SORPTION OF PENTACHLOROPHENOL TO HUMIC ACIDS AND SUBSEQUENT EFFECTS ON BIODEGRADATION AND SOLVENT EXTRACTION

by

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(ABSTRACT)

The focus of this research was to acquire a better understanding of the sorption and desorption of pentachlorophenol to soil organic matter. In order to separate the reactions controlling the interactions with the soil organic matter from those associated with mineral surfaces, these experiments used only humic acids extracted from soil samples. The major focus of this study was to examine the effects of solution pH, humic acid concentration and contact time on the degree of sorption. The association reactions proceeded slowly. Even after 28 days, many solutions had not attained equilibrium. An increase in the solution pH led to a reduction in the amount of partitioning onto the humic material. At solution concentrations between 100 mg/L and 800 mg/L of total organic carbon (TOC), an increase in the humic acid concentration resulted in a lower partition coefficient. However, above a concentration of 800 mg/L TOC, further increases in the amount of humic material caused enhanced sorption. The particulate humic acids demonstrated a higher affinity for the pentachlorophenol than did the dissolved polymers. In the concentrated solutions, the majority of the humic acids were present in the particulate form.

Two experiments focused on the effect of sorption on the bioavailability and solvent extraction of pentachlorophenol. The bioavailability data suggested that the sorbed contaminant was not readily accessible to the microorganisms. The humic acids prevented the extraction of the sorbate by methyl-tert-butyl ether and methylene chloride. Recovery of the pentachlorophenol sorbed to the dissolved humic acids ranged from zero to 42.9 percent, depending on the solution pH. The removal of pentachlorophenol

from the particulate matter varied from 25 percent to 90 percent. Longer contact times diminished the transfer of PCP associated with the solid humic acids to the solvent phase.

The experimental results were not consistent with a simple, one mechanism model. The best explanation of the data was provided by a model which included liquid-liquid partitioning, surface sorption, absorption and chemisorption. The dominant process depended on the contact time, solution pH, and concentration and nature of the humic acids.

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Chapter 1: Introduction

Within the past decade, pentachlorophenol (PCP) has gained widespread recognition as a major environmental pollutant. This chemical was once commonly used as a pesticide in both agriculture and industry (Fishbein, 1975). Pentachlorophenol's extreme toxicity causes it to be an excellent fungicide, herbicide, insecticide and bactericide. This compound's toxicity is not confined to only the agricultural and industrial pests. "PCP is known to accumulate in fish and the mean survival time LD50 is about one hour at one ppm" (Fishbein, 1975, p.391). In humans, chronic exposure can lead to liver and kidney damage. Clearly it is not desirable to permit this chemical to remain, much less accumulate, in the natural environment. Unfortunately, agricultural runoff, industrial site runoff and industrial waste disposal sites containing pentachlorophenol have caused widespread contamination of soils and groundwater.

In order to estimate the extent of contamination and to determine the most effective subsurface remediation approach, it is necessary to understand the behavior of pentachlorophenol within the soil and groundwater matrix. Since sorption of a given compound to the natural organic matter influences contaminant transport, this reaction is of particular importance. Compounds associated with dissolved organic material follow the groundwater flow. Solutes which strongly adhere to the organic matter coating the mineral surfaces are not moved far from their point of release. The kinetics of sorption affect this retardation of subsurface contaminant movement. Specific sorption reactions will determine the kinetics and reversibility of the reaction. If a fraction of the sorbed PCP is not readily desorbed, typical pump-and-treat remediation techniques may not remove that irreversibly held or slowly released solute.

Subsurface microorganisms are capable of degrading PCP (Mikesell and Boyd, 1986). However, the sorbed fraction may not be accessible to the soil microorganisms, resulting in biodegradation rates that are controlled by desorption. The association with the humic matter might be strong enough to shield pentachlorophenol from solvent extraction and thereby interfere with this contaminant's quantification by conventional methods.

Since the 1970's, much research has been conducted on the sorption of hydrophobic organic compounds to soil. The majority of these studies have focused on the interactions between nonionizable contaminants and the soil as a whole. In the literature, the general consensus is that a given compound associates primarily with the organic matter but minimally, or negligibly, with mineral surfaces. Controversy shrouds the actual mechanism(s) which govern these interactions. Chiou (1983, 1985, 1986), Rutherford, *et al.* (1991), and Hassett and Anderson (1979), to list a few authors, claimed that liquid-liquid partitioning constitutes the sorption process. Lagas (1988), Murphy, *et al.* (1990) and Isaacson and Frink (1984) stated that surface sorption controls these associations. A third model, proposed by Wershaw (1986), suggested that the humic acid polymers engulf the hydrophobic organic compounds, similar to an absorption process.

This research concentrated on the sorption of pentachlorophenol to only the humic acid fraction of the soil organic matter. The objectives of this study were:

- to determine the influence of organic matter concentration, pH and contact time on the association of pentachlorophenol with dissolved and particulate humic matter.

- to examine the efficiency of methyl-tert-butyl ether (MTBE) and methylene chloride (MeCl) in extracting the humic bound PCP.

- to determine the bioavailability of humic bound PCP.

- to attempt to gain a better understanding of which of the previously mentioned reactions actually dominate the sorption of PCP to humic matter.

Chapter 2: Literature Review

Section 2.1: Introduction

In response to the growing problem posed by organic pollutants in the environment, much research has been conducted on the fate and behavior of these compounds. Hydrophobic organic contaminants tend to associate with the organic matter present in the soil and groundwater. This natural organic matter is either dissolved or attached to mineral surfaces as a precipitate coating. If pollutants were to strongly sorb to the solid organic matter, then they would not be transported far from their point of release into the subsurface system. However, compounds which either remain in the aqueous phase or interact with the dissolved organic matter will follow the groundwater flow.

The type and degree of association influences the choice of remediation techniques. Since a significant fraction of the sorbed contaminant may be irreversibly held, compounds which bind with the solid organic matter may not prove amenable to typical pump-and-treat removal procedures. Sorption to the humic materials may protect the contaminants from biodegradation (Ogram, *et al.*, 1985) and interfere with their analytical detection (Hassett and Anderson, 1979). In order to estimate the extent of contamination and to design the most appropriate remediation method, it is necessary to understand how a given chemical will interact with the soil humic and fulvic acids.

Liquid-liquid partitioning and surface sorption have been the most commonly proposed sorption mechanisms. Wershaw (1986) has suggested that hydrophobic contaminants become assimilated within humic polymer aggregates. Each theory has different implications for the fate and transport of hydrophobic contaminants. Since the interactions between organic pollutants and natural organic matter are not completely understood, controversy surrounds these theories.

Section 2.2: Pentachlorophenol

Pentachlorophenol is an extremely toxic compound which has been widely used as an insecticide, bactericide, fungicide and herbicide. The majority

of PCP produced was incorporated into the lumber industry as a wood preservative (Fishbein, 1975). Due to its once prevalent use, PCP has become a widespread, major environmental contaminant (Hickman, 1982).

Pentachlorophenol is a weak acid with a pKa of 4.75 (Lee, *et al.*, 1990). Consequently, under most natural environmental conditions, this chemical is present primarily in its dissociated form. Although the hydroxyl group lends polarity to PCP, the presence of the five chlorines causes the molecule to be extremely hydrophobic. Its aqueous solubility is 14 milligrams per liter (mg/L) and its log octanol-water partition coefficient (Kow) is 5.01 (for further information on PCP's chemistry, see Hickman, 1982). Often a compound's log Kow is used to predict the degree of sorption in the subsurface. A high log Kow, such as pentachlorophenol's value, is correlated with a high amount of sorption.

Section 2.3: The Nature of Humic Acids

Humic acids and fulvic acids are operationally defined. Humic acids are the natural organic compounds which are in dissolved form above pH 12 and are particulate below pH 2. Fulvic acids are soluble throughout the entire pH range. Both are stable byproducts of the breakdown of vegetative matter. Although these organic acids are extremely heterogeneous, some general characteristics are applicable to each type of organic matter. According to Stevenson (1985), humics consist of more carbon and less oxygen, mainly as part of ether or ester linkages, than do fulvics. Both types of organic matter contain ionizable functional groups. However, fulvic acids are characterized by more ionizable functional groups, primarily carboxyl groups, than humic acids and are thus the most polar.

> "Oxygen containing functional groups greatly influence the reactivities of humic substances in the soil environment. Undoubtedly the carboxyl and phenolic structures are the most important of these because they are the major groups responsible for the contribution by organic matter to the cation exchange capacity of soils and they can have chelating effects."
>
> (Hayes and Swift, 1978, p.195)

Thus the fulvic acids should possess a greater cation exchange capacity than do the humics.

The second general defining characteristic is molecular size. The molecular weights of humic acids range from 2000 atomic mass units (amu) to 20,000 amu, while those for fulvics are less than 2000 amu. In the natural environment, most of the organic matter is associated with some mineral surface while a small, but important, fraction is dissolved.

Section 2.4: Mechanisms of Association

Section 2.4.1: Theoretical Isotherms

The association between organic chemicals and natural organic matter results from physical, chemical and electrostatic reactions. The primary mechanisms listed by Voice and Weber (1983) were Van der Waal interactions, hydrophobic forces which drive a given molecule out of the aqueous phase, and charge repulsion/attraction. Several isotherms attempt to model sorption using equations derived from the thermodynamic laws which govern these forces. According to the Langmuir saturation model, the amount of adsorption depends on the number of sites at which this physical reaction may occur and the equilibrium liquid concentration (Voice and Weber, 1983). One linear form of this model is:

$$q_e = Q^o - q_e/bC_e$$

where q_e is the amount sorbed per unit mass of sorbent, C_e is the equilibrium solution concentration, Q^o is the maximum amount which can be sorbed to the solid and b is a constant which depends on the entropy (Voice and Weber, 1983).

The Brunauer Extended Langmuir (BET) isotherm (as cited in Voice and Weber, 1983) takes into account the possibility that multiple layers of the compound may sorb to the sorbent, and that a complete monolayer might not be present prior to the formation of subsequent layers. Including the liquid

saturation concentration and a constant which encompasses the heats of adsorption and condensation for the solute with the sorbent, this equation is more complex than the simple Langmuir:

$$q_e = B(C_e)(Q^o)/\{(C_s-C_e)(1+(B-1)(C_e/C_s))\}$$

where C_s is the solute saturation concentration, B is a constant relating to the energy of adsorption, and the other terms are defined as previously.

From the Langmuir and BET equations, one can note that two of the primary variables which control the distribution of a solute between two phases at equilibrium are the liquid concentration and the amount of surface area available for sorption. As the equilibrium concentration and/or the number of sorption sites increase, the amount adsorbed per unit mass of sorbent should also increase. Thus, if the association between organic compounds and humic acids were strictly a surface sorption phenomenon, raising the humic acid concentration of the solution should increase the q_e term.

The Gibbs equation adopts a different theoretical approach and "considers the change in surface concentration necessary to achieve a thermodynamic balance between two homogeneous phases" (Voice and Weber, 1983, p.1435-36). Thus with this model, more attention is focused on the thermodynamic forces behind the reactions which comprise the association. Considering that organic matter is not homogeneous, the appropriateness of this equation for modeling sorption to humic acids is questionable.

Although of theoretical interest, the assumptions needed to simplify the theory and derive the equations may cause these models to be of little practical value. The Langmuir equation, originally designed for gas-solid adsorption but adapted to liquid-solid systems, is partly based on the assumptions that adsorbate molecules do not affect each other and that the energy of binding is the same for all sorption sites (Voice and Weber, 1983). It seems inappropriate to use this equation to model liquid-liquid systems. Also, the energy of binding assumption does not hold for the functional groups on humic acids. The Langmuir isotherm includes the concept that only a monolayer will form at maximum adsorption. The BET isotherm contains the first assumption, but does allow for the formation of multiple layers of a sorbed solute. Although more

realistic, this theoretical extension causes the equation to be more cumbersome than its predecessor. In short, "these isotherms often fail to describe sorption data adequately" (Voice and Weber. 1983, p.1436).

Section 2.4.2: Empirical Approach

The general consensus within the literature is that the empirical Freundlich isotherm better describes the observed data than do the theoretical models. According to this empirical approach:

$$x/m = K_p C_e^n$$

where x is the sorbed mass, m is the sorbate mass, n is an empirical constant, C_e is the equilibrium sorbent concentration and K_p is the empirical partitioning constant or partition coefficient. Frequently for soil systems n is assumed to be unity, resulting in the linear Freundlich equation. "This model for description of sorption equilibria has gained widespread acceptance due to its lack of mathematical complexity" (Voice and Weber, 1983, p.1436).

This linear partitioning model is usually applied to the soil mass as a whole, not to the mineral or organic fractions separately. Although the constant varies from compound to compound, research has demonstrated that dividing the K_p by the percent organic matter yields a value which differs little for a given chemical over a wide range of soil types (Schellenberg, *et al.*, 1984; Voice and Weber, 1983). This finding implies that the soil mineral fraction plays a very minor role in the sorption of hydrophobic species. "Adsorption of these compounds by soil mineral surfaces is considered to be relatively insignificant in wet soils" (Chiou, 1985, p.9). Indeed, this notion is the reasoning proposed by some researchers to allow the inclusion of the mineral fraction in the experimental set-up but the exclusion of any possible influences of this part of the soil in the analysis of the data.

It has been proposed that the partition coefficient depends primarily on a compound's lipophilicity, of which the octanol-water coefficient (K_{ow}) provides a good measure. Thus the Kow may be used to predict the Kp:

$$K_p = (f_{oc})(K_{oc}) = (f_{oc})(b)(K_{ow})^a$$

where "the values of a and b are primarily determined by the type of compounds (i.e., compound class(es), range of lipophilicity) on which the relationship is established, and only to a smaller degree by the type of natural sorbents used" (Schellenberg *et al.*, 1984, p.652). The implication is that the type(s) of organic matter present will not significantly influence the degree of binding. Because fulvic and humic acids possess different structures, molecular weights and polarities, this logical conclusion from the aforementioned articles seems unrealistic.

Since K_{ow} may be related to a compound's aqueous solubility, several researchers, Chiou, *et al.* (1983, 1986) and Karickhoff (Voice and Weber, 1983), among others, have attempted to form a mathematical equation to predict the amount of sorption from this property. For a variety of reasons, aqueous solubility alone provides an unreliable means for estimating the degree of association with natural organic matter. First, the methods used to determine a compound's aqueous solubility yield varied results (Voice and Weber, 1983). Secondly, "the thermodynamics of saturated aqueous solutions differ significantly from those in two-phase systems where neither phase approaches saturation" (Voice and Weber, 1983, p.1438). Attempting to model sorption solely on a compound's aqueous solubility oversimplifies the process. However, solubility should indicate qualitatively how well a given compound will associate with organic matter. In general, the least soluble compounds will sorb in the highest quantities.

Section 2.4.3: Liquid-Liquid Partitioning

The fact that the K_{ow} has been used successfully to estimate the partition coefficients of hydrophobic chemicals implies that this sorption may be a liquid-liquid partitioning process in which the organic matter assumes the role played by the octanol. "Chiou *et al.* (1979, 1983) suggested that the sorption of nonionic organic compounds from water consists primarily of solute partition (dissolution), rather than adsorption, into soil humic phase" (Chiou *et al.*, 1985,

p.9). This theory implies that the organic matter is not itself dissolved into the water, but forms its own separate matrix within the solution.

If liquid-liquid partitioning were the dominant mechanism, then the association of hydrophobic compounds with humic acids should be fully reversible. Equilibrium should be rapidly achieved. The distribution of a given compound between the aqueous and organic phases should be a function of their relative polarities. Since this phenomenon does not depend on a finite number of sorption sites, the partitioning should display no competitive effects between cosolutes (Chiou, *et al.*, 1983). This mechanism is not a surface sorption phenomenon, thus it would not be appropriate to model the process using Langmuir or BET equations. According to Chiou, *et al.* (1983, 1985) and Rutherford, *et al.* (1992), the linear Freundlich isotherm should provide the best mathematical description of the process.

Numerous studies lend support to the theory of liquid-liquid partitioning. Hassett and Anderson (1979) examined the interaction of cholesterol and polychlorinated biphenyl with dissolved aquatic humic matter. Using gel permeation chromatography, they noted that a significant fraction of these compounds was associated with the organics. "It was found that dissolved organic matter inhibited adsorption of cholesterol and tetrachlorobiphenyl {to the Sephadex gel}, probably by binding these compounds and holding them in solution" (Hassett and Anderson, 1979, p.1528). These results indicated that preferential dissolution into the organic phase overwhelmed surface sorption tendencies with the gel. Hassett and Anderson (1979) also observed that the presence of dissolved organic matter inhibited the ability of carbon tetrachloride to extract cholesterol. However, these results did not conclusively prove that liquid-liquid partitioning is the dominant mechanism driving sorption. Liquid-liquid partitioning should be fully reversible. Considering that the extractions were performed thrice with a solvent in which the cholesterol is highly soluble, one could claim that these significantly reduced extraction efficiencies indicated that some irreversible complexation had occurred.

"Several studies have demonstrated that dissolved organic matter can increase the apparent aqueous solubility of hydrophobic compounds" (Hassett and Anderson, 1979, p.1526). It is not that the actual water solubility is enhanced, but that more of the compound is held in solution by the organic

matter and in these studies no attempt was made to separate these two phases. A more recent study did distinguish between the water and the organic matter. Abdul and others (1990) observed that higher quantities of hydrophobic compounds bound to sand desorbed into a humic acid solution than into a strictly aqueous one. The extent of this increase depended on the lipophilicity of the solute. The humic acids were most effective in removing compounds of the greater hydrophobicities. These observations suggested that a form of dissolution into the organic phase took place.

Chiou and others (1983, 1985, 1986) have also examined the apparent water solubility enhancement of nonionic, hydrophobic compounds in the presence of dissolved organic matter. Their results yielded linear isotherms and no obvious competitive effects between cosolutes, even when the equilibrium concentration was as high as 90% of saturation. The log of the partition coefficient was modeled as a linear function of the log K_{ow} with a r^2 value of 0.989 (Chiou, *et al.*, 1983). These data conformed to anticipated results from a liquid-liquid partitioning process. One must note that Chiou's experiments used the entire soil, not simply the organic fraction. These authors did not contemplate the possibility of surface sorption to organic matter bound to the mineral component. Perhaps the Freundlich isotherms were linear and no competitive interactions were observed because there was an excess of sorption sites on the particulate organic matter. These data did not conclusively prove that liquid-liquid partitioning controls the sorption process.

The molecular weight of the dissolved organic phase appears to influence the degree of partitioning. High molecular weight humic acids enhance water solubility to a greater degree than do the lower molecular weight fulvics (Chiou, *et al.*, 1986). These results were consistent with the model promulgated by Wershaw:

> "who proposed that the structural units of humic acid are arranged into membranes and/or micelles having hydrophobic interiors and hydrophilic exteriors . . . By this model the hydrophobic NPOC {nonpolar organic compound} became trapped within the hydrophobic interior of the humic acid"
>
> (cited in Abdul, *et al.*, 1990, p.332)

The humic acids possess a large volume which may engulf the contaminants. A compound may also diffuse across the semipermeable membrane and become trapped within the hydrophobic interior of the humic aggregates (Wershaw, 1986). However, the above model is a form of absorption, not dissolution. Perhaps the compound initially partitions into the organic phase, then gradually becomes absorbed within the humic molecular structure.

Rutherford, *et al.* (1992) demonstrated that the polarity of the sorbent influences these interactions. Nonpolar compounds tended to associate with the less polar humics in greater quantities than with the more polar fulvic acids. "The effect of sample polarity on the observed partition coefficient is intimately consistent with the well-known effect of solvent polarity on solute solubility" (Rutherford, *et al.*, 1992, p.338). Stated more simply, like dissolves like. These data supported the liquid-liquid partitioning theory.

Liquid-liquid partitioning is one mechanism by which hydrophobic organic compounds bind to organic matter. However, to state emphatically that this dissolution is the primary mechanism, particularly based on experiments that do not directly address the possibility of surface sorption or absorption, would be to oversimplify a complex situation.

Section 2.4.4: Surface Sorption

In contrast to Chiou, Hassett, Abdul and others, there are some researchers who espouse that the primary mechanism of association is surface sorption. Several studies demonstrated that the data do not always follow linear, fully reversible Freundlich isotherms (Gschwend and Wu, 1985). Gschwend and Wu (1985) claimed that any deviations from the liquid-liquid partitioning model resulted from experimental artifacts. They observed that the colloidal fraction which is difficult to remove via centrifugation influenced the resulting partition coefficients. "The observed partition coefficients (determined with no precautions against NSP {nonsettling particles} effects) were found to diminish with suspended solids loadings as reported previously by many workers" (Gschwend and Wu, 1985, p.91).

Chiou, *et al.* (1983, 1985, 1986) considered the attachment to the organic solids/colloids to be a liquid-liquid partitioning phenomenon. The partition

coefficients were ratios normalized to a per unit mass basis. The fact that the partition coefficient depended on the suspended solids content implied that the particulate organic matter and dissolved organic matter had differing affinities for the compounds. If the sorption process were simple dissolution, this implication should not be true. Other authors have observed this same relationship between the solids concentration and the partition coefficients (Voice, *et al.*, 1983). Gschwend and Wu did not attempt to separate the truly dissolved organic matter from the remainder of the solution by ultrafiltration, dialysis or gel permeation chromatography.

Using a continuous flow system with a hydraulic retention ranging from 1.7 hours to 50 hours, Isaacson and Frink (1984) found the sorption of chlorinated phenols to sediments to reach a limiting maximum concentration. The method employed probably mimicked groundwater flow better than batch equilibration studies. In this same paper, the authors noted that the desorption isotherms were significantly different from the corresponding sorption ones. A portion of the chlorophenols were resistant to removal. An experiment by Lagas (1988) yielded data which supported the notion of an irreversibly held fraction. The actual partition coefficients "greatly exceed those predicted on the basis of sorption controlled solely by hydrophobic forces" (Isaacson and Frink, 1984, p.46). These results implied that surface sorption may play an important role. However, it was unclear from this study whether these inconsistencies with liquid-liquid partitioning were attributable to only the organic fraction or whether the mineral components interacted significantly with the phenols.

There is further evidence which demonstrates the importance of surface sorption reactions. In one study it was found that the type of mineral to which the humic matter was attached influenced the degree of sorption of several hydrophobic compounds (Murphy, *et al.*, 1990). These results suggested that there was a three way interaction between the mineral surface, organic material and contaminant which affected the actual sorption reactions. Such behavior was not consistent with the hypothesis that liquid-liquid partitioning controls sorption. These same authors observed that their data yielded nonlinear Freundlich isotherms "on the mineral-humate sorbents {which} suggest that the sorbed humic substance is behaving as a hydrophobic surface rather than a hydrophobic phase" (Murphy, *et al.*, 1990, p.1515). Murphy, *et al.* (1990) noted

that the K_{OC} was in part a function of the amount of organic matter which coated the minerals. This relationship was a predictable consequence of associations dominated by surface reactions.

Evidence from the literature indicates that dissolution, surface sorption and solute entrapment play roles in the association of hydrophobic organic contaminants with organic matter. Westall, *et al.* (1985), listed the first two mechanisms, along with the complexation of the organic compound onto metal surfaces, as the possible processes by which a given contaminant can be removed from the aqueous phase. Carter and Suffet (1982) stated that neither dissolution nor surface sorption adequately explained the interactions between organic contaminants, DDT in their experiments, and natural organic matter:

> "Both liquid partitioning and surface sorption require the presence of a second bulk phase where the DDT will either accumulate at the interface or dissolve in the nonaqueous phase. In the case of dissolved humic materials, there is no second bulk phase. Furthermore, the DDT and the humic acid have sizes within the same order of magnitude . . . One could just as well speculate about the 'adsorption' or 'partitioning' of humic materials to DDT and investigate whether or not this association affected the aqueous behavior of the humic material." (p.737)

The comment on size does not apply to pentachlorophenol. However, many of the articles cited herein did support dissolution or adsorption based on experiments using compounds similar to DDT. Carter and Suffet (1982) indicated that the chemistry of association is more complex than what either "school of thought" might lead one to believe. The absorption model eliminates the above concerns. The amorphous, physical structure of the humic acid, influenced by pH and neighboring molecules, may be the main factor affecting these hydrophobic associations. The contaminant may react with the favorable sites on the humic acid, after which the humic polymer may change form to encompass within itself the contaminant. Desorption would result only after the humic polymer had shifted its shape such that the contaminant could break free of the organic matrix or solution conditions caused the initial diffusion to be reversed across the humic "membrane" (Dove, 1992).

To state emphatically that only one of the aforementioned mechanisms governs these interactions would be a gross oversimplification. The natural environment tends to be a complex, dynamic system. It seems more likely that a variety of reactions govern the association of contaminants with soil humic acids.

Section 2.5: Kinetics of Association

Although the actual mechanisms of sorption in the subsurface system are a source of controversy, in general it is agreed that the process rapidly approaches equilibrium. Most of the researchers assumed that the vast majority of the relevant interactions occurred within 24 hours. Lagas (1988) did note that a small fraction of the contaminant required days to sorb. Robinson (1990) observed that both the amount of contaminant sorbed in the slowly sorbing fraction and the necessary equilibration time increased with increasing organic carbon content. These findings were consistent with those of Karickhoff and Morris, and DiToro and Horzempa, as cited in Robinson's thesis (1990). The slow reaction rates were attributed to the time needed for the compound to reach sorption sites within the organic matrix by diffusion.

Recent evidence suggested that equilibrium might not be as readily achieved as previously thought. A study by Ball and Roberts (1991) demonstrated that significant amounts of sorption continued to occur over a period of months. The change was so slow as to not be noticeable if one were to take measurements only over a period of several days. Ball and Roberts (1991) concluded that it is possible that many of the experiments cited in the literature compiled data collected under nonequilibrium conditions. In a review of recent articles, Pignatello stated that both sorption and desorption proceed more slowly than previously believed. This length of equilibration time could explain the "irreversible" fraction and hysteresis noted in the literature (Pignatello, 1989).

Slow kinetics are not necessarily inconsistent with the proposed mechanisms of association. With liquid-liquid partitioning, it is possible that a long period of time is required to completely assimilate the contaminant into the interior of the organic phase. Adsorption might be slow since it is in part a

function of the probability that the contaminant comes into contact with an appropriate sorption site on a humic polymer. Some of the sorption sites might not be readily accessible. With the amorphous polymer entrapment of the hydrophobic compounds, time might be necessary for either the humic acid to change its structure such that the contaminant is enveloped within the polymer's hydrophobic interior or the compound to be transported from the hydrophilic exterior into the hydrophobic region. Wershaw (1986) did not indicate whether the process was envisioned to follow rapid or slow kinetics. Steinberg (1987) suggested that the slowly sorbing fraction resulted from the slow diffusion of the compound into the soil inner pore structure as opposed to the kinetics of the actual sorption mechanism.

Although contrary to the predominant view of the literature, recent evidence indicates that the theory of rapid kinetics is not accurate. Since most groundwater transport models assume that equilibrium is rapidly achieved, proof of slow kinetics would have a significant impact in that area.

Section 2.6: Influence of pH

The literature discussed deals primarily with nonionic hydrophobic compounds. Pentachlorophenol is weak acid with a pKa of 4.75 (Lee, *et al*, 1990). Ionization increases slightly the polarity of this compound. The negatively charged hydroxyl on the phenolate would be repulsed by dissociated carboxyl groups on the humic acid. However, it has been demonstrated that a significant portion of the phenolate ions form organic-inorganic ion pairs with free cations in the aqueous solution (Westall, *et al.*, 1985). "According to Bjerrum's theory of ionic association, ion pairs can form in the solution phase and then be transferred to the three-dimensional organic phase as a neutral species in the same manner as a HOC {hydrophobic organic compound}" (Lee, *et al.*, 1990, p.655). That pentachlorophenol which forms an ion-pair should sorb to humic acids in a manner similar to that of the neutral species.

It appears that pentachlorophenolate sorption becomes significant only above pH 7 (Lee, *et al.*, 1990). In this pH range, only a slight fraction of the

pentachlorophenol would be present in its neutral form. "There is strong evidence that the sorption of phenolate species is predominantly a partitioning process between the aqueous phase and the organic phase present in a natural sorbent" (Schellenberg, *et al.*, 1984, p.657). Thus the sorption is perceived to follow the same mechanisms as outlined previously. However, due to its slightly lower hydrophobicity and negative charge, the phenolate ion partitions to a lesser degree than its neutral counterpart.

Although the mechanisms of phenolate sorption are subjects of controversy, it is clear that the anion does not sorb as readily as neutral PCP. Several studies (Lee, *et al.*, 1990; Schellenberg, *et al.*, 1984) demonstrated that increasing the pH decreased the association of PCP with the soil/sediment sample. The log of the partition coefficients followed a linear, inverse trend with respect to increasing solution pH.

Section 2.7: Biodegradation of Sorbed Pentachlorophenol

Natural subsurface microorganisms are capable of converting pentachlorophenol to carbon dioxide and water. It is not known if the microbes are able to directly degrade PCP sorbed to humic acids or if the organisms must wait until the contaminant desorbs before they are able to use it as a food source.

Larsson and Lemkemeier (1989) proposed that the presence of humic acids promoted the degradation of phenolic compounds. Microbial communities within a humic matrix have adapted themselves to using phenolic structures associated with humic material as a food source. "Aromatic, chlorinated hydrocarbons showing structural similarity to aromatic, humic compounds may thus be degraded by relatively unspecific enzymes produced by these microbial communities" (Larsson and Lemkemeier, 1989, p.1081). This statement was based on experimental results (Larsson and Lemkemeier, 1988) which showed that PCP was more readily degraded in a high humic content solution than a nearly humic free solution. The presence of natural sediment matter enhanced the complete biological decomposition of PCP (Larsson and Lemkemeier, 1989). This observation supported the findings of

Pignatello (as cited in Larsson and Lemkemeier, 1989, p.1085) "that surface-attached bacteria were the type most efficient at mineralizing pentachlorophenol". These studies did not distinguish between the mineralization of the humic bound PCP and PCP free in solution.

