HOC sorption onto soil OM (Chiou et al., 1979). A large body of research findings supports the partitioning theory. Partitioning behavior of HOCs between soil OM and water has been successfully described by applying the Flory-Huggins theory, which was developed to model interactions between solute and amorphous synthetic polymers (Chiou et al., 1983). The basic assumptions of the partitioning theory is that sorption is uniform and independent of solute concentration. Hence, the sorption isotherm is expected to be linear, and there should be no competition between solutes. But recent studies on soil OM structure suggest that it is composed micropores and voids (Maurice and Namjesnik-Dejanovic, 1999) that allow molecules to penetrate and diffuse. The reports of nonlinear sorption isotherms of HOC with soil OM, would support the diffusion mechanism.

Recently, the rubbery versus glassy polymer theory has received much attention by researchers in attempting to explain sorption of HOC onto soil OM. Carroll et al. (1994) developed this theory to explain HOC sorption onto soils and river sediments

based on differences between molecular diffusion into rubbery and glassy polymers. McGinley et al. (1996) found nonlinear sorption isotherms and competitive sorption between tetrachloroethylene and trichlorobenzene in one of the soils, while an additive effect with the other soil. They suggested that sorption occurred on or within tightly ordered or condensed OM for soil that exhibited nonlinear sorption isotherms and competitive sorption. Sorption by the other soil was viewed as occurring within the more amorphous parts of soil OM. Xing et al. (1996) and Xing and Pignatello (1996) found that HOC sorption was linear and noncompetitive with rubbery polymers, while with peat soil and glassy polymers, HOCs exhibited nonlinear isotherms and competition. These two studies were the first attempt to apply the polymer theory to explain HOC sorption onto soil OM by using amorphous and glassy polymers as model sorbents.

Basically, isotherms for HOC sorption onto soil can be linear or nonlinear. The linear isotherms suggest partitioning processes, while the nonlinear isotherms suggest that other mechanisms are responsible for the sorption processes, such as diffusion and specific sorbate-sorbent interaction.

Factors affecting HOC sorption onto soil OM

There are many possible reasons for the variability of HOC sorption data. First, soils are heterogeneous, consisting of a wide range of types of minerals and OM. Therefore, when one compares HOC sorption onto soils, soil physical and chemical characteristics are important factors that should be considered. Soil OM content especially, must be similar in order to make valid comparisons of HOC sorption with different soils. OM structure, polarity, molecular weight, and diagenesis can greatly

influence HOC sorption (Grathwol, 1990; Rutherford et al., 1992; Young and Weber, 1995; Stuer-Lauridsen and Pedersen, 1997; Piatt and Brusseau, 1998; Kleineidam et al., 1999). OM also differs in pore size, fraction of hydrophilic and hydrophobic regions, and chemical constituents, depending on its source and the residence time in soil (Ghosh and Schnitzer, 1980).

Although HOCs are sorbed predominantly by organic constituents of soil, other soil constituents also sorb HOCs. A list of reported studies on HOC sorption onto mineral surfaces can be found in Schwarzenbach et al. (1993). The mechanisms for HOC sorption onto mineral surfaces include diffusion into micropores as well as weak hydrogen bonding and van der Waal's forces (Schwarzenbach et al., 1993). As both the mineral and the organic constituents of soils can sorb the HOCs, their relative amounts are important in sorption process. However, studies suggest that the contribution from the organic fraction is more important. For example, Kleineidam et al. (1999) studied sorption of phenanthrene onto a wide variety of heat-treated and nontreated lithocomponents (constituents of sand and gravel sediments) and unweathered rock fragments, and concluded that sorption was solely due to the organic constituents.

Another factor that contributes to differing results from studies of HOC sorption onto soil is the concentration of HOC. Depending on the sorption mechanism, sorbate concentrations can greatly influence the sorption processes. Maxin and Kögel-Knabner (1995) showed that sorption of polycyclic aromatic hydrocarbons (PAHs) to water-soluble soil OM was linear up to 30% of the PAH solubility. Above 30%, the sorption no longer obeyed the linear partitioning rule. They attributed the nonlinear isotherms at higher sorbate concentrations to experimental artifacts and decreasing PAH affinity to the

OM. In addition to the sorbate concentrations, sorbent concentrations may also affect HOC sorption. O'Connor and Connolly (1980) showed that sorption coefficients decreased as the sorbate concentrations increased.

