SLOW SORPTION KINETICS OF PENTACHLOROPHENOL ON SOIL

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences

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EPIGRAM

"The world we are told was made for man. A presumption that is totally unsupported by facts....Nature's object in making animals and plants might possibly be first of all the happiness of each one of them, not the creation of all for the happiness of one. Why ought man to value himself as more than an infinitely small composing unit of the one great unit of creation, and what creature of all that the lord has taken the pains to make is less essential to the grand completeness of that unit?"

-John Muir, 1867

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ABSTRACT

We investigated the slow sorption kinetics of both the protonated (neutral) and ionized (charged) forms of pentachlorophenol (PCP) on a silt loam soil using batch techniques. A multiple spiking methodology was employed to circumvent the solubility limitation of neutral PCP. Both forms of PCP reached an apparent equilibrium in about 42 h. A slow sorption stage for the protonated form was detected within 12 days (14 days total time) following the apparent equilibrium.

The partition coefficient (K_p) of neutral PCP at the apparent equilibrium was concentration dependent. It decreased from 90 L/kg to 60 L/kg with a four fold increase in the total PCP concentration, from 5 to 20 mg/L. Increasing residence times resulted in slow increases in K_p. The onset of the slow sorption kinetics was also concentration dependent. At higher PCP concentrations the slow sorption kinetics were much more pronounced. However, there was not a clear definable trend in which concentration could be correlated to K_p. Desorption st ıdies demonstrated that the extent of hysteresis was also concentration dependent. At higher PCP concentrations, a

smaller percent of the sorbed PCP at equilibrium was desorbed. The hysteresis also increased with increasing residence time and was greater for higher concentration samples.

The ionized PCP took roughly 69 days before a discernible slow sorption stage could be detected. The hindrance of the slow sorption stage for the ionized PCP could not be attributed to differences in the apparent equilibrium sorbed concentrations. Oxidation of the soil organic matter (SOM) resulted in a substantial reduction in the slow sorption of the protonated PCP, thus suggesting the importance of PCP diffusion into the SOM. Sorption isotherms were linear out close to the solubility limit of the protonated form and nonlinear for the ionized form. Desorption and methanol extraction studies demonstrated that hysteresis of the neutral PCP is mainly a kinetic phenomenon but residual fractions do form. The ionized PCP was relatively resistant to desorption.

It was concluded that speciation of pentachlorophenol, and other ionizable organic compounds, should be considered for environmental fate modeling and when considering remediation strategies.

Chapter 1

INTRODUCTION

The extensive use of organic chemicals in both agriculture and industry has led to a national awareness of the potential problems associated with their presence in the environment. Their introduction into the environment occurs in a number of ways including: agricultural runoff, waste disposal, spills, and leakage from underground storage tanks. An entire array of these organic chemicals has been found in ground water, surface water, drinking water, wastewater effluent, soil, and the atmosphere. Many of these compounds are carcinogenic or toxic to both humans and animals.

These health and environmental concerns have been the catalyst for the emergence of extensive research on the fate of organic chemicals in the environment. One of the most prominent and important areas of research has been the sorption and desorption of organic compounds on soil, sediments, and aquifer solids. Soil acts as a buffer zone between anthropogenic sources of pollution and our natural water supply. Understanding how organic contaminants interact with the soil is paramount to predicting the fate

of these chemicals in the environment. It is also a necessity for predicting the stability of a contaminated site and developing a sound and cost effective remediation strategy.

An understanding of the sorption process is essential because this reaction directly affects the distribution of the organic pollutant within the environment. It will alter significantly the physical transport and chemical and biological reactivity of the contaminant. The desorption process is of utmost concern for the understanding of leaching, runoff and soil remediation. To fully comprehend these processes one needs an understanding of the kinetics and mechanisms of these reactions (Sparks, 1995).

Several of the U.S. Environmental Protection Agency's list of 129 priority pollutants belong to the class of chemicals known as hydrophobic organic compounds (HOCs). This group of chemicals can further be divided into hydrophobic ionizable organic compounds (HIOCs) and hydrophobic nonionizable organic compounds (HNOCs). Because of HOCs' persistence and slow rates of subsurface transport, additional cases of ground water contamination are likely to be detected for years to come

Rate-limited or slow sorption has been implicated as the cause of slow and incomplete desorption. The

mechanisms of sorption can play an important role in deciding on a remediation strategy. An understanding of the spatial distribution of the organic pollutant within the soil matrix is an important step forward in advancing our remediation technology.

Rate-limited sorption of organic chemicals by natural sorbents can have environmental implications that are far reaching. The linear partition coefficient (K_p) that is often used to predict the fate of organic chemicals in the soil environment will be directly affected. In addition, the desorption resistant fractions so often found for organic chemicals with long soil residence times are the result of rate-limited sorption. This slow and incomplete desorption could be the rate-limiting step in many of the soil remediation technologies presently practiced (e.g., soil flushing, pump and treat, in situ bioremediation). It could affect the time needed to flush a contaminated aquifer. Also, microbial degradation of organic chemicals in the environment will be affected by the sorption-desorption process. Sorption often inhibits the biodegradation process and desorption is usually the rate limiting step.

Furthermore, during field testing, soil contaminant concentrations are often determined by aqueous phase analyses of soil-water mixtures, assuming complete

desorption of the soil contaminant. This will underestimate pollutant concentrations substantially, depending on the residence time of the pollutant in the soil.

If the goal is to model these processes and to predict the fate of organic chemicals under varying conditions, then it is necessary to understand both the kinetics and mechanisms. The reason there is such a difference between K_p values predicted from the laboratory and those actually found in the field is the result of an incomplete understanding of the mechanisms and controlling factors involved. For practical reasons, it is important to be able to relate laboratory results, where equilibrium times are typically on the order of days, to field data where exposure times are on the order of years.

If there are differences between the slow sorption of HIOCs and HNOCs, then they need to be elucidated. The remediation strategy for a particular site could well depend on the state of the organic chemical. Diffusion into the soil organic matter by a HNOC might have to be treated differently than a HIOC that reacts specifically with the surface. The principal concern here is bioavailability for any intended bioremediation strategy. Sorption, diffusion and biodegradation occur simultaneously and are tightly coupled. Another concern might be the

availability of the organic chemical for surfactant soil washing. If one species is more intractable, then altering the pH might be a possible step in remediating a contaminated soil.

Relatively little long-term soil sorption-desorption research has been carried out on comparisons between charged and neutral organic chemicals. Hydrophobic ionizable organic compounds (HIOCs) offer a unique chance to look at both the charged and uncharged species. Many HIOCs, such as the chlorophenols, have a dissociation constant (pK_a) within an environmentally relevant pH range. Therefore they can exist in either the protonated (neutral) or deprotonated (ionized) forms. The physicochemical properties such as solubility, octanol-water partition coefficient (K_{ow}), Henry's Law constant (H), and soil-water partition coefficients (K_p) vary orders of magnitude for the two species. Comparisons between the two forms can help to elucidate different sorption mechanisms.

Due to the recalcitrance of many HOCs, the frequent lack of the necessary microbial community to degrade the chemicals, and the present failure to successfully introduce nonindigenous organisms into a contaminated site, it is extremely important to understand the long-term fate of organic contaminants in soil. Furthermore, the location and bonding of the chemical in the soil will determine the

success of certain remediation strategies such as soil washing and bioremediation, and could also determine the availability of the compound for leaching into groundwater.

There is a need to establish correlations between the linear partition coefficient (K_p), residence time and desorption resistant fractions. This will eliminate the need to always do site specific analysis. In addition, the desorption kinetics of hydrophobic organic compounds need to be better characterized.

The goal of this research was to address some of these questions. The objectives of this project were as follows:

- Investigate the long-term kinetics for the protonated and ionized forms of pentachlorophenol (PCP) on a silt loam soil.
- Examine the effect of concentration and soil organic matter on the slow sorption stage of PCP.
- Characterize the desorption of PCP as a function of both sorption time and concentration.

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Sparks, D. L. (1995). Environmental Soil Chemistry. San Diego, Academic Press.

Chapter 2

LITERATURE REVIEW

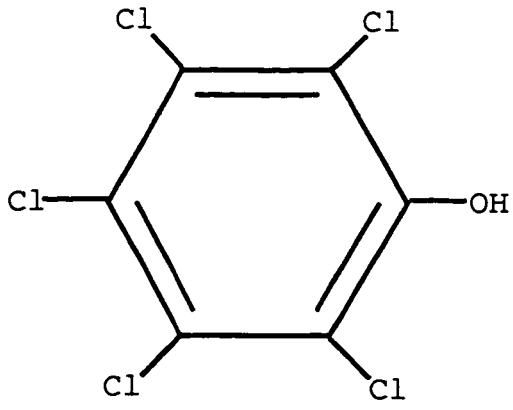
2.1 Environmental Importance

Various chlorophenols, including pentachlorophenol (PCP), tetrachlorophenol, trichlorophenols, and their precursors, have been used since the 1930's as fungicides, herbicides, and insecticides. Total world production of chlorophenols in the late 1970s was approximately 200 million kg of which PCP accounted for 91 million kg. Approximately 23 million kg were produced in the United States alone (Ahlborg and Thunberg, 1980).

Pentachlorophenol has been used worldwide to control mold, mildew, and termites in wood. In the past PCP was used as a pre- and post-emergence herbicide in pineapple and sugarcane fields (Weiss et al., 1982). Pentachlorophenol also has industrial application such as controlling mold and slime in food-processing plants. Additionally PCP has been used as a fungicide and bactericide in the production of oils, paints, textiles, rubber, and leather goods.