"Surfaces may influence the degradability of organic chemicals either by adsorbing the molecules to make them less available or by increasing the microbial density at surfaces as compared to that in solution" (Subba-Rao and Alexander, 1982, p.659). Research conducted by Ogram, *et al.* (1985), indicated that both solution and surface microbes are able to degrade (2,4-dichlorophenoxy)acetic acid, but that the acid sorbed to the organic matter was not accessible to either type of bacteria. Robinson (1990) examined the bioavailability of 2,4,6-trichlorophenol associated with dissolved humic acids. The free trichlorophenol was rapidly mineralized. Degradation of the sorbed fraction was slow and linear, indicating that desorption controlled the rate of biodegradation. Scribner, *et al.* (1992) observed that simazine which had been associated with a soil for several years was not bioavailable, while recently applied simazine was readily degraded by microorganisms. Not only the sorption itself, but the length of contact time with the sorbent appeared to affect biodegradation.

Section 2.8: Solvent Extraction of Sorbed Compounds

Hassett and Anderson (1979) observed that the presence of dissolved humic matter decreased the efficiency of carbon tetrachloride extractions of cholesterol by nearly half. However, if the humic solutions were irradiated with ultraviolet rays prior to the addition of cholesterol, the extraction efficiencies were similar to percent removals from distilled water solutions.

Data from the study by Hassett and Anderson (1979) indicated that the humic matter is capable of interfering with the solvent extraction of a sorbed compound. If dissolution were the only mechanism driving the association with the humic acids, one would anticipate that the solvent would remove virtually all of the solute. Even after three extractions, 60 percent of the cholesterol in Hassett and Anderson's experiment was not extracted by the solvent. These results supported the absorption model. A surface sorption model including

complexation reactions would not be inconsistent with reduced extraction efficiencies.

Steinberg, *et al.* (1987) noted that 1,2-dibromoethane which had been in contact with soil for times ranging from several months to 19 years was substantially more resistant to extraction than recently sorbed 1,2-dibromoethane. The longterm association of 1,2-dibromethane with the soil prevented the removal of this contaminant by conventional means.

Chapter 3: Materials and Method

Introduction

The techniques employed in this research and described below were either standard procedures or were adapted from similar, prior work.

Section 3.1: Experimental Design

The initial intent of this research was to determine if the pentachlorophenol bound to humic acids were resistant to solvent extraction and biodegradation. Under the preliminary experimental conditions, only one to two percent of the PCP sorbed to the dissolved organic matter. Considering PCP's high octanol-water partition coefficient, one would have anticipated that a significantly greater amount of sorption would have occurred. The preliminary results demonstrated that a more thorough understanding of the actual sorption process was necessary prior to examination of the possible influence of sorption on analytical detection. Thus it was decided to shift the primary research focus from analytical detection to the actual sorption.

According to the literature, the solution pH influences the degree of association between hydrophobic ionic organic compounds and humic acids (Lee, *et al.*, 1990; Westall, *et al.*, 1985). The preliminary solutions' pH's were approximately 7. A decrease in the pH should have promoted sorption. A series of solutions were prepared with the purpose of obtaining isotherms at different humic acid concentrations, pH values and contact times. Comparisons between these isotherms should yield insights on the relationships between pH, organic content and kinetics of sorption.

In order to address at least part of the issue of the analytical detection of PCP, a series of extractions were performed to note if sorbed PCP were removed by solvents. Since it appeared that both contact time and pH may affect the sorption mechanism, the extracted solutions ranged in contact time from one to 92 days and in pH from 5 to 8.

Section 3.2: Extraction of Humic Acids

Because commercially available humic acids do not accurately reflect the behavior of natural humic acids (Robinson, 1990), it was necessary to extract this organic matter from soil. A portion of the humic precipitates used in this study were extracted by Kevin Robinson during the course of his dissertation research at Virginia Polytechnic Institute and State University. The remainder were isolated from Newport News soil following the procedure briefly outlined by Robinson (1990). This soil is classified as a sandy loam, with 57 percent sand, 27.1 percent silt, 15.8 percent clay and 2.2 percent organic matter (Robinson, 1990). Since various extraction techniques yield humics with slightly different characteristics (Pierce and Felback, 1973; Ponomareva and Plotnikova, 1968), care was taken to extract all of the humic acids in as similar a manner as possible.

Initially, the soil was suspended in a 0.1 N sodium hydroxide (NaOH) solution for approximately 24 hours under a nitrogen atmosphere. This method causes minimum change to the humic acids (Ponomareva and Plotnikova, 1968) while removing the maximum amount of organic matter (Levesque and Schnitzer, 1966). The mixture was centrifuged in a Beckman model J-21C centrifuge at 18000 rpm for 20 to 30 minutes to remove the suspended mineral fraction. By addition of 6 N hydrochloric acid, the pH of the supernatant was reduced to below two, at which point the humic acids precipitated out of solution. The fulvic acids were siphoned off and the humic solids were dried at a temperature of 105 degrees Fahrenheit. The entire extraction procedure was repeated to purify the humics. Once dry, the solid humics were stored at 4 degrees Celsius. The only deviation from this process occurred when the centrifuge broke, and it was necessary to store the 0.1 N NaOH soil mixture at 4 degrees Celsius for several days. A nitrogen atmosphere was maintained during this waiting period in order to prevent oxidation of the humic acids.

Section 3.3: Preparation of Dissolved Humics

To prepare the humic acid solution, the precipitates were washed with distilled water and then dissolved by addition of 6 N sodium hydroxide. The pH was then reduced to pH 6 - 7 using concentrated sulfuric acid (H_2SO_4). The

first stock solution contained a 10^{-3} M phosphate buffer. However, once it became apparent that the pH was changing over time, the use of a buffer was discontinued. Instead, the solution pH's were monitored and adjusted when necessary. In terms of both elution profile and longterm pH variations, there did not appear to be any difference between solutions with and without the phosphate buffer. The total organic carbon content (TOC) of each stock solution was measured on a Horiba PIR-2000 general purpose infrared gas analyzer. All humic acid concentrations are expressed in terms of mg/L TOC. The stock solutions were stored at 4 deg C.

Section 3.4: Pentachlorophenol

Unlabeled pentachlorophenol from Sigma constituted the bulk of the PCP in the humic acid solutions. Prior to addition of the organic matter, approximately 0.2 μCi of ^{14}C labeled PCP was thoroughly mixed with the diluted stock PCP. The radiolabeled chemical was obtained from Sigma, and had a purity of >98% with a specific activity of 11.9 mCi/mmol. All radioactivity measurements were made by placing the given sample in a borosilicate glass scintillation vial, filling the vial with Fisher Scientific Scintiverse BD scintillation cocktail until the total volume was 15 ml and analyzing the contents in a Beckman LC250 liquid scintillation counter. The scintillation counter was set to an analysis time of ten minutes.

The use of radiolabeled PCP allowed precise and reproducible quantification of the compound. Periodically throughout the research, five or six samples would be withdrawn from a single solution and analyzed for radioactivity. The maximum sample deviation of the counts per minute was three percent. The majority of the sample deviations were between one and two percent.

Section 3.5: Fractionation of Humic Acid/PCP Solutions

A number of techniques have been used in the literature to separate compounds bound to dissolved humics from the portion remaining in the

aqueous phase. Since an earlier, similar study had used gel permeation chromatography, this method was chosen for this research.

In gel permeation chromatography, the solution flows through a column packed with polymer beads. The large, high molecular weight molecules, such as humic acids, are excluded from the small, inner pores and consequently follow the shortest path. The low molecular weight compounds enter the convoluted inner pore structure and are thereby retarded in their passage.

Retardation of a compound by the gel is theoretically due only to molecular weight. However, the shape of the molecule will influence the elution of the compound (Robionson, 1990). Often the gel will interact chemically with the molecules of interest. The Sephadex gel is composed of polymers which contain ionizable functional groups. Under certain conditions, compounds will sorb to these sites until a change in the pH, ionic strength and/or concentration of the eluent causes desorption (Heizlar, 1987). Heizlar likened the process to one of weak cation exchange. Aromatic, hydrophobic compounds, of which pentachlorophenol is an example, are likely to undergo these associations with the gel. Unfortunately, "the validity of gel permeation is dependent on the extent to which gel-solute interactions other than purely size exclusion are operating" (Hine and Bursill, 1984, p.1461). After consideration of these problems concerning the reliability of gel permeation chromatography, it was decided to use this technique primarily because the gel had been employed with success in similar work (Robinson, 1990).

After centrifugation for three minutes at 13000 rpm in a Fisher Scientific microcentrifuge, model 235C, each one milliliter fractionation sample was passed by gravity flow through 100 ml of Sephadex G-25. The eluate was collected in 5 ml fractions and then analyzed. Distilled water was the eluent.

Unlabeled stock solutions of pentachlorophenol, 4-monochlorophenol and 2,4,6-trichlorophenol were passed through the column to determine the volumes at which they elute. Blue dextran and vitamin B12 were used to determine the void and inner pore volumes, respectively, of the Sephadex gel. A Beckman DU-6 UV spectrophotometer was used to analyze the fractions for the presence of these compounds. The wavelength settings were 319 nm for pentachlorophenol, 267 nm for 4-monochlorophenol, 293 nm for 2,4,6-trichlorophenol, 580 nm for blue dextran and 361 nm for vitamin B12. In order

to determine the elution pattern of the humic acids, several humic solutions were separated in the gel column and the resulting fractions were analyzed for TOC content.

Section 3.6: Sorption Study

The goal of the sorption study was to determine the influence of pH on the sorption of PCP to humic acids. Four concentrations of humic acids - 100 mg/L TOC, 400 mg/L TOC, 800 mg/L TOC, 2000 mg/L TOC - were combined with 0.25 mg/L, 1 mg/L and 4 mg/L of radiolabeled PCP in an attempt to yield a 4 x 3 matrix at various pH's. The solution pH ranged from 3.7 to 7.9. The pH of each solution was adjusted by addition of weak NaOH and/or weak H_2SO_4. If the pH varied by more than 0.3 pH units over time, the data were not used. The 25 ml solutions were agitated on a shaker table for a week then placed in a stationary location for the remainder of the contact time. To prevent photodegradation, exposure to light was minimized by placing the flasks in a dark incubator. Two samples of one milliliter each were withdrawn after 1 day, 7 days and 28 days. One sample was fractionated on the gel columns. The remaining milliliter was analyzed directly. Some solutions were sampled after 3 months in order to observe the effects of extended contact times.

Section 3.7: Analysis of Particulate vs Dissolved Humics

Since the overall sorption of PCP can be divided into PCP bound to particulate matter and PCP associated with the dissolved organics, it was necessary to quantify the distribution of TOC between these two phases. Four TOC concentrations - 100 mg/L, 400 mg/L, 800 mg/L, 2000 mg/L - were adjusted to pH 4.4 - 4.8, pH 5.1 - 5.4, and pH 6.3 - 7. After 24 hours on the shaker table, these solutions were centrifuged in a Beckman model J-21C at 13000 rpm for three minutes. The TOC concentrations of the initial solutions and supernatants were then measured.

Section 3.8: Bioavailability Study

Microorganisms able to degrade PCP were cultured from a Newport News soil. Soil and pentachlorophenol were suspended in tap water. After one week, 10 ml of the suspension were transferred to a flask and diluted until the volume was approximately 750 ml. Until the conclusion of the study, only tap water, distilled water, air and pentachlorophenol were added to the flask. The amount of PCP added was sufficient to maintain the solution in a supersaturated state. To remove any organic impurities, the air was filtered through activated carbon. The microorganisms were cultured at room temperature and were exposed to light for approximately 12 hours per day. The culture was established five months prior to its initial use. Biological activity was monitored by periodically observing the organisms under a microscope.

Only solutions which had been allowed to equilibrate for at least three months were included in this experiment. Similar solutions which had been prepared at the same time as the inoculated solutions constituted the experimental controls. After an initial sample had been removed for fractionation, a couple of milliliters of the PCP culture were pipetted into the test solution. To collect carbon dioxide and thereby determine mineralization, in the first six solutions 100 μl of methylbenzyl amine was placed in a well hanging from a septum inserted into the flask cap, similar to Robinson's (1990) procedure. Unfortunately, after two days it became apparent that the CO_2 trap caused the solution pH to increase from 5.4 - 5.8 to 9.2 - 9.7. Such a drastic change in the pH promoted desorption. Thus, it was impossible to determine if any loss in PCP associated with the humics was due to desorption or biodegradation. Since it was more important to maintain the initial pH than to obtain actual CO_2 production rates, it was deemed prudent to not use CO_2 traps. Furthermore, the overall mineralization rates do not yield information pertaining to the actual goal of this experiment: to determine whether or not the sorbed fraction is available for biodegradation. Once the microbes had been added, the flasks remained on the shaker table to promote oxygen transfer. Sampling times ranged from two days to 63 days.

Section 3.9: Solvent Extraction

The purpose of the extraction experiment was to determine if common solvents were able to remove the pentachlorophenol sorbed to the particulate and dissolved humic acids. Small amounts of the solvent were added to five ml of the PCP/humic solutions. These solutions were not pH adjusted prior to extraction nor did they contain a buffer. Solution pH's ranged from 4 to 7.5. The two phases were mixed by manual shaking. The solvent layer was removed by Pasteur pipette, and the process repeated twice. After the third extraction, a sample from the aqueous phase was fractionated and compared to an initial fractionation sample. All components of the process were analyzed on the liquid scintillation counter in order to calculate a mass balance for percent recovery purposes.

The solvents used were methyl-tert-butyl ether (MTBE) and methylene chloride (MeCl). From six extractions of a solution of 4 mg/L PCP and 100 mg/L TOC, a sample deviation of 6.92 percent was calculated. The extraction technique yielded reproducible results.

Chapter 4: Results and Discussion

Section 4.1: Characterization of Humic Acids

During the course of this research, two different stock solutions of humic acids were used, both extracted from Newport News soil. The two stock solutions differed greatly in the proportion of organic matter which was present in particulate and dissolved forms (see Table 1). The definition of a humic acid is organic matter which precipitates from solution when the solution pH is below 2. At any pH, there was a humic acid concentration above which a portion of the organic matter was present as particulate matter. The maximum TOC concentration at which the organic acids were completely dissolved decreased with decreasing solution pH. At a given pH and humic acid concentration, the second soil extraction yielded organic matter which tended to form more solid humic material than the first stock solution.

Table 1: Proportion of the Humic Acids in Dissolved and Particulate Form

First Stock:			
TOC (mg/L)	pH	% Solid	% Dissolved
100	3.7 - 7.9	0	100
400	5.4	33	67
400	7.05	0	100
800	5.15	77.6	22.4
800	6.35	45	55
2000	5.15	87.3	12.7
2000	6.3	61.1	38.9
Second Stock:			
TOC (mg/L)	pH	% Solid	% Dissolved
100	4.45	87.5	12.5
100	5.5	80.9	19.1
100	7.05	76.9	23.1
400	4.45	90.43	9.57
800	5.45	92.12	7.88
800	6.9	72.4	27.6
2000	5.05	92.7	7.3
2000	5.55	90	10

The variations in the organic matter removed from soil from the same location demonstrated the heterogeneous nature of soil organic matter. As will be shown later in this chapter, the distribution of the organic material between

the particulate and dissolved phases influenced the degree of sorption. However, solutions derived from the two stocks exhibited similar trends in both sorption and solvent extraction efficiencies.

Section 4.2: Gel Permeation Chromatography

Gel permeation chromatography proved to be a reliable method for separating the pentachlorophenol associated with the humic matter from unbound or free PCP. The elution pattern of both the humic acids and free pentachlorophenol were consistently reproducible. The humic acids eluted in two separate peaks. Between 70 percent and 80 percent of the dissolved organics eluted between 35 ml and 45 ml, while the rest eluted between 70 ml and 80 ml (Figure 1). From a total sample size of six fractionations, the percent recovery of humic acids at solution pH's of 4.5, 5.5 and 6.5 was determined to be 99.8 percent, with a sample deviation of 11.2 percent.

In the pH range used for the sorption study, 3.7 to 7.9, the free pentachlorophenol passed through the column in a defined peak, usually 10 to 15 ml in width, somewhere between 70 ml and 100 ml (Figure 1). The percent recovery of the ^{14}C PCP depended on the solution pH, but averaged 88.2 percent, with a standard deviation of 13.9 percent (n = 115). Generally, the percent recovery decreased with decreasing solution pH. Using blue dextran (MW > 2 million amu) and vitamin B12 (MW = 1355 amu) as tracer compounds, the inner pore volume was determined to be 70 ml and the large pore volume to be 40 ml for 100 ml of Sephadex G-25. These volumes were consistent with the elution volumes for pentachlorophenol and humic acids, respectively.

As mentioned previously, the recovery of the ^{14}C PCP depended on the pH of the sample. However, the bound PCP was not retained by the gel. This observation provided the basis for calculating the partition coefficients when the amount of radioactivity eluted from the column differed from the initial sample. The sorbed fraction was subtracted from the known initial solution concentration to determine the free solute concentration.

In order to demonstrate the ability of the gel to separate the bound compound from the free molecules, the sorbed and free PCP elution volumes from an equilibrated humic acid solution were each refractionated separately.

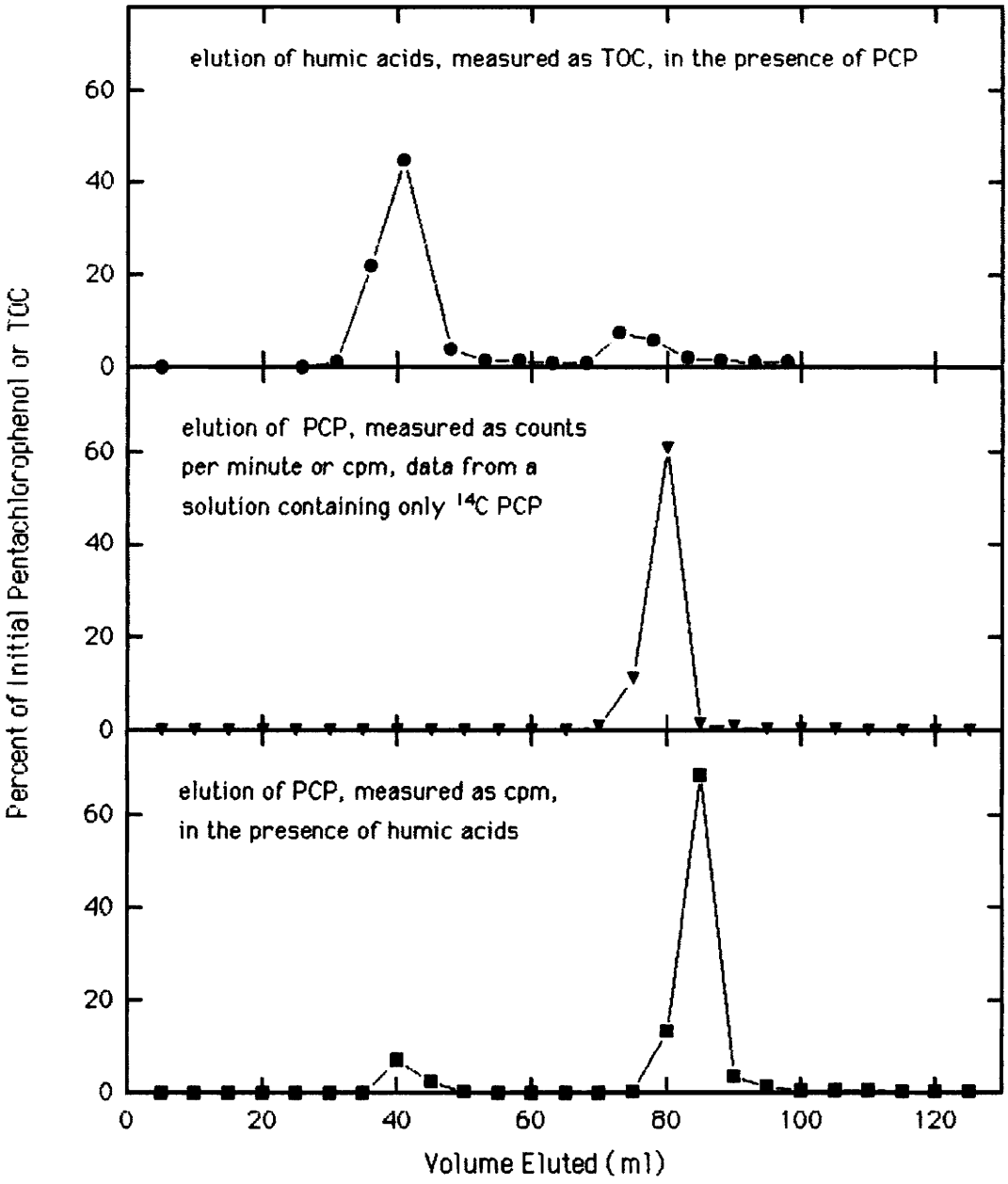

Figure 1. Typical gel column chromatographs which depict the elution patterns of PCP and humic acids in the experimental solution pH range of pH 4 to pH 8.

As can be seen in figure 2, the high molecular weight solution did not elute any ^{14}C beyond 50 ml, the volume which marked the upper limit of the humic acid fractions. The refractionated free PCP sample did not elute any pentachlorophenol in the region which contained the high molecular weight organic matter. Thus it appears that the gel was effective in separating the bound from the free PCP.

Even though a few difficulties are associated with the use of gel permeation chromatography, it was a valid method for these experiments. The purpose was not to distinguish between compounds of only slightly differing molecular size, but to separate molecules whose weights varied by at least an order of magnitude. In this task the gel performed consistently well. If it were necessary to determine the concentrations of a number of chlorinated phenols, whose molecular weights differ by only a chlorine or two, then gel permeation chromatography would not be an appropriate method.

Section 4.3: Preliminary Results

In the first set of preliminary experiments, no sorption appeared to occur. Initially, 250 μl samples were withdrawn from each five ml fraction eluted from the gel column and placed within scintillation vials for analysis. Even after 30 days of contact time, the humic acid fractions did not contain radioactivity levels which could be distinguished from the background activity (Figure 3). It was necessary to increase both the radioactivity of the solutions and the sample size quantified by the scintillation counter before any sorption to the humic material was discernible. Even with this alteration, after one day at the most only one to two percent of the pentachlorophenol was associated with the humic acids (Figure 4). These values were lower than the sorption reported by Robinson (1990) for trichlorophenol (TCP) under similar experimental conditions (Table 2). In one day, more sorption of TCP occurred in solutions of 20 mg/L TOC than with PCP in solutions of 800 mg/L TOC.

Since PCP is considerably more hydrophobic and less water soluble than TCP, the amount of PCP associated with the organic matter was expected to be at least as much as, if not more than, the quantity of sorbed TCP. It was repeatedly mentioned in the literature that PCP sorption was both rapid and

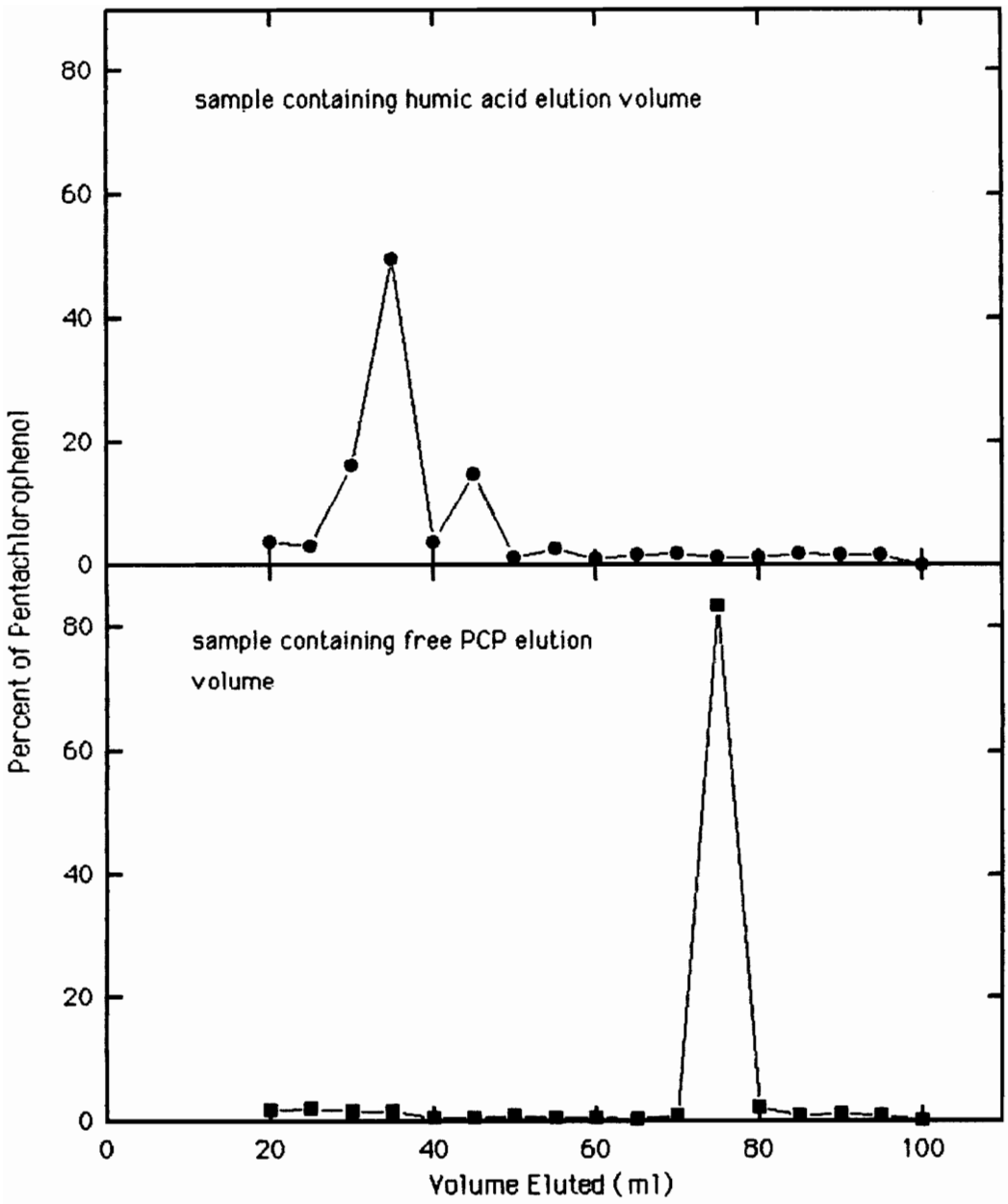

Figure 2. Chromatographs which demonstrate the ability of the gel column to cleanly separate the humic bound PCP from the PCP free in solution.