Postulation of HOC sorption mechanisms based on sorbent properties

The mechanism of HOC sorption can be postulated from the structure of sorbents. There are two possible mechanisms for HOC sorption regardless of the type of sorbent: partitioning and diffusion. Partitioning of HOCs between the soil organic phase and water can be considered to be similar to that between an organic solvent phase and water. Hydrophobic forces drive the partitioning process. Water molecules form stronger hydrogen bonds between themselves and polar surfaces than with hydrophobic molecules or surfaces. Detailed discussion of the mechanisms and the thermodynamics of the partitioning processes can be found in Israelachvili (1991) and Schwarzenbach et al. (1993). Briefly, organic molecules orient themselves in a phase that has a polarity similar to theirs because of the more favorable thermodynamics. Polar surfaces form hydrogen bonds with water. The water molecules are tightly bound to the surfaces; replacing them is energetically unfavorable. Therefore, HOCs will move to a phase that does not require replacement of the tightly bound water molecules. Accordingly, a prerequisite for a partitioning process is the presence of a hydrophobic phase. This phase can be discrete (e.g., an organic solvent) or a continuum of phases such as in soil-water systems. Partition of organic solutes between an organic solvent phase and water can be described by a ratio of the concentration of the organic solute in solvent to its concentration in water. Similarly, partitioning of HOCs between water and the soil OM phase should in

theory be linear. Mathematical derivation of linear partition coefficients between organic phases and water is provided by Schwarzenbach et al. (1993).

Sorption of DCB onto cellulose

In the present study, sorption of DCB onto cellulose was relatively linear up to an initial DCB concentration of 25 μg/mL for all treatments, above which the sorption increased (Fig. 4, 10, 16, and 22). Increasing the equilibration time only increased sorption of DCB onto the cellulose at lower concentrations (Fig. 4 and 5). But at an initial DCB concentration of 50 μg/mL, the evidence did not indicate that equilibration time affected DCB sorption. This suggests that sorption onto the cellulose was only affected by the equilibration time when the driving force, i.e., the concentration gradient, was small. Desorption of DCB from cellulose was affected by both the initial DCB concentration and length of time the DCB was in contact with cellulose (Table 5). At initial DCB concentrations of 5 and 10 μg/mL, no detectable amount of DCB was desorbed from the sorbent. For DCB initial concentrations of 25 and 50 μg/mL, desorption from the sorbent equilibrated for only 1 d was significantly higher than the sorbent equilibrated with the DCB for 15 and 30 d. Slower desorption with increasing equilibration time suggests that diffusion was the mechanism of the sorption process.

I hypothesized that initial DCB sorption onto cellulose created a hydrophobic environment in the cellulose structure, which would then allowed further sorption. This is supported by the fact that cellulose pre-treated with naphthalene increased DCB sorption at initial DCB concentrations up to 25 μg/mL (Fig. 16 and 17). It would be expected that at lower DCB concentrations, diffusion into the structure is time-dependent.

At higher concentrations, however, an increase in the sorbent hydrophobicity and a higher concentration gradient would allow DCB to be sorbed more rapidly onto the cellulose. Results from the other experiments also support the hypothesis that sorption was facilitated at higher concentrations by an increase in sorbent hydrophobicity and a higher concentration gradient. At higher initial DCB concentrations, increasing naphthalene equilibration time with cellulose did not reduce DCB sorption (Fig. 10). Sorption of DCB onto the cellulose was reduced with increasing ionic strength (Fig. 22 and 23) probably because the calcium ions bind with the polar functional groups of the cellulose, causing it to compress and rendering it less open for the diffusion of DCB molecules.