The extensive production and use of PCP accounts for its occurrence in soil, sediment, air, food, humans (Ahlborg and Thunberg, 1980), drinking water, rainwater, surface waters and effluents (Callahan et al., 1979). Currently, the use of PCP as a wood preservative has been restricted by the U.S. Environmental Protection Agency (USEPA) due to its toxic properties (Federal Register, 1984a; Federal Register, 1984b). The structure and some important properties of PCP are shown in Figure 2.1.

Exposure of humans to chlorophenols can come from an array of sources. Figure 2.2 shows a schematic of some of the possible exposure pathways for humans. For many of the reasons mentioned above the USEPA now lists PCP as a priority pollutant (Keith and Telliard, 1979).



pK_a = 4.75

log K_{ow} = 5.01

Solubility = 14 mg/L

Vapor Pressure = 0.0147 Pa

Figure 2.1 Structure and properties of PCP. The K_{ow} and vapor pressure are for the neutral species. The solubility is given at the pK_a. The temperature in each case is 20 °C.

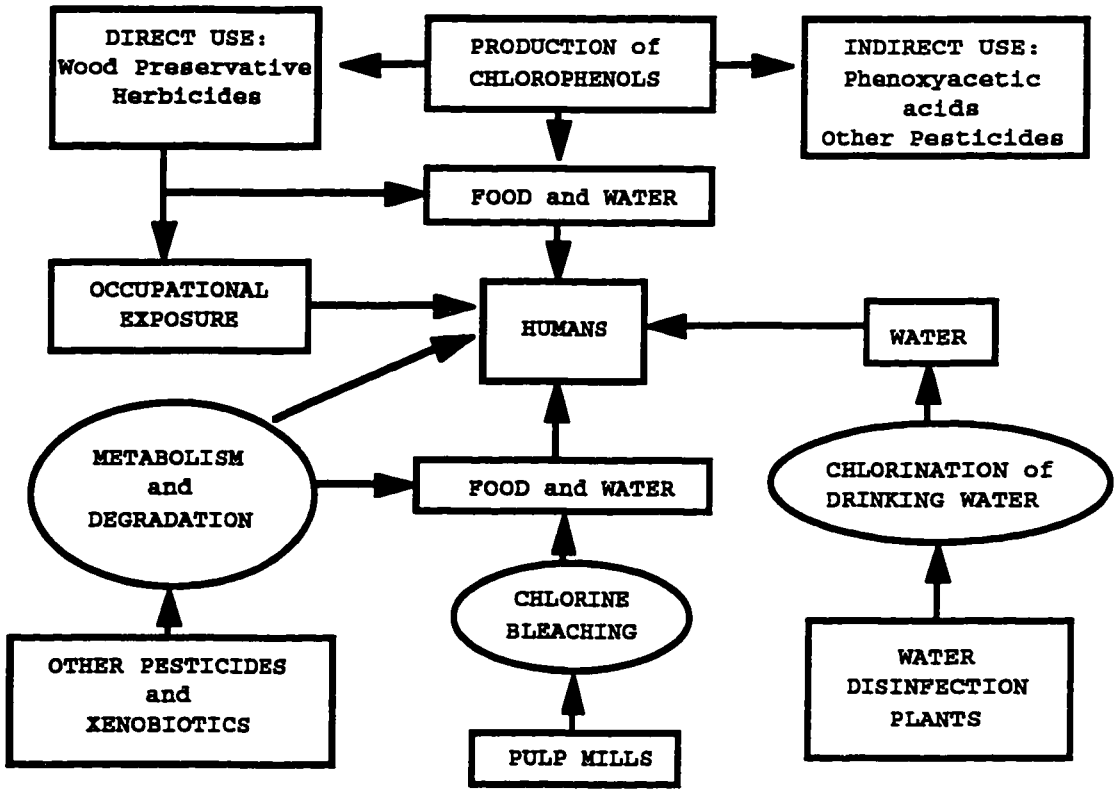


Figure 2.2 Schematic for sources of exposure to chlorophenols.

Table 2.1 shows a list of some priority pollutants which are hydrophobic ionizable organic chemicals (HIOC). The important point to note is the pK_a values. The pK_a is the $-\log K_a$, where K_a is the acid dissociation constant. The equilibrium relationship of an acid such as PCP may be represented as

$$HA_{(aq)} \Leftrightarrow H^+_{(aq)} + A^-_{(aq)} \qquad (2.1)$$

with

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2.2)$$

where [HA] is defined as the aqueous concentration of the neutral species, $[H^+]$ is the hydrogen ion concentration, and $[A^-]$ is the concentration of the anion. This assumes that the activity coefficients (γ) are equal to one.

These K_a values are within an environmentally relevant pH range. Agricultural soils range from 4.5-8.5 but hazardous waste sites may have pH values as low as 3. Therefore, the pollutants can exist in either the neutral (protonated-uncharged) or ionized (deprotonated-charged) forms within the environment.

Table 2.1. Priority Pollutants.

Compound	pK_a
2-chlorophenol	8.52
2,4-dichlorophenol	7.85
2,4,6-trichlorophenol	5.77
pentachlorophenol	4.75
2-nitrophenol	7.21
4-nitrophenol	7.15
2,4-dinitrophenol	4.09
2-methyl-4,6-dinitrophenol	4.35

Aqueous chemistry tells us that the two species have drastically different properties. Solubility, octanol-water partition coefficient (K_{ow}), and Henry Law constant (H) can vary orders of magnitude between the two species. Stapleton et al. (1994) demonstrated the solubility differences between the two species and Kaiser and Valdmanis (1982) calculated K_{ow}s as a function of pH. Since the Henry Law constant is dependent on solubility it will also vary dramatically. For these reasons it is essential to delineate any differences in the environmental behavior of the two species.

The fate and the ability to remediate a contaminated site may very well depend on the speciation of the contaminant. In order to be cost effective, one needs to be able to predict the availability of the contaminant. This eliminates the need to always do site specific analysis. In order to accomplish this goal a sound understanding of the kinetics and mechanism of the reactions is essential (Sparks, 1995).

2.2 Equilibrium Sorption Mechanisms

There are generally two accepted mechanisms of sorption for hydrophobic organic compounds (HOCs) on soil. Sorption here refers to the absence of any mechanistic implications. It is simply the removal of the chemical

from the aqueous phase followed by association with the solid phase. That is, accumulation of the chemical within or on the solid phase.

The first of the two mechanisms is partitioning. This is analogous to partitioning into an organic phase such as octanol. There are no specific bonds formed and the chemical is uniformly distributed within the organic phase. It permeates the entire solid phase structure and is not simply accumulated at the interface. This mechanism was first proposed by Chiou et al. (1979) for the sorption of hydrophobic nonionizable organic compounds (HNOCs) on soil.

The supposition was that the organic matter of the soil was acting as the organic phase for the hydrophobic pollutant to partition into. Earlier studies examining the interaction of organic compounds with soil had shown that the sorptive binding was well correlated with the organic content of the sorbent (Lambert, 1967; Lambert, 1968; Lambert et al., 1965). Since then numerous studies have supported this conclusion (Chiou et al., 1983; Gabarini and Lion, 1986; Hassett and Anderson, 1979; Rutherford et al., 1992; Saltzman et al., 1972; Walker and Crawford, 1968). Equilibrium sorption for partitioning can be described graphically by the linear isotherm model. This is a plot of the pollutant concentration in the sorbed phase (q_e)

versus pollutant concentration in solution (C_e), described by,

$$q_e = K_p C_e \qquad (2.1)$$

where K_p is the equilibrium partition coefficient.

It is also claimed in many studies that K_p can be determined directly as a linear function of the organic content of the sorbent. That is,

$$K_p = K_{oc}(OC) \quad \text{or} \quad K_p = K_{om}(OM) \qquad (2.2)$$

where OC is the mass fraction of organic carbon, OM is the mass fraction of organic matter and the K_{om} or K_{oc} (the carbon normalized partition coefficient) can be estimated from the octanol:water partition coefficient (K_{ow}) for the sorbate in question. This can be done by any one of several empirical equations (Chiou et al., 1983; Karickhoff et al., 1979; Schwarzenbach and Westall, 1981). The general form is:

$$\log K_{om} = a \log K_{ow} + b \qquad (2.3)$$

where a is the slope of the relationship of log K_{om} (or K_{oc}) versus log K_{ow} and b is the intercept. Values of a and b are empirically determined by linear regression using the above equation. The correlation coefficient for most data comparisons is greater than 0.91, suggesting that the organic portion of the soil is the major medium for sorption of organic pollutants.

Although the literature seems to suggest strong correlations between K_{oc} and K_{ow}, there are considerable variations in the numbers. Karickhoff et al. (1979) suggests that the variations arise from three main points: hydrophilic contributions to sorption, kinetic or steric inhibition to sorption and the use of computed K_{ow}'s which are often overestimated.

There are two important points about these and other studies in the literature that need to be pointed out. First, these investigations are almost always done in the presence of large amounts of water (small soil:solution ratio) insuring that the soil is saturated. Due to the strong dipole interaction between the water and the mineral fraction of the soil, sorption of the organic chemical by the mineral is suppressed (Khan, 1980). Second, the strong correlation between organic matter and sorption of the organic compound holds mainly for nonionic and nonpolar organic compounds. Also, in the absence of large amounts of organic matter and/or the presence of a large mineral fraction, the inorganic portion of the soil could play a much more important role.