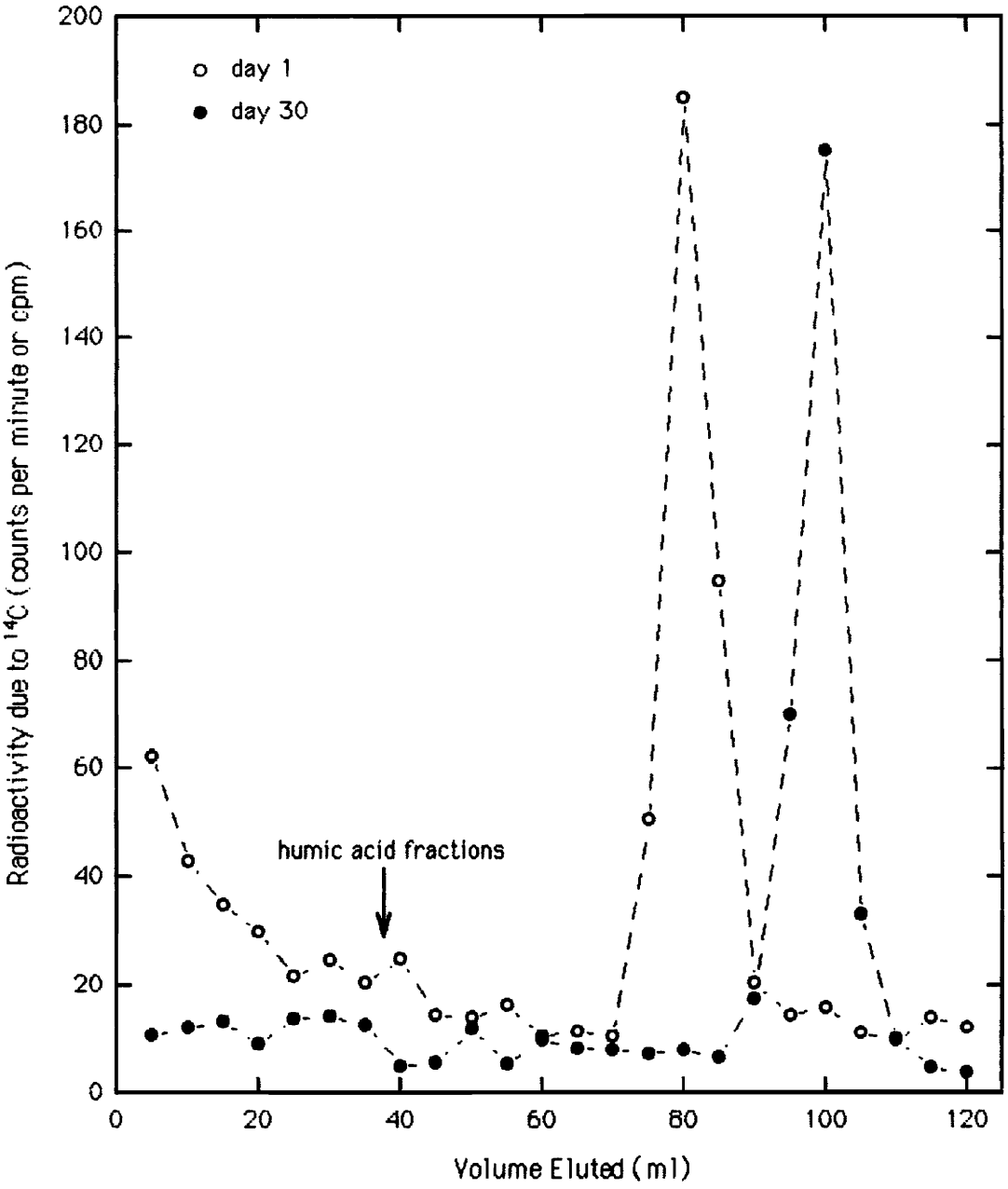

Figure 3. Gel chromatographs representative of the preliminary results with the initial sampling technique. From a solution of 100 mg/L TOC, 4 mg/L PCP and neutral pH.

note: slight variations in the amount of gel present cause the peaks to shift

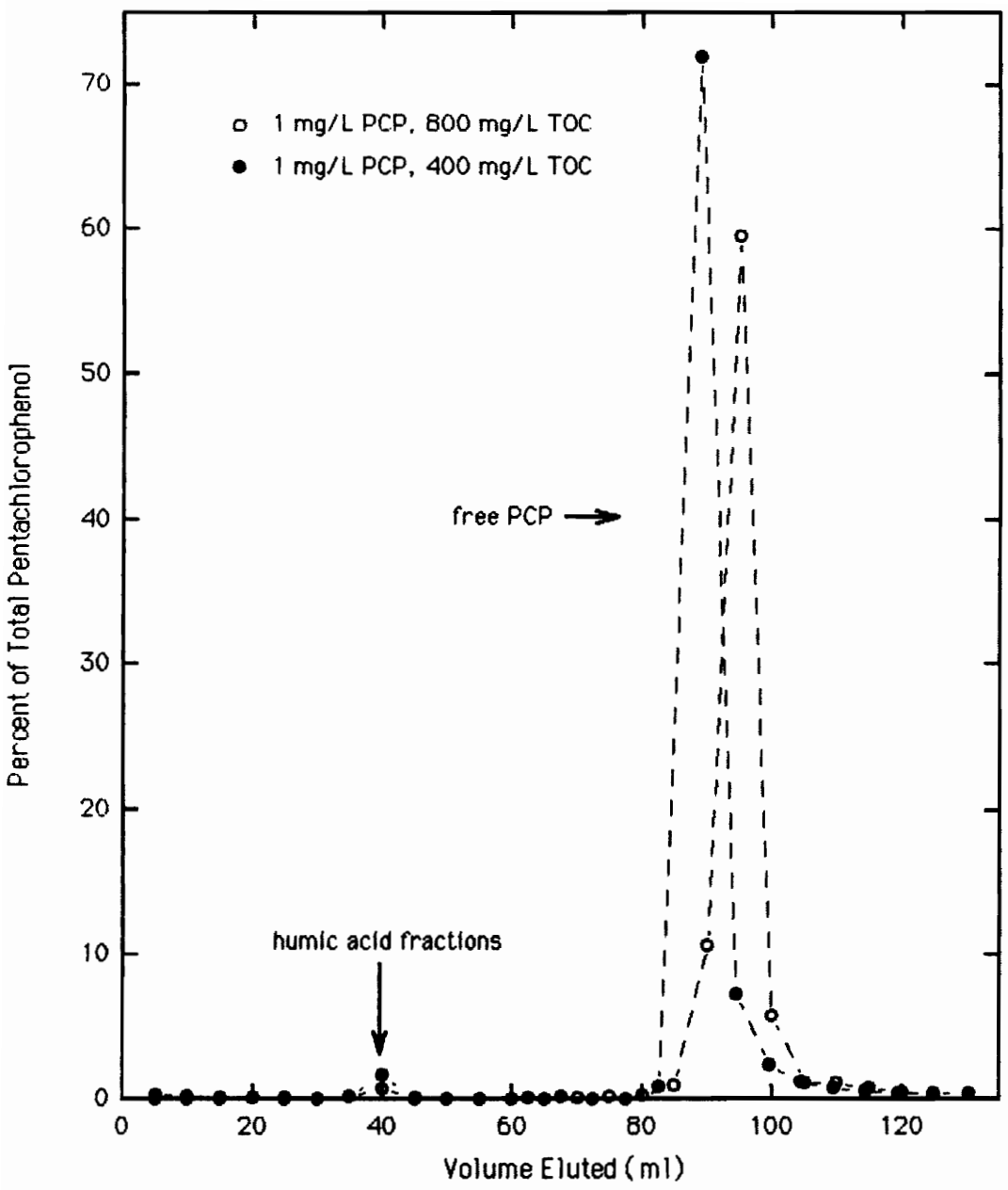

Figure 4. Representative gel chromatographs from the revised sampling approach. In the fractions which contain the humic acids, there is enough radioactivity to form a peak which can be distinguished from the background levels.

measurable, even when the contaminant was primarily in its dissociated form (Lee, *et al.*, 1990). The preliminary results did not coincide with this observation. Prior to the examination of any possible interferences in the quantification of PCP caused by its association with humic acids, it was necessary to acquire a better understanding of the factors which influence the sorption of pentachlorophenol to organic matter. Therefore a sorption study was conducted in which solution pH was a major variable. The following section describes the results of these experiments.

Table 2: Comparison of Sorption of PCP and TCP to Humic Acids

TCP Sorption:		
TOC (mg/L)	Time (days)	% Sorbed to Humics
500	1	8
500	30	12
100	1	8
100	25	11
50	1	7
50	25	12
PCP Sorption:		
TOC (mg/L)	Time (days)	% Sorbed to Humics
800	1	1
400	1	1.92
100	1	not measurable
100	30	not measurable
50	1	not measurable

Section 4.4: Sorption Study

Section 4.4.1: Influence of PCP Concentration

As discussed in the literature review section, the sorption of hydrophobic organic compounds to soil organic matter is best described by a linear isotherm. Representative data shown in figure 5 demonstrate the approximately linear fit of the data to the Freundlich equation. This equation is:

$$x/m = K_p C_e^n$$

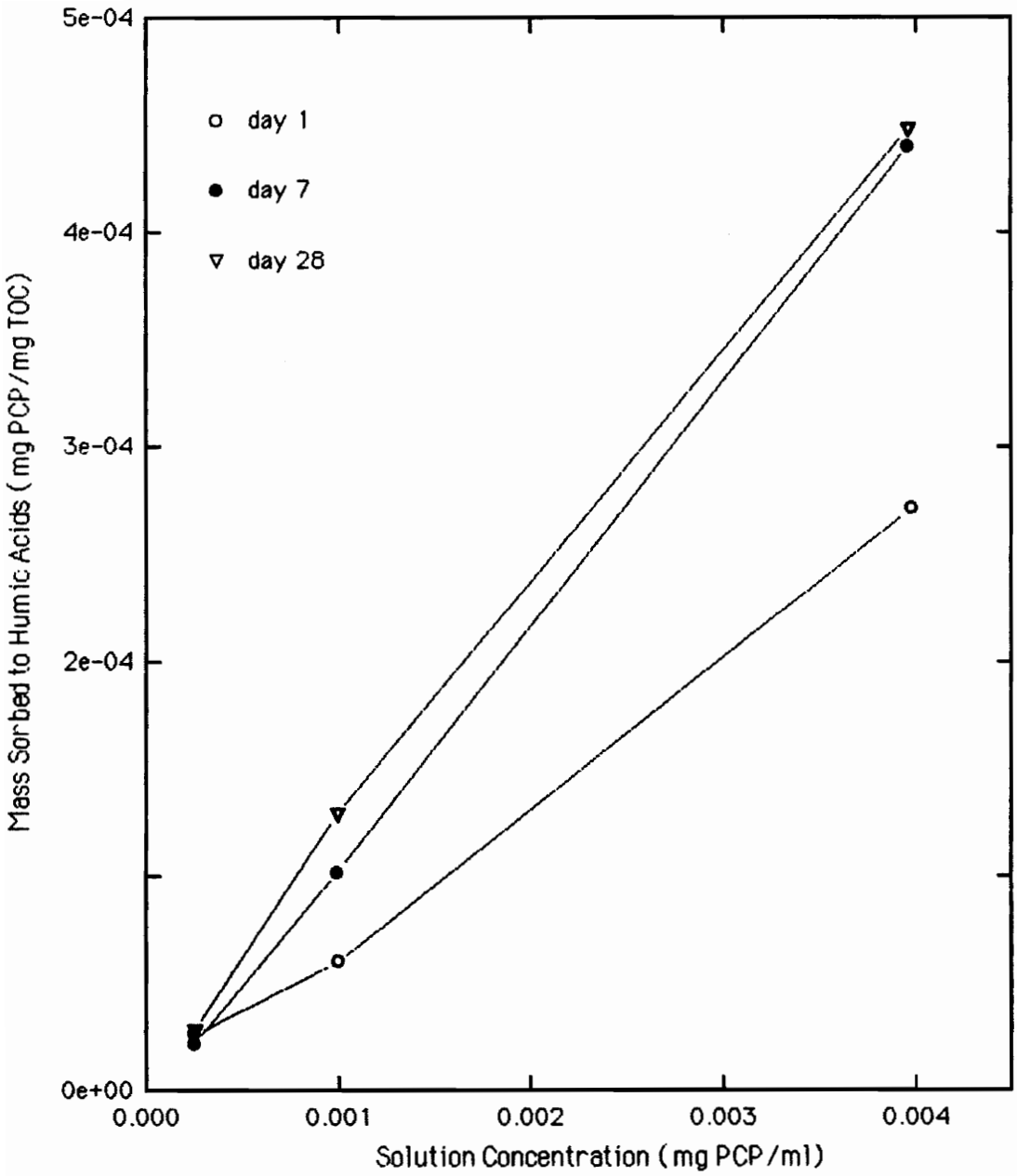

Figure 5. Typical example of the linear Freundlich isotherms produced by the data. Data from solutions of 100 mg/L TOC, pH 7.7-7.9, first humic stock.

where x is the solute mass, m is the sorbent mass, C_e is the equilibrium free solute concentration, n is an empirical constant and K_p is the partition coefficient or constant. When the value of n approximates one, the equation becomes the linear isotherm. The partitioning constant in the Freundlich equation implies that the relative amount of a given compound sorbed to a specific sorbent does not depend on the initial solute concentration, but on the characteristics of the reacting compounds. This premise provides the theoretical basis for the prediction of the partition coefficient from a solute's lipophilicity (Schellenberg, *et al.*, 1984). Accordingly, under similar experimental conditions, the Freundlich constant should be equivalent for the three initial PCP concentrations.

The data indicated that, at solution pH's above 6, the initial solution PCP concentration did not affect the degree of partitioning (Figure 6). In the acidic samples, it appeared that the solute concentration strongly influenced the amount of sorption. A series of standard t-tests were performed to determine the validity of these observations (Appendix A). These analyses provided statistical proof that, regardless of pH, the amount of partitioning was not controlled by the solute concentration.

The sample variances in the data from neutral and basic solutions were statistically lower than the variances calculated from the acidic solutions (Appendix A). This observation suggests that the sorption process differed between the low pH and high pH solutions.

From the data, one can only speculate as to the cause of the differing variances. Acidic conditions promote the precipitation of humic acids. As the solution pH is reduced, the humic acids may become less stable, precipitating but unable to remain in the solid phase when the pH is above 2. The humic precipitates associate with greater quantities of PCP than the dissolved organic matter. The acidic samples were close to the pKa of PCP. The neutral and ionized species exhibit varying affinities for humic acids (Schellenberg, *et al.*, 1984). At low solution pH's, slight differences in the pH could lead to large variations in the ratio of neutral to dissociated solutes. The experimental results do not provide any evidence for or against either possible explanation.

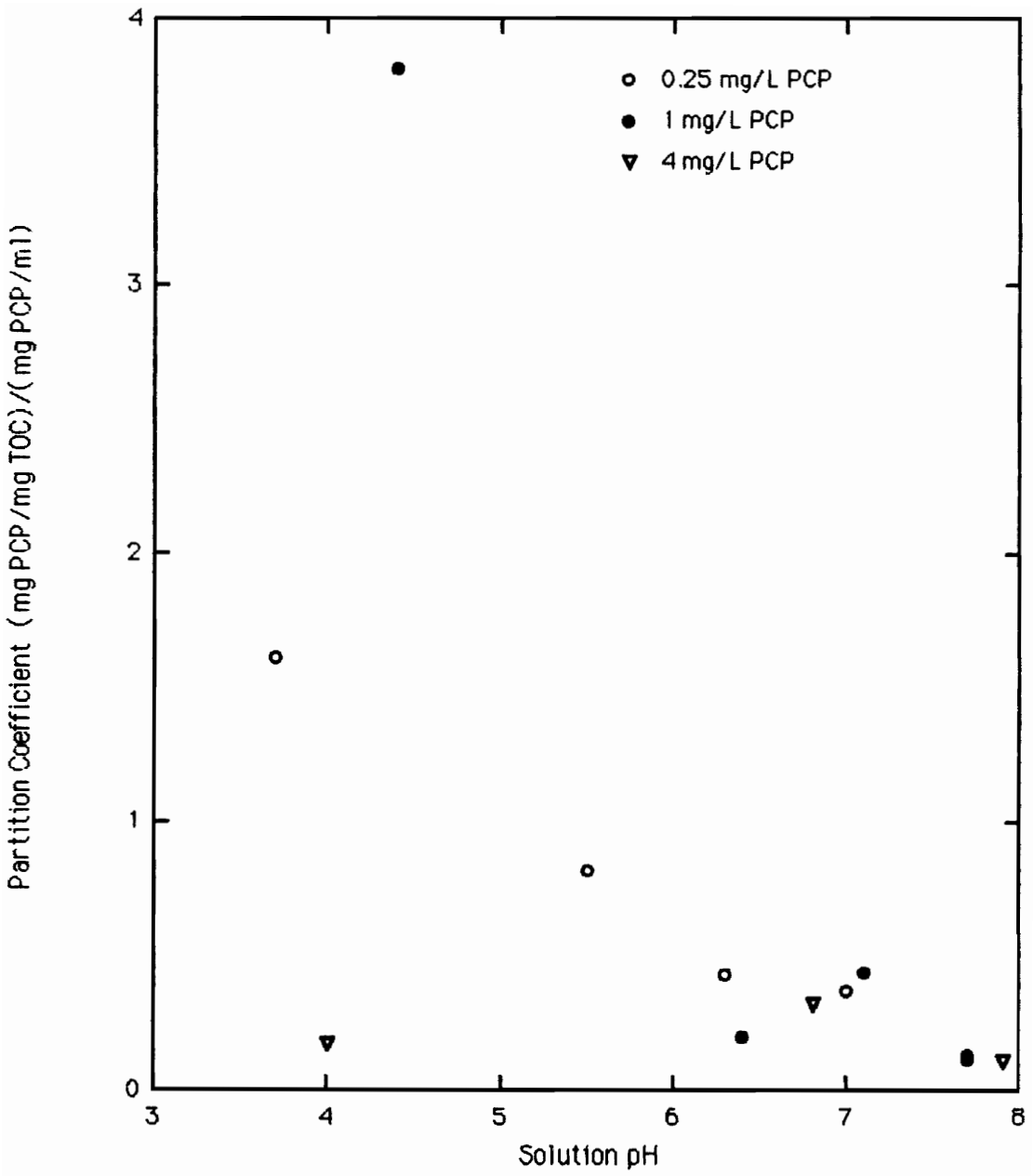

Figure 6. Comparison of partition coefficients from solutions of different initial PCP concentrations. Data from solutions of 28 days contact time and 100 mg/L TOC, first humic stock.

Section 4.4.2: Influence of pH

The experimental results followed a pattern similar to those described by Lee, *et al.* (1990) and Schellenberg, *et al.* (1984). These authors depicted the degree of partitioning to be strong and constant below pH 4. Between pH 4 and pH 7, the log partition coefficient decreased dramatically and linearly with increasing pH. Above pH 7, the partitioning was constant with respect to pH again, but at a much reduced level.

The experimental solutions ranged from pH 4 to pH 8. After contacting with the PCP for 28 days, the humic matter in the more acidic solutions bonded with greater amounts of pentachlorophenol than did the organic material in the neutral and basic solutions (Figure 7). In some of the solutions from the first humic stock, this trend was less noticeable at the one and seven day contact times. Both figures 7 and 8 illustrate similar amounts of sorption at pH 5 and pH 7 until day 28. Solutions derived from the second humic stock also exhibited this trend of decreasing sorption with increasing solution pH (Figure 9).

Figure 7 appears to depict an inverse, linear relationship between solution pH and the partition coefficient. Regression analyses were performed for linear and log-linear models of several data sets from day 28, and for only a log-linear equation at days one and day seven (Table 3). After 28 days of contact, the log-linear equation yielded the best fit of the results. The inverse, log-linear trend coincided with the findings of Lee, *et al.* (1990), except that time was necessary for this relationship to develop. Data from the first stock samples after one day and seven days resulted in low r square values, indicating that the log-linear equation should not be used to describe the relationship between partition coefficient and pH. This research offered no explanation why the partition coefficients from the second stock solution yielded an excellent fit to the log-linear model regardless of contact time. The difference between these data sets was that the solutions from the second stock consisted primarily of particulate humic matter while the TOC content of the first stock solution samples was mostly in dissolved form.

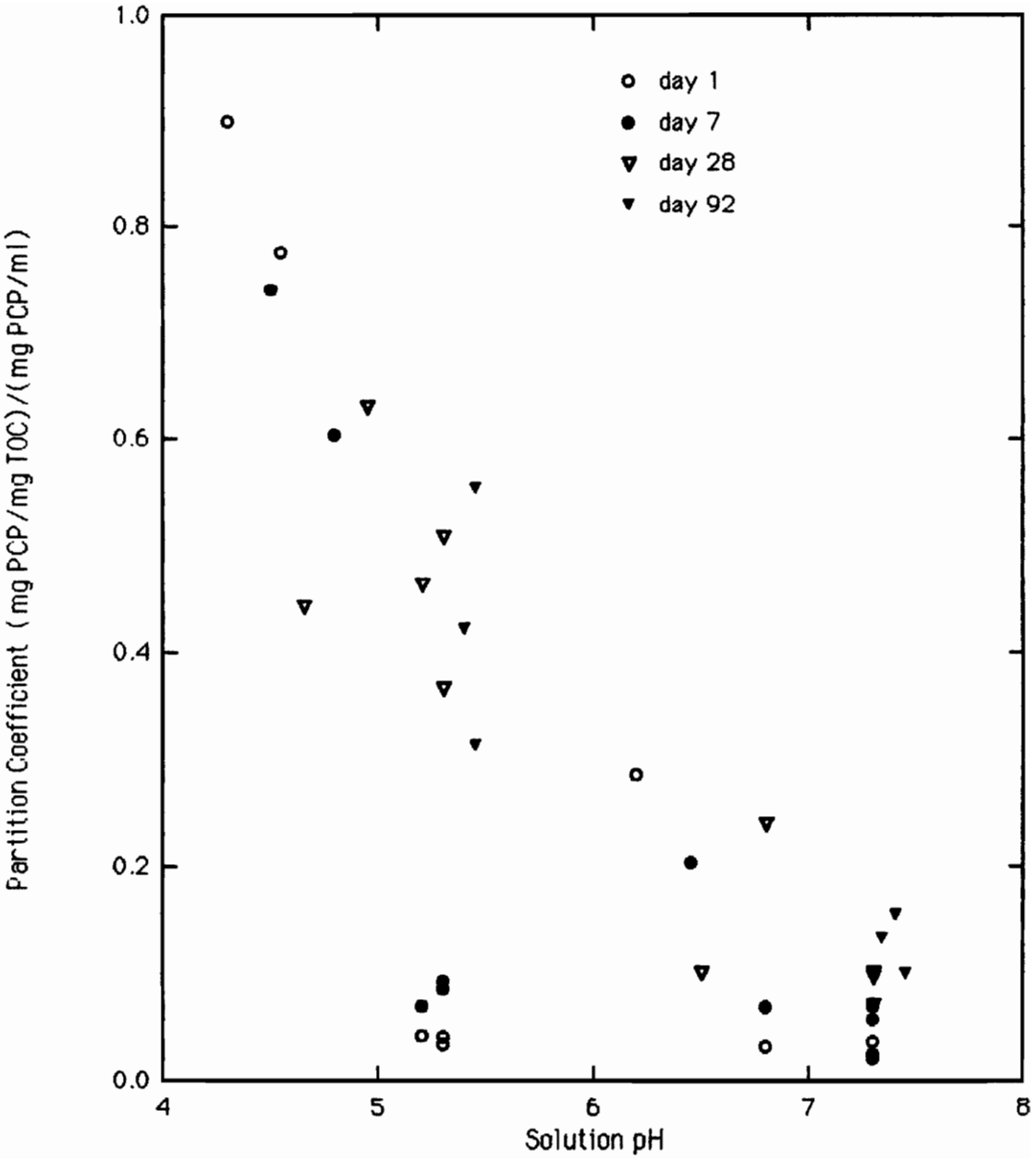

Figure 7. The influence of pH on the degree of partitioning at various sampling times. Data from solutions of 400 mg/L TOC, first humic stock.

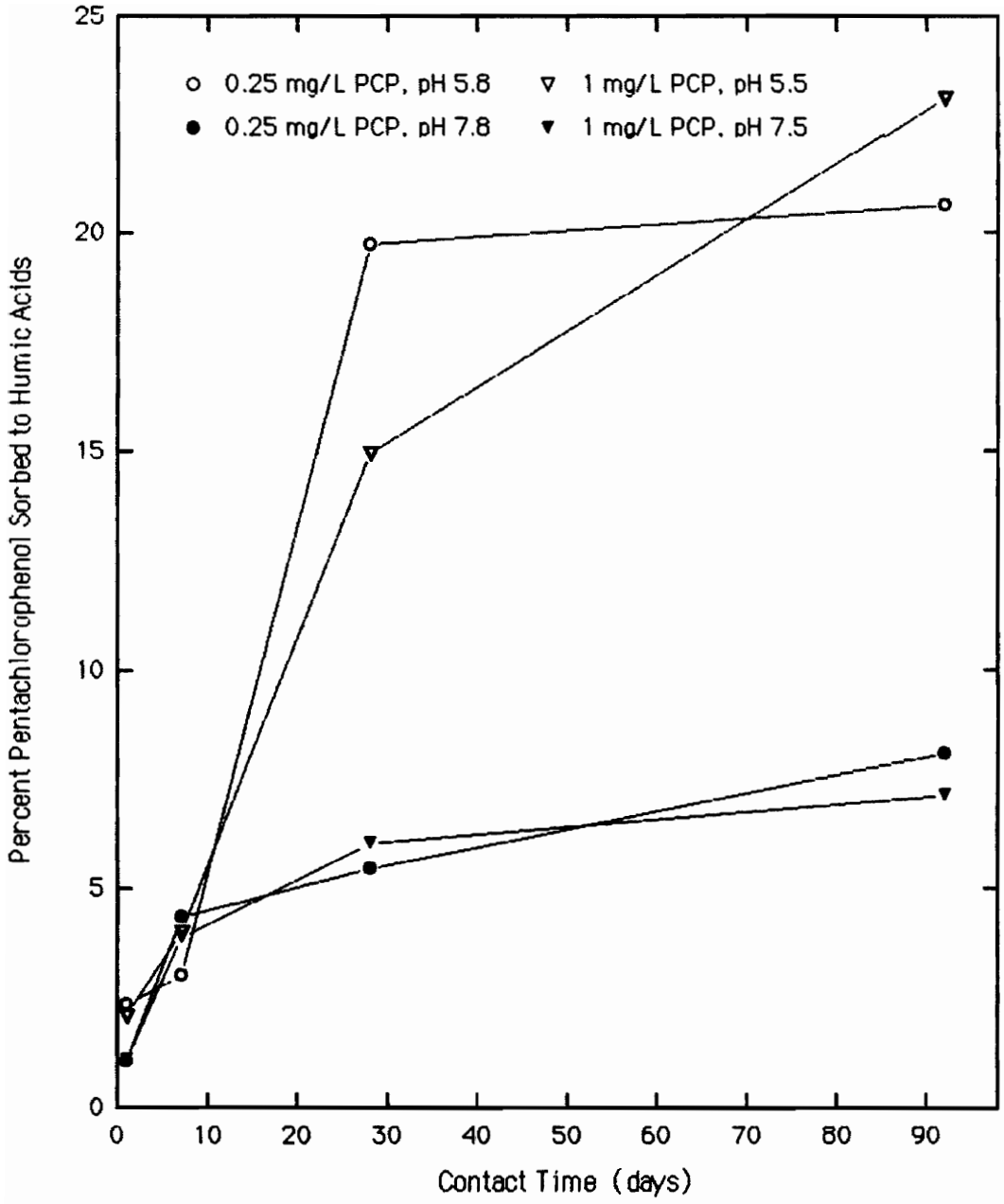

Figure 8. The influence of pH and contact time on the degree of sorption. Data from solutions of 800 mg/L TOC, first humic stock.

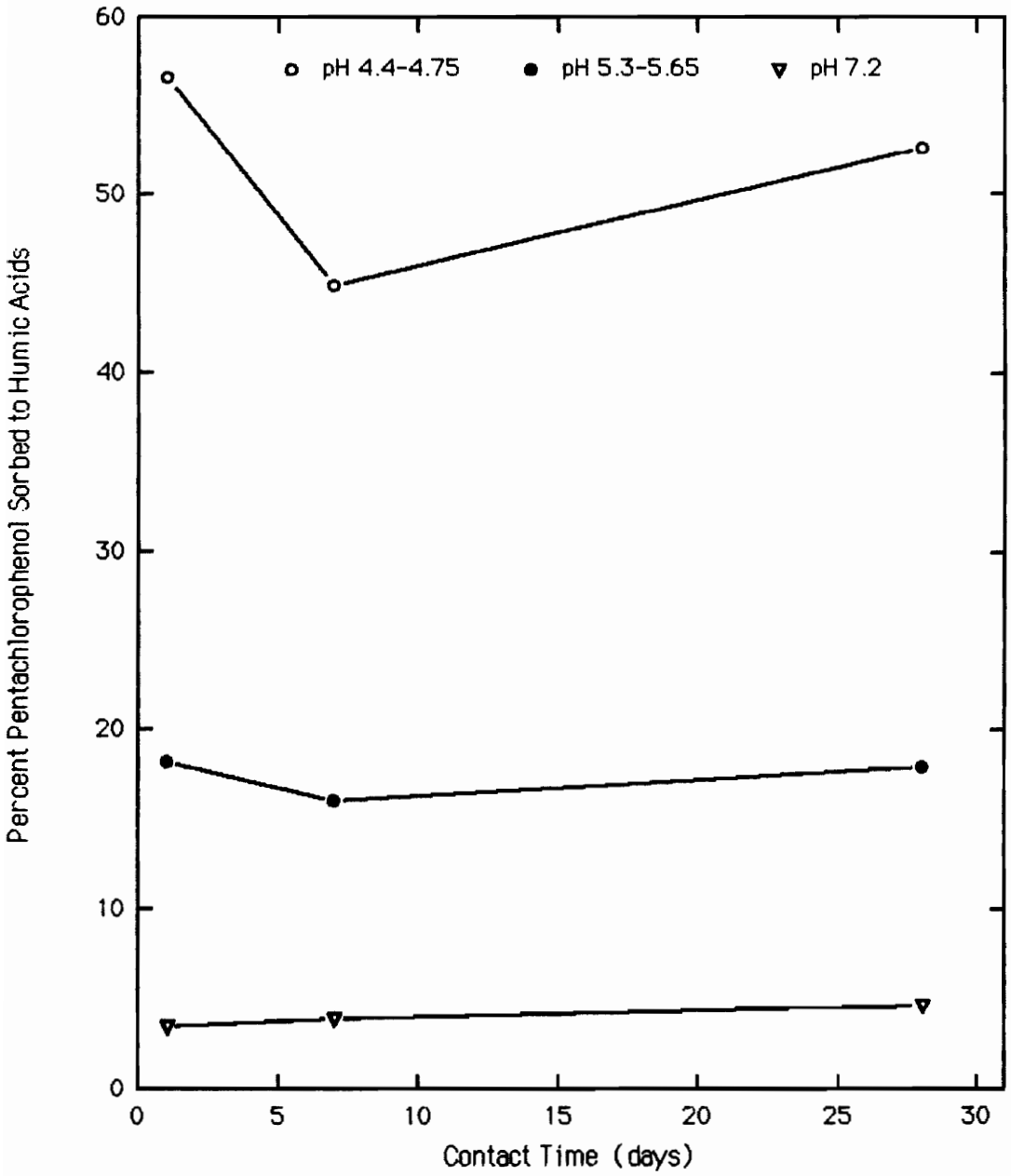

Figure 9. The influence of contact time and pH on sorption. Data from solutions of 4 mg/L PCP and 100 mg/L TOC, second humic stock.

Table 3: Results of Regression Analyses

Samples	Sample Size	Contact Time (days)	r Square
100 mg/L TOC, first humic stock, Kp vs. pH	11	28	0.599
100 mg/L TOC, first humic stock, log Kp vs. pH	11	28	0.831
100 mg/L TOC, first humic stock, log Kp vs. pH	12	7	0.603
100 mg/L TOC, first humic stock, log Kp vs. pH	12	1	0.0423
400 mg/L TOC, first humic stock, Kp vs. pH	10	28	0.843
400 mg/L TOC, first humic stock, log Kp vs. pH	10	28	0.853
400 mg/L TOC, first humic stock, log Kp vs. pH	10	7	0.449
400 mg/L TOC, first humic stock, log Kp vs. pH	10	1	0.483
100 mg/L TOC, second humic stock, Kp vs. pH	5	28	0.771
100 mg/L TOC, second humic stock, log Kp vs. pH	5	28	0.973
100 mg/L TOC, second humic stock, log Kp vs. pH	5	7	0.966
100 mg/L TOC, second humic stock, log Kp vs. pH	5	1	0.96

The dependence of the pH effect on contact time is further illustrated in figure 10. Excluding the pH 5.2 at day 28 line, all of the isotherms are clustered close together. The solutions in figure 8 showed similar amounts of sorption regardless of pH until at least the seventh day. The relationship between contact time and the observed pH effects for humics from the first stock solution suggests that the experimental system was more dynamic than reported in the literature. According to the literature, the relationship between solution pH and the partition coefficient should be quickly apparent and should not change over time. For the second stock humics, contact time appeared to have little influence on the effect of pH (Figure 9).