The results from this study suggest that sorption of DCB onto the cellulose is controlled by diffusion rather than partitioning because there is no hydrophobic domain in the cellulose structure. Results from desorption studies (Table 5) also lend support for diffusion as the main mechanism for DCB sorption. Desorption from cellulose was less for sorbents equilibrated for longer periods of time. Since equilibrium by partitioning is achieved in a relatively short time period compared to diffusion, the effect of equilibration time on DCB desorption suggests that diffusion was the major mechanism controlling the sorption onto the cellulose. All these factors can be attributed to diffusion mechanism rather than partitioning. Sorption of DCB onto cellulose did not obey the characteristics of molecular diffusion onto amorphous polymers as predicted by the polymer theory.

Sorption of DCB onto PVC

DCB sorption onto PVC was affected by factors that control diffusion. Sorption was increased with increasing equilibration time (Fig. 2). The K_f values for sorption isotherms at 1- and 15-d equilibration were 274.7 and 972.5 mL/g, respectively. These values are higher than those reported by Xing and Pignatello (1996) for 1,3-dichlorobenzene sorption onto PVC which were 65.9 and 671 mL/g for 1- and 15-d equilibration times, respectively. The *n* values for DCB sorption isotherms in the present study were closer to unity than the values reported by Xing and Pignatello (1996). The *n* values for DCB sorption isotherms for 1- and 15-d equilibration times were 0.96 and 1.07, respectively. The *n* values for 1,3-dichlorobenzene sorption isotherms reported by Xing and Pignatello (1996) were 0.879 for both 1- and 15-d equilibration times. Since equilibrium takes longer for diffusion than partitioning, the results suggest that diffusion was the controlling mechanism for DCB sorption. The effect of equilibration time was significant over the entire DCB initial concentration range, unlike the situation with cellulose.

Desorption was affected by the DCB equilibration time with the sorbent (Table 4) as well the initial sorbate concentrations. At an initial DCB concentration of 5 μg/mL, no detectable amount of desorbed DCB was measured. At DCB initial concentrations of 10, 25, and 50 μg/mL, the percentage of DCB desorbed decreased with increasing equilibration time and also the initial DCB concentrations. The results indicate that diffusion was the controlling mechanism in the sorption process. As equilibration time and DCB concentration are increased, more DCB will diffuse into the micropores of PVC. Desorption of DCB molecules from PVC will be more difficult after 30-d

equilibration and at higher concentrations because DCB molecules penetrate deeper into PVC molecules as equilibration time and initial DCB concentration increase.

The presence of naphthalene increased DCB sorption onto PVC. This may be due to an increase in the hydrophobicity of the pores, enhancing further sorption either by partitioning or diffusion. Since diffusitivities of a solution are influenced by the viscosity of water (Schawarzenbach, 1993), initial sorption of the naphthalene may have reduced the viscosity of water at the vicinity where diffusion took place. Increased naphthalene residence time with the sorbent decreased DCB sorption. The longer the naphthalene residence time the lesser the amount of DCB that can diffuse onto PVC.

Sorption of DCB onto PVC followed the characteristics of molecular diffusion into a crystalline polymer in some cases but not in others. PVC appeared to be a highly reactive sorbent for DCB as reflected by its large K_f values compared to the other sorbents. Almost 100% of the DCB was sorbed at an initial DCB concentration of 5 μg/mL. This suggests that there may have been interactions between DCB and PVC molecules such as van der Waals forces.

Sorption of DCB to Pahokee peat

The Pahokee peat used in this study is almost mineral free (93% OM). Previous studies have indicated that sorption of HOCs was almost exclusively onto the organic fraction of soils. There are two mechanisms that can control DCB sorption onto the soil OM, diffusion and partitioning. Diffusion is partially controlled by the sorbent porosity. Sorbent hydrophobicity is the main factor that controls partitioning. Clearly, an

understanding of the structure of the soil OM is important to the understanding of the sorption of HOCs.