The second of the two mechanisms is adsorption. This is a surface phenomenon that results in the concentration of the compound on the surface by either chemical or physical bonding. Adsorption usually reaches a

maximum, suggesting there is a finite number of sites. Therefore it cannot be described using a linear isotherm and is usually described by the Langmuir or Freundlich equations, given below, respectively:

$$\frac{q_e}{q_{max}} = \frac{bC_e}{1 + bC_e} \qquad (2.4)$$

$$q_e = K_F C_e^{1/n} \qquad (2,5)$$

where q_{max} is the adsorption maximum, b is the adsorption constant that depends on the strength of the sorbate-sorbent interaction, K_F is the Freundlich equilibrium sorption coefficient, n is an empirical constant and q_e and C_e are as defined earlier (Equation 1).

Hydrophobic ionizable organic compounds whose pK_a is well below the solution pH usually exhibit this type of behavior since the majority of the compound is in the deprotonated (ionized) form (Lee et al., 1990). They are generally more reactive with the surface and may form specific physical or chemical bonds. When the pH is below the pK_a the compounds tend to behave the same as the nonionizable compounds (Schellenberg et al., 1984).

2.3 Slow Sorption

The organic matter fraction of the soil was implicated as the cause of slow sorption as early as 1966 by Hamaker et al (1966). Karickhoff (1980) modeled the sorption of hydrophobic aromatic hydrocarbons as a two

stage chemical process. The chemical was considered to be fractionated into a "labile" state (equilibrium occurring within a short amount of time) and a "nonlabile" state (equilibrium occurring over a much longer time frame).

Recently, there was a series of papers by Brusseau (Brusseau et al., 1991a,b,d; Brusseau and Rao, 1989a) that address the idea of intraorganic matter diffusion as the cause for the nonlabile sorption of nonpolar uncharged organic chemicals. Through a series of comparative studies (Brusseau et al., 1991a) they were able to eliminate physical and chemical surface reactions and retarded intraparticle diffusion. However, they stress that for the more polar and ionizable organics, such as atrazine or pentachlorophenol, chemical surface reactions are a contributing factor (Brusseau and Rao, 1989a). The structure of the sorbate is of extreme importance in determining the extent of rate-limited sorption (Brusseau and Rao, 1991).

Ball and Roberts (1991a,b) investigated the long-term sorption of halogenated organic chemicals on an aquifer material and concluded that intraparticle diffusion was the cause of the slow sorption, and not intraorganic matter diffusion. Regardless if one or both mechanisms are correct both studies support strongly that the cause of the slow sorption for HNOCs is rate-limited diffusive mass

transfer. In addition, film diffusion has been shown to be negligible in comparison to other mechanisms (Brusseau and Rao, 1989b).

Similar conclusions to those discussed above were reached by McCall and Agin (1985) and Steinberg et al (1987). These are two of the very few comprehensive studies looking at comparisons between short and long term sorption-desorption of organic chemicals on soil. Steinberg et al. (1987) used soil samples that were contaminated with EDB (native) for a number of years (0.9-13). Desorption of the native EDB was negligible, while desorption of fresh EDB applied to the same soils was greater than 90%. Further tests showed that pulverization of the soil increased the release of the native EDB into the aqueous and volatile phases. It was concluded that the EDB was entrapped in intraparticle micropores.

The above discussions would suggest that the kinetics of organic sorption on soils could take much longer than was previously believed. If equilibrium is not reached before the onset of desorption, this could lead to the nonsingularity (hysteresis) observed in many lab studies (Di Toro and Horzempa, 1982; Rao and Davidson, 1980). However, the hysteresis could be real and not just an artifact of the lab technique.

2.4 Residence Time

A quick survey of the literature on organic pollutants in soil will immediately alert the reader to the frequency of use of the linear partition coefficient (K_p) and the carbon normalized partition coefficient (K_{oc}). They are also the major criterion used by the U.S. Environmental Protection Agency (USEPA) in predicting chemical fate of organic contaminants. The frequency of use would suggest an inherent understanding of their reliability. However, in actuality the opposite is true.

Although some studies have been conducted to explore the dependence of K_{oc} on different physical parameters (sorbent type, sorbent concentration, ionic strength, pH, etc.), the more important issue is the reliability of the partition coefficient. The K_{oc} value for the same compound in different studies can vary as much as two orders of magnitude (Brusseau and Rao, 1989). This is probably due to the fact that there is no standard method for the measurement of these values. Inconsistencies in the parameters mentioned above will all cause variations in the measured K_{oc} values.

K_p has no validity for HIOCs at higher concentrations, and when the solution pH is above the pKa, since the isotherm is no longer linear. It seems to hold form for the entire concentration range of HNOCs, even as

the solubility limit is approached (Chiou et al., 1979). However, now that our understanding of the sorption kinetics seems to suggest a slow approach to equilibrium, it is necessary to investigate the possible variation of K_p with varying sorption time.

Recent studies have begun to show that field soils with long pollutant residence times have much larger K_p values than would be predicted from lab equilibrium studies, and they also exhibit a desorption resistant fraction (Pignatello, 1990a,b; Pignatello et al., 1993; Pignatello and Huang, 1991; Steinberg et al., 1987). This reinforces the idea of a slow sorption stage. The longer the contaminant is in contact with the soil, commonly referred to as "aging", the larger the K_p and the more likely there is to be a greater desorption resistant fraction. This phenomenon is further explained as the desorption K_p being greater than the sorption K_p. This is commonly referred to as desorption hysteresis.

Recently it has been demonstrated in the literature that the sorption of an organic chemical to soil slows its rate of biodegradation and lessens the amount that is ultimately available to the degrading microbes (Fu et al., 1994; Guerin and Boyd, 1992; Ogram et al., 1985; Rijnaarts et al., 1990; Scow, 1993; Scribner et al., 1992). Some studies have dealt specifically with the aging effect on

biodegradation. Two studies were able to directly compare field aged soil with freshly added chemical to the same soil (Scribner et al., 1992; Steinberg et al., 1987). They accomplished this by using ^{14}C labeled chemicals. The addition to the same soil eliminates any discrepancies arising from differences in soil characteristics and the possibility that some toxic by-products were produced during the long-term degradation in the field.

Steinberg et al. (1987) were able to show that aged 1,2-dibromoethane (EDB) was unavailable for biodegradation. After 24 days the fresh EDB showed 90% degradation while the native EDB showed essentially no degradation. The authors then concluded that the aged EDB was entrapped within intraparticle micropores.

The work of Scribner et al. (1992) supported the findings of Steinberg et al. (1987). Scribner et al. (1992) investigated the biodegradation of aged and freshly added simazine. They carried out their biodegradation studies for 34 days and saw no change in the aged simazine concentration, as opposed to fresh simazine, where 11% was completely mineralized.

Furthermore, lab studies (Fu et al., 1994; Guerin and Boyd, 1992; Lehmann et al., 1992; Robinson et al., 1990) also showed there to be an aging effect. Biodegradation studies were carried out on soil samples

with varying contact times. In all cases, the longer the contact time the slower the rate of biodegradation and the less that was ultimately available to the bacteria.

This has vast implications in both predicting the fate of organic chemicals and developing remediation strategies. Compounds that are readily biodegraded might be limited by the bioavailability of the compound determined by the sorption dynamics. The success of bioremediation will depend on the residence time of the chemical in the field.

2.5 Bound Pesticide Residues

The literature is filled with references to bound pesticide residues (Capriel and Kahn, 1985; Helling and Krivonak, 1978a,b; Khan, 1982a,b). Most pesticides today have reactional functional groups that can be protonated or deprotonated (Calderbank, 1989). Therefore, they will behave similar, and in fact are, in most cases, HIOCs. This implies that the bound residues, which would be the result of rate-limited sorption, are due to a specific surface reaction as opposed to a slow diffusion into pores or soil organic matter (Brusseau and Rao, 1989a). However it is possible that both mechanisms are occurring simultaneously. Whether the distinction between these two mechanisms can be delineated, remains to be seen.

The ongoing debate about bound pesticide residues is whether the residual state renders the pesticide innocuous or if it is a continued toxic source. One important aspect is the availability for biodegradation. Although there have been investigations into the effect of sorption on biodegradation of organic chemicals (e.g., (Fu et al., 1994; Guerin and Boyd, 1992; Ogram et al., 1985; Rijnaarts et al., 1990; Scow, 1993; Scribner et al., 1992), one important question remains to be addressed. If the sorption mechanism is truly different for the protonated and deprotonated form of a HIOC, then how does that sorption affect both the extent and rate of biodegradation? Is one form more readily available for degradation, or is there no difference between the two species? The different mechanisms might result in different spacial distributions for the chemical within the soil matrix. Outside of the actual pH effect on the microbes, the availability of the contaminant within the soil might vary with the sorption mechanism.

2.6 Sorption-Desorption Kinetics

An understanding of the sorption-desorption kinetics is extremely important for remediation of contaminated soil sites and modeling the fate and movement of organic chemicals in the environment. Perhaps this is

the reason for the reemergence of research in this area (Boesten and Van Der Pas, 1988; Connaughton et al., 1993; Gilchrist et al., 1993; Karickhoff and Morris, 1985; McCall and Agin, 1985; Pavlostathis and Jaglal, 1991; Pavlostathis and Mathavan, 1992; Wu and Gschwend, 1986).