One way in which the influence of pH manifested itself was through the ionization of pentachlorophenol and the humic polymer acidic groups. The repulsive forces between the PCP hydroxyl group and the organic carboxyl and hydroxyl groups caused their association to be energetically less favorable. Differences in the amount of pentachlorophenol which binds to humic acids

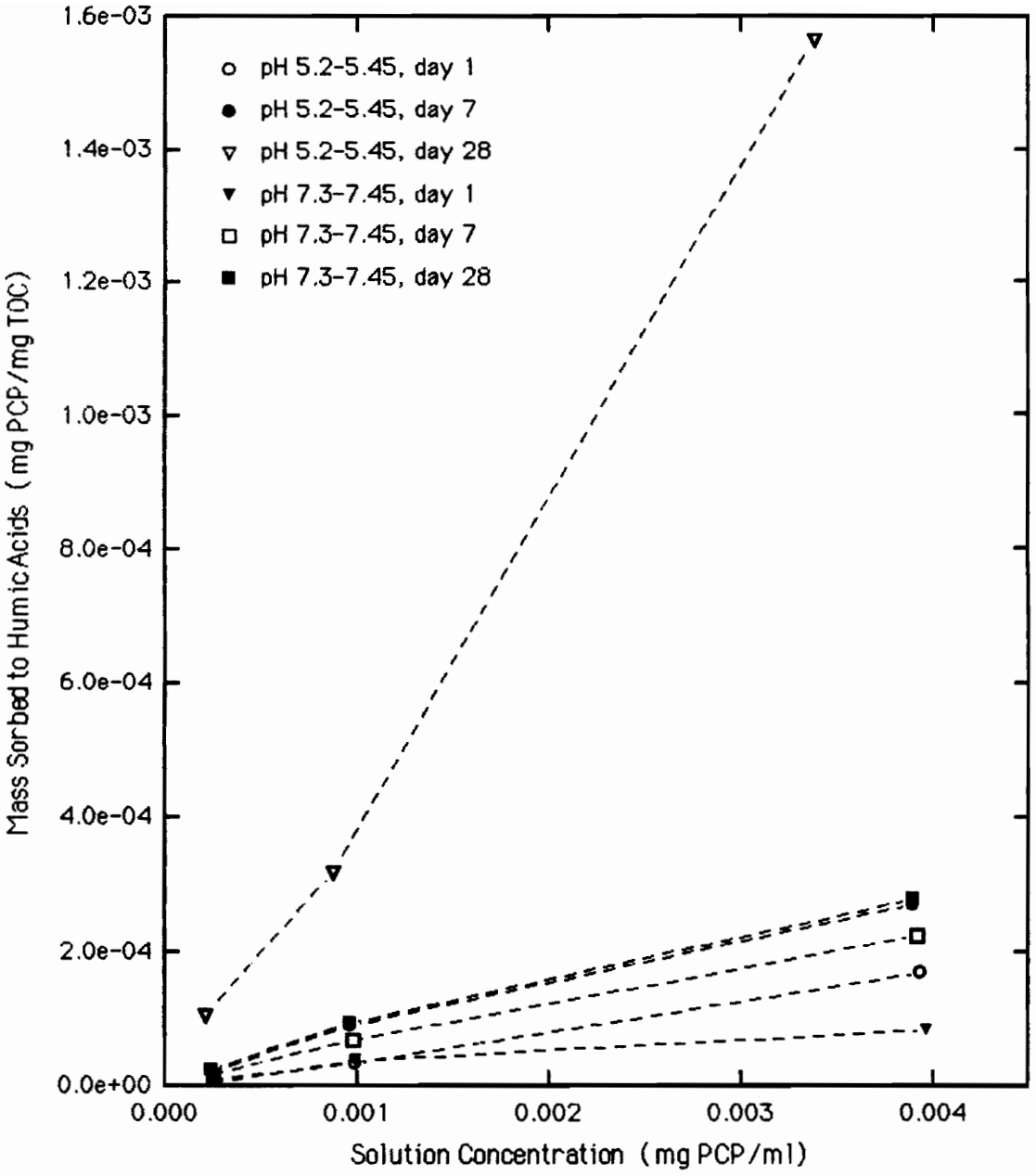

Figure 10. Freundlich isotherms which compare the sorption at pH 5.3 and pH 7.3 over time. Solutions of 400 mg/L TOC, first humic stock.

from various sources might be due in part to variations in the pH at which the soil organic acids dissociate.

The solution pH in part controlled the distribution of the humic acids between the particulate and dissolved phases. Reduction of the pH promoted the precipitation of humic acids. The data indicate that PCP preferentially binds with the particulate humic matter as opposed to the dissolved organic polymers, even after the values are normalized to account for differences in the amount of TOC present in each phase. Thus, under acidic conditions, most of the sorbent was present in the physical form which interacted with pentachlorophenol to the greatest degree.

Section 4.4.3: Influence of Humic Acid Concentration

The solutions which contained primarily particulate humic acids (low pH and/or high TOC samples) were thought to provide an approximation of the processes which occur in the actual subsurface system, where the majority of the organic matter is attached to mineral surfaces as a solid coating. The fraction removed by centrifugation was thought to be the experimental equivalent of this immobile organic matter. However, there is no evidence from this research to support either claim.

An increase in the mass of sorbent led to a higher percentage of the pentachlorophenol being sorbed. As shown in figure 11, this trend was less pronounced in the neutral and basic solutions. Once the sorption had been normalized to the mass of PCP per unit mass of humic acids, the partition coefficients first decreased to a minimum value and then increased with increasing organic carbon content. Figure 12 shows the partitioning to decrease as the humic acid content rose from 100 mg/L TOC to 800 mg/L TOC. As the humic material became more concentrated beyond 800 mg/L TOC, the partition constants increased. A series of standard t-tests verified this parabolic pattern (Appendix A). This trend was not as obvious in the high pH solutions. The enhanced sorption under acidic conditions is likely the reason why the low pH solutions most noticeably demonstrated the influence of changing organic carbon content.

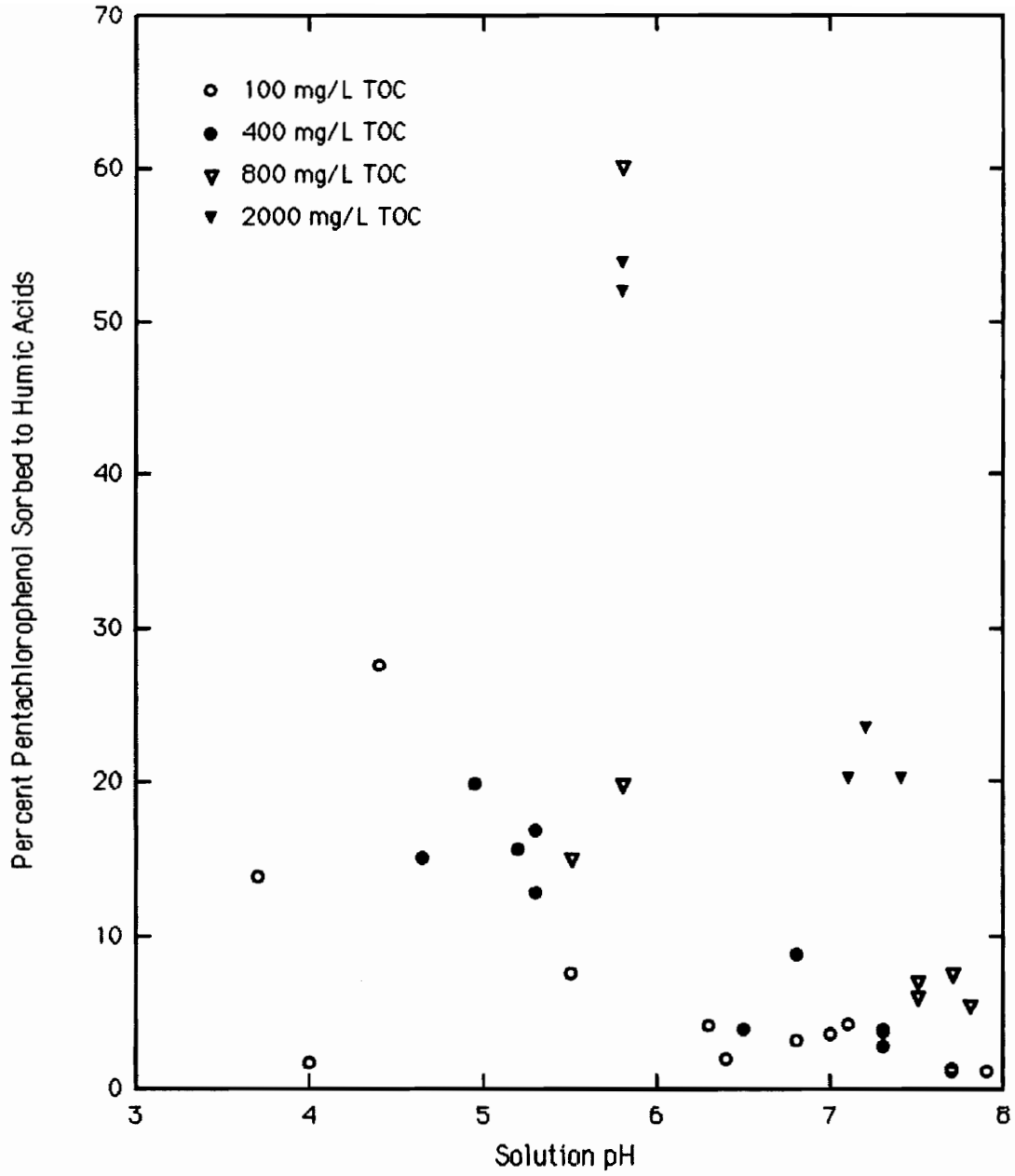

Figure 11. The influence of pH and organic carbon content on the amount of PCP sorbed to humic acids. Solutions from the first humic stock and sampled after 28 days of contact..

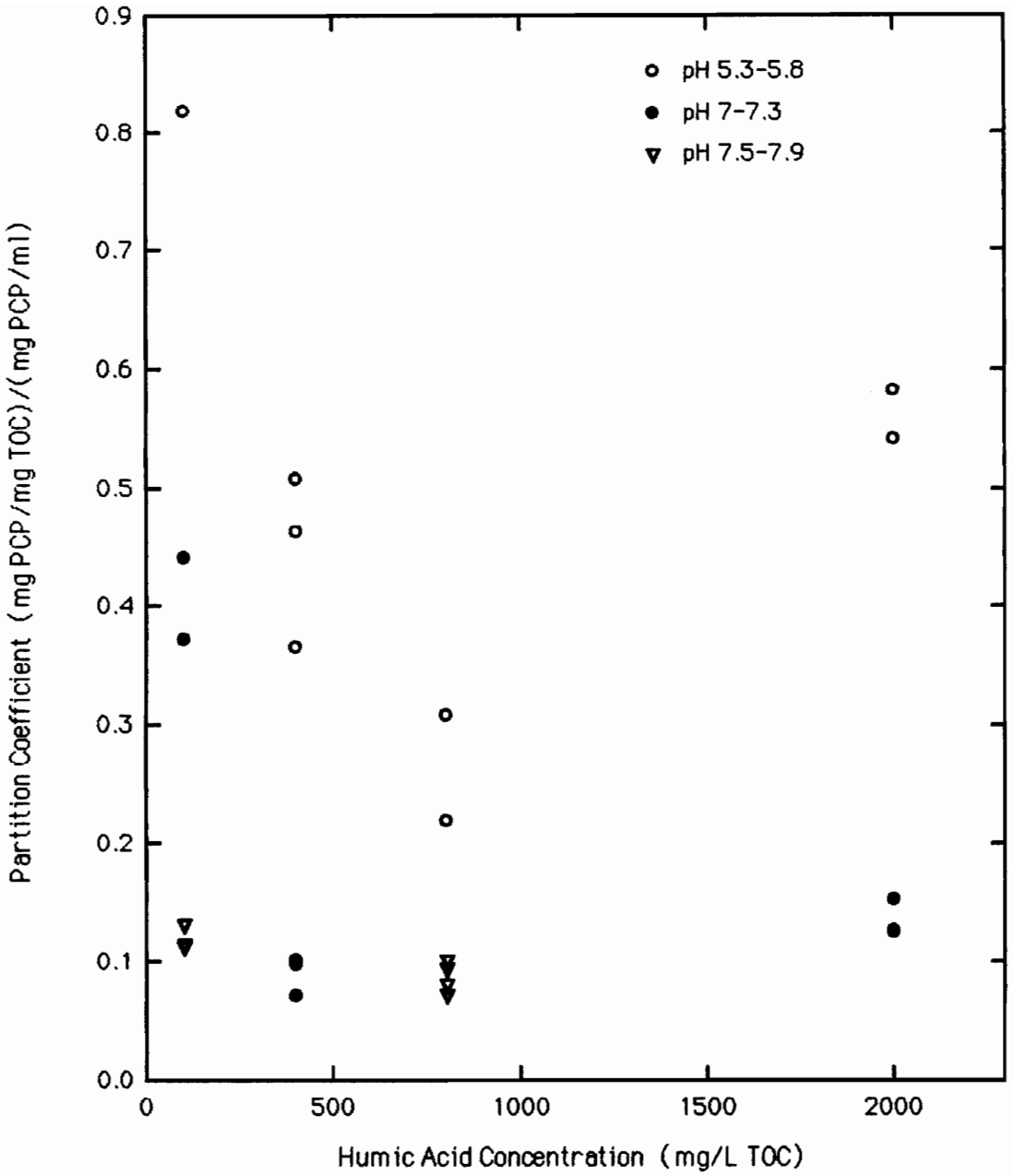

Figure 12. Influence of organic carbon content on partition coefficients. Data from solutions of 28 days contact time and first humic stock.

Along with the solution pH, the humic acid concentration controlled the distribution of the organic matter between the particulate and dissolved phases. It can be seen in figures 13, 14 and 15 that more pentachlorophenol, both in terms of percentage and mass per unit mass of TOC, was typically associated with the solid phase. Regardless of humic acid concentration, the curves depicting the sorption to the particulates were consistently higher than the equivalent ones for the dissolved phase. This behavior was consistent for the duration of the sampling time and over the entire experimental pH range.

The fact that the form of the organic matter affected the degree of sorption implies that at least two different mechanisms governed the sorption process. If only dissolution into the organic matrix dominated the interactions, then the solidification of the organic matter should not have increased sorption.

The importance of at least two mechanisms may explain why the partition coefficients followed a parabolic pattern with respect to humic acid concentration. At a given pH, as solutions became more concentrated, the amount of particulate matter increased. Transformation from the dissolved to the solid form would, by decreasing the volume of the material, have resulted in the simultaneous reduction of the volume into which the solute could dissolve and an increase in the area available for surface sorption interactions. The former decreases sorption while the latter process promotes these reactions. The net effect would depend on which mechanism was dominant under a given set of conditions. The transformation of the humic acids from the dissolved state to the colloidal and particulate forms influenced the sorption process.

According to Schellenberg, *et al.* (1984), the quantity, but not the type, of organic matter controls subsurface interactions. This statement was not supported by these results. Although extracted by the same process from soil from the same location, the two stock solutions of humic acids demonstrated vastly different affinities for PCP. Typical of the data, figure 16 illustrates that the normalized sorption values for the second stock solution were consistently higher than those for the first extracted humic acids. This trend was apparent throughout the experimental pH range, but was accentuated in the acidic samples (Figure 17). The particulate humics demonstrated this pattern more dramatically than did the dissolved phase.

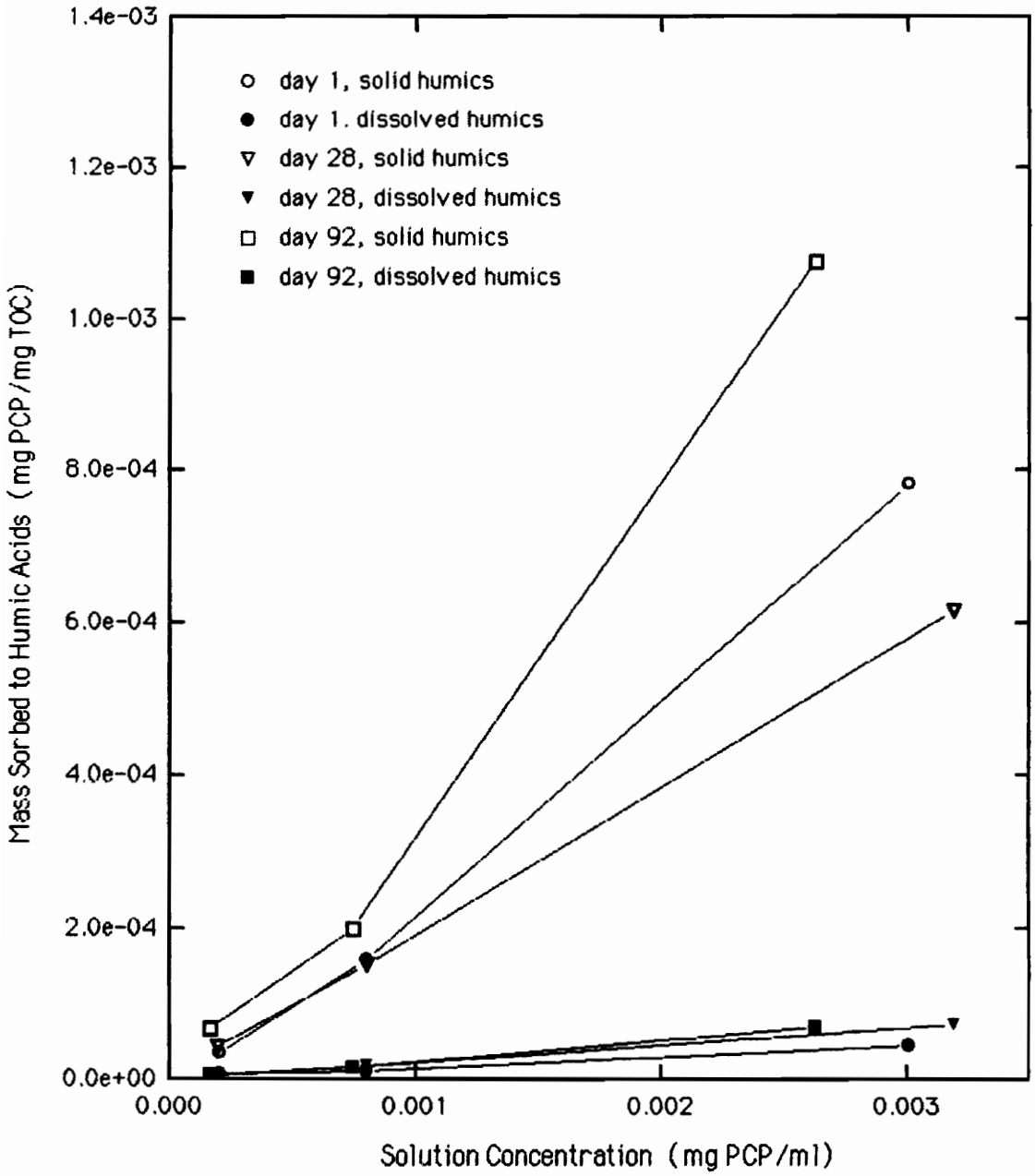

Figure 13. Freundlich isotherms which compare the sorption of PCP to the two humic phases over time. From solutions of 2000 mg/L TOC, pH 7.1-7.4, first humic stock.

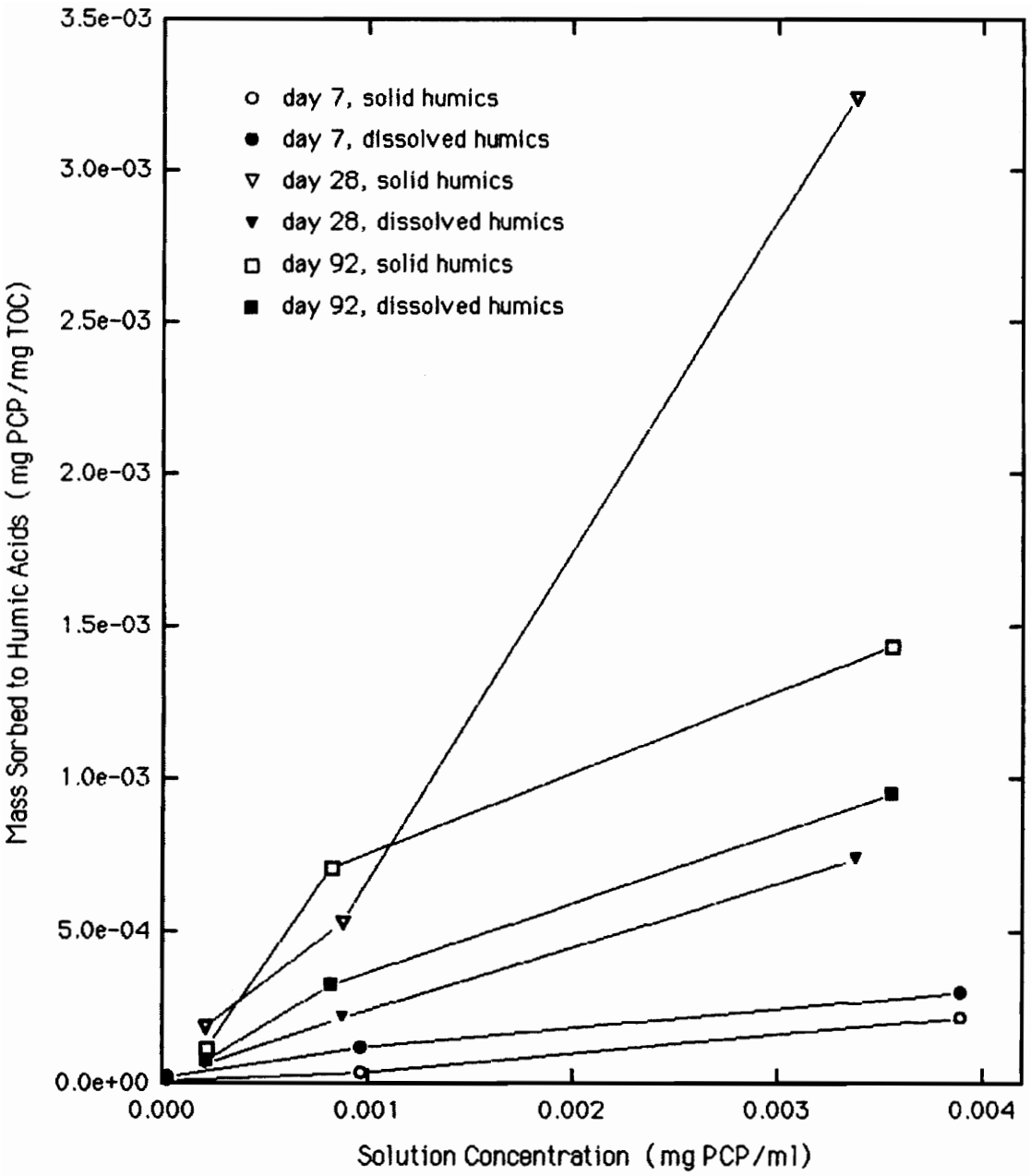

Figure 14. Freundlich isotherms which compare the sorption of PCP to the dissolved and particulate humic acids over time. Data from solutions of 400 mg/L TOC, first humic stock, pH 5.2-5.4.

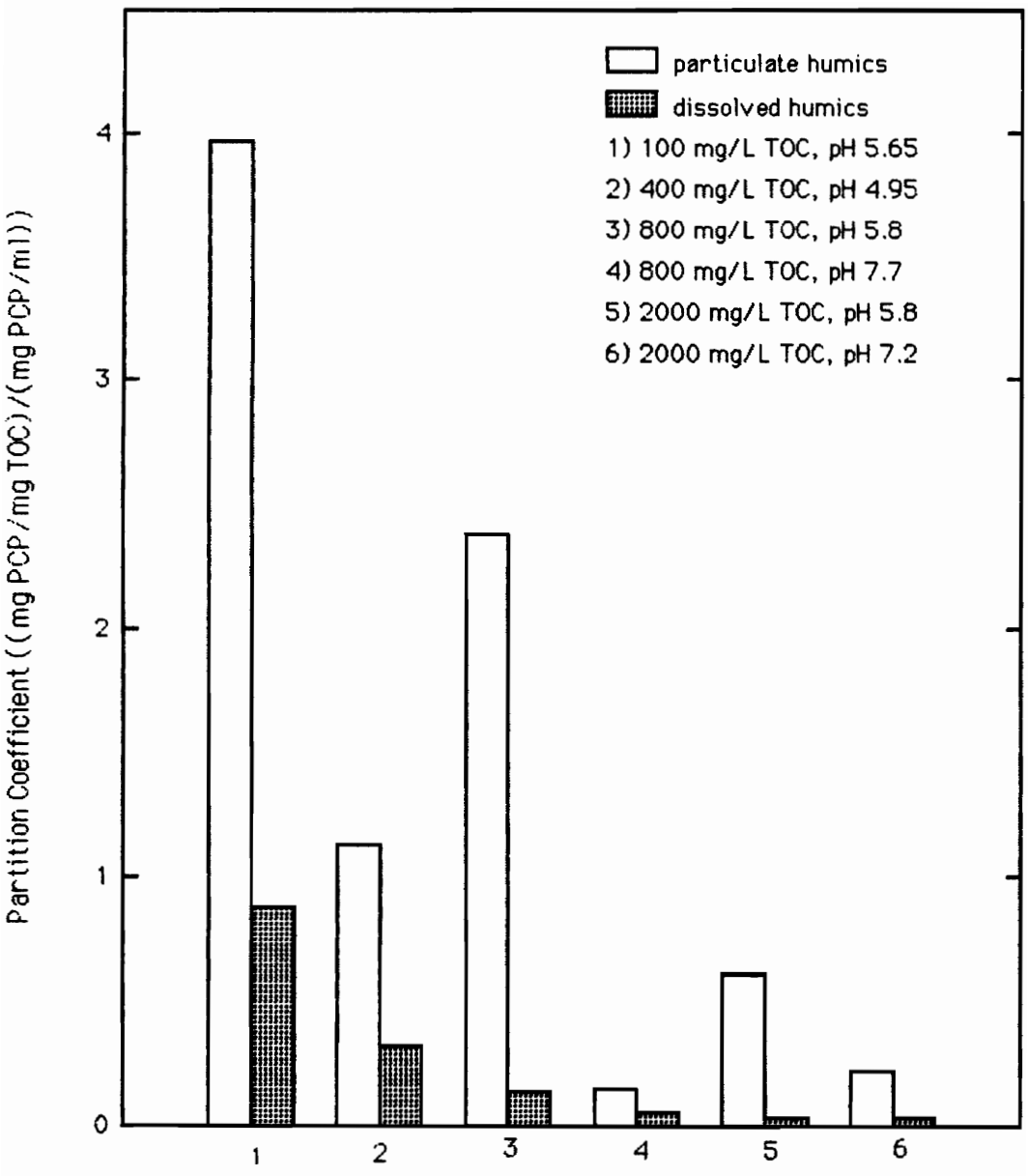

Figure 15. Regardless of solution pH and humic acid concentration, the particulate humic acids had a greater affinity for PCP than did the dissolved. Data from samples at 28 day contact time.

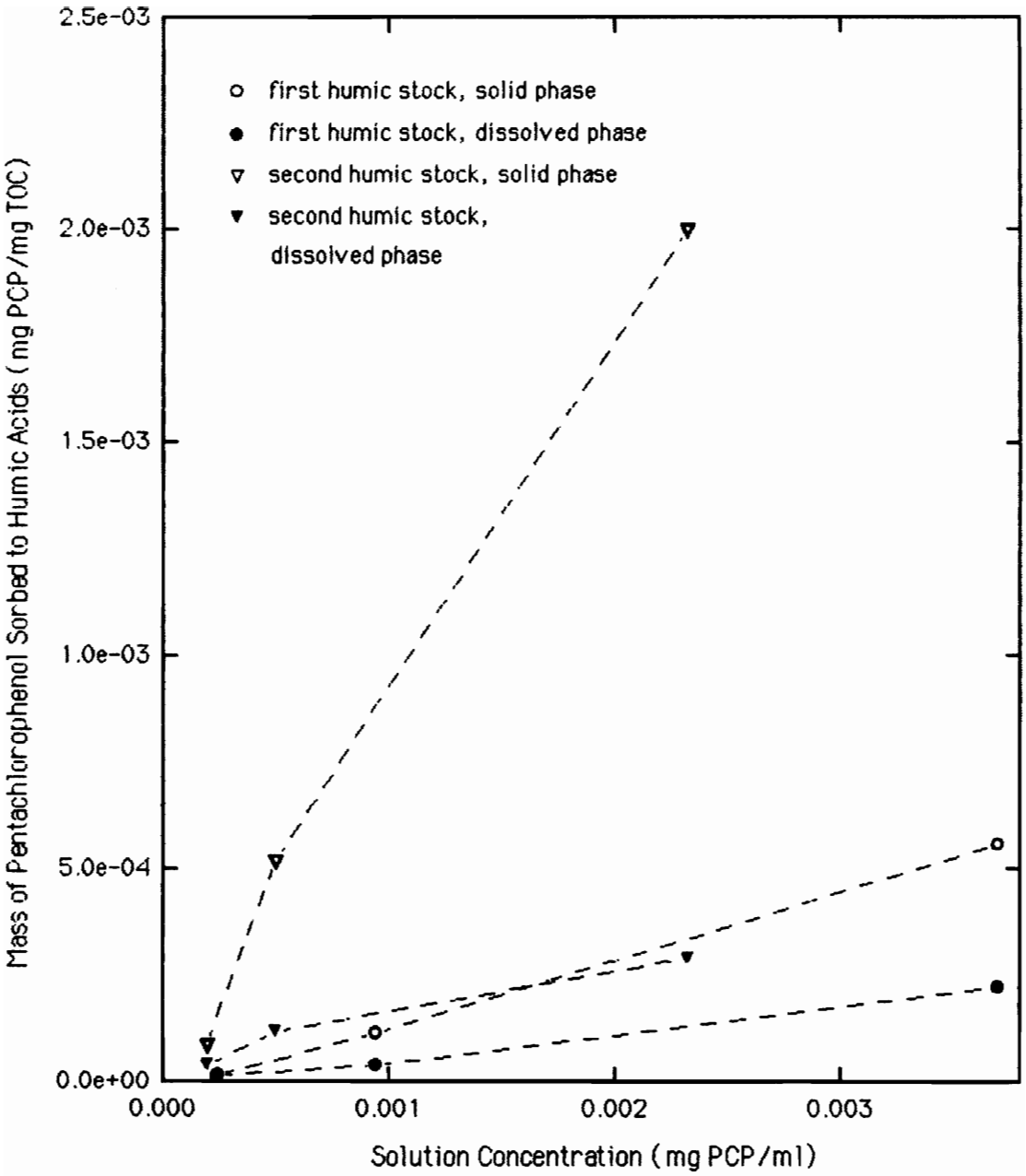

Figure 16. Freundlich isotherms which demonstrate that both phases of the second humic stock solution sorbed more PCP per unit mass of TOC than the first stock humic acids. Data from solutions of 800 mg/L TOC, 28 day contact time, pH 7.5-7.8 (first stock) and pH 7.2-7.5 (second stock).