All humic matter substances regardless of their origins have hydrophilic and hydrophilic regions (Schnitzer and Khan, 1972; Wershaw, 1993). The hydrophobic regions are mostly made up of waxes, resins, lipids, and alkyl side chains. A pyroanalysis-mass spectrometry study of OM, soil extracts, and whole soils conducted by Schnitzer and Schulten (1995) provided detailed analysis of OM. Microscopic evidence has shown that soil OM contains nanopores, which would be important in HOC sorption (Maurice and Namjesnik-Dejanovic, 1999). Whether partitioning or diffusion is more important is still unclear. Both linear sorption isotherms (Deitsch et al., 1998) and nonlinear sorption isotherms (Xing et al., 1996; Xing and Pignatello, 1996; Xing and Pignatello, 1998) for HOC sorption onto soil OM have been reported.

The sorption isotherms for DCB with Pahokee peat are relatively linear (Fig. 6 and 7) compared to the isotherms for the other two sorbents and are not affected by equilibration time, as reflected by the n values of the sorption isotherms (Table 3). In general, desorption of DCB from Pahokee peat was not affected by either equilibration time or initial DCB concentrations, which clearly suggests that partitioning was the controlling mechanism for sorption. As partitioning is not energy driven, desorption of sorbate from the sorbent should not be affected by the residence time of the sorbate in the sorbent.

The results from the sorption and desorption experiments clearly support the view that partitioning is the controlling mechanism for DCB sorption to the peat. However, sorption of DCB was decreased by the increase in the naphthalene equilibration time

(Fig. 12 and 13). If sorption were a pure partitioning process, there should not be any effect of naphthalene equilibration time on DCB sorption. This could be explained by a slow diffusional process, which was only apparent at the longer equilibration times.

Pre-equilibration of Pahokee peat with naphthalene increased sorption of DCB at low initial DCB concentrations, but at higher initial concentration sorption was reversed. These results suggest that increasing hydrophobicity of the sorbents did not increase sorption when the concentration gradient was high. Neither a pure partitioning process nor a diffusional mechanism alone can explain this.

Ionic strength had no effect on the sorption of DCB onto Pahokee peat. Ionic strength can alter the size of micropores in the OM structure but not its hydropbobicity. These results suggest that partitioning controlled DCB sorption.

With Pahokee peat, in some experiments a partitioning mechanism could explain the results, while in other experiments the results could only be explained by a combination of partitioning and diffusional mechanisms. It is reasonable to conclude that both partitioning and diffusion mechanisms were involved. Which mechanism is more important in any sorbate-sorbent system depends on many factors, including sorbate concentrations, sorbent concentrations, presence of a cosolute, and ionic strength.

CHAPTER VI

SUMMARY AND CONCLUSIONS

This study was conducted to evaluate the applicability of the rubbery versus glassy polymer theory in describing 1,2-dichlorobenzene (DCB) sorption onto organic sorbents. The polymer theory predicts sorption of HOCs onto amorphous polymers would yield linear isotherms while sorption onto glassy polymers would yield nonlinear isotherms. DCB was the sorbate and PVC, cellulose, and Pahokee peat the sorbents used in this study. Experiments were conducted to determine:

1. The effects of equilibration time on DCB sorption and desorption from the sorbents.
2. The effects of naphthalene on DCB sorption.
3. The effects of equilibration time on naphthalene competition with DCB for sorption sites.
4. The effects of ionic strength on DCB sorption.

PVC had a very high affinity for DCB and sorption increased as the equilibration time was increased. Sorption of DCB to PVC was the highest among the sorbents as reflected by high K_f values. Sorption of DCB onto cellulose showed partitioning-like isotherms at DCB concentrations up to 25 μg/mL. Sorption increased with increasing equilibration time at DCB concentrations up to 25 μg/mL but the pattern was not

observed at 50 μg/mL. Sorption of DCB onto Pahokee peat was the closest to unity among the sorbents, and in general was not affected by equilibration time.

No detectable DCB was desorbed from PVC that had been equilibrated with DCB at a concentration of 5 μg/mL. At higher concentrations, desorption was affected by both equilibration time and initial DCB concentration. Percentage of DCB desorbed from PVC decreased inversely with equilibration time and initial sorbate concentration. No detectable DCB desorption was found with cellulose equilibrated with DCB at concentrations of 5 and 10 μg/mL. At 50 μg/mL, desorption was generally affected by equilibration time and sorbate concentration, which was similar to the pattern observed for PVC. Desorption of the DCB from Pahokee peat was not affected by either equilibration time or initial sorbate concentration.