Brusseau and Rao (1989b) reviewed the mass-transfer and diffusion-based models that have been developed to describe sorption kinetics. These models have only been partially successful in describing rate-limited sorption. The one-site model is described as:

$$S \xrightarrow[k_d]{} C \qquad (2.6)$$

where S is the concentration of the sorbed contaminant (g/g), k_d is the first-order desorption rate coefficient (min^{-1}) and C is the concentration of the aqueous phase contaminant (g/ml). The sorption rate is a first-order function of concentration difference between the aqueous phase and the sorbent (considered a completely mixed compartment). This model is not very useful since it cannot describe the biphasic sorption/desorption kinetic data (Connaughton et al., 1993).

An improvement in the modeling approach involves utilizing a two compartment system. The physical significance is that there are two types of sorption sites. One corresponding to the labile sorbate (fast sorbing) and

one for the nonlabile sorbate (slow sorbing). The equation is as follows:

$$S_1 \underset{k_1/k_{-1}}{\longleftrightarrow} C \underset{k_2/k_{-2}}{\longleftrightarrow} S_2 \qquad (2.7)$$

where S_1 and S_2 are the two sorption compartments and k_1/k_2 and k_{-1}/k_{-2} are the forward and reverse rate constants, respectively for the two compartments.

The two compartment model as written above (equation 2.7) is a parallel model. The series model is written as:

$$C \underset{k_1/k_{-1}}{\longleftrightarrow} S_1 \underset{k_2/k_{-2}}{\longleftrightarrow} S_2 \qquad (2.8)$$

The models are kinetically indistinguishable in describing the rate of change in S_2 as long as equilibrium is assumed between S_1 and C. The series model seems more suited for relating the idea of rate-limited sorption. It distinguishes sorption sites differing primarily in diffusion path lengths for access to and/or from bulk water, whereas the parallel model distinguishes sites based on differing effective diffusion coefficients (Karickhoff and Morris, 1985).

The major limitation of the two compartment model is that it cannot describe the slow, reversible, rate-limited desorption for residual sorbed compounds (Karickhoff and Morris, 1985). In addition, it has three fitting parameters (i.e., k_1, the exchange rate from the

solution to the first compartment; k_2, the exchange rate from the first compartment to the second compartment; X_1, the fraction of the bulk sorbed contaminant that is in equilibrium with the aqueous concentration) as opposed to one fitting parameter for the one-site model (i.e., k_d).

Wu and Gschwend (1986) overcame the limitation of three fitting parameters by developing a radial diffusive penetration model modified by a retardation factor. The model is based on the premise that intraparticle diffusion is the limiting factor for sorption kinetics. The model is described by the equation:

$$S' \xleftrightarrow[K_p]{} C' \xrightarrow[D_{eff}]{} C \qquad (2.9)$$

where K_p is the equilibrium sorption partition coefficient (ml/g), S' is the concentration of contaminant in the immobile bound state (mol/g), C' is the concentration of contaminant free in the pore fluid (mol/cm^3) and D_{eff} is defined as:

$$D_{eff} = f(n,t)D_m n \;/\; (1-n)r_s K_p \qquad (2.10)$$

where $f(n,t)$ is the pore geometry factor, D_m is the pore fluid diffusivity of the sorbate (cm^2/s), n is the porosity of the sorbent (cm^3 fluid/cm^3 total) and r_s is the specific gravity of the sorbent (g/cm^3).

This model has a sound physical basis and is fairly flexible. The sorbent properties (organic content,

porosity and particle size) and the compound properties (hydrophobicity and diffusivity in solution) can be used in the model to predict *a priori* sorption kinetics for each chemical and/or sorbent of interest.

However, the model is most certainly not without problems. It cannot describe instantaneous uptake without an additional correction factor (Connaughton et al., 1993). In addition, as Wu and Gschwend (1986) pointed out, the model cannot describe kinetic data for times greater than 10^6 minutes.

A more recent model was developed called a dual resistance surface diffusion model (Miller and Pedit, 1992). The equation for this model is:

$$S' \xleftrightarrow{D_s} C'_s \xrightarrow{K_b} C \qquad (2.11)$$

where D_s is the surface diffusion coefficient (m^2/s), K_b is the boundary layer mass transfer coefficient (m/s) and C'_s is the aqueous phase contaminant concentration which is in equilibrium with the solid phase contaminant concentration at the exterior of the particle (g/L). When calibrated with the sorption data, this model over estimated desorption (Miller and Pedit, 1992).

The last model to be discussed, to the author's knowledge, is the most recently developed. It is based on a strong physical significance that appears to be the best equipped to handle rate-limited sorption.

It is generally accepted that natural porous materials, such as organic matter, contain a multitude of differing sorptive sites or compartments (Gabarini and Lion, 1986; Gauthier et al., 1987; Rutherford et al., 1992). Regardless of whether the diffusion is within particles (Ball and Roberts, 1991b) or soil organic matter (Brusseau et al., 1991a) it is unlikely that the single mass-transfer coefficient of the two-site model will suffice in describing pollutant release from soil. Therefore, the logical next step to take in applying a kinetic model to the sorption of hydrophobic organic compounds, is to use multiple compartments instead of just two. The problem with this approach is that with each additional compartment an additional two fitting parameters are needed.

Connaughton et al. (1993) solved this problem by employing a continuum of compartments with a continuous distribution of desorption rate coefficients. They modeled this approach by using the continuous mathematical Γ function of statistics. The resulting function for accumulated release is:

$$\ln[1 - F(t)] = -\alpha \ln(1 + t/\beta) \qquad (2.12)$$

where $F(t)$ is the fraction of initial mass released up through time t and α and β are adjustable parameters that correspond to pore sizes or binding sites.

Although the model fits well to naphthalene desorption data, it needs to be tested for varying sorbents and compared more closely with the other kinetic models discussed above. In addition, the Γ model's ability to describe experimental sorption data needs to be explored.

2.7 Solids Concentration Effect

In order to correctly understand the desorption hysteresis and to model the kinetics accurately, one has to be certain that the hysteresis is real and not an artifact of the lab technique. Rao and Davidson (1980) identified three possible causes of hysteresis: (i) artifacts of the methods used, (ii) failure to establish complete sorption equilibrium, and (iii) chemical and/or biological transformations of the compound during the experiment.

The third cause can be addressed. By choosing compounds that are resistant to chemical transformations (e.g., chemical hydrolysis) and biological degradation, or using a bacteriological inhibitor, one can minimized this problem. The second cause is the subject of much of this research. That is, to try and establish the distinction between "apparent" equilibrium and "true" equilibrium and how it affects the desorption.

The first cause can be addressed by identifying that the method of choice does not cause hysteresis. Rao

et. al. (1978) suggested using a dilution method since they found that the centrifugation-resuspension step in the batch sorption-desorption method might be responsible for at least some of the hysteresis. However, Horzempa and Di Toro (1983) used a modified dilution method and reported that the centrifugation was apparently not the cause of hysteresis in their studies.

There is another phenomenon apparently related to this desorption hysteresis. In the past there have been reports in the literature (Mackay and Powers, 1987; O'Connor and Connolly, 1980; Voice and Weber, 1985) suggesting that the solids concentration used in the isotherm study can affect the partition coefficient; that is, K_p decreases with increasing sorbent concentration.

One common explanation for this phenomenon is the presence of macromolecules, dissolved organic matter (DOM) and/or nonsettling microparticles (NSP) (Gschwend and Wu, 1985), in the aqueous phase which can greatly affect the apparent results. As the sorbent concentration increases there is an increase in the macromolecules. After any filtering step there are microparticles less than the pore size of the filter and DOM still in the aqueous phase. Any organic chemical, the amount of which is potentially substantial, bound to these particles is analytically

attributed to the solution phase when in fact it is sorbed. This will decrease the apparent K_p value.

Secondly, there is the possibility of a particle collision effect (Di Toro, 1985; Mackay and Powers, 1987). Mackay and Powers (1987) claim that if a significant fraction of the sorbate is sorbed, collision-induced desorption becomes important and limits the sorbed concentration. This becomes particularly important for a weak sorption model (partitioning). This situation would also ultimately lead to a decrease in the partition coefficient.

Gschwend and Wu (1985) demonstrated that the effect could be eliminated with repeated washings of the soil. Apparently each wash removed more and more of the macromolecules that would break away from the soil matrix. In addition, the prewashed soil showed no desorption hysteresis. It appears that it's not the actual centrifugation-resuspension that causes the hysteresis, but the removal of the macromolecules that contribute to the aqueous phase concentration. When the solids are resuspended in water the aqueous phase concentration of the chemical decreases and there is an apparent nonsingular isotherm.

It is certainly clear that desorption hysteresis is a real phenomenon. There are methods used for desorption

studies not subject to the solids concentration effect (e.g., gas purge) that still exhibit hysteresis. Also, Gschwend and Wu (1985) used a 24 hour sorption equilibrium time. Increasing this time could result in a true hysteresis effect. The important point is that if one wants to characterize the hysteresis effect, one must be certain that the method chosen is not part of the cause of hysteresis.

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Chapter 3

CHARACTERIZATION OF EXPERIMENTAL SYSTEM

3.1 Introduction

This chapter describes the preliminary experiments that were conducted in order to characterize and define the experimental system. Initially, the parameters of the gas chromatography (GC) were worked out. Choices of column, internal standard, and temperature profile were addressed. For GC analysis the aqueous samples must be extracted into an organic solvent before injection onto the GC column. The efficiency of this extraction procedure was examined.

Specific surface area analyses were performed on the soil. Additionally, the effect of the soil solids concentration on the equilibrium sorption partition coefficient (K_p) was examined. The sorption of pentachlorophenol (PCP) onto surfaces during the filtering step, necessary before GC analysis, was also explored.