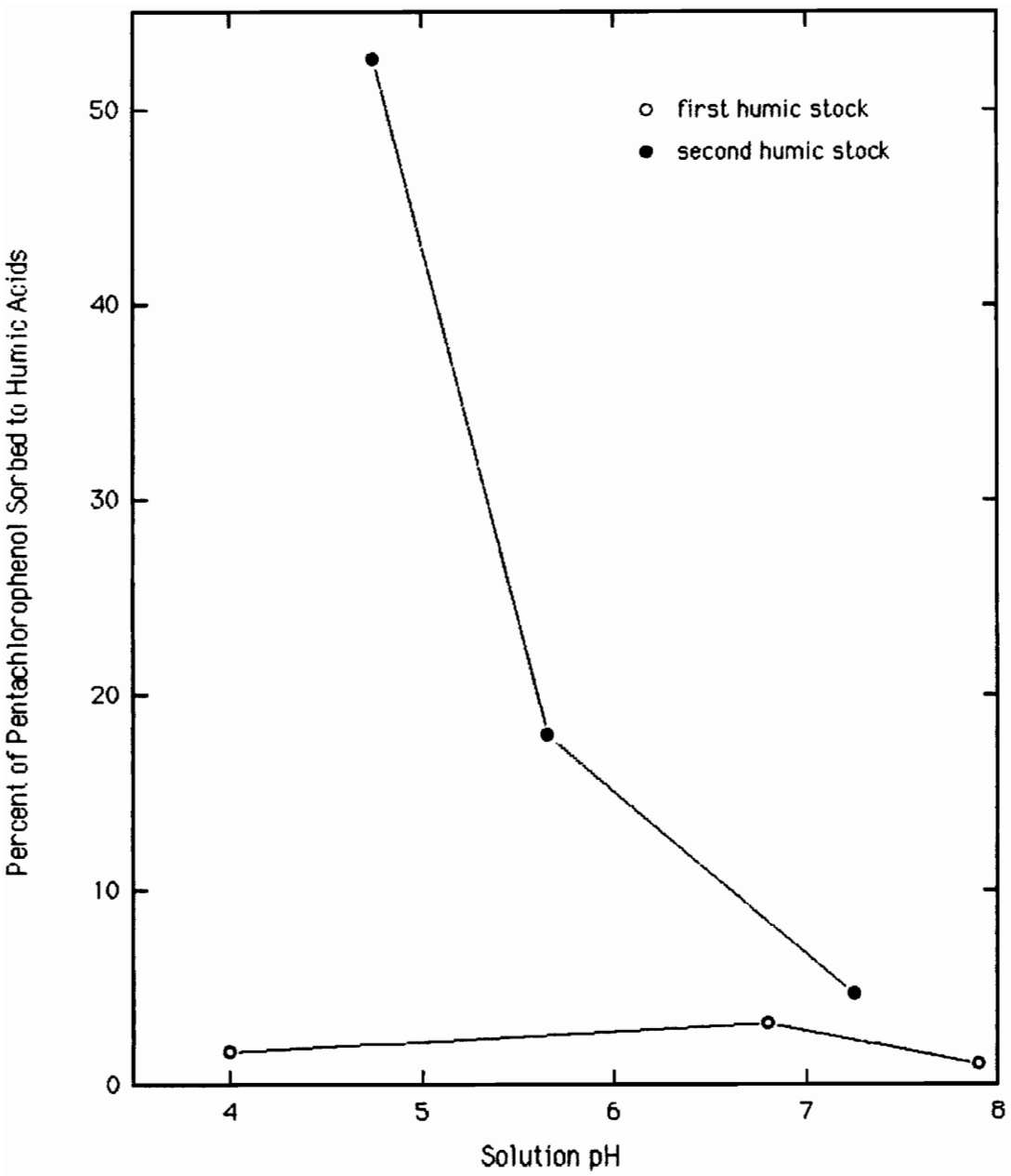

Figure 17. Comparison of the ability of the humic acids from the two humic stock solutions to sorb the PCP. Data from solutions of 4 mg/L PCP, 100 mg/L TOC, 28 day contact time. Note that the differences are more pronounced under acidic conditions.

The differences in partitioning of PCP to humic acids from the two stock solutions underline the heterogeneous nature of this organic material. These results indicate that the characteristics of the organic matter play an important role. Subtle structural variations in the number and type of functional groups affect the attractive and repulsive forces. For example, a polymer which contains a relatively high number of polar groups will be more soluble in the aqueous phase and the nonpolar PCP will not as readily associate with this organic molecule.

Not only the quantity, but the phase and source of the humic acids control the degree of sorption. The nature of the soil organic material is dynamic and poorly understood, but should not be ignored when deriving models to estimate the extent of partitioning.

Section 4.4.4: Kinetics

According to Chiou, *et al.* (1983, 1985, 1986), Lee, *et al.* (1990) and Schellenberg, *et al.* (1984), equilibrium is essentially achieved within 24 hours. Robinson (1990) noted that sorption of trichlorophenol occurred between day one and day 30, but the quantity was small compared to the total amount sorbed. The assumption of rapid kinetics is used in models which estimate the extent of subsurface contamination. However, Ball and Roberts (1991) observed that substantial amounts of a solute continued to sorb slowly over a period of months. The experimental results from this study supported the latter trend. Figures 18 and 19 show that only a minor fraction of the total recorded sorption occurred within the first day. In several solutions, a measurable increase in the amount of PCP which bonded with the humic acids was recorded between days 28 and 92 (Figure 18). These rates were different from those reported by Robinson (1990) for 2,4,6-trichlorophenol. The trichlorophenol completed 60 percent of its total sorption within the first day and virtually 100 percent within the first month.

A series of statistical tests were performed in order to analyze the changes in the partition coefficients over time (Appendix A). In the low pH solutions, the change in sorption from day one to day seven was not great enough to yield a statistically significant increase in the partition coefficients.

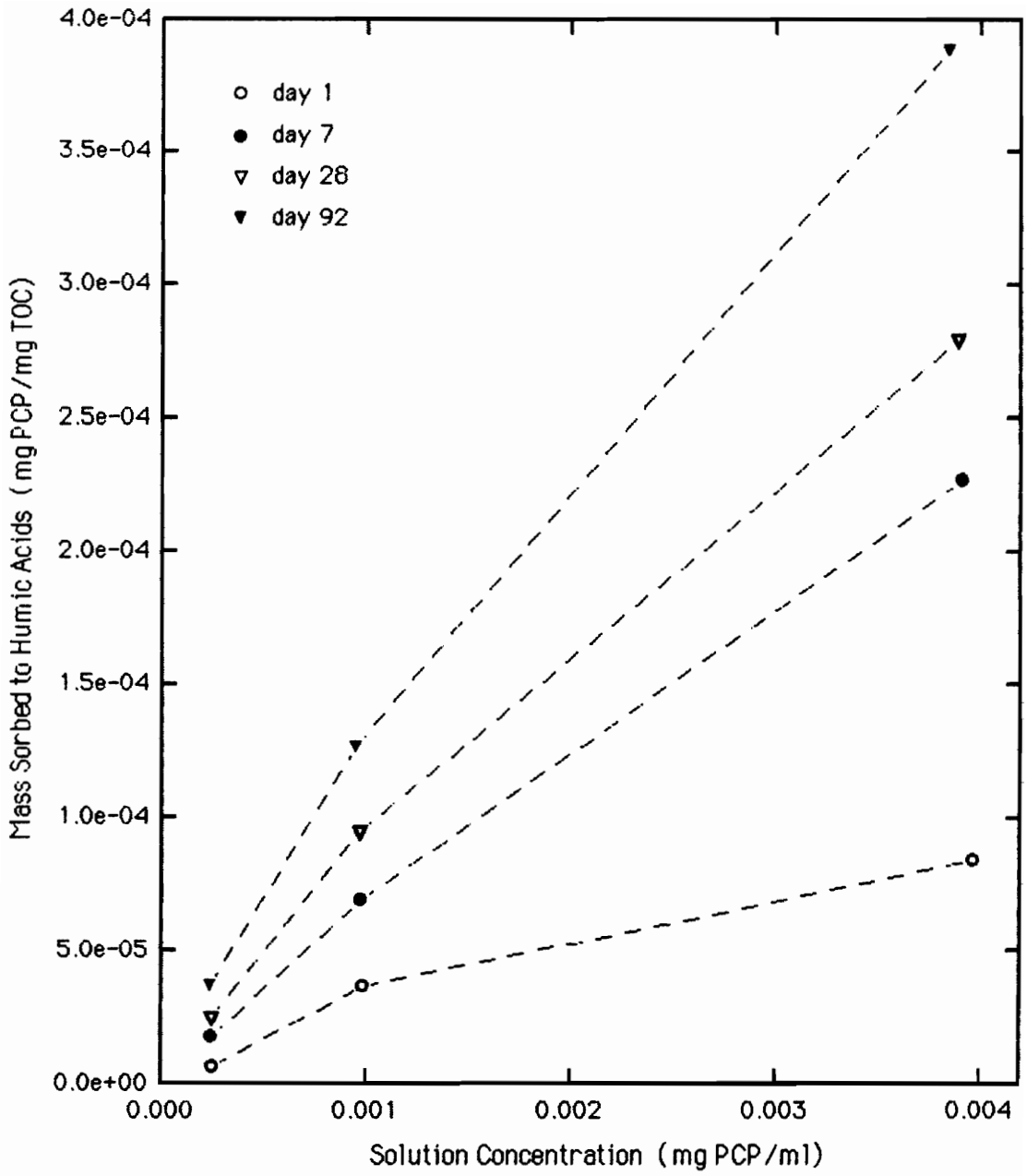

Figure 18. Freundlich isotherms which illustrate the significant amount of PCP which bound to the humic acids after the first day of contact. Data from solutions of 400 mg/L TOC, first humic stock, pH 7.3 - 7.45.

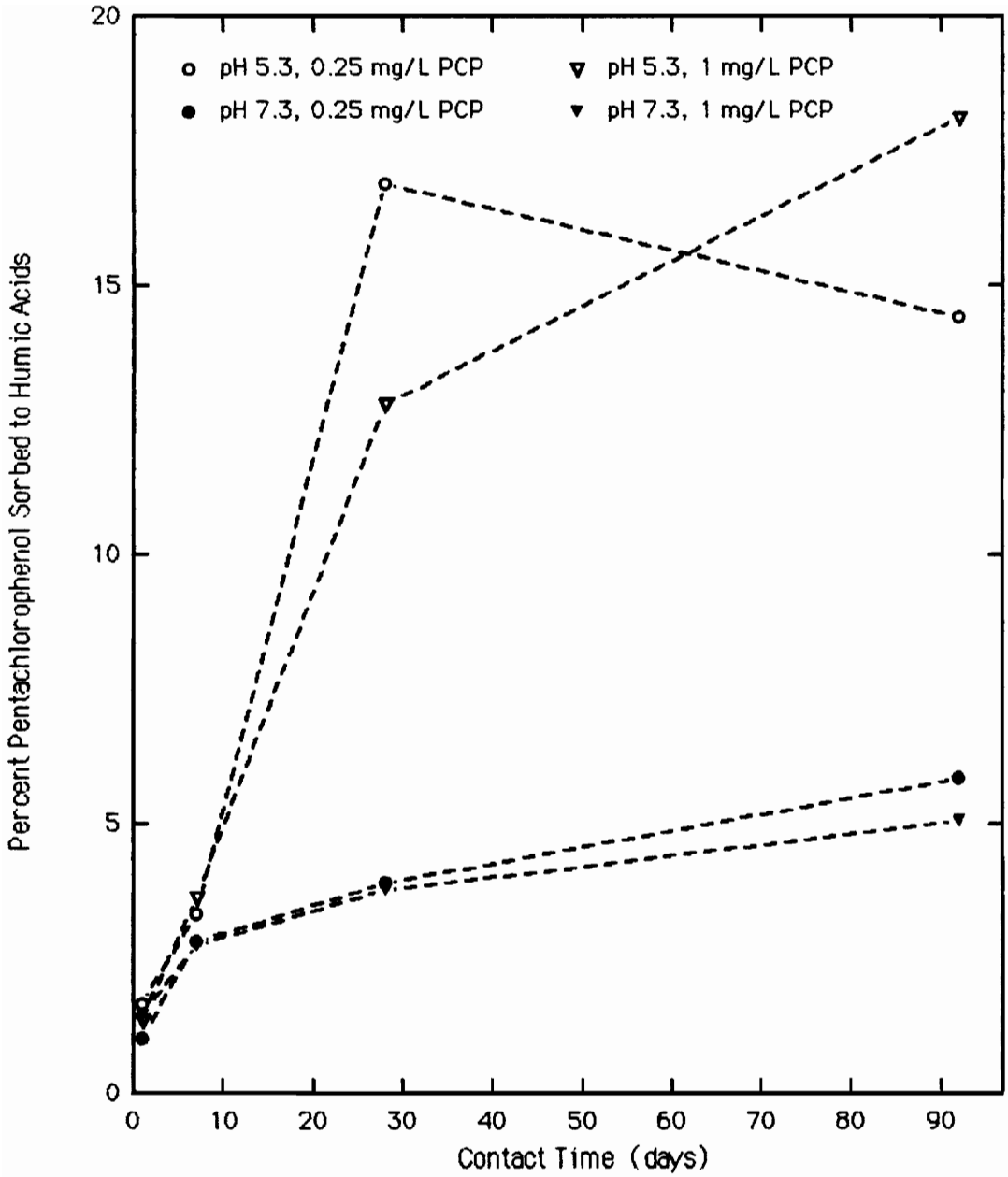

Figure 19. Percent sorption over time which demonstrates the slow sorption kinetics at both pH 5.3 and pH 7.3. Data from solutions of 400 mg/L TOC, first humic stock.

On average, the partition coefficients from day 28 were significantly higher than those from day 7. For neutral and basic solutions, the degree of association rose steadily between day one and day 28. The latter increases are not readily apparent in the graphs. However, the amount of sorption was generally low in the neutral and basic solutions. Small changes in absolute values became large in terms of percentages. These calculations did not address the actual rates of sorption, but simply served to ascertain that equilibrium was not attained within the first seven days, and most likely not within the first month. Not enough data were collected to make valid statistical comparisons between partition coefficients from day 92 and day 28.

Even though the sorption increased greatly from day seven to day 28 in the acidic solutions, the changes in the sorption to the dissolved and particulate phases individually were not statistically significant. Only seven samples with high variability comprised this test. More data is necessary to verify this observation. In the neutral and basic samples, the trends in the association with the particulate phase were statistically similar to the acidic ones. However, association with the dissolved phase increased significantly throughout the duration of the experiment. Regardless of the statistical results, the averages of the partition coefficient ratios were greater than one, indicating that the amount of sorbed PCP generally increased with lengthening contact time.

In some solutions, the amount of PCP sorbed to the humics actually decreased between two of the sampling times, but otherwise increased, creating a sorption/desorption pattern. Three 2000 mg/L TOC, basic solutions were the most dramatic examples of this trend (Figure 20). Several 800 mg/L TOC, pH 6.9-7.2 solutions derived from the second stock of humic acids behaved in a similar manner (Figure 21). In these solutions, association with the dissolved phase increased consistently, while that to the solid humic matter followed the sorption/desorption pattern. Each set of solutions graphically depicted did not constitute isolated instances of this phenomenon from either humic stock. The uptake and release of pentachlorophenol is not confined to these experimental results. Galil (1991) noted that after the initial sorption of PCP to the soil, some of the PCP was desorbed into solution.

The solutions in which this unexpected sorption/desorption behavior was the most apparent were the ones with a high content of particulates. The

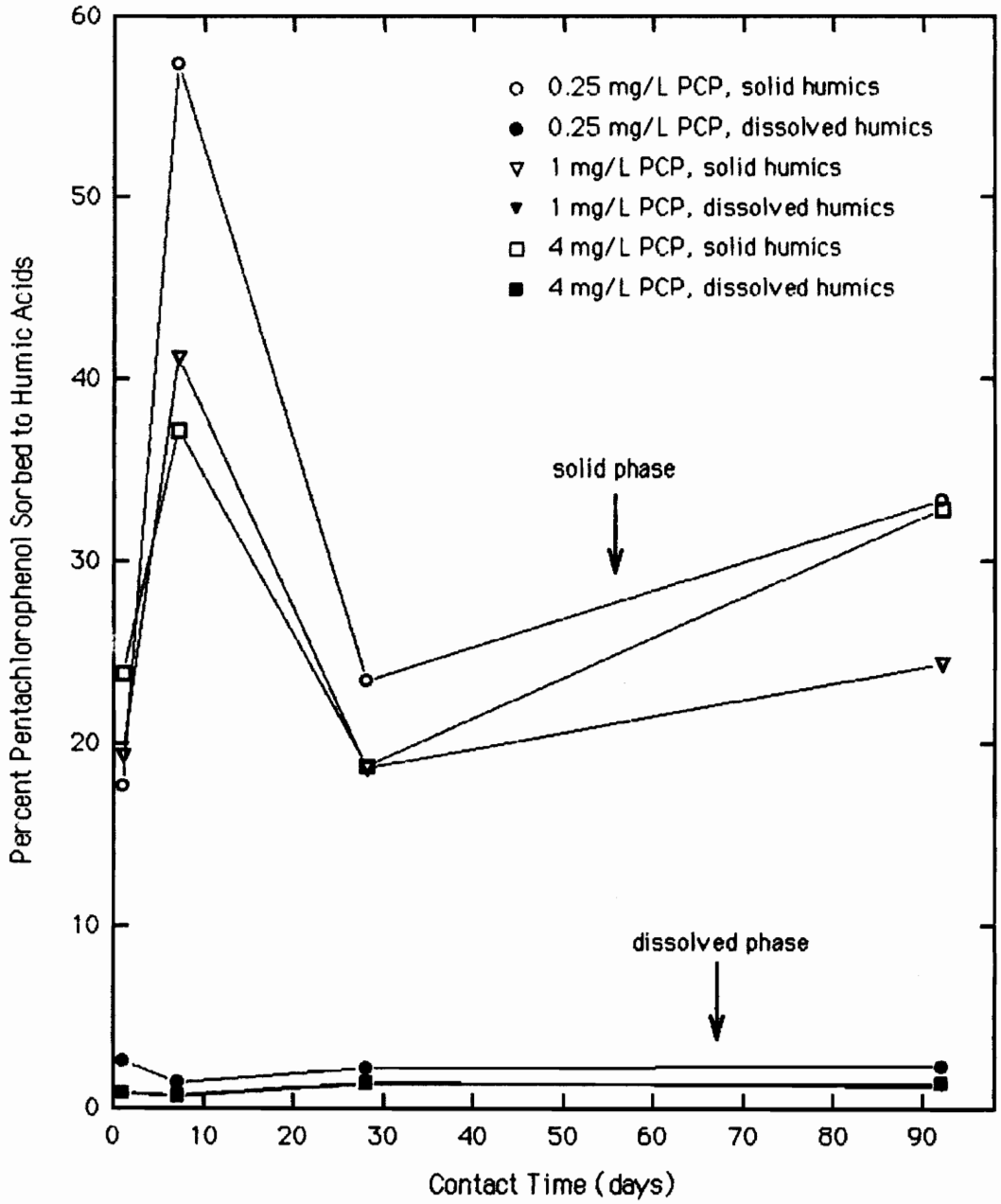

Figure 20. Influence of contact time on sorption to the dissolved and particulate humic acids. Data from solutions of pH 7.1-7.4, 2000 mg/L TOC, first humic stock.

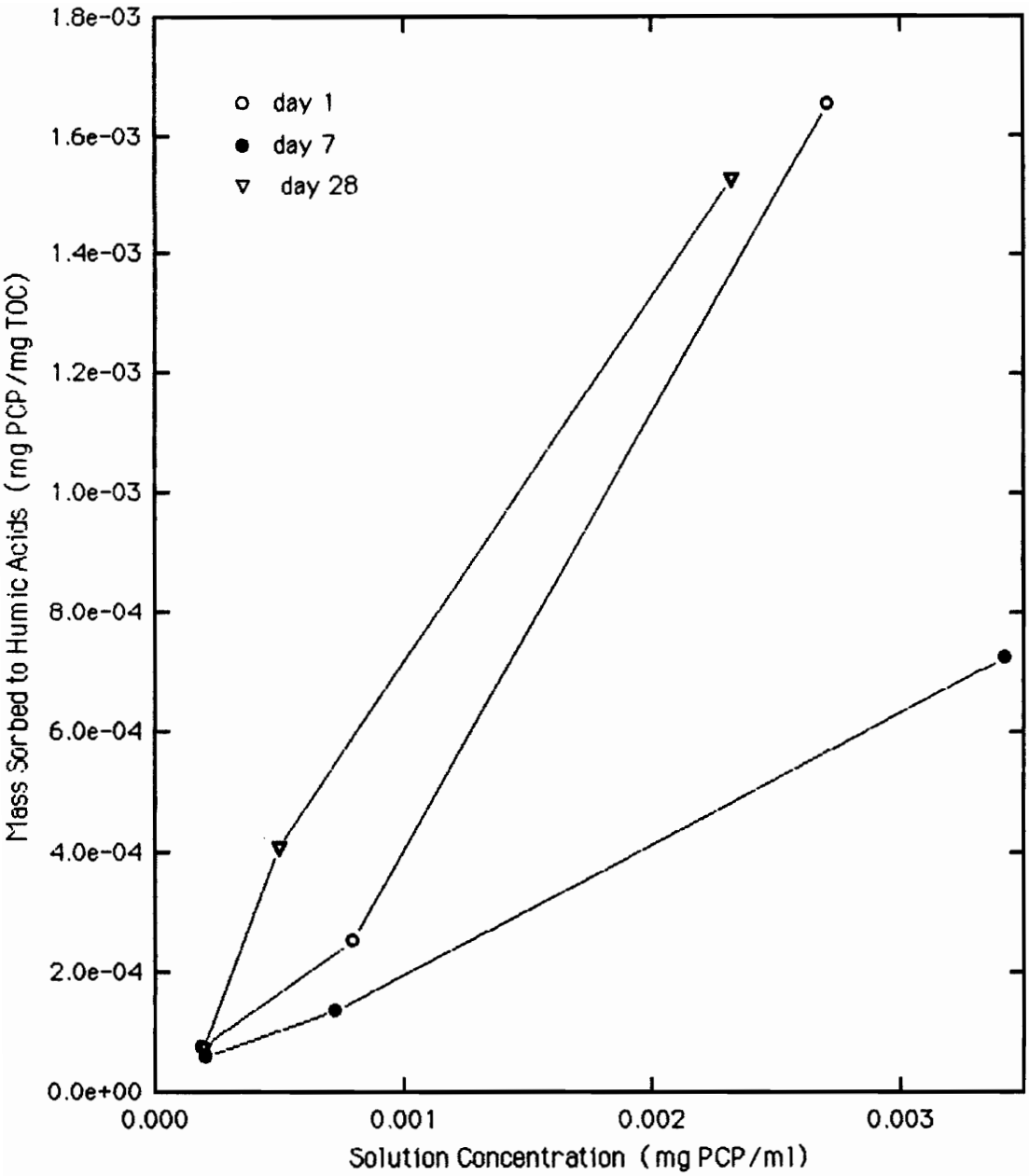

Figure 21. Freundlich isotherms which illustrate the variability of the amount of sorbed PCP over time. The dissolved humics associated with a minor fraction of the PCP. Data from solutions of pH 6.9-7.2, 800 mg/L TOC, second humic stock.

dissolved phase interacted with a small amount of PCP which was either constant or slowly increasing. The solids tended to sorb large amounts with considerable variation over time. These two observations support the theory that different mechanisms control the sorption to the individual humic phases. The occurrence of only one mechanism cannot possibly explain why, in a given solution, the sorption pattern over time was vastly different for the particulate and dissolved humic acids. None of the proposed sorption mechanisms are able to explain the initial uptake then release of PCP. Without information on possible changes in the distribution of the humic acids between the dissolved and particulate phases over the course of this uptake/release process, no explanation can be offered.

Based on these data, it is proposed that physical surface sorption initially controlled the binding to the solid phase, while liquid-liquid partitioning dominated the associations with the dissolved humic acids. The primary reaction was determined by the relative amounts of each organic phase present. These reactions proceeded rapidly. Gradually, humic absorption of the PCP became the dominant reaction, accounting for the slowly sorbing fraction. Steinberg, *et al.* (1987) and Scribner, *et al.* (1992) suggested that the slowly sorbing fraction was due to continued diffusion of the contaminant into sorbent micropores as opposed to the actual kinetics governing the sorption mechanisms. This explanation clearly does not apply to the dissolved humic acids. It is doubtful that the particulate humic material in the experimental solutions contained such inaccessable micropores. This micropore model does not seem to be appropriate for these experimental conditions.

Section 4.5: Bioavailability

The first five equilibrated solutions to which the microorganisms were added were initially at a pH between 5.2 and 5.8. The methylbenzylamine carbon dioxide traps caused the pH to increase to above 9 overnight. Over the course of a week, after which time the solutions were acidified and analyzed for mineralization, no evidence of biodegradation was recorded (Appendix B). Consistent with the proposed sorption processes, the dramatic increase in pH did induce desorption. At a solution pH of 7.5, the humic acids should sorb

more PCP than in comparable solutions at pH 9.5. The observed desorption was not strong enough to cause the amount of PCP associated with the humic acids to become less than the quantity bound to the organic matter in similar solutions of pH 7.3 to 7.5 (Figure 22).

This sorption irreversibility was not isolated to these experiments. Similar desorption hysteresis was mentioned by Lagas (1988) and Isaacson and Frink (1984). The desorbed fraction might have represented the portion of PCP which was sorbed via physical surface interactions and liquid-liquid partitioning. The irreversibly held PCP could have been that portion which went through either chemical surface reactions or envelopment by the humic acid.

To guarantee that the pH remained constant, the second set of five solutions did not contain any CO_2 traps. During the first 20 days, neither a decrease in the solution radioactivity within typical experimental variation (ten percent) nor an alteration in the gel column elution pattern was noted. Between day 20 and day 63, evidence developed which indicated biodegradation. The overall solution radioactivity decreased by as much as 30 percent in some solutions, indicating complete degradation of part of the PCP to carbon dioxide (Table 4). The elution pattern of the free ^{14}C was altered to follow a pattern consistent with the presence of species characterized by molecular weights less than that of PCP. Figures 23 and 24 show typical results. Only one solution of the second set of flasks did not exhibit any sign of biodegradation. Since the microorganisms had been cultured for five months in a strong pentachlorophenol solution, the lag time and slow rate of degradation were not expected. It was thought that the microorganisms would degrade the free PCP during the first few days, similar to the results that Robinson (1990) obtained with trichlorophenol.

The elution of the free radiolabeled solutes between 100 ml and 130 ml indicated that species with molecular weights lower than PCP were present. The radioactivity in the 65 ml to 100 ml fractions was due to the presence of free PCP. Trichlorophenol elutes within the 100 ml to 130 ml region, while monochlorophenol elutes between 150 ml and 170 ml (Figure 25). Measurement of only the counts per minute did not permit the determination of which specific phenols were present. Thus it was not possible to identify the compounds which contributed to the radioactivity in the 100 ml to 130 ml elution

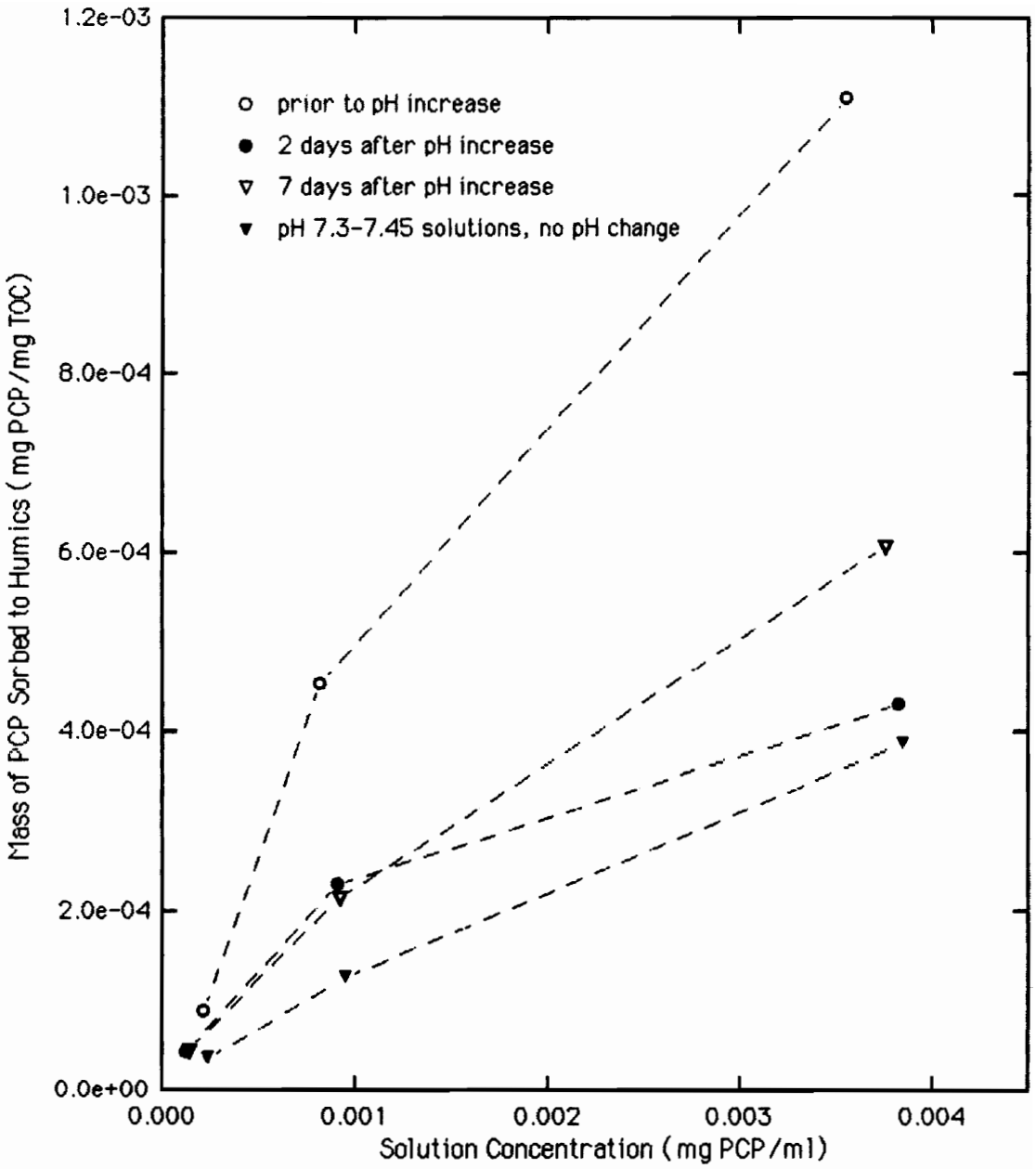

Figure 22. Freundlich isotherms which illustrate the presence of an irreversibly held PCP fraction after the pH increase from 5.3-5.4 to 9.2-9.5 induced desorption. Note that little change in the amount of sorbed PCP occurred between day 2 and day 7.