Previous equilibration of the sorbents with naphthalene increased DCB sorption. However, the effect of equilibrating the sorbent with naphthalene on DCB sorption was significant only at the lower range of concentrations. At higher concentrations, the effect was reduced. This was true for all sorbent types.

Sorption of DCB onto PVC initially equilibrated with naphthalene for 100 d was less than sorption onto PVC equilibrated with naphthalene for only 1 d. For cellulose at lower DCB concentrations, sorption of DCB for 100 d was less than sorption onto DCB equilibrated for 1 d. However, at higher concentrations, the effect was reversed.

Amounts of DCB sorbed onto PVC and cellulose were higher at lower ionic strength. But there was no significant effect of ionic strength on the DCB sorption onto Pahokee peat. Based on these results, it can be concluded that:

1. The patterns of sorption and desorption of DCB with PVC and cellulose did not support the glassy versus rubbery polymer theory.
2. The glassy and polymer theory was unable to describe the pattern of DCB sorption and desorption with Pahokee peat.
3. The sorption and desorption patterns of the DCB with Pahokee peat was best described by a partitioning mechanism.
4. In general, the Freundlich model was able to fit the sorption data of DCB with all three sorbents.

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APPENDICES

APPENDIX I.

An example of SAS code used to determine the statistical significant of K_f and n values of the DCB sorption isotherms.

```
options nodate;
data PVC;
input days Cs logCs Cw logCw;
cards;

1       619.89        2.79       1.90       0.28
1       553.86        2.74       2.23       0.35
1       556.55        2.75       2.22       0.35
1       1101.63       3.04       4.49       0.65
1       1037.44       3.02       4.81       0.68
1       1128.58       3.05       4.36       0.64
1       2777.53       3.44       11.11      1.05
1       2789.85       3.45       11.05      1.04
1       2955.34       3.47       10.22      1.01
1       5584.18       3.75       22.08      1.34
1       5397.35       3.73       23.01      1.36
1       5325.86       3.73       23.37      1.37
15      1672.05       3.22       1.64       0.21
15      1664.52       3.22       1.68       0.22
15      1660.08       3.22       1.70       0.23
15      4187.47       3.62       4.06       0.61
15      4252.84       3.63       3.74       0.57
15      4225.76       3.63       3.87       0.59
15      8413.35       3.92       7.93       0.90
15      8485.77       3.93       7.57       0.88
15      8499.34       3.93       7.50       0.88
30      1869.27       3.27       0.65       -0.18
30      1865.94       3.27       0.67       -0.17
30      1890.14       3.28       0.55       -0.26
30      4501.30       3.65       2.49       0.40
30      4515.37       3.65       2.42       0.38
30      4522.91       3.66       2.39       0.38
30      9012.45       3.95       4.94       0.69
30      9019.59       3.96       4.90       0.69
30      9051.54       3.96       4.74       0.68
;
proc glm;
class days;
model logCs = days logCw days*logCw;
run;
```

APPENDIX II.

An example of a SAS code used to determine the statistical significant of the mean of DCB desorbed from the sorbent.

```
options nodate;
data PVC;
input days Iconc desorbed;
cards;
1  5   0.00
1  5   0.00
1  5   0.00
1  10  8.12
1  10  13.42
1  10  13.31
1  25  19.82
1  25  24.40
1  25  22.79
1  50  36.51
1  50  37.60
1  50  36.95
15 5   0.00
15 5   0.00
15 5   0.00
15 10  0.00
15 10  7.94
15 10  8.07
15 25  17.52
15 25  18.40
15 25  19.77
15 50  36.46
15 50  33.11
15 50  35.00
30 5   0.00
30 5   0.00
30 5   0.00
30 10  0.00
30 10  0.00
30 10  0.00
30 25  14.72
30 25  13.80
30 25  14.84
30 50  27.50
30 50  26.81
30 50  25.12
;
```

```
proc sort;
by Iconc;
proc glm;
class days Iconc;
model desorbed = days Iconc;
lsmeans days/pdiff;
by Iconc;
run;
```