In order for the same soil to be used for both the protonated (pH 4) and ionized (pH 8) PCP studies, it was necessary to buffer the system at the desired pH. No single buffer could be used at both pH 4 and pH 8. This

presented a concern since we were trying to compare the behavior of the two different PCP species. The goal was to minimize any differences in the two systems outside of different pH values. Furthermore, any buffers available at pH 4 were organic and could interfere with the sorption of PCP. For this reason it was desirable to use the soils' natural inherent buffering capacity. Experiments to address this possibility were carried out.

3.2 Materials

Pentachlorophenol was purchased from Sigma (purity > 95%) and used as received. Hexane (extracting solvent) was HPLC grade. 2,4,5-trichlorophenol was used as an internal standard for GC analysis (Sigma, purity > 95%). All inorganic reagents used were analytical grade (Fisher Chemicals).

The soil used was a Matapeake silt loam (Typic Hapludult) from the Ap-horizon. Physicochemical and mineralogical properties of the soil were as follows: pH = 6.1, cation exchange capacity (CEC), 5.02 cmol/kg, 1.7% organic matter, 29.6% sand, 58.6% silt, and 11.8% clay. The mineral suite of the < 2 μm clay fraction was kaolinite ≈ chloritized vermiculite > quartz > mica. A standard N_2/BET analysis yielded a surface area of 5.52 m^2/g.

3.3 Methods

3.3.1 Experimental Procedure

The following general protocol was used for all soil sorption-desorption studies:

- The soil (< 2 mm) is weighed out into 25 ml tubes.
- 24.9 ml of the background electrolyte solution is added to all tubes.
- The tubes are then spiked with a stock PCP solution and capped.
- The samples are then mixed by hand and placed into the incubation chamber.
- After incubation the phases are separated by either centrifugation or settling.
- For desorption studies 20 ml of solution is removed and replaced with 20 ml of PCP-free solution.
- Additional desorption steps remove 5 ml of solution and replace with PCP-free solution.
- After phases are separated 5 ml is removed to a new 25 ml tube.
- Internal standard (2,4,5-trichlorophenol) is added to all samples.
- 20 µl of 3 M HCl is added to all samples.

- Hexane is added to all tubes.
- The tubes are capped and vortexed for 30 s.
- The phases are allowed to separate.
- 1.5 ml is removed from the upper hexane phase and added to a 3 cc plastic syringe fitted with a filter unit holing a 13 mm 0.2 µm membrane filter.
- The sample is filtered directly into a 2 ml brown glass GC vial and fitted with a crimp cap.
- 2 µl of sample is then injected into the GC.

3.3.2 Gas Chromatography Parameters

Gas chromatography (GC) analysis was carried out on a Hewlett Packard HP 5890 II with chemstation software and mass spectrometer (MS) detector. The column was an HP-5 MS (cross-linked 5% phenyl methyl silicone), with a 30 m x 0.25 mm x 0.25 µm film. The column head pressure was set at 8 psi. The injection port purge was set to 1.0 minute. The temperature program was initially at 100 °C for 2 minutes and then a 20 °C/min increase up to 300 °C and held for 2 minutes. The injection temperature was 250 °C and the detector temperature was 280 °C. Two microliters (≈ 2-8 ng) of each sample were injected into the GC. The practical limit of detection was roughly 1 ng. The retention times for 2,4,5-trichlorophenol (internal

standard) and PCP were 6.13 and 9.01 min, respectively. Representative chromatography peaks are shown in Figure 3.1.

The extraction of the PCP from the aqueous phase of soil sorption-desorption experiments was examined by testing three different concentrations with three replicates each. Aqueous PCP samples were prepared at 2, 4, and 6 mg/L. Five milliliter samples were acidified with 20 µl of 3 M HCl to a pH less than 2.2. Hexane was added and the samples were vigorously vortexed for 30 s and the phases allowed to separate. The aqueous phase was then analyzed on a Hewlett Packard HP 8452A diode array uv-visible spectrophotometer at 214 nm. This would help determine if any appreciable amount of PCP remained within the aqueous phase after extraction with hexane.

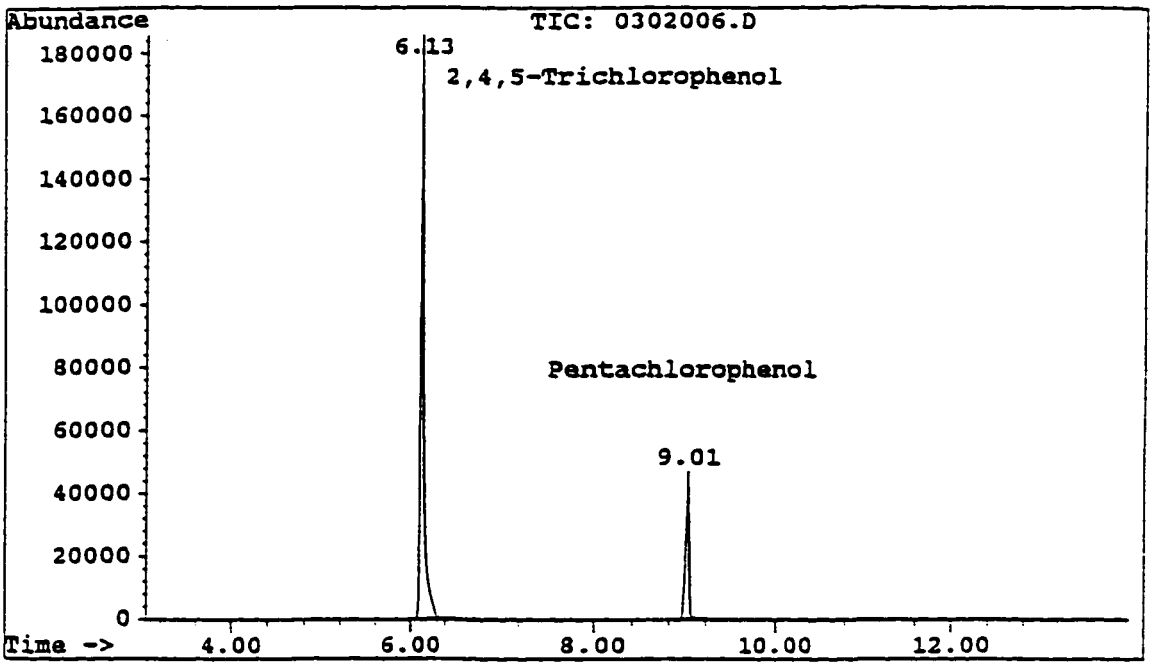

Figure 3.1 Representative gas chromatography peaks. The first peak at 6.13 min is the internal standard 2,4,5-trichlorophenol. The second peak is PCP. 2 µl (≈ 2-8 ng) samples were injected.

3.3.3 Surface Area Analysis

The soil was air dried and screened to pass through a US Standard No. 10 mesh (2 mm) sieve prior to any analyses or experiments. The surface area of the soil was measured using a Quantachrome Quantasorb QS-7 BET with an LMFC-4 flow control accessory. The adsorbate was nitrogen gas and the inert mixture gas was helium. The system was set up and calibrated with a known standard (aluminum oxide, 100 m^2/g). All samples were outgassed for 48 hr at 100 °C. Samples were weighed to five significant figures before and after outgassing to account for sample loss. Repeated samples were done to insure < 10% variation.

The required total flow of nitrogen plus helium was 20 cc/min. Due to the limitations of the BET method of surface area estimation, the relative pressure must be within a certain range to prevent over or underestimation of surface area of the sorbent. This range is $0.05 \leq P/P_o \leq 0.35$, where P is the pressure of nitrogen (mm Hg) and P_o is the saturated vapor pressure of nitrogen (mm Hg). This is equivalent to specifying the flow rate of N_2 at $\geq$ 2 cc/min and $\leq$ 7 cc/min. For this reason the flow rate of nitrogen was varied from 2 to 7 cc/min. The sample was run three times at each flow rate to insure accuracy. The Quantasorb was allowed to reequilibrate after each change

in the flow. Each run was calibrated against a pure N_2 injection of 1 ml (V_{cal}).

The N_2 gas was allowed to adsorb onto the soil surface and then the desorption signal was measured (A). A pure 1 ml sample of N_2 was withdrawn from the Quantasorb and injected into the sampling line and the signal recorded (A_{cal}). After repeating this procedure three times, the data were graphed with the x-axis equal to the relative pressure (P/P_o) and the y-axis equal to

$$\frac{1}{X\left\{\frac{P_o}{P} - 1\right\}} \tag{3.1}$$

X is equal to $X_{cal}(A/A_{cal})$ and

$$X_{cal} = \frac{P_a M_a V_{cal}}{6.235 \times 10^4 T} \tag{3.2}$$

where P_a is the ambient pressure (mm Hg), M_a is the molecular weight of the adsorbate (g) and T is the ambient temperature (K).

The mass of the adsorbate on the soil (X_m) can then be calculated as the inverse of the slope plus the intercept. The total surface area (S_t) can then be described by,

$$S_t = \frac{X_m\left(6.02 \times 10^{23}\right)A_{cs}}{M_a} \tag{3.3}$$

where A_{cs} is the cross sectional area of the adsorbate (1.62×10^{-19} m^2 for nitrogen). The specific surface area (S) is then simply S_t/W (m^2/g), where W is the sample weight after outgassing (g).