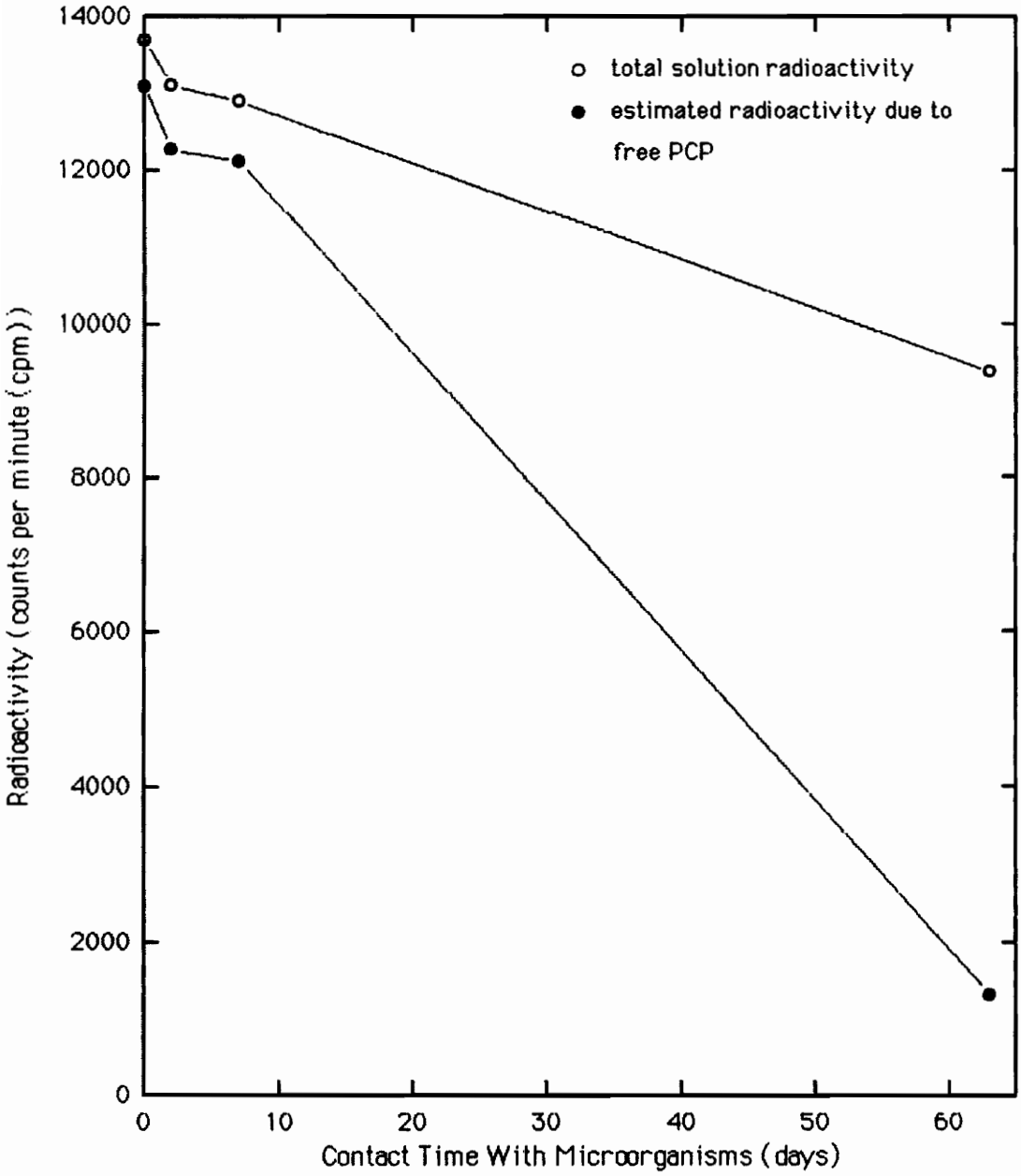

Figure 23. Influence of contact time with microbial PCP degraders on the total solution radioactivity and the estimated radioactivity due to free PCP. Data from solution of 1 mg/L PCP, 400 mg/L TOC, pH above 7. The cpm due to free PCP were estimated using the gel column elution patterns.

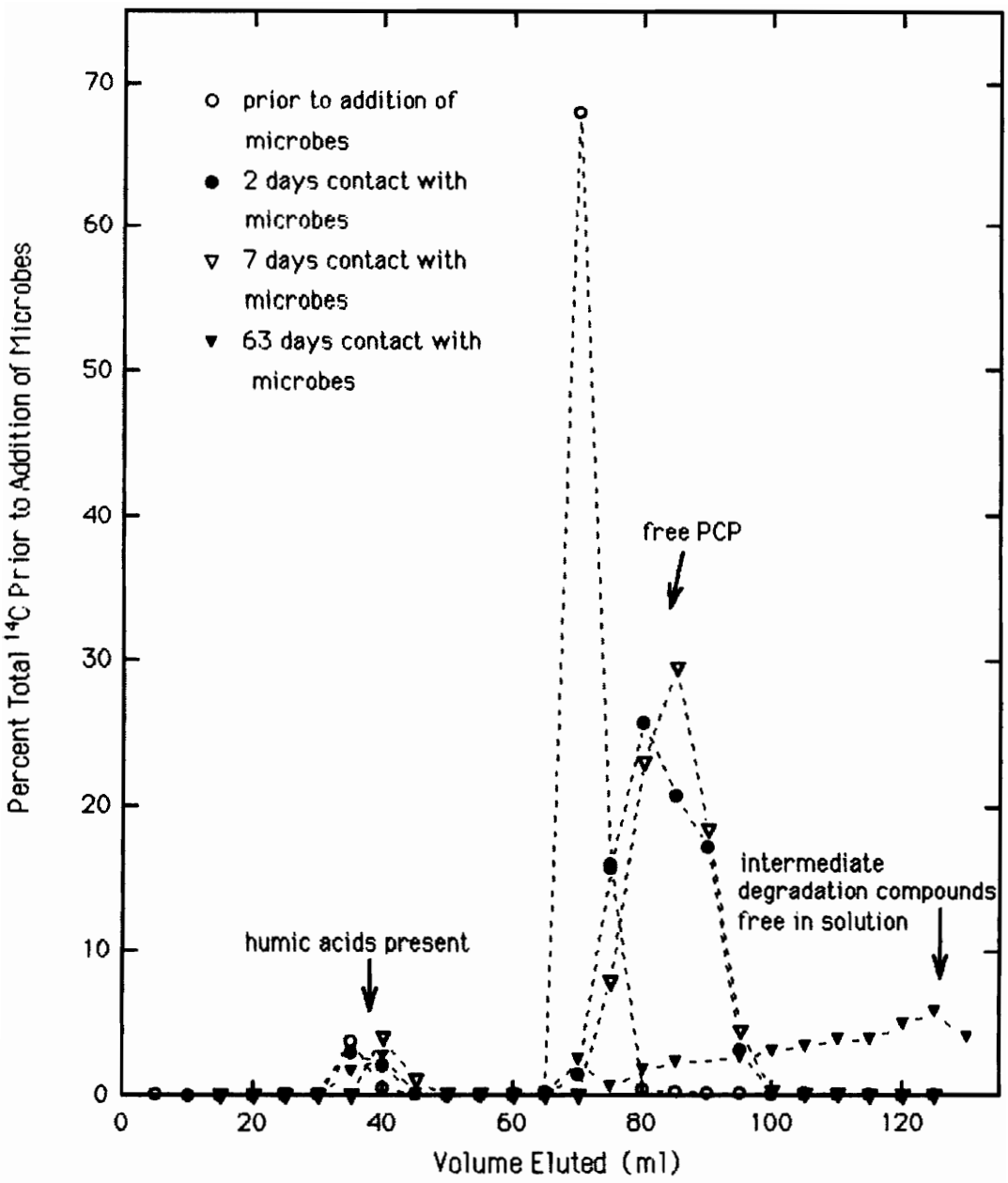

Figure 24. Gel chromatographs which depict the lack of PCP biodegradation until day 63. The delayed free solute peak for the day 63 peak indicates the presence of chlorinated phenols with molecular weights lower than PCP's. Solution of 1 mg/L PCP, 400 mg/L TOC, pH above 7, first humic stock.

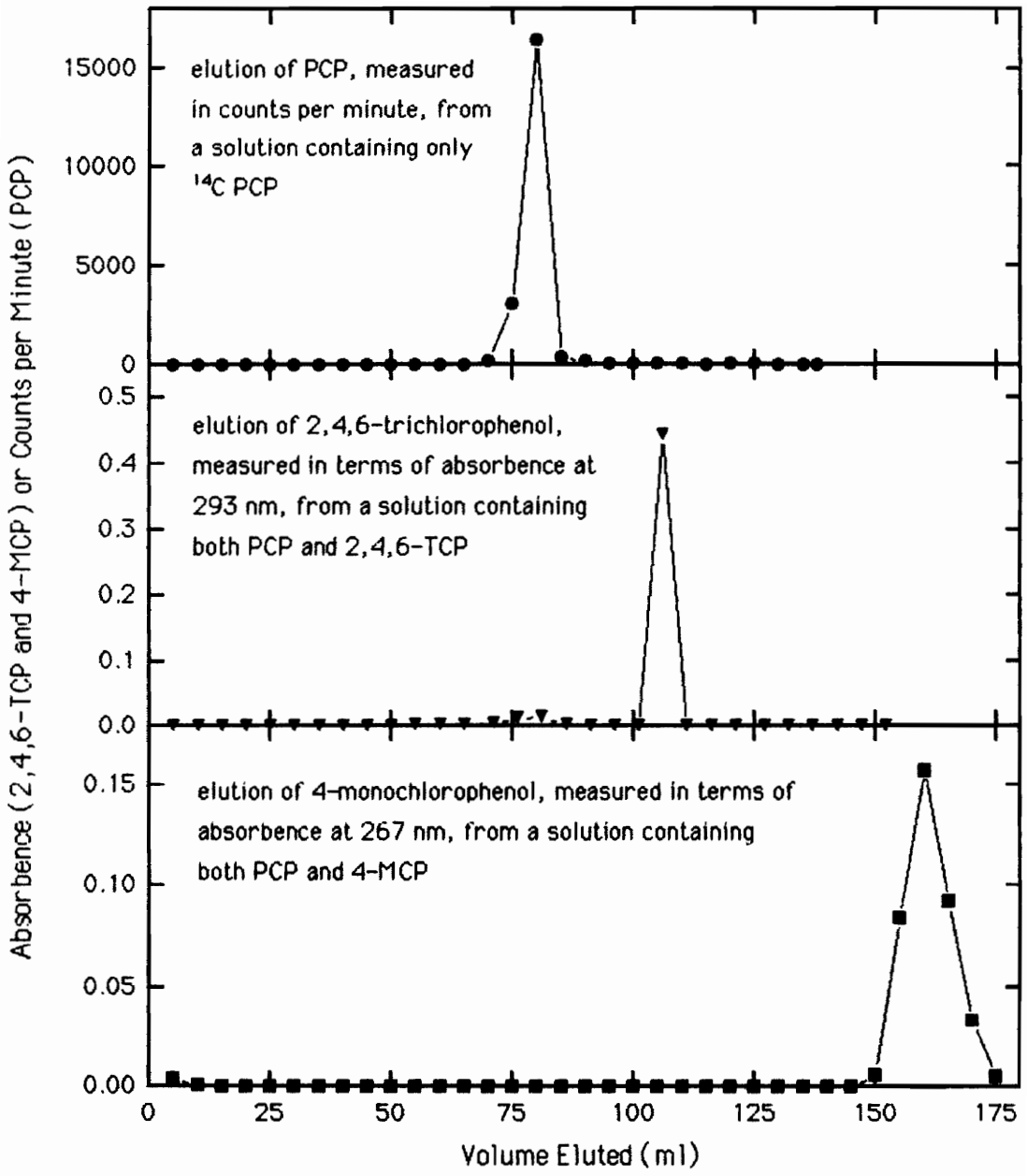

Figure 25. Typical elution patterns of PCP, 2,4,6-TCP and 4-MCP from the Sephadex gel column.

volume. However, given the elution volumes, one can conclude that the molecular weights of the degradation products were similar to that of trichlorophenol but not as low as that of monochlorophenol. Reductive dehalogenation is one process by which aerobic microorganisms degrade PCP (Topp, *et al*, 1988). Tetrachlorophenol has been identified as a product of the aerobic metabolism of PCP (Portier and Fujisaki, 1986). It seems likely that the unidentified, radiolabeled compounds were tetrachlorophenol and trichlorophenol.

Table 4: Distribution of ^{14}C With Degradation Time

Solution	Contact Time With Microbes (days)	Percent ^{14}C in Solution	Percent ^{14}C Sorbed to Humic Acids	Percent Estimated Free PCP
0.25 mg/L PCP, 400 mg/L TOC	0	100	5.83	94.17
	2	90.7	5.53	85.17
	7	90.3	6.49	83.81
	63	78.6	5.84	20.1
1 mg/L PCP, 400 mg/L TOC	0	100	4.34	95.66
	2	95.8	6.33	89.47
	7	94.3	6.11	88.19
	63	68.6	5.12	12.2
4 mg/L PCP, 400 mg/L TOC	0	100	3.88	96.12
	2	95.1	3.1	92
	63	86.6	3.04	9.78
0.25 mg/L PCP, 800 mg/L TOC	0	100	8.09	91.91
	2	95.1	5.37	89.73
	20	80.3	4.72	75.58
	63	74.8	5.34	8.73
1 mg/L PCP, 800 mg/L TOC	0	100	7.13	92.87
	2	93.8	7.06	86.74
	20	83.8	5	78.8
	63	89.2	NA	NA

note: NA means not available

As with the free solute, the sorbed radiolabeled compounds could not be identified. The radioactivity in the humic fractions could have been due to the presence of PCP, intermediate degradation products or biomass which had incorporated the radiolabeled carbon within itself. All that can be stated is that the amount of sorbed radioactivity did not vary as biodegradation proceeded (Figure 26).

There is evidence in the literature to support the premise that the bound ^{14}C was due to the PCP and that the PCP was not accessible to the microorganisms (Falatko, 1992; Ogram, *et al.*, 1985; Robinson, 1990; Scribner, *et al.*, 1992). However, by decreasing the concentration of the free PCP, degradation should have caused desorption of the sorbed PCP. If one were to assume that the bound PCP were not bioavailable, then the radioactivity associated with the humic acids should have decreased. It is possible that the PCP was irreversibly bound, or slowly released such that the desorption could not be measured. In this situation, the amount of ^{14}C bound to the humic acids should have increased due to the sorption of degradation products and biomass. Trichlorophenol sorbs rapidly to humic acids (Robinson, 1990). If one assumes that the bound PCP were not bioavailable, then the only explanation for the constancy of the quantity of sorbed ^{14}C is that the amount of desorbed PCP was completely offset by the sorption of the degradation products. This scenario seems unlikely.

The data clearly demonstrated that aerobic soil microorganisms are capable of completely and incompletely degrading PCP. The results concerning the bioavailability of humic bound PCP were inconclusive. Qualitative information on the radiolabeled compounds sorbed to the humic acids is necessary before any conclusions can be drawn.

Section 4.6: Solvent Extractions

Pentachlorophenol is highly soluble in both MTBE and MeCl. Theoretically, in the presence of a solvent into which PCP readily dissolves, both surface sorption and liquid-liquid partitioning should be reversible. The experimental results indicated the presence of some irreversibly held pentachlorophenol. While the PCP free in solution was between 90 percent

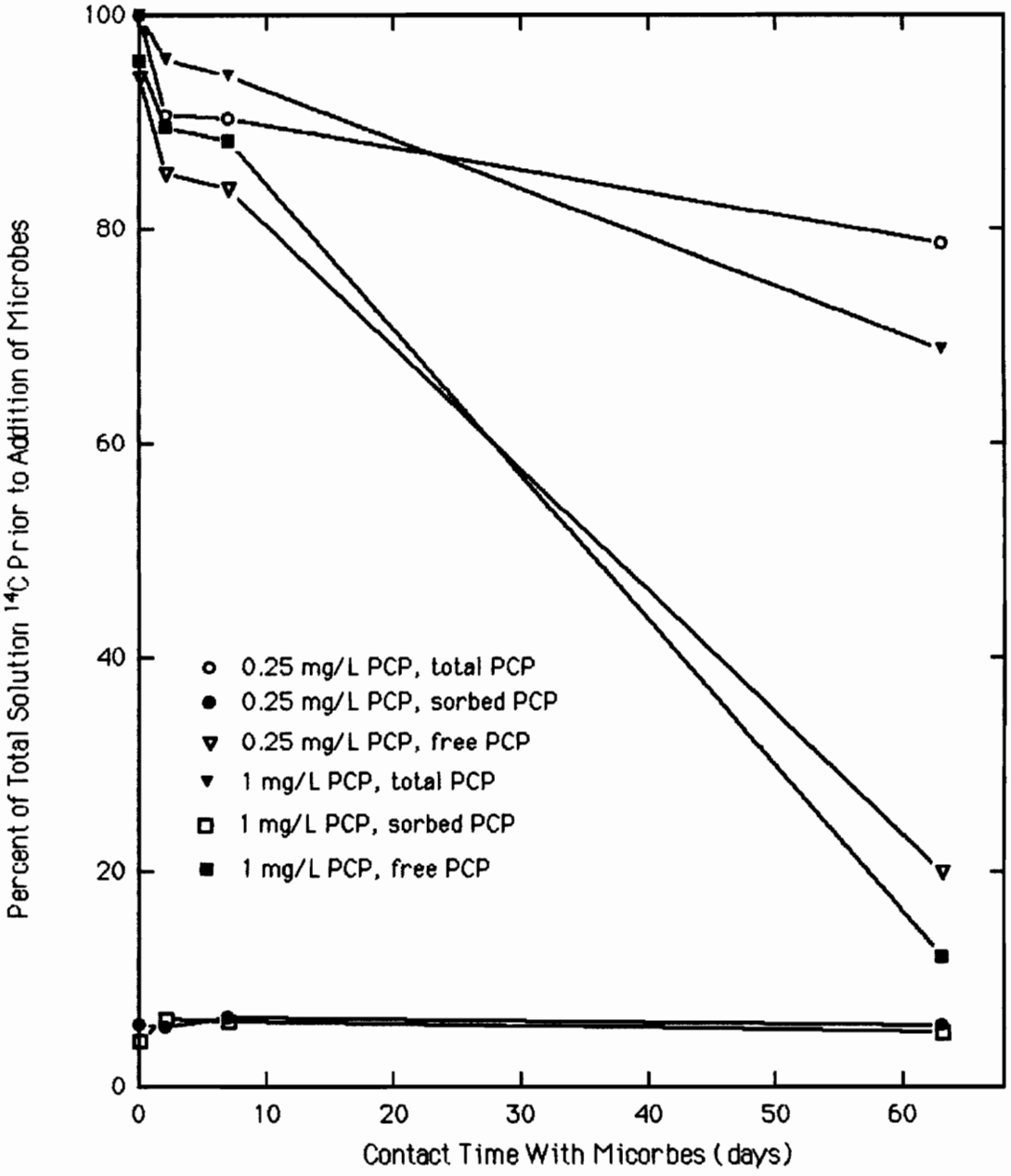

Figure 26. Influence of contact time with microbial PCP degraders on the amount of sorbed ^{14}C, estimated ^{14}C due to free PCP and total solution ^{14}C. Data from solutions of pH above 7, 400 mg/L TOC, first humic stock. Amount of free PCP estimated from gel column elution patterns.

and 98 percent collected by the MTBE and between 70 percent and 80 percent by the MeCl, the extraction efficiencies for the sorbed pentachlorophenol were much lower (Table 5). Figures 27 and 28 are gel chromatographs which illustrate the inability of both solvents to remove the PCP associated with the dissolved humic acids.

Table 5: Average Solvent Extraction Efficiencies:

Stock Solution	pH range	Contact Time (days)	Percent Extracted from Solid Humic Phase	Percent Extracted from Dissolved Humic Phase	Percent of Free PCP Extracted
first	4.8	92	54.5	42.9	95.6
first	5.75	92	77.6	20.5	86.8
first	6.5 - 6.8	92	74.6	22.8	97.4
first	7.1 - 7.9	92	63.6	2.64	92.6
second	4.4 - 4.8	1	85.2	NA	95.2
second	5.7	1	65.4	NA	98.7
second	7-7.2	1	63.6	NA	95.9
second	4.6 - 5	35	56.1	NA	92.3
second	5.4 - 5.7	35	50.8	30.7	88.7
second	7.3 - 7.8	35	67.3	4.7	93.5
first, MeCl	7.1 - 7.9	92	75.1	10.8	78.4

note: NA means not available, the amount of PCP initially sorbed to the dissolved phase was too small to be accurately measured

Over the experimental pH range for each humic stock at each contact time, an average extraction efficiency of the PCP sorbed to the solid phase was calculated and compared to the corresponding average removal of PCP from the aqueous phase. The results of these one-tailed, standard t-tests provided statistical evidence that the solvents were less efficient at extracting the PCP attached to the humic precipitates. Two of the three tests were characterized by p-values less than 0.001. The third p-value was less than 0.025.

The PCP associated with the dissolved organics was particularly resistant to solvent extraction. The highest amount of PCP removed from the dissolved phase was 42.9 percent. In several solutions, no extraction was even measured. The transfer of the PCP from the dissolved organics to the solvent

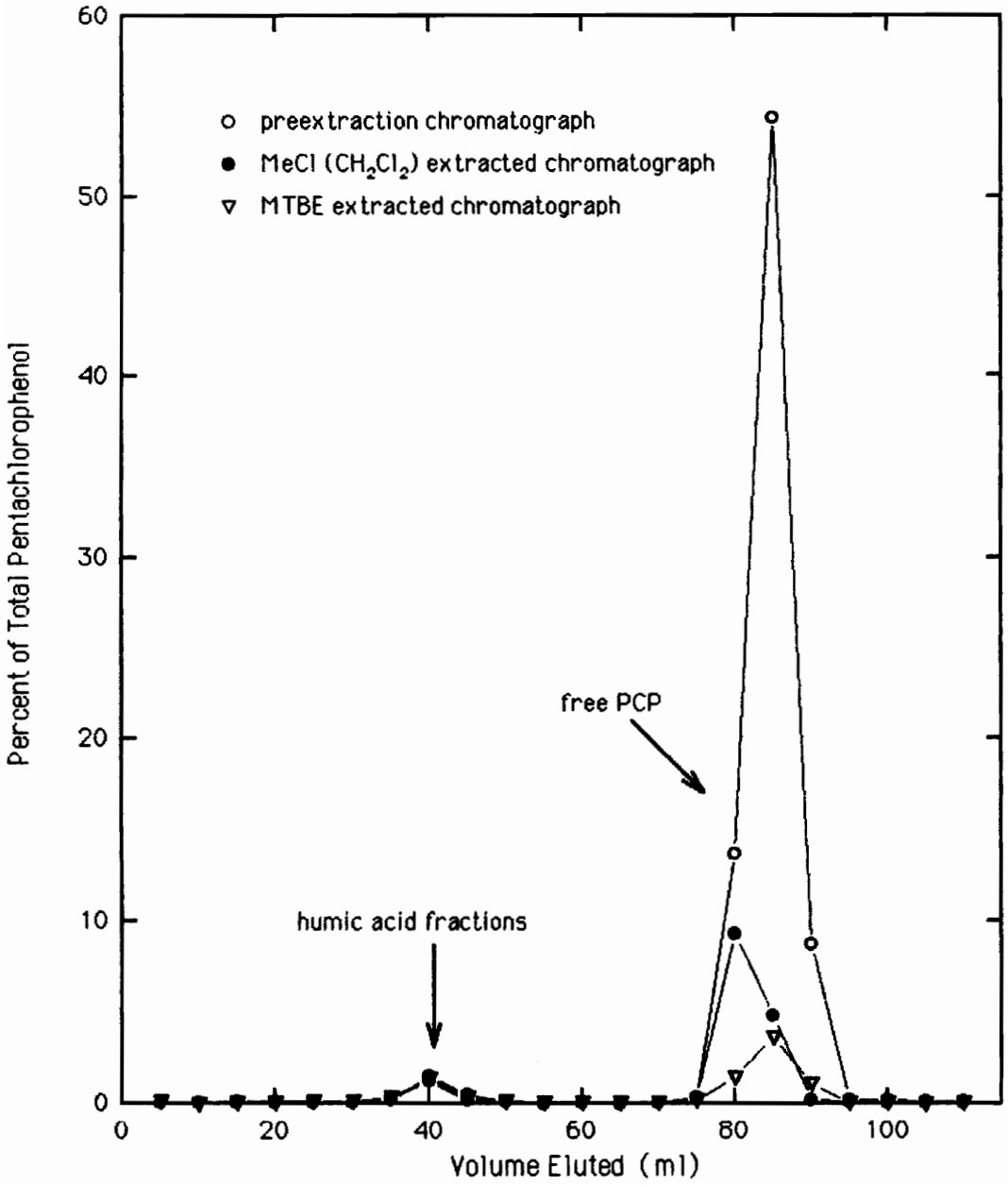

Figure 27. Typical gel column elution patterns before and after solvent extraction. Data from a solution of 0.25 mg/L PCP, pH 7.2, 2000 mg/L TOC from the first humic stock, and a contact time of three months.

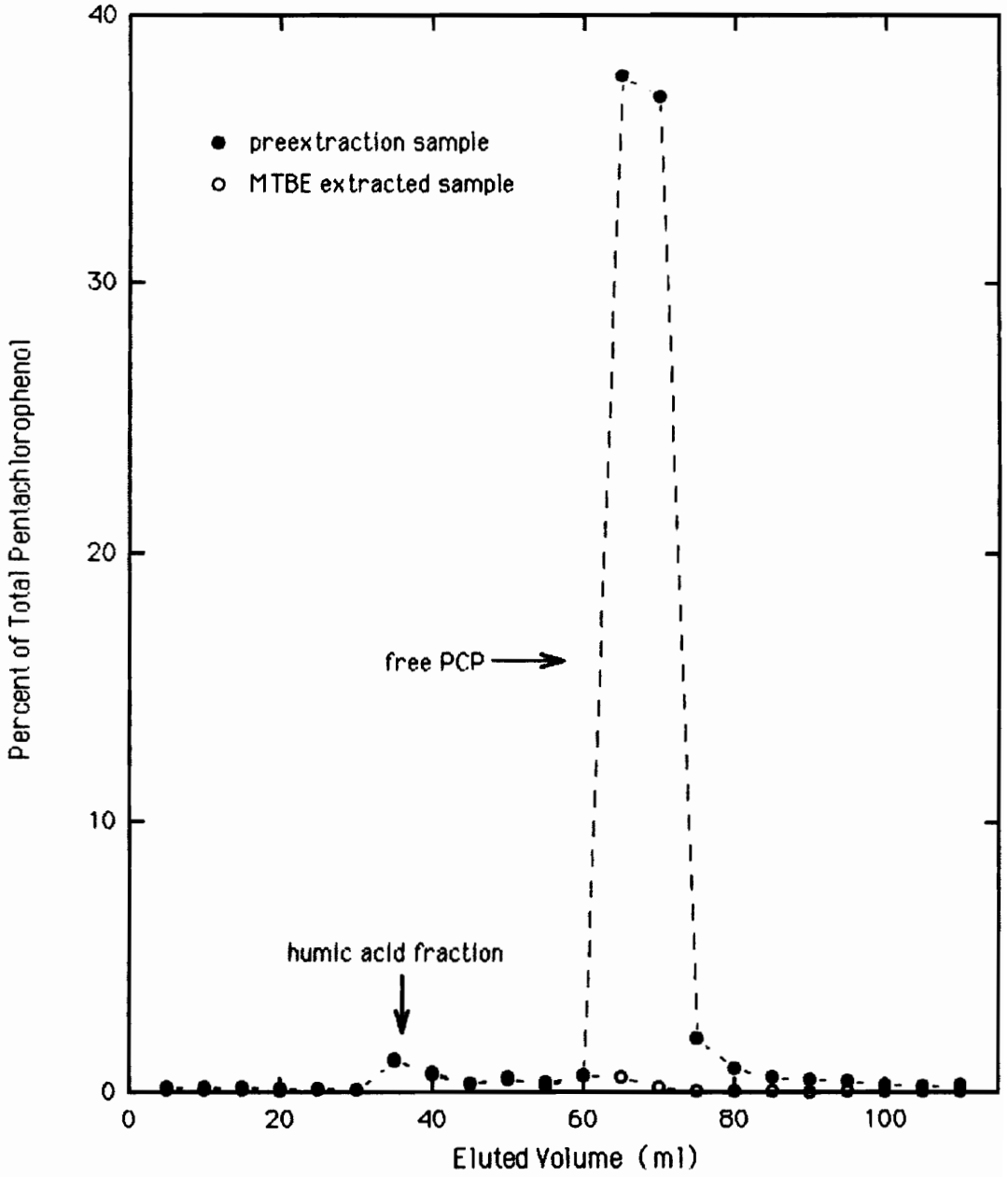

Figure 28. Gel chromatographs which illustrate MTBE's inability to remove the humic bound PCP. From solution of 1.75 mg/L PCP, 100 mg/L TOC, first humic stock, pH 6.8, two months contact time.

phase appeared to be pH dependent. The data collected concerning the dissolved phase extractions of solutions derived from the second humic stock supported this observation. Solution pH did not appear to affect the removal of PCP from the particulate humic acids nor from the aqueous phase (Figure 29). Regardless of the degree of pentachlorophenol ionization, MTBE was consistently effective in extracting the free solute. The fact that pH influences the dissolved phase extractions but not the particulate ones indicates that different mechanisms dominate the interactions between PCP and each type of humic acid.