3.3.4 Solids Concentration

Varying soil masses (< 2mm) ranging from 0.1-2.1 g were weighed into 25 ml glass centrifuge tubes. Three replicates were used for each soil mass. Twenty-four and 9/10 ml of a 0.01 M $CaCl_2$, 0.02% NaN_3 (bacteriological inhibitor), 2 mg/L PCP solution was added to each tube and the tubes were fitted with Teflon® lined screw caps and weighed. The samples were equilibrated on an orbital shaker at 50 rpm in the dark (to avoid photolysis) for 48 h. Equilibrium was assumed to be reached. Samples were then centrifuged at 6315g for 15 min and the pH measured. Five ml of the aqueous solution was removed to a new tube, the internal standard was added (2,4,5-trichlorophenol), and the sample was acidified with 20 µl of 3 M HCl. Hexane was then added to the samples and vortexed for 30 s. The sample was then filtered through a 0.2 µm membrane filter and analyzed by gas chromatography.

3.3.5 Filter Sorption

Solution samples of PCP were prepared at four different concentrations (5.1, 2.6, 1.3, 0.5 mg/L). Twelve

replicates were used at each concentration. The internal standard was added to all samples and then acidified with 3 M HCl. After extraction into hexane six samples from each concentration were filtered and six were not filtered. They were then all analyzed by gas chromatography.

3.3.6 Mixing Test

Eighteen replicate samples were prepared with 1.00 g of soil each. Twenty-four and 9/10 ml of a 0.01 M $CaCl_2$, 0.02% NaN_3 solution were added to each tube. Each tube was spiked with a 5 g/L stock solution of PCP (pH ≈ 11) to a final concentration of 6.93 mg/L. Nine samples were shaken on an orbital shaker at 50 rpm and 25 °C for 4 days. Nine samples were mixed initially and then allowed to sit for the entire 4 days.

Samples were then centrifuged at 6315g for 15 min and the pH measured. Five ml of the aqueous solution was removed to a new tube, the internal standard was added (2,4,5-trichlorophenol), and the samples were acidified with 20 µl of 3 M HCl. Hexane was then added to the samples and vortexed for 30 s. The upper phase of the sample was then filtered through a 0.2 µm membrane filter and analyzed by gas chromatography.

3.3.7 pH Buffer

Several replicate samples were prepared as described in section 3.2.3 with a single solids mass of 2.0 g. The initial solution pH was lowered to 3.5 with 6 M HCl. The samples were equilibrated for 48 h as described above. The samples were then centrifuged and the supernatant replaced with a fresh solution of pH 3.5 and equilibrated again. The pH was measured at various time intervals. At 12 days the solution was acidified with HCl. The pH of the system was then monitored out to 44 days.

This procedure was repeated on different samples using a solution of pH 8.5 and raising the pH with 4 M NaOH five times over the course of eight hours. This was carried out in a glove box to limit the contribution of CO_2 in lowering the suspension pH.

3.4 Results and Discussion

3.4.1 Extraction Efficiency

Pentachlorophenol was undetectable on the uv-visible spectrophotometer in all of the samples. The limit of quantitation of the spectrophotometer was determined by analyzing a blank sample and choosing a mean for the background noise. One standard deviation (s) from the noise was drawn in to include 99% of the noise. The limit of quantitation was assumed to be 10(s) (Clesceri et al.,

1989). This resulted in an absorbance value of 4.000 x 10^{-3}. However, this yielded a negative number for the concentration when applied to the calibration curve. Therefore the number was increased to yield a positive value (1.210 x 10^{-1}). This resulted in a limit of quantitation for concentration of 2.5 µg/L.

Assuming that the amount remaining is dependent on the initial concentration, but that the ratio between the two is constant, we can calculate the extraction efficiency. Using the lowest initial concentration yields: 100(2.0 mg/L - 2.5 x 10^{-3} mg/L)/2.0 mg/L = 99.9%. This value will be even greater if the amount remaining is independent of concentration. Hence, the extraction procedure was successful at removing nearly all of the PCP from solution.

3.4.2 Surface Area Analysis

The results from the BET surface area analysis (Figure 3.2) resulted in a specific surface area of 5.52 m^2/g, which was calculated as mentioned above. Four relative pressure values were employed. The data were very well correlated with an r^2 value of 0.997.

3.4.3 Solids Concentration

The linear equilibrium sorption partition coefficient (K_p) decreased with increasing sorbent

concentration (Figure 3.3). There is little to no effect beyond sorbent concentrations of 30 g/kg. At sorbent concentrations below this, there is a significant effect. The first sampling point at roughly 4 g/kg has 4 replicates of which three have a K_p of 44 L/kg. The average and standard deviation are 39.9 ± 8.3. The second sampling point (12 g/kg) has an average and standard deviation of 23.4 ± 7.6.

In the past there have been reports in the literature (DiVincenzo and Dentel, 1996; Mackay and Powers, 1987; O'Connor and Connolly, 1980; Voice and Weber, 1985) suggesting that the solids concentration in the experimental system can affect the partition coefficient; that is, K_p decreases with increasing sorbent concentration.

The research that has been carried out in this area was discussed previously in Chapter 2 (Literature Review). However, it will briefly be repeated here for the sake of completeness.

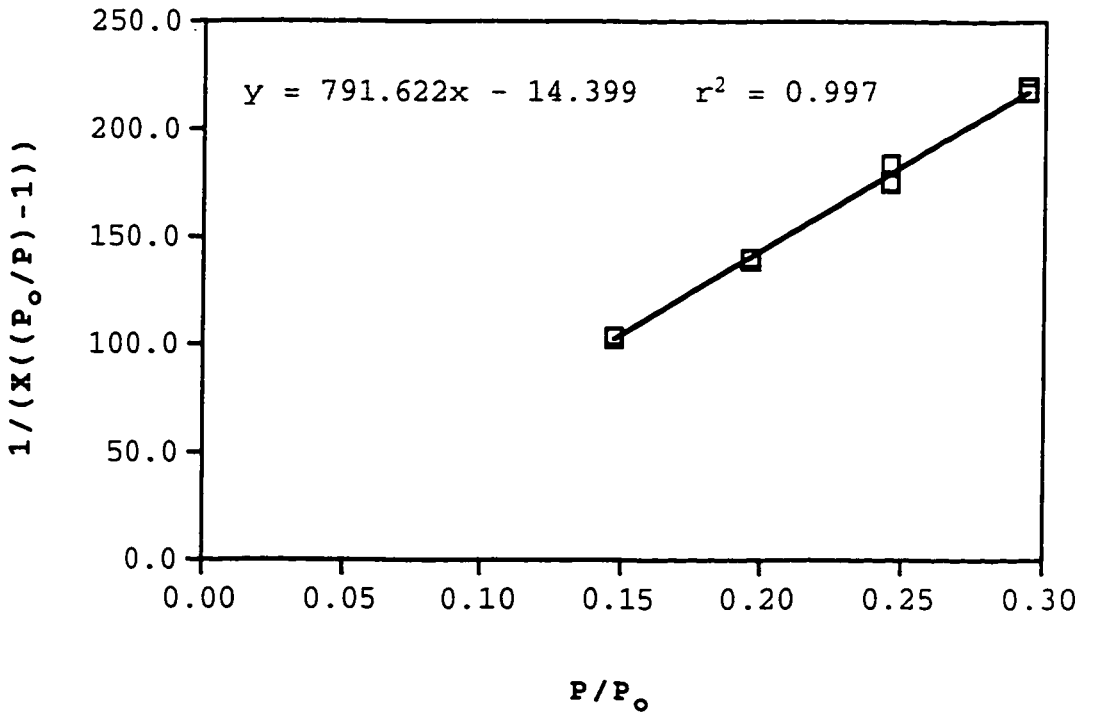

Figure 3.2 **BET surface area analysis.** The soil was passed through a US standard No. 10 mesh (2mm) sieve. The sample was outgassed for 48 h at 100 °C. The adsorbate was nitrogen.

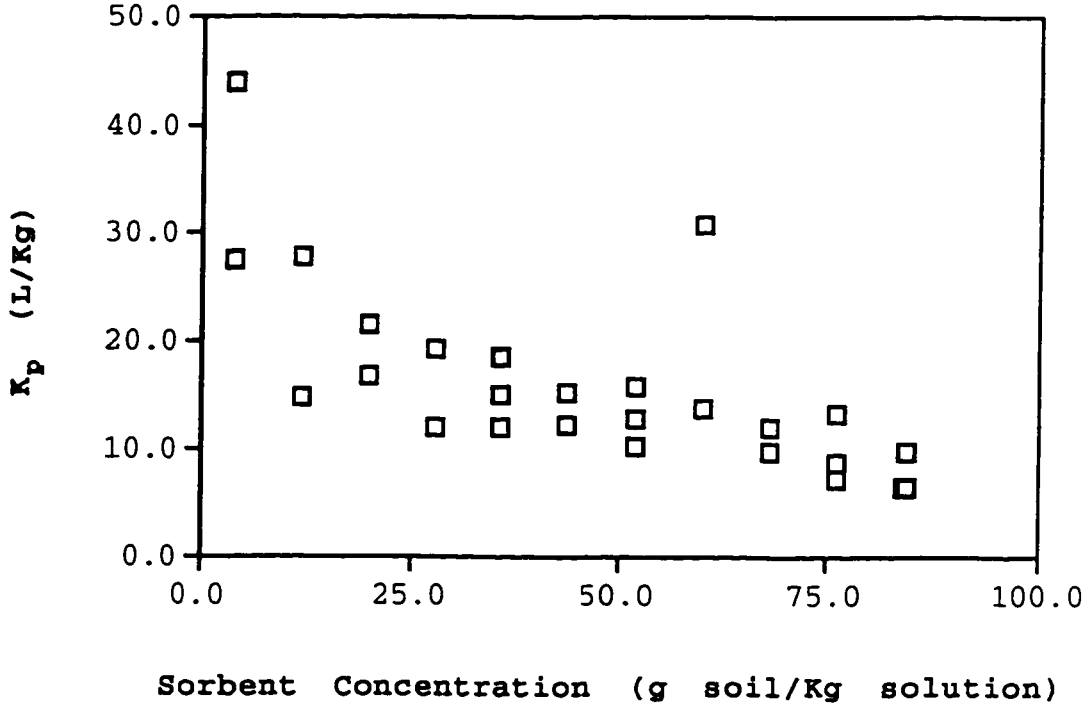

Figure 3.3 **Effect of sorbent concentration on the partition coefficient.** All tubes had a background electrolyte concentration of 0.01 M $CaCl_2$, 0.02% NaN_3 and an initial PCP concentration of 2 mg/L.

One common explanation for the solids concentration effect is the presence of dissolved organic matter (DOM), which can greatly affect the apparent results. As the sorbent concentration increases more and more colloidal particles (DOM plus any other suspended particulate matter) become suspended, and as a result, the DOM concentration also increases. Any PCP, the amount of which is potentially substantial due to the high surface area to volume ratio of these particles, bound to these colloids is analytically attributed to the solution phase when in fact it may be sorbed PCP. The reasoning here is that during the extraction step the PCP bound to the colloids will preferentially partition into the hexane phase. This will decrease the apparent K_p value.

Secondly, there is the possibility of a particle collision effect (Di Toro, 1985; Mackay and Powers, 1987). Mackay and Powers (1987) claim that if a significant fraction of the sorbate is sorbed, collision-induced desorption becomes important and limits the sorbed concentration. This becomes particularly important for a weak sorption model (partitioning). This situation would also ultimately lead to a decrease in the K_p value.

A third possibility that has been proposed is that at low solids masses the amount of organic chemical in the solution phase is high. At concentrations greater than 50%

of the solubility, there may be an increase in sorption due to the hydrophobic nature of the compound (DiVincenzo and Dentel, 1996).

Gschwend and Wu (Gschwend and Wu, 1985) demonstrated that during batch sorption-desorption studies these nonsettling microparticles can cause an artifactual desorption hysteresis. After the sorption stage is complete, a volume of solution is removed which contains these particles with bound PCP. The solution is replaced with a solution free of these particles. The result is less particles in solution during the desorption stage. More PCP will now sorb to the settled solids and be attributed to the sorbed phase. The conclusion will be hysteresis due to the larger K_p for desorption when compared to the K_p for sorption. They further demonstrated that by repeatedly washing the soil prior to any studies, most of the nonsettling microparticles could be removed, and the unreal hysteresis eliminated.

3.4.4 Filter Sorption

The results from the filter sorption tests are shown in Table 3.1. The means and standard deviations (s) for each set of samples are shown. A statistical t-test was performed to see if the means were statistically different. This was done on the highest concentration

samples since they had the greatest difference and the largest standard deviations. The pooled standard deviation (s_p) was calculated first:

$$s_p = \sqrt{\frac{s_1^2 \times (n_1 - 1) + s_2^2 \times (n_2 - 1)}{N - p}} \qquad (3.4)$$

where n is the number of samples for each treatment, N is the total number of samples, and p is the number of treatments. This yielded a value of 0.447. The experimental difference in means was then compared to that computed using the t-statistic with the following equation:

$$\overline{x_1} - \overline{x_2} = \pm t s_p \sqrt{\frac{n_1 + n_2}{n_1 \times n_2}} \qquad (3.5)$$

where $\overline{x}$ is the mean of the respective samples and t is the test statistic for the particular level of confidence chosen. If the experimental difference, $\overline{x_1} - \overline{x_2}$, is smaller than the computed value, the null hypothesis ($\overline{x_1} = \overline{x_2}$) is not rejected, and no significant difference between the means has been established.

Table 3.1 **Filter Sorption Tests.** Each concentration is the average of six replicates.

	Avg. Conc. (mg/L)		Standard Deviation (s)	
C_o (mg/L)[a]	Filtered	Unfiltered	Filtered	Unfiltered
5.1	5.0	5.2	0.20	0.60
2.6	2.6	2.6	0.20	0.10
1.3	1.1	1.2	0.09	0.08
0.5	0.6	0.6	0.00	0.00

[a] Initial PCP Concentration.

A 95% confidence level was chosen. With 10 degrees of freedom ($n_1 + n_2 - 2$) the t-value was 2.23. The right side of Equation (3.5) yielded a value of 0.576. The difference in the experimental means (0.2) was smaller than the computed value and therefore no significant difference in the means was demonstrated.

However, the standard deviation for the unfiltered sample was unusually high. For all other concentrations the filtered sample showed the higher standard deviation, which is what one would expect. Using a standard deviation of 0.2, equivalent to what it was for the filtered sample, yielded a value of 0.257 for the right side of Equation (3.5). This is still larger then the difference in the means. It was concluded that the filtering step did not significantly affect the pentachlorophenol concentration.

3.4.5 Mixing Test

The amount of sorption for the mixed and unmixed samples was compared. The average amount sorbed for the mixed samples was 132.94 mg/kg ± 3.91 (standard deviation). The average amount sorbed for the unmixed samples was 135.86 mg/kg ± 3.37. Using Equation 3.4 the spooled standard deviation (s_p) was 3.65. The experimental difference in means was then compared to that computed using the t-statistic with the Equation 3.5. With 16

degrees of freedom and a 95% confidence interval the test statistic was 3.61. This is greater than the difference in the means so no significant difference has been established. For incubation times of 4 or more days mixing should not be a factor.

3.4.6 pH Buffer

These experiments demonstrated that the buffering capacity of the soil, with a natural pH of 6.1, could be overcome, and that the pH of the system stabilized after a certain amount of equilibration time (Figure 3.4). With either resuspension or acidification the pH could be lowered to 4.0 and stabilized. Although the pH 8.5 data was not followed over time, the pH did stabilize at 8.0.

With the concern of the solids concentration effect on the partition coefficient, it was decided that the soil would be resuspended rather than the solution acidified. This served to wash the soil free of the nonsettling microparticles in addition to adjusting the pH. The pH of the solutions was 4.0 or 8.0. These values were chosen to avoid dissolution of the solid phase which could occur at pH values outside this range. It was still necessary to add base (4 N NaOH) several times during the first wash of the pH 8.0 equilibration.

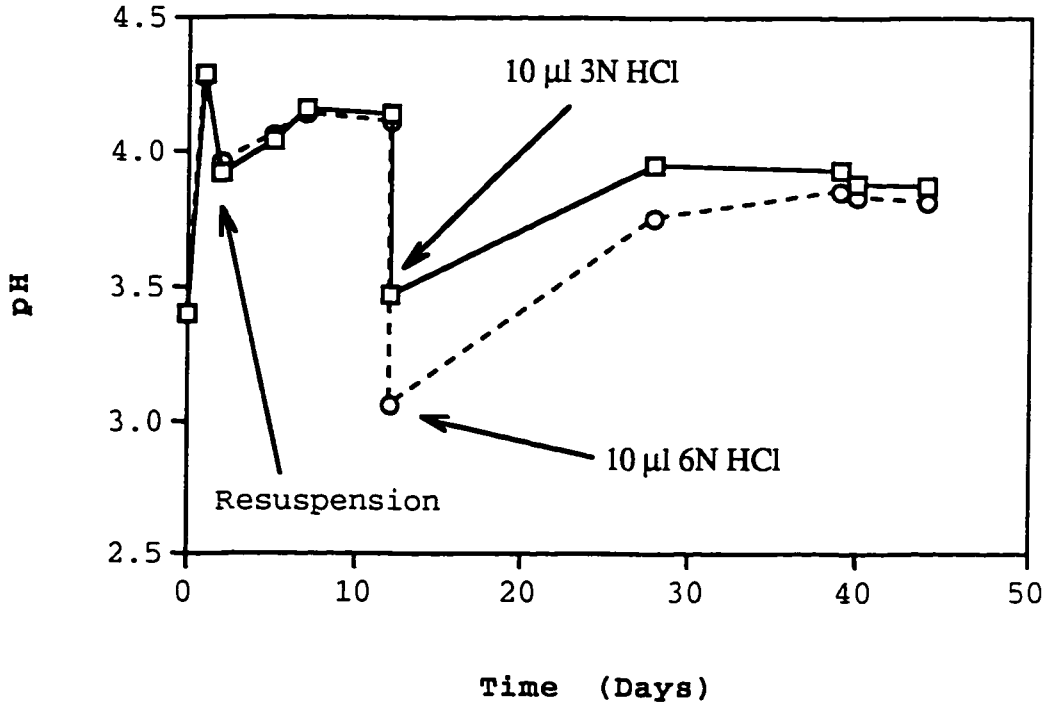

Figure 3.4 **Equilibration of soil pH.** The data points are the average of two replicates. Resuspension involves centrifugation, decanting, and addition of pH 3.5 solution. Two different treatments are shown.

3.5 Conclusions

The same soil (Matapeake silt loam) could now be used for the studies of both the protonated (pH 4) and the ionized (pH 8) species of PCP. This was accomplished by preequilibrating the soil to the desired pH prior to being used in any sorption-desorption studies. This preequilibration step also served to wash the soil and remove nonsettling microparticles. This helped to eliminate artifactual hysteresis in the batch sorption-desorption studies.

The author recognizes the limitations of using only one soil. Different soils may lead to significantly different results. However, behavioral trends of the two species of PCP may very well be similar on different soils.