After one day of contact, 71.1 percent of the PCP was removed from the solid phase. In solutions which had stood for 35 days, only 56.6 percent was extracted. By performing a one-tailed t-test to compare two means, it was determined that these two averages were statistically different (p-value < 0.05). Lengthening the contact time increased the quantity of irreversibly sorbed pentachlorophenol. No data for the dissolved phase extractions at different contact times were available. This observation was consistent with the findings of Steinberg, *et al.* (1987), who noted that 1,2-dibromoethane was more difficult to extract after it had been in contact with a soil for several years than after recent application.

The methylene chloride was less effective than the MTBE at extracting the aqueous phase PCP. The extraction efficiencies for the sorbed compounds appeared to follow the same trends described for MTBE. However, the sample size was not large enough to permit valid statistical comparisons.

Liquid-liquid partitioning and physical surface sorption do not adequately explain the solvents' inability to extract the sorbed pentachlorophenol. The time dependency implies that at least one of the reactions which inhibited the extraction proceeded slowly. The absorption model fits this requirement. The question remains as to whether or not absorption could account for half of the sorption to the solid phase. The fact that, after only one day of equilibration time, an average of 30 percent of the PCP sorbed to the solid phase was not removed suggests that some rapid, irreversible process also took place. Perhaps this portion of the PCP was bound by chemical sorption. Although much is not yet understood, it is clear that the contact time, and the degree and

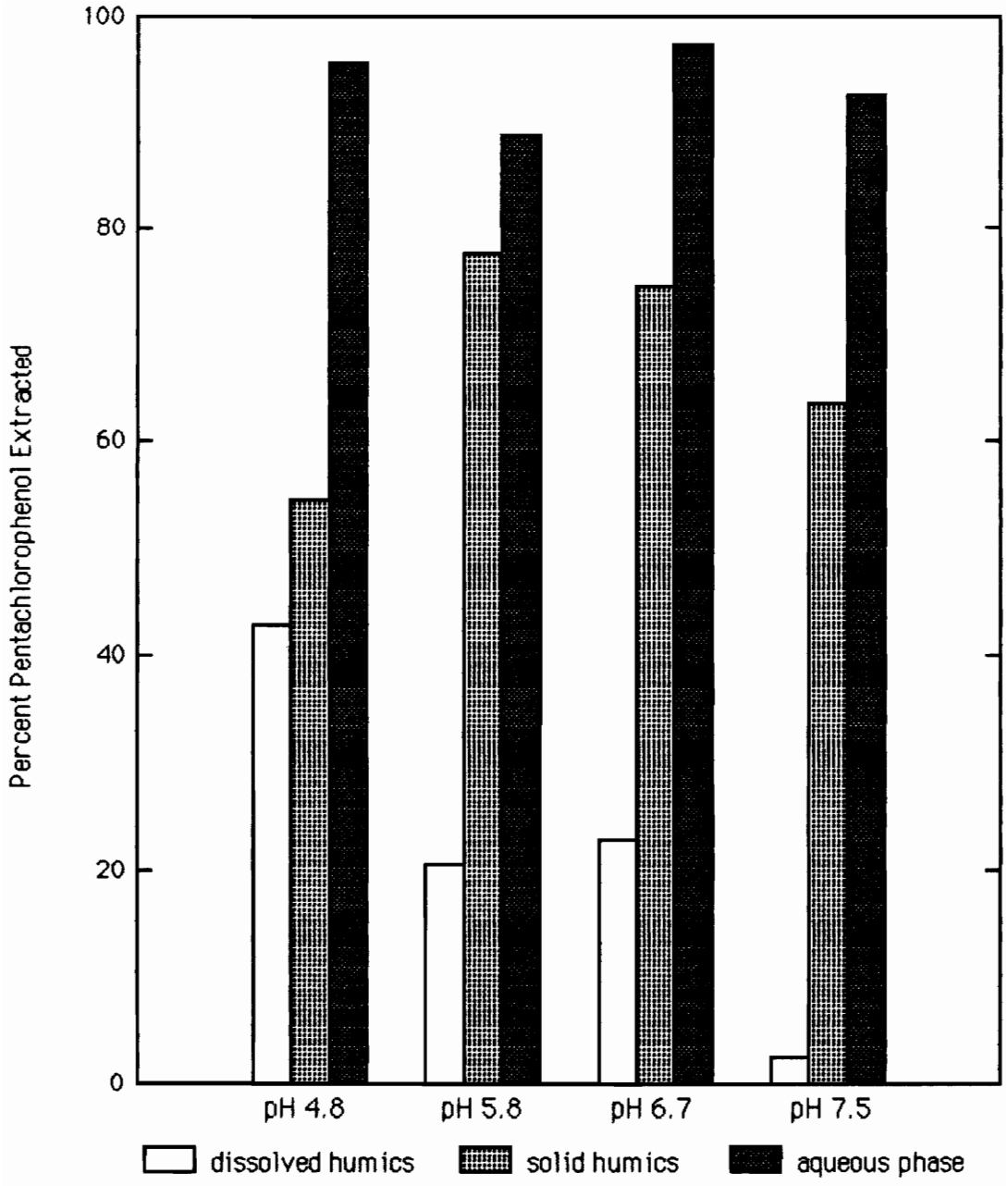

Figure 29. The influence of pH on the MTBE extraction efficiencies of PCP associated with the humic phases and dissolved in the aqueous phase. Data are averages of removals from solutions derived from the first humic stock and allowed to equilibrate for more than three months.

mechanism of partitioning determine the amount of PCP extracted and hence detected by conventional methods.

Section 4.7: Summary

Researchers have proposed three mechanisms to explain the association of pentachlorophenol with humic acids. Liquid-liquid partitioning is the dissolution of the PCP into the organic matrix. The humic acids form a separate phase within the aqueous solution. Surface sorption results from physical attractive forces between the pentachlorophenol hydroxyl group and specific sites on the humic polymer. Absorption describes the process whereby the humic acids form aggregates and trap the PCP molecule inside the polymeric structure. The relative importance of these mechanisms has been the subject of much debate.

The fact that a fraction of the PCP sorbed quickly to the dissolved phase suggests that some liquid-liquid partitioning did occur. Linear Freundlich isotherms are another indication of this dissolution process (Chiou, 1983, 1985). However, the solid phase bonded with more PCP per unit mass than did the dissolved polymers. Theoretically, the molar volume can be used to predict the degree of association caused by liquid-liquid partitioning (Voice and Weber, 1983). The particulate phase encompassed less volume than did the dissolved, and thus, by dissolution alone, should have sorbed less PCP. The experimental results suggest that surface sorption occurred.

Murphy, *et al.* (1990) presented results that supported surface sorption. With surface sorption, the association would have been primarily the result of interactions between the functional groups on the PCP molecule and the humic acid polymer. In neutral and basic solutions, the majority of these groups would have been ionized, causing electrostatic repulsive forces which would have inhibited the interactions. Consistent with this model, the Freundlich constants of the particulate humic acids decreased log-linearly as the pH increased.

Above pH 7, only a fraction of a percent of the PCP would have been in its neutral form. The amount of sorption by the anion is considered to be insignificantly small (Schellenberg, *et al.*, 1984). The fact that substantially more than one percent of the PCP partitioned to the solid phase in the high pH

solutions suggested that the entire process was not simple physical surface sorption. Absorption, chelation and chemisorption are possible explanations for this observation.

Sorption to the dissolved phase was also pH dependent. If liquid-liquid partitioning governed these interactions, then the relative polarities of the PCP and the humic acids would influence the sorption. By causing dissociation of the acidic functional groups and thus enhancing the polarity of the PCP relative to water, increasing the solution pH would have resulted in more PCP remaining in the aqueous phase. The trend observed with changing pH was consistent with this model.

The slow kinetics demonstrated by both humic phases suggest that another mechanism besides surface sorption and liquid-liquid partitioning governs sorption. For the first week of contact time, the flasks were kept on a shaker table. The continuous agitation should have provided enough mixing to counter any retardation of the reactions caused by the slow diffusion of PCP into the organic phase. Absorption can explain the continued sorption reported at the long sampling times. Time is needed for the humic polymers to change shape and envelop the solute. Longterm kinetic studies should be conducted to determine the full extent of the slow sorption reactions.

Absorption can account for the increase in the nonextractable sorbed PCP fraction over time. PCP enveloped within a humic molecule would be less likely to partition into a solvent than PCP sorbed by surface interactions or dissolution. Yet even after only one day, approximately 30 percent of the PCP associated with the particulate phase was not removed by MTBE. It is doubtful that enough humic acids could alter shape overnight and prevent the extraction of 30 percent of the PCP. This preliminary information implies the possibility of irreversible chemical reactions.

Microorganisms indigenous to the soil are capable of degrading PCP. Concerning the bioavailability of sorbed PCP, the data were inconclusive. Nor do the data provide any evidence to support the various theories of sorption mechanisms. The results do suggest that desorption is slow and that a fraction of the PCP is irreversibly bound. If biodegradation of the sorbed compound were controlled by desorption, as indicated in the literature (Ogram, *et al.*, 1985;

Robinson, 1990; Scribner, *et al.*, 1992), then a portion of the contaminant would not be available to the microbial population.

This research has raised some important questions that should be addressed in future studies. The nature of the sorbent itself appears to be as, if not more, important than the character of the solute. Further work is necessary in order to fully understand the dynamic nature of the humic acids. The intermediate degradation products and the sorbed compounds in the bioavailability study should be identified. More work should focus on the solvent extraction of the sorbed contaminant. It is difficult to quantify the concentration of a given compound if it cannot be fully extracted from the soil or groundwater sample.

The experimental results suggest that sorption of PCP to the organic matter is more complicated and dynamic than indicated in the literature. A few reactions, each at a different rate, govern the interactions. The controlling process(es) depends on the solution pH, the humic acid concentration, the distribution of the humic acids between the particulate and dissolved phases, the source of humic acids and the contact time.

Chapter 5: Conclusions

The intent of this research was to gain a more thorough understanding of the association of pentachlorophenol with soil organic matter. The results have indicated the following conclusions:

1.) Equilibrium is not rapidly achieved. With time, sorption to the particulate organic matter varies more than the association with the dissolved phase. The kinetics of the reactions depend on both the solution pH and phase in which the humic matter is present. The experimental results contradict the assumption of instantaneous equilibrium typically used when modeling the subsurface transport of hydrophobic compounds.

2.) Pentachlorophenol has a substantially higher affinity for the solid organic matter than for the dissolved phase. Along with the total humic acid concentration, the degree of partitioning depends on the type of organic matter present. Humic matter from different soil samples demonstrate varying affinities for the solute. Thus prediction of the partition coefficients should not be based solely on the percent organic matter.

3.) The reactions with the organic matter depends on the solution pH. Increasing the pH leads to decreasing sorption. Above pH 7, or two pH units above pentachlorophenol's pKa, this change appears to be relatively small as solutions become more basic. The degree of the ionizable, hydrophobic compound's dissociation affects its partitioning to the soil organic matter.

4.) More than one sorption mechanism is required to adequately explain the data. A combination of physical surface sorption, liquid-liquid partitioning, humic acid envelopment of the solute and chemical sorption appear to govern the binding process. Contact time, solution pH, humic acid concentration and humic acid type dictate the relative importances of these reactions.

5.) If given enough time, microorganisms cultured from a soil sample are capable of completely degrading a portion of the free PCP. Production of intermediate compounds also occurs. Preliminary observations suggest that the pentachlorophenol associated with the humic material is protected from biodegradation.

6.) The humic acids interfere with solvent extraction of PCP. The extent of the shielding depends on the contact time, the solution pH and the form of the

humic acids. Solvents more readily extract PCP associated with the particulate rather than the dissolved organic polymers. By preventing the transfer of the sorbed solute to the liquid which will be analyzed, the soil organic matter can cause significant underestimates of the amount of the contaminant actually present in groundwater and soil samples.

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Appendix A: Statistical Tests:

Comparison of Partition Coefficients with Respect to PCP Concentration:

The data were divided into basic and neutral solutions, and acidic samples. Ratios were calculated of partition coefficients from solutions of the same pH, contact time, and humic acid concentration but differing initial PCP concentration. If the PCP concentration had no influence on the amount of sorption, then theoretically the ratios should equal one. Standard t-tests with a significance level of 0.05 were used to compare the ratio averages to a value of one. The average ratios, sample deviations and p-values are listed in Table A-1.

Table A-1 : Results of t-tests to Determine Influence of PCP Concentration

Category	Average Ratio	Sample Deviation	p-value
(0.25 mg/L Kp)/ (1 mg/L Kp), low pH	1.441	1.787	$p > 0.2$
(0.25 mg/L Kp)/ (1 mg/L Kp), high pH	1.13	0.4226	$0.1 < p < 0.2$
(1 mg/L Kp)/ (4 mg/L Kp), lowpH	1.542	2.17	$p > 0.2$
(1 mg/L Kp)/ (4 mg/L Kp), high pH	1.159	0.4001	$0.1 < p < 0.2$
(0.25 mg/L Kp)/ (4 mg/L Kp), low pH	1.292	1.833	$p > 0.2$
(0.25 mg/L Kp)/ (4 mg/L Kp), high pH	1.07	0.4315	$p > 0.2$

Statistically, the average ratios were not different from one. From Table A-1, there appeared to be higher sample variances in results from the low pH range than data from solutions at pH above 7. To determine if these deviations were statisically different, F-tests were calculated on the variances. The results are provided in Table A-2. The variances differ substantially.

Table A-2: Results of F-tests to Compare Sample Variances

Category	Observed F Value	p-value
(0.25 mg/L Kp)/ (4 mg/L Kp), low pH/high pH	17.9	< 0.001
(1 mg/L Kp)/ (4 mg/L Kp), low pH/high pH	29.3	< 0.001
(0.25 mg/L Kp)/ (4 mg/L Kp), low pH/high pH	18.05	< 0.001

TOC Comparisons:

Ratios of partition coefficients from solutions with the same PCP concentration, pH and contact time but differing humic acid concentrations were computed. Tests similar to the ones outlined in the PCP section were performed. The null hypothesis for each of the tests stated that the partition coefficients were equal. These standard t-tests were two-tailed with a significance level of 0.05. Table A-3 presents the results.

Table A-3: Results of Statistical Analyses on the Influence of TOC

Category	Average Ratio	Sample Deviation	p-value	Conclusion
100 mg/L Kp/ 400 mg/LKp	3.989	5.135	$0.02 < p < 0.05$	reject null
100 mg/L Kp/ 800 mg/L Kp	3.007	4.097	$0.05 < p < 0.1$	barely accept null
100 mg/L Kp/ 2000 mg/L Kp	3.87	5.409	$0.02 < p < 0.05$	barely reject null
400 mg/L Kp/ 800 mg/L Kp	1.453	0.6512	$0.05 < p < 0.1$	barely accept null
400 mg/L Kp/ 2000 mg/L Kp	0.5571	0.5913	$0.02 < p < 0.05$	reject null
800 mg/L Kp/ 2000 mg/L Kp	4.845	5.204	$0.05 < p < 0.1$	barely accept null

The partition coefficients for 100 mg/L TOC were higher than those at 400 mg/L TOC and 2000 mg/L TOC. With more data, it is likely that this conclusion would have been reached regarding 100 mg/L TOC and 800 mg/L TOC. On average, the 400 mg/L TOC coefficients were lower than those for 2000 mg/L TOC. However, statistically the 400 mg/L TOC constants were not different from the 800 mg/L TOC coefficients. The 800 mg/L TOC values were similar to the 2000 mg/L constants. These statistical conclusions verify the parabolic curve which resulted when the partition coefficients were plotted against the humic acid concentration. Most of the sample deviations were high. It is possible that with more data of less variability, the borderline statistical conclusions might change.

Comparison of Partition Coefficients over Time:

Similar to the previous analyses, ratios of partition coefficients from the same solutions at one, seven and 28 day contact times were calculated. If no or minimal sorption had occurred within those time frames, then the average of the ratios should have equalled one. The data were divided into low pH solutions and neutral and basic sooutions. Where applicable, the tests were conducted on the amount sorbed to the particulate and dissolved phases separately. Table A-4 provides the average ratios, sample deviations and sample sizes. Table A-5 lists the actual comparisons and their conclusions.

Table A-4: Ratios of Partition Coefficients at Various Times

Ratio	Average	Sample Deviation	Sample Number
low pH, day 7 Kp/ day 1 Kp	1.48	1.396	18
low pH, day 28 Kp/ day 7 Kp	3.044	3.593	20
high pH, day 7 Kp/ day 1 Kp	2.009	1.219	18
high pH, day 28 Kp/ day 7 Kp	1.451	0.8038	18
low pH, dissolved phase, day 28 Kp/ day 7 Kp	2.064	1.432	7
low pH, solid phase, day 28 Kp/ day 7 Kp	4.602	6.946	7
high pH, dissolved phase, day 7 Kp/ day 1 Kp	2.699	1.544	10
high pH, dissolved phase, day 28 Kp/ day 7 Kp	1.566	0.8109	10
high pH, solid phase, day 7 Kp/ day 1 Kp	1.786	1.726	10
high pH, solid phase, day 28 Kp/ day 7 Kp	1.939	2.043	10

Table A-5: Results of t-tests to Analyze Kinetics

Null Hypothesis	p-value	Conclusion
low pH, day 7 Kp = day 1 Kp	$0.1 < p < 0.2$	accept null
low pH, day 28 Kp = day 7 Kp	$p < 0.02$	reject null
low pH, solid phase day 28 Kp = day 7 Kp	$p > 0.05$	accept null
low pH, dissolved phase day 28 Kp = day 7 Kp	$p > 0.05$	accept null
high pH, day 7 Kp = day 1 Kp	$0.002 < p < 0.01$	reject null
high pH, day 28 Kp = day 7 Kp	$0.02 < p < 0.05$	reject null
highpH, dissolved phase day 7 Kp= day 1 Kp	$0.002 < p < 0.01$	reject null
high pH, dissolved phase day 28 Kp = day 7 Kp	$0.05 < p < 0.1$	barely accept null
high pH, solid `phase day 7 Kp = day 1 Kp	$p > 0.05$	accept null
high pH, solid phase day 28 Kp = day 7 Kp	$p > 0.05$	accept null
low pH, (day 28 Kp/ day 7 Kp) = (day 7 Kp/ day 1 Kp)	$p > 0.05$	accept null
(low pH day 7 Kp/ day 1 Kp) = (high pH day 7 Kp/ day 1 Kp)	$p > 0.05$	accept null
(low pH day 28 Kp/ day 7 Kp) = (high pH day 28 Kp/ day 7 Kp)	$p > 0.05$	barely accept null
low pH, (dissolved day 28 Kp/ day 7 Kp) = (solid day 28 Kp/day 7 Kp)	$p > 0.05$	accept null
high pH, (dissolved day 28 Kp/ day 7 Kp) = (solid day 28 Kp/day 7 Kp)	$p > 0.05$	accept null
high pH, (dissolved day 7 Kp/ day 1 Kp) = (solid day 7 Kp/day 1 Kp)	$p > 0.05$	accept null

Appendix B: Bioavailability and Solvent Extraction Data

Bioavailability Data:

As the data in Table B-1 show, the solutions which contained the CO_2 traps did not exhibit any signs of biological activity after one week. These solutions were terminated before a sufficient lag time had passed to allow the microorganisms to adapt themselves to the experimental conditions.

Table B-1: Data Which Demonstrates Lack of Degradation in First Experimental Solutions

Sample	Initial ^{14}C (cpm/ml)	Solution ^{14}C After 7 Days (cpm/ml)	Percent Initial ^{14}C After 7 Days	Percent of Total Initial ^{14}C Recovered by CO_2 Trap
0.25 mg/L PCP, 400 mg/L TOC	9543	9271	97.1	4.1
1 mg/L PCP, 400 mg/L TOC	13940	13810	99.1	0.99
4 mg/L PCP, 400 mg/L TOC	13820	13520	97.8	1.25
0.25 mg/L PCP, 800 mg/L TOC	15350	12860	83.8	1.29
1 mg/L PCP, 800 mg/L TOC	15960	13940	87.3	0.81
4 mg/L PCP, no TOC	15230	14800	97.2	0.36
4 mg/L PCP, no TOC, no microorganisms	14900	14520	97.4	3.5

Solvent Extraction Data:

The individual solution solvent extraction data are provided below. Unless specified, the data refer to MTBE extractions and contact time is the time which the solutions equilibrated prior to solvent extractions. Only a few of the samples from the second stock solution were fractionated on the gel column after extraction.

Table B-2: Solvent Extraction Efficiencies, First Humic Stock, Three Month Contact Time

Solution	pH	Percent Extracted from the Dissolved Phase	Percent Extracted from the Solid Phase	Percent Extracted from the Aqueous Phase
1 mg/L PCP, 400 mg/L TOC	4.8	42.9	54.5	95.6
only high molecular weight humics	5.75	42.7	NA	90
0.25 mg/L PCP, 2000 mg/l TOC	5.75	0	74.4	50.7
1 mg/L PCP, 2000 mg/L TOC	5.75	18.9	80.8	83.5
0.25 mg/L PCP, 100 mg/L TOC	6.5	9.8	74.6	97.2
1.75 mg/L PCP, 100 mg/L TOC	6.8	35.8	NA	97.5
4 mg/L PCP, 2000 mg/L TOC	7.1	0	70.5	91.5
0.25 mg/L PCP, 2000 mg/L TOC	7.25	3.2	56.4	91.4
1 mg/L PCP, 2000 mg/L TOC	7.6	0	55.8	91.5
4 mg/L PCP, 800 mg/L TOC	7.85	7.36	71.5	93.5

Table B-3: Solvent Extraction Efficiencies of MeCl, First Humic Stock, Three Months Contact Time

Sample	pH	Percent Extracted from Solid Phase	Percent Extracted from Dissolved Phase	Percent Extracted from Aqueous Phase
4 mg/L PCP, 800 mg/L TOC	7.85	63.5	22.7	70
0.25 mg/L PCP, 2000 mg/L TOC	7.25	83	20.4	80.3
1 mg/L PCP, 2000 mg/L TOC	7.55	77	none	83
4 mg/l PCP, 2000 mg/L TOC	7.1	77	none	80

Table B-4: Solvent Extraction Efficiencies, Second Humic Stock, 35 Day Contact Time

Solution	pH	Percent Extracted from the Solid Phase	Percent Extracted from the Aqueous Phase
0.25 mg/L PCP, 100 mg/L TOC	4.6	61	94.2
4 ng/L PCP, 100 mg/L TOC	4.65	70.9	92.7
4 mg/L PCP, 400 mg/L TOC	4.65	57.3	93.2
4 mg/L PCP, 2000 mg/L TOC	5	35.2	89.1
4 mg/L PCP, 100 mg/L TOC	5.4	56.3	96.8
0.25 mg/L PCP, 2000 mg/L TOC	5.45	24.9	70.4
0.25 mg/L PCP, 800 mg/L TOC	5.5	47.6	88.2
1 mg/L PCP, 2000 mg/L TOC	5.5	51.4	84.6
4 mg/L PCP, 800 mg/L TOC	5.55	77.8	94.2
4 mg/l PCP, 2000 mg/L TOC	5.5	39.7	91.2
1 mg/L PCP, 100 mg/L TOC	5.65	57.7	95.4
1 mg/L PCP, 800 mg/L TOC	7.35	55.5	88.4
4 mg/L PCP, 800 mg/L TOC	7.4	90.1	93.7
4 mg/L PCP, 100 mg/L TOC	7.45	74.2	96.7
0.25 mg/L PCP, 800 mg/L TOC	7.55	49.3	95.1

One should note that the solutions in which the least PCP was removed from the solid phase were those which contained the highest humic acid concentrations. Four of the solutions listed above were fractionated on the gel column. The results are presented in Table B-5.

Table B-5: Removal of PCP from the Dissolved Phase, Second Humic Stock, 35 Day Contact Time

Sample	Solution pH	Percent PCP Extracted from the Dissolved Humic Acids
4 mg/L PCP, 100 mg/L TOC	5.4	27.5
0.25 mg/L PCP, 800 mg/L TOC	5.5	33.9
4 mg/L PCP, 100 mg/L TOC	7.45	none
0.25 mg/L PCP, 800 mg/L TOC	7.55	9.4

In general, the MTBE removed a higher percentage of PCP after one day of equilibration than after 35 days. The solvent extraction data from the short contact time are presented in Table B-6.

Table B-6: Solvent Extraction Efficiencies, Second Humic Stock, One Day Contact Time

Solution	pH	Percent Extracted from the Solid Phase	Percent Extracted from the Aqueous Phase
0.25 mg/L PCP, 100 mg/L TOC	4.45	82.1	97.6
4 mg/l PCP, 2000 mg/l TOC	4.8	88.2	92.76
0.25 mg/l PCP, 100 mg/l TOC	5.7	65.4	98.71
0.25 mg/L PCP, 800 mg/L TOC	7.05	80.2	96.81
4 mg/L PCP, 100 mg/L TOC	7.15	42.7	97.59
0.25 mg/L PCP, 2000 mg/L TOC	7.2	67.8	93.32

Appendix C: Raw Data

Abbreviations:

* second humic stock solution

** the sorption to the dissolved phase was too slight to accurately measure

NA not available, typically refers to solutions which did not contain particulate humic matter

Table C-1: Partition Coefficients {Kp, (mg PCP/mg TOC)/(mg PCP/ml)}

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	Kp, total TOC	Kp, TOC in solid phase	Kp, TOC in dissolved phase
0.25	100	3.7	1	0.117	NA	NA
0.25	100	3.7	7	0.482	NA	NA
0.25	100	3.7	28	1.61	NA	NA
* 0.25	100	4.5	1	7.18	**	**
* 0.25	100	4.55	7	7.54	**	**
* 0.25	100	4.6	28	10.8	12.3	0.434
0.25	100	5.1	1	0.852	NA	NA
0.25	100	5.3	7	0.893	NA	NA
0.25	100	5.5	28	0.819	NA	NA
0.25	100	5.8	1	0.515	NA	NA
0.25	100	6.1	7	0.346	NA	NA
0.25	100	6.3	28	0.432	NA	NA
0.25	100	7	1	0.0746	NA	NA
0.25	100	7	7	0.146	NA	NA
0.25	100	7	28	0.372	NA	NA
0.25	100	7.7	1	0.109	NA	NA
0.25	100	7.7	7	0.0888	NA	NA
0.25	100	7.7	28	0.115	NA	NA
0.25	400	4.55	1	0.776	2.02	0.16
0.25	400	4.8	7	0.603	1.35	0.232
0.25	400	4.95	28	0.59	1.13	0.323
0.25	400	5.3	1	0.0422	NA	NA
0.25	400	5.3	7	0.0865	0.0505	0.104
0.25	400	5.3	28	0.508	0.908	0.311
0.25	400	5.4	92	0.421	0.542	0.361
0.25	400	6.8	1	0.0329	NA	NA
0.25	400	6.8	7	0.0696	NA	NA
0.25	400	6.8	28	0.241	NA	NA
0.25	400	7.3	1	0.026	NA	NA

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	Kp, total TOC	Kp, TOC in solid phase	Kp, TOC in dissolved phase
0.25	400	7.3	7	0.0728	NA	NA
0.25	400	7.3	28	0.102	NA	NA
0.25	400	7.4	92	0.155	NA	NA
* 0.25	800	5.7	1	1.2	1.29	0.0945
* 0.25	800	5.45	7	1.64	1.76	0.334
* 0.25	800	5.5	28	1.65	1.75	0.535
0.25	800	5.8	1	0.0305	0.0142	0.0865
0.25	800	5.8	7	0.0392	0.0103	0.139
0.25	800	5.8	28	0.308	0.196	0.692
0.25	800	5.8	92	0.325	0.212	0.714
* 0.25	800	6.95	1	0.408	0.554	0.0252
* 0.25	800	7.4	7	0.299	0.379	0.0903
* 0.25	800	7.2	28	0.388	0.455	0.212
0.25	800	7.8	1	0.0293	0.0347	0.0249
0.25	800	7.8	7	0.0573	0.0354	0.0751
0.25	800	7.8	28	0.0723	0.0811	0.0652
0.25	800	7.75	92	0.11	0.118	0.103
0.25	2000	4.8	1	0.358	NA	NA
0.25	2000	5.5	7	0.592	0.673	0.0361
0.25	2000	5.8	28	0.583	0.657	0.0699
* 0.25	2000	5.65	1	0.243	0.267	0.0223
* 0.25	2000	5.5	7	1.57	1.73	0.089
* 0.25	2000	5.45	28	0.475	**	**
0.25	2000	7.2	1	0.128	0.182	0.0429
0.25	2000	7.2	7	0.716	1.14	0.0466
0.25	2000	7.2	28	0.153	0.227	0.038
0.25	2000	7.25	92	0.278	0.425	0.0462
1	100	4.4	1	0.0555	NA	NA
1	100	4.4	7	0.276	NA	NA
1	100	4.4	28	3.81	NA	NA
* 1	100	5.5	1	2.11	2.58	0.285
* 1	100	5.35	7	3.78	4.41	1.1
* 1	100	5.65	28	3.38	3.97	0.883
1	100	6.2	1	0.89	NA	NA
1	100	6.3	7	0.437	NA	NA
1	100	6.4	28	0.2	NA	NA
1	100	7.1	1	0.0766	NA	NA
1	100	7.1	7	0.144	NA	NA
1	100	7.1	28	0.442	NA	NA
1	100	7.7	1	0.0614	NA	NA
1	100	7.7	7	0.103	NA	NA

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	Kp, total TOC	Kp, TOC in solid phase	Kp, TOC in dissolved phase
1	100	7.7	28	0.131	NA	NA
1	400	4.3	1	0.9	2.39	0.166
1	400	4.5	7	0.74	1.79	0.225
1	400	4.65	28	0.444	0.835	0.251
1	400	5.3	1	0.0345	NA	NA
1	400	5.3	7	0.0944	0.037	0.123
1	400	5.3	28	0.366	0.607	0.248
1	400	5.45	92	0.553	0.866	0.398
1	400	6.2	1	0.286	NA	NA
1	400	6.45	7	0.204	NA	NA
1	400	6.5	28	0.102	NA	NA
1	400	7.3	1	0.0373	NA	NA
1	400	7.3	7	0.071	NA	NA
1	400	7.3	28	0.0982	NA	NA
1	400	7.35	92	0.133	NA	NA
1	800	5.5	1	0.0272	NA	NA
1	800	5.5	7	0.0524	0.0175	0.172
1	800	5.5	28	0.22	0.147	0.472
1	800	5.55	92	0.377	0.257	0.788
* 1	800	6.9	1	0.321	0.436	0.0188
* 1	800	7.2	7	0.474	0.626	0.0736
* 1	800	7.25	28	0.824	1.05	0.242
1	800	7.5	1	0.0139	0.014	0.0138
1	800	7.5	7	0.0509	0.0176	0.0781
1	800	7.5	28	0.0804	0.125	0.0438
1	800	7.75	92	0.173	0.112	0.0825
1	2000	4.8	1	0.471	NA	NA
1	2000	5.45	7	0.382	0.43	0.05
1	2000	5.8	28	0.541	0.614	0.0385
* 1	2000	5.55	1	0.231	**	**
* 1	2000	5.3	7	0.19	**	**
* 1	2000	5.5	28	1.69	**	**
1	2000	7.1	1	0.127	0.199	0.0147
1	2000	7.1	7	0.361	0.581	0.0166
1	2000	7.4	28	0.126	0.192	0.0235
1	2000	7.55	92	0.173	0.269	0.0223
4	100	4	1	0.0812	NA	NA
4	100	4	7	0.366	NA	NA
4	100	4	28	0.175	NA	NA
* 4	100	4.4	1	13.4	**	**
* 4	100	4.45	7	8.15	**	**

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	Kp, total TOC	Kp, TOC in solid phase	Kp, TOC in dissolved phase
* 4	100	4.75	28	11.4	**	**
* 4	100	5.3	1	2.23	2.65	0.467
* 4	100	5.4	7	1.91	2.11	1.08
* 4	100	5.65	28	2.16	2.34	1.43
4	100	6.8	1	0.0658	NA	NA
4	100	6.8	7	0.149	NA	NA
4	100	6.8	28	0.327	NA	NA
* 4	100	7.2	1	0.358	0.426	0.135
* 4	100	7.25	7	0.409	0.406	0.419
* 4	100	7.25	28	0.492	0.483	0.522
4	100	7.9	1	0.0685	NA	NA
4	100	7.9	7	0.111	NA	NA
4	100	7.9	28	0.113	NA	NA
* 4	400	4.4	1	7.91	**	**
* 4	400	4.45	7	3.58	**	**
* 4	400	4.65	28	11.6	**	**
4	400	5.2	1	0.0432	NA	NA
4	400	5.2	7	0.0702	0.0553	0.0775
4	400	5.2	28	0.464	0.961	0.219
4	400	5.45	92	0.313	0.404	0.268
4	400	7.3	1	0.0213	NA	NA
4	400	7.3	7	0.0581	NA	NA
4	400	7.3	28	0.0718	NA	NA
4	400	7.45	92	0.101	NA	NA
4	800	4.8	1	1.32	1.69	0.0479
4	800	5.45	7	1.73	2.21	0.0928
4	800	5.8	28	1.88	2.38	0.14
4	800	5.9	92	1.01	1.26	0.146
* 4	800	5.55	1	1.87	**	**
* 4	800	5.45	7	2.85	**	**
* 4	800	5.5	28	2.31	**	**
4	800	6.3	1	0.289	0.598	0.0352
4	800	6.45	7	0.22	0.441	0.039
4	800	7.5	28	0.0937	0.13	0.0638
* 4	800	6.9	1	0.611	0.836	0.02
* 4	800	7.25	7	0.212	0.269	0.064
* 4	800	7.55	28	0.659	0.862	0.125
4	800	7.6	1	0.0492	0.0748	0.0283
4	800	7.6	7	0.0582	0.084	0.0371
4	800	7.7	28	0.101	0.151	0.0604
4	800	7.85	92	0.0935	0.136	0.0584

PCP conc (mg/L)	humic acid conc mg/L TOC)	solution pH	contact time (days)	Kp, total TOC	Kp, TOC in solid phase	Kp, TOC in dissolved phase
* 4	2000	5.05	1	0.292	**	**
* 4	2000	4.75	7	0.0572	**	**
* 4	2000	4.95	28	0.805	**	**
* 4	2000	5.7	1	0.259	**	**
* 4	2000	5.45	7	0.2	**	**
* 4	2000	5.5	28	0.199	**	**
4	2000	7.1	1	0.165	0.26	0.015
4	2000	7.1	7	0.305	0.49	0.0149
4	2000	7.1	28	0.127	0.193	0.0229
4	2000	7.1	92	0.261	0.41	0.0268

Table C-2: Percent PCP Sorbed to Total Humic Matter and Each Humic Phase

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	percent PCP sorbed to total TOC	percent PCP sorbed to solid phase	percent PCP sorbed to dissolved phase
0.25	100	3.7	1	1.16	NA	NA
0.25	100	3.7	7	4.6	NA	NA
0.25	100	3.7	28	13.85	NA	NA
* 0.25	100	4.5	1	41.8	41.8	**
* 0.25	100	4.55	7	43	43	**
* 0.25	100	4.6	28	51.7	51.7	**
0.25	100	5.1	1	7.85	NA	NA
0.25	100	5.3	7	8.2	NA	NA
0.25	100	5.5	28	7.57	NA	NA
0.25	100	5.8	1	4.9	NA	NA
0.25	100	6.1	7	3.34	NA	NA
0.25	100	6.3	28	4.14	NA	NA
0.25	100	7	1	0.74	NA	NA
0.25	100	7	7	1.44	NA	NA
0.25	100	7	28	3.59	NA	NA
0.25	100	7.7	1	1.08	NA	NA
0.25	100	7.7	7	0.88	NA	NA
0.25	100	7.7	28	1.14	NA	NA
0.25	400	4.55	1	23.68	20.4	3.28
0.25	400	4.8	7	19.42	14.4	5.02
0.25	400	4.95	28	19.1	12.1	7
0.25	400	5.3	1	1.66	NA	NA
0.25	400	5.3	7	3.34	0.644	2.7
0.25	400	5.3	28	16.88	9.96	6.92
0.25	400	5.4	92	14.48	6.2	8.28
0.25	400	6.8	1	1.3	NA	NA
0.25	400	6.8	7	2.71	NA	NA
0.25	400	6.8	28	8.79	NA	NA
0.25	400	7.3	1	1.03	NA	NA
0.25	400	7.3	7	2.83	NA	NA
0.25	400	7.3	28	3.92	NA	NA
0.25	400	7.4	92	5.83	NA	NA
* 0.25	800	5.7	1	48.2	47.9	0.3
* 0.25	800	5.45	7	56.81	55.9	0.91
* 0.25	800	5.5	28	56.95	55.5	1.45
0.25	800	5.8	1	2.38	NA	NA
0.25	800	5.8	7	3.04	0.62	2.42

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	percent PCP sorbed to total TOC	percent PCP sorbed to solid phase	percent PCP sorbed to dissolved phase
0.25	800	5.8	28	19.75	9.75	10
0.25	800	5.8	92	20.65	10.45	10.2
* 0.25	800	6.95	1	24.62	24.2	0.4
* 0.25	800	7.4	7	19.31	17.7	1.61
* 0.25	800	7.2	28	23.67	20.1	3.57
0.25	800	7.8	1	2.29	1.22	1.07
0.25	800	7.8	7	4.38	1.22	3.16
0.25	800	7.8	28	5.47	2.76	2.71
0.25	800	7.75	92	8.09	3.91	4.18
0.25	2000	4.8	1	41.7	41.7	**
0.25	2000	5.5	7	54.22	53.8	0.42
0.25	2000	5.8	28	53.82	53	0.82
* 0.25	2000	5.65	1	32.7	32.4	0.3
* 0.25	2000	5.5	7	75.83	75.4	0.43
* 0.25	2000	5.45	28	48.7	48.7	**
0.25	2000	7.2	1	20.36	17.7	2.66
0.25	2000	7.2	7	58.89	57.4	1.49
0.25	2000	7.2	28	23.46	21.2	2.26
0.25	2000	7.25	92	35.71	33.4	2.31
1	100	4.4	1	0.55	NA	NA
1	100	4.4	7	2.69	NA	NA
1	100	4.4	28	27.59	NA	NA
* 1	100	5.5	1	17.5	17	0.5
* 1	100	5.35	7	27.42	25.9	1.52
* 1	100	5.65	28	25.26	24	1.26
1	100	6.2	1	8.17	NA	NA
1	100	6.3	7	4.19	NA	NA
1	100	6.4	28	1.96	NA	NA
1	100	7.1	1	0.76	NA	NA
1	100	7.1	7	1.42	NA	NA
1	100	7.1	28	4.23	NA	NA
1	100	7.7	1	0.61	NA	NA
1	100	7.7	7	1.02	NA	NA
1	100	7.7	28	1.29	NA	NA
1	400	4.3	1	26.47	23.2	3.27
1	400	4.5	7	22.85	18.2	4.65
1	400	4.65	28	15.08	9.36	5.72
1	400	5.3	1	1.36	NA	NA
1	400	5.3	7	3.64	0.47	3.17

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	percent PCP sorbed to total TOC	percent PCP sorbed to solid phase	percent PCP sorbed to dissolved phase
1	400	5.3	28	12.78	6.99	5.79
1	400	5.45	92	18.1	9.36	8.74
1	400	6.2	1	10.26	NA	NA
1	400	6.45	7	7.54	NA	NA
1	400	6.5	28	3.92	NA	NA
1	400	7.3	1	1.47	NA	NA
1	400	7.3	7	2.76	NA	NA
1	400	7.3	28	3.78	NA	NA
1	400	7.35	92	5.06	NA	NA
1	800	5.5	1	2.13	NA	NA
1	800	5.5	7	4.02	1.04	2.98
1	800	5.5	28	14.97	7.74	7.23
1	800	5.55	92	23.15	13.4	10.9
* 1	800	6.9	1	20.4	20.1	0.3
* 1	800	7.2	7	27.48	26.3	1.18
* 1	800	7.25	28	39.73	36.5	3.23
1	800	7.5	1	1.1	0.5	0.6
1	800	7.5	7	3.91	0.61	3.3
1	800	7.5	28	6.04	4.23	1.81
1	800	7.75	92	7.13	3.76	3.37
1	2000	4.8	1	48.5	48.5	**
1	2000	5.45	7	43.3	42.6	0.7
1	2000	5.8	28	51.97	51.5	0.47
* 1	2000	5.55	1	31.56	31.2	0.36
* 1	2000	5.3	7	27.5	27.5	**
* 1	2000	5.5	28	77.2	77.2	**
1	2000	7.1	1	20.27	19.36	0.91
1	2000	7.1	7	41.95	41.2	0.75
1	2000	7.4	28	20.16	18.7	1.46
1	2000	7.55	92	25.69	24.4	1.29
4	100	4	1	0.81	NA	NA
4	100	4	7	3.53	NA	NA
4	100	4	28	1.72	NA	NA
* 4	100	4.4	1	56.6	56.6	**
* 4	100	4.45	7	44.9	44.9	**
* 4	100	4.75	28	52.6	52.6	**
* 4	100	5.3	1	18.23	17.5	0.73
* 4	100	5.4	7	16.03	14.3	1.73
* 4	100	5.65	28	17.96	15.7	2.26

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	percent PCP sorbed to total TOC	percent PCP sorbed to solid phase	percent PCP sorbed to dissolved phase
4	100	6.8	1	0.65	NA	NA
4	100	6.8	7	1.47	NA	NA
4	100	6.8	28	3.17	NA	NA
* 4	100	7.2	1	3.19	3.16	0.3
* 4	100	7.25	7	3.93	3	0.93
* 4	100	7.25	28	4.69	3.54	1.15
4	100	7.9	1	0.68	NA	NA
4	100	7.9	7	1.1	NA	NA
4	100	7.9	28	1.12	NA	NA
* 4	400	4.4	1	75.1	75.1	**
* 4	400	4.45	7	58.9	58.9	**
* 4	400	4.65	28	82.3	82.3	**
4	400	5.2	1	1.7	NA	NA
4	400	5.2	7	2.73	0.71	2.02
4	400	5.2	28	15.65	10.7	4.95
4	400	5.45	92	11.12	5.89	6.38
4	400	7.3	1	0.85	NA	NA
4	400	7.3	7	2.27	NA	NA
4	400	7.3	28	2.79	NA	NA
4	400	7.45	92	3.88	NA	NA
4	800	4.8	1	51.32	50.9	0.42
4	800	5.45	7	58.1	57.4	0.7
4	800	5.8	28	60.01	59	1.01
4	800	5.9	92	44.65	43.2	1.45
* 4	800	5.55	1	59.9	59.9	**
* 4	800	5.45	7	69.5	69.5	**
* 4	800	5.5	28	64.9	64.9	**
4	800	6.3	1	18.76	17.5	1.26
4	800	6.45	7	14.96	13.5	1.46
4	800	7.5	28	6.97	4.36	2.61
* 4	800	6.9	1	33.1	32.8	0.3
* 4	800	7.25	7	14.51	13.3	1.21
* 4	800	7.55	28	34.51	32.7	1.81
4	800	7.6	1	3.79	2.59	1.2
4	800	7.6	7	4.45	2.89	1.56
4	800	7.7	28	7.48	5.02	2.46
4	800	7.85	92	6.96	4.57	2.39
* 4	2000	5.05	1	36.9	36.9	**
* 4	2000	4.75	7	11.4	11.4	**

PCP conc. (mg/L)	humic acid conc. (mg/L TOC)	solution pH	contact time (days)	percent PCP sorbed to total TOC	percent PCP sorbed to solid phase	percent PCP sorbed to dissolved phase
* 4	2000	4.95	28	61.7	61.7	**
* 4	2000	5.7	1	34.1	34.1	**
* 4	2000	5.45	7	28.6	28.6	**
* 4	2000	5.5	28	28.5	28.5	**
4	2000	7.1	1	24.78	23.9	0.88
4	2000	7.1	7	37.92	37.2	0.72
4	2000	7.1	28	20.22	18.8	1.42
4	2000	7.1	92	34.27	32.9	1.37

Table C-3: Free solute concentrations and x/m terms

note: all x/m terms in units of (mg PCP/mg TOC)

PCP (mg/L)	TOC (mg/L)	solution pH	contact time (days)	Ce (mg PCP per ml)	total x/m	x/m of solid phase	x/m of dissolved phase
0.25	100	3.7	1	2.47E-04	2.90E-05	NA	NA
0.25	100	3.7	7	2.39E-04	1.15E-04	NA	NA
0.25	100	3.7	28	2.15E-04	3.46E-04	NA	NA
* 0.25	100	4.5	1	1.46E-04	1.05E-03	**	**
* 0.25	100	4.55	7	1.43E-04	1.08E-03	**	**
* 0.25	100	4.6	28	9.80E-05	1.06E-03	1.21E-03	4.24E-05
0.25	100	5.1	1	2.30E-04	1.96E-04	NA	NA
0.25	100	5.3	7	2.30E-04	2.05E-04	NA	NA
0.25	100	5.5	28	2.31E-04	1.89E-04	NA	NA
0.25	100	5.8	1	2.38E-04	1.23E-04	NA	NA
0.25	100	6.1	7	2.42E-04	8.35E-05	NA	NA
0.25	100	6.3	28	2.40E-04	1.04E-04	NA	NA
0.25	100	7	1	2.48E-04	1.85E-05	NA	NA
0.25	100	7	7	2.46E-04	6.00E-06	NA	NA
0.25	100	7	28	2.41E-04	8.98E-05	NA	NA
0.25	100	7.7	1	2.47E-04	2.70E-05	NA	NA
0.25	100	7.7	7	2.48E-04	2.20E-05	NA	NA
0.25	100	7.7	28	2.47E-04	2.85E-05	NA	NA
0.25	400	4.55	1	1.91E-04	1.48E-04	3.86E-04	3.06E-05
0.25	400	4.8	7	2.01E-04	1.21E-04	2.73E-04	4.68E-05
0.25	400	4.95	28	2.02E-04	1.19E-04	2.29E-04	6.53E-05
0.25	400	5.3	1	2.46E-04	1.04E-05	NA	NA
0.25	400	5.3	7	2.42E-04	2.09E-05	1.22E-05	2.52E-05
0.25	400	5.3	28	2.08E-04	1.06E-04	1.89E-04	6.46E-05
0.25	400	5.4	92	2.14E-04	9.00E-05	1.16E-04	7.72E-05
0.25	400	6.8	1	2.47E-04	8.13E-06	NA	NA
0.25	400	6.8	7	2.43E-04	1.69E-05	NA	NA
0.25	400	6.8	28	2.28E-04	5.49E-05	NA	NA
0.25	400	7.3	1	2.47E-04	6.44E-06	NA	NA
0.25	400	7.3	7	2.43E-04	1.77E-05	NA	NA
0.25	400	7.3	28	2.40E-04	2.45E-05	NA	NA
0.25	400	7.4	92	2.35E-04	3.64E-05	NA	NA
* 0.25	800	5.7	1	1.26E-04	1.51E-04	1.62E-04	1.19E-05
* 0.25	800	5.45	7	1.08E-04	1.78E-04	1.90E-04	3.61E-05
* 0.25	800	5.5	28	8.15E-05	1.35E-04	1.43E-04	4.36E-05
0.25	800	5.8	1	2.44E-04	7.44E-06	3.47E-06	2.11E-05

PCP (mg/L)	TOC (mg/L)	solution pH	contact time (days)	Ce (mg PCP per ml)	total x/m	x/m of solid phase	x/m of dissolved phase
0.25	800	5.8	7	2.42E-04	9.50E-06	2.50E-06	3.36E-05
0.25	800	5.8	28	2.01E-04	6.17E-05	3.93E-05	1.39E-04
0.25	800	5.8	92	1.98E-04	6.45E-05	4.21E-05	1.42E-04
* 0.25	800	6.95	1	1.88E-04	7.69E-05	1.04E-04	4.75E-06
* 0.25	800	7.4	7	2.02E-04	6.03E-05	7.64E-05	1.82E-05
* 0.25	800	7.2	28	1.91E-04	7.40E-05	8.68E-05	4.04E-05
0.25	800	7.8	1	2.44E-04	7.16E-06	8.47E-06	6.08E-06
0.25	800	7.8	7	2.39E-04	1.37E-05	8.47E-06	1.80E-05
0.25	800	7.8	28	2.36E-04	1.71E-05	1.92E-05	1.54E-05
0.25	800	7.75	92	2.30E-04	2.53E-05	2.72E-05	2.38E-05
0.25	2000	4.8	1	1.46E-04	5.21E-05	**	**
0.25	2000	5.5	7	1.14E-04	6.78E-05	7.70E-05	4.13E-06
0.25	2000	5.8	28	1.15E-04	6.73E-05	7.59E-05	8.07E-06
* 0.25	2000	5.65	1	1.68E-04	4.09E-05	4.50E-05	3.75E-06
* 0.25	2000	5.5	7	6.04E-05	9.48E-05	1.05E-04	5.38E-06
* 0.25	2000	5.45	28	9.97E-05	4.73E-05	**	**
0.25	2000	7.2	1	1.99E-04	2.55E-05	3.62E-05	8.55E-06
0.25	2000	7.2	7	1.03E-04	7.36E-05	1.17E-04	4.79E-06
0.25	2000	7.2	28	1.91E-04	2.93E-05	4.34E-05	7.26E-06
0.25	2000	7.25	92	1.61E-04	4.46E-05	6.83E-05	7.42E-06
1	100	4.4	1	9.94E-04	5.52E-05	NA	NA
1	100	4.4	7	9.73E-04	2.69E-04	NA	NA
1	100	4.4	28	7.24E-04	2.76E-03	NA	NA
* 1	100	5.5	1	8.26E-04	1.75E-03	2.10E-03	2.36E-04
* 1	100	5.35	7	7.26E-04	2.74E-03	3.20E-03	7.96E-04
* 1	100	5.65	28	6.19E-04	2.09E-03	2.46E-03	5.46E-04
1	100	6.2	1	9.18E-04	8.17E-04	NA	NA
1	100	6.3	7	9.58E-04	4.19E-04	NA	NA
1	100	6.4	28	9.80E-04	1.96E-04	NA	NA
1	100	7.1	1	9.92E-04	7.60E-05	NA	NA
1	100	7.1	7	9.86E-04	1.42E-04	NA	NA
1	100	7.1	28	9.58E-04	4.23E-04	NA	NA
1	100	7.7	1	9.94E-04	6.10E-05	NA	NA
1	100	7.7	7	9.90E-04	1.02E-04	NA	NA
1	100	7.7	28	9.87E-04	1.29E-04	NA	NA
1	400	4.3	1	7.35E-04	6.62E-04	1.76E-03	1.22E-04
1	400	4.5	7	7.72E-04	5.71E-04	1.38E-03	1.74E-04
1	400	4.65	28	8.49E-04	3.77E-04	7.09E-04	2.13E-04
1	400	5.3	1	9.86E-04	3.40E-05	NA	NA

PCP (mg/L)	TOC (mg/L)	solution pH	contact time (days)	Ce (mg PCP per ml)	total x/m	x/m of solid phase	x/m of dissolved phase
1	400	5.3	7	9.64E-04	9.10E-05	3.56E-05	1.18E-04
1	400	5.3	28	8.72E-04	3.20E-04	5.30E-04	2.16E-04
1	400	5.45	92	8.19E-04	4.53E-04	7.09E-04	3.26E-04
1	400	6.2	1	8.97E-04	2.57E-04	NA	NA
1	400	6.45	7	9.25E-04	1.89E-04	NA	NA
1	400	6.5	28	9.61E-04	9.80E-05	NA	NA
1	400	7.3	1	9.85E-04	3.68E-05	NA	NA
1	400	7.3	7	9.72E-04	6.90E-05	NA	NA
1	400	7.3	28	9.62E-04	9.45E-05	NA	NA
1	400	7.35	92	9.49E-04	1.27E-04	NA	NA
1	800	5.5	1	9.79E-04	2.66E-05	NA	NA
1	800	5.5	7	9.60E-04	5.03E-05	1.68E-05	1.66E-04
1	800	5.5	28	8.50E-04	1.87E-04	1.25E-04	4.02E-04
1	800	5.55	92	7.69E-04	2.89E-04	1.98E-04	6.06E-04
* 1	800	6.9	1	7.96E-04	2.55E-04	3.47E-04	1.49E-05
* 1	800	7.2	7	7.25E-04	3.44E-04	4.54E-04	5.34E-05
* 1	800	7.25	28	4.96E-04	4.09E-04	5.19E-04	1.20E-04
1	800	7.5	1	9.89E-04	1.38E-05	1.39E-05	1.36E-05
1	800	7.5	7	9.61E-04	4.89E-05	1.69E-05	7.50E-05
1	800	7.5	28	9.40E-04	7.55E-05	1.18E-04	4.11E-05
1	800	7.75	92	9.29E-04	2.53E-05	2.72E-05	2.38E-05
1	2000	4.8	1	5.15E-04	2.43E-04	**	**
1	2000	5.45	7	5.67E-04	2.17E-04	2.44E-04	2.83E-05
1	2000	5.8	28	4.80E-04	2.60E-04	2.95E-04	1.85E-05
* 1	2000	5.55	1	6.84E-04	1.58E-04	**	**
* 1	2000	5.3	7	7.25E-04	1.38E-04	**	**
* 1	2000	5.5	28	1.74E-04	2.94E-04	**	**
1	2000	7.1	1	7.97E-04	1.01E-04	1.58E-04	1.17E-05
1	2000	7.1	7	5.81E-04	2.10E-04	3.37E-04	9.64E-06
1	2000	7.4	28	7.98E-04	1.01E-04	1.53E-04	1.88E-05
1	2000	7.55	92	7.43E-04	1.28E-04	2.00E-04	1.66E-05
4	100	4	1	3.97E-03	3.22E-04	NA	NA
4	100	4	7	3.86E-03	1.41E-03	NA	NA
4	100	4	28	3.93E-03	6.88E-04	NA	NA
* 4	100	4.4	1	1.69E-03	2.26E-02	**	**
* 4	100	4.45	7	2.20E-03	1.80E-02	**	**
* 4	100	4.75	28	1.60E-03	1.83E-02	**	**
* 4	100	5.3	1	3.27E-03	7.29E-03	8.65E-03	1.53E-03
* 4	100	5.4	7	3.36E-03	6.41E-03	7.07E-03	3.62E-03
* 4	100	5.65	28	2.90E-03	6.27E-03	6.77E-03	4.13E-03
4	100	6.8	1	3.97E-03	2.62E-04	NA	NA

PCP (mg/L)	TOC (mg/L)	solution pH	contact time (days)	Ce (mg PCP per ml)	total x/m	x/m of solid phase	x/m of dissolved phase
4	100	6.8	7	3.94E-03	5.88E-04	NA	NA
4	100	6.8	28	3.87E-03	1.27E-03	NA	NA
* 4	100	7.2	1	3.86E-03	1.38E-03	1.64E-03	5.19E-04
* 4	100	7.25	7	3.84E-03	1.57E-03	1.56E-03	1.61E-03
* 4	100	7.25	28	3.81E-03	1.88E-03	1.84E-03	1.99E-03
4	100	7.9	1	3.97E-03	2.72E-04	NA	NA
4	100	7.9	7	3.97E-03	4.40E-04	NA	NA
4	100	7.9	28	3.96E-03	4.48E-04	NA	NA
* 4	400	4.4	1	9.50E-04	7.51E-03	**	**
* 4	400	4.45	7	1.64E-03	5.89E-03	**	**
* 4	400	4.65	28	7.08E-04	8.23E-03	**	**
4	400	5.2	1	3.93E-03	1.70E-04	NA	NA
4	400	5.2	7	3.89E-03	2.73E-04	2.15E-04	3.01E-04
4	400	5.2	28	3.37E-03	1.57E-03	3.24E-03	7.39E-04
4	400	5.45	92	3.56E-03	1.11E-03	1.44E-03	9.52E-04
4	400	7.3	1	3.97E-03	8.45E-05	NA	NA
4	400	7.3	7	3.91E-03	2.27E-04	NA	NA
4	400	7.3	28	3.89E-03	2.79E-04	NA	NA
4	400	7.45	92	3.84E-03	3.88E-04	NA	NA
4	800	4.8	1	1.95E-03	2.57E-03	3.28E-03	9.33E-05
4	800	5.45	7	1.68E-03	2.91E-03	3.70E-03	1.56E-04
4	800	5.8	28	1.60E-03	3.00E-03	3.81E-03	2.24E-04
4	800	5.9	92	2.21E-03	2.23E-03	2.79E-03	3.22E-04
* 4	800	5.55	1	1.60E-03	3.00E-03	**	**
* 4	800	5.45	7	1.22E-03	3.48E-03	**	**
* 4	800	5.5	28	1.40E-03	3.25E-03	**	**
4	800	6.3	1	3.25E-03	9.38E-04	1.94E-03	1.15E-04
4	800	6.45	7	3.40E-03	7.48E-04	1.50E-03	1.33E-04
4	800	7.5	28	3.72E-03	3.49E-04	4.84E-04	2.37E-04
* 4	800	6.9	1	2.71E-03	1.66E-03	2.27E-03	5.43E-05
* 4	800	7.25	7	3.42E-03	7.26E-04	9.19E-04	2.19E-04
* 4	800	7.55	28	2.32E-03	1.53E-03	2.00E-03	2.90E-04
4	800	7.6	1	3.85E-03	1.90E-04	2.88E-04	1.09E-04
4	800	7.6	7	3.82E-03	2.23E-04	3.21E-04	1.42E-04
4	800	7.7	28	3.70E-03	3.74E-04	5.58E-04	2.24E-04
4	800	7.85	92	3.72E-03	3.48E-04	5.08E-04	2.17E-04
* 4	2000	5.05	1	2.52E-03	7.38E-04	**	**
* 4	2000	4.75	7	2.84E-03	1.63E-04	**	**
* 4	2000	4.95	28	1.01E-03	8.15E-04	**	**
* 4	2000	5.7	1	2.64E-03	6.82E-04	**	**
* 4	2000	5.45	7	2.86E-03	5.72E-04	**	**

PCP (mg/L)	TOC (mg/L)	solution pH	contact time (days)	Ce (mg PCP per ml)	total x/m	x/m of solid phase	x/m of dissolved phase
* 4	2000	5.5	28	2.86E-03	5.70E-04	**	**
4	2000	7.1	1	3.01E-03	4.96E-04	7.82E-04	4.52E-05
4	2000	7.1	7	2.48E-03	7.58E-04	1.22E-03	3.70E-05
4	2000	7.1	28	3.19E-03	4.04E-04	6.15E-04	7.30E-05
4	2000	7.1	92	2.63E-03	6.85E-04	1.08E-03	7.04E-05

Vita:

Cynthia E Crane was born October 1, 1967, in Concord, Mass., the youngest of four children, to Robert and Emma Crane. She received a B.A. in economics from the University of New Hampshire in 1989. Currently, she is attempting to live up to the motto she adopted while conducting the research for this thesis:

Carpe Diem
(Sieze the Day!)

Cynthia E Crane