3.6 References

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Chapter 4

pH EFFECTS

4.1 Introduction

The slow sorption of organic chemicals on soil complicates the predictability of both the environmental fate and the potential for remediation of sites contaminated with these chemicals. Long field residence times result in contaminants that appear resistant to desorption (Di Toro and Horzempa, 1982; Hatzinger and Alexander, 1995; Horzempa and Di Toro, 1983; Kan et al., 1994; Pignatello, 1990; Pignatello et al., 1993; Pignatello and Huang, 1991). The cause of increased resistance to desorption, with increasing contact time, is still largely unknown. The mechanism may vary with both the type of organic compound and the nature of the sorbent.

Sorption and desorption reactions on soil represent the controlling reactions that determine whether a contaminant remains in the soil matrix or leaches into the groundwater. A sound understanding of the rates of these chemical reactions helps to predict the long term fate of organic chemicals. Many hydrophobic organic compounds

(HOCs) demonstrate a slow sorption stage that can last for months or even years (Gilchrist et al., 1993; Karickhoff, 1984; Karickhoff and Morris, 1985). Diffusion deep into the matrix of the soil often results in entrapment in intraparticle micropores (Ball and Roberts, 1991; Steinberg et al., 1987). Compounds in this state may not represent a major threat to groundwater supplies and can be considered unavailable for leaching. They are also unavailable for biodegradation and can remain in the soil for long periods of time. However, chemicals aged in field soils for years have also been shown to slowly diffuse outward (Connaughton et al., 1993; Pavlostathis and Jaglal, 1991; Pignatello, 1990). This scenario would represent a continued source of groundwater pollution.

Compounds such as pesticides, that often have charged functional groups, can react more specifically with the surface (Brusseau and Rao, 1991). This often results in a hindrance of the diffusion process to particle interiors. Compounds in this state could remain more available to leach downward into the groundwater. However, these chemicals frequently bond strongly to the surface over time, forming bound residues (Calderbank, 1989; Scribner et al., 1992). This can often render the compound innocuous, especially in the presence of microbial

activity. The compound eventually gets incorporated into the organic matter of the soil.

In terms of environmental health it is extremely important to distinguish between these two types of mechanisms. An organic contaminant that is truly irreversibly bound to the soil may not be a threat to ground or surface waters. However, if the pollutant is slowly diffusing outward it remains a constant threat to our water resources.

The objectives of this research were to compare the sorption-desorption of the protonated (neutral) and ionized (charged) forms of pentachlorophenol (PCP) on a silt loam soil. PCP is a hydrophobic ionizable organic compound (HIOC) with a pK_a of 4.75. In the protonated form, PCP can behave similarly to other hydrophobic nonionizable organic compounds (HNOCs). In the ionized form the charged functional group may result in a more specific reaction with the surface. The effect of both residence time and pH on the sorption-desorption of PCP was examined.

4.2 Materials

Pentachlorophenol was purchased from Sigma (purity > 95%) and used as received. Hexane was HPLC grade. 2,4,5-trichlorophenol was used as an internal standard for

GC analysis (Sigma, purity > 95%). All inorganic reagents used were analytical grade (Fisher Chemicals).

The soil used was a surface (Ap) horizon of a Matapeake silt loam (Typic Hapludult). Physicochemical and mineralogical properties of the soil are as follows: pH = 6.1, cation exchange capacity (CEC), 5.02 cmol/kg, 1.7% organic matter, 29.6% sand, 58.6% silt, and 11.8% clay. The mineral suite of the < 2 μm clay fraction was kaolinite ≈ chloritized vermiculite > quartz > mica. A standard N_2/BET analysis yielded a surface area of 5.52 m^2/g.

4.3 Methods

4.3.1 Preequilibration of Soil

The natural soil pH was 6.1. Experiments were conducted at both pH 4 and pH 8 to compare the protonated and ionized forms of PCP. Due to the soil's relatively high buffering capacity it was necessary to preequilibrate the soil to the desired pH of the experiment. This would allow for a constant pH over the course of the entire experiment. The soil (20 g) was washed three times with a 250 ml solution (pH 4.0 or pH 8.0) of 0.01 M $CaCl_2$, 0.02% NaN_3 (bacteriological inhibitor) by shaking at 150 cycles/min in 250 ml plastic screw capped bottles for 24, 48 and 48 h. The samples were spun down in between washes for 20 min at 514g. The soil was then oven dried at 50 °C

for approximately 48 h and screened to pass through a US standard No. 10 mesh (2 mm).

A modification of the procedure was necessary for the pH 8.0 studies. During the first wash it was necessary to repeatedly spike the suspensions with 4 M NaOH. This was done every few hours over the course of 10 hours until the pH was stabilized at 8.0. The washing procedure was then carried out identical to that described above except for that the entire process was performed in a glove box purged with nitrogen. This limited the presence of CO_2 so that an equilibrium pH of 8.0 could be obtained.

4.3.2 Sorption Studies

The pH 4 studies used a 0.01 M $CaCl_2$, 0.02% NaN_3 solution adjusted with 3 M HCl to a pH of 4.0. Preliminary studies demonstrated that a pH of 8 was not maintainable even with the preequilibrated soil. For these studies a $CaCO_3$-CO_2/N_2 buffered solution was prepared. A 10^{-3} M $CaCO_3$, 0.02% NaN_3 solution was stirred for several hours with a CO_2/N_2 gas mixture bubbling through the solution. This was continued until the system came to equilibrium as determined by a stable pH. N_2 was then bubbled through to adjust the pH to 8.0. The solution was then filtered through Whatman 42 filter paper to remove any undissolved $CaCO_3$.

One or two grams of soil (determined to be appropriate in previous experiments) and 24.9 ml of solution were used in all experiments. All samples were spiked with aqueous PCP stocks (pH ~ 11.0) and then mixed on an orbital shaker at 50 rpm, in the dark (to prevent photolysis) at 25 ± 1 °C, for a minimum of 48 h. Additional mixing beyond this point proved to have no effect on sorption (see Chapter 3). In all experiments there was a minimum of 20% of the samples used as controls (no soil or no PCP).

All *sorption kinetic studies* were mixed continuously at 50 rpm. Particle degradation was shown to be negligible as determined by N_2/BET analysis before and after mixing. Any percent difference in surface area was less than the inherent error of the BET analysis. In these studies, 25 ml glass centrifuge tubes with Teflon® lined screw caps were placed in a test tube rack lain on its side on the orbital shaker. This increased mixing efficiency and the contact area between the solution and solid phase. Samples were collected and centrifuged at 6315g for 15 min. A portion of the aqueous phase was then stored for analysis. All sampling times were conducted in duplicate and certain random times had multiple replicates.

Additional sorption kinetic studies used 25 ml brown glass bottles with Teflon® lined screw caps. Samples

were upright at all times. The bottles were removed from the shaker after two days of equilibrating and then allowed to incubate for additional times. Samples were collected and a portion of the liquid phase removed and saved for analysis. Five replicates were used at each time interval.

Sorption isotherms were carried out identical to the sorption kinetics described above (centrifuge tubes), with one exception. After two days of mixing, the samples were removed from the shaker and stood upright, in the same incubation chamber. Also, the multiple spiking method described below was employed for the pH 4 studies. All samples were conducted in triplicate.

4.3.3 Multiple Spiking

The solubility of the protonated form of PCP at 25 °C is 28 μM (7.46 mg/L) (Stapleton et al., 1994). In order to do pH 4 sorption studies at higher concentrations than the solubility, we employed a multiple spiking approach. The samples were spiked every two hours after the initial spike, for a total of 10 h (6 spikes). The concentrations of the spikes were calculated based on the kinetics, which showed substantial sorption after 2 h (~ 80% of the total amount sorbed). The aqueous PCP concentration never exceeded the solubility limit.

4.3.4 Desorption Studies

Desorption kinetic studies were conducted on samples that had sorbed PCP for 12 days. The PCP was sorbed using the multiple spiking technique. After sorption 80% of the solution volume was removed (20 ml) and replaced with PCP-free solution. Samples were then placed back on the orbital shaker at 50 rpm for 2 days. The samples were then removed from the shaker and collected over time. Aqueous samples were separated and stored. Five replicates were used at each time interval. Seventeen percent of all the samples were controls (no soil or no PCP).

4.3.5 Analysis

An internal standard was added to all samples (2,4,5-trichlorophenol) and the samples were then diluted if necessary and acidified with 3 M HCl. A volume of hexane was added to all samples for extraction. The observation was made that the mass spectrometer (MS) analysis was most consistent within the concentration range of 0.5-2.5 mg/L of PCP. Therefore, the amount of hexane added varied depending on the predicted aqueous concentration of PCP. An attempt was made to have all the samples analyzed within this concentration range in order to reduce error. Hence, samples were often either diluted

prior to extraction or concentrated in hexane as deemed necessary.

After the addition of hexane the samples were vigorously vortexed. UV spectrophotometric analysis showed no detectable amount of PCP remaining in the aqueous phase (see Chapter 3). An aliquot of the hexane was then removed and filtered through a 0.2 μm membrane filter. Each sample was then injected twice into a gas chromatograph equipped with an MS detector. Two qualifying ions for PCP were used in all cases. The integrity of the chromatography and the nonexistence of any aberrant peaks suggested the absence of any degradation.

4.4 Results and Discussion

The soil preequilibration (washing) procedure stabilized the pH of the soil at 4.1 ± 0.1 or 7.9 ± 0.2. As mentioned in the Methods it was necessary to use a $CaCO_3$-CO_2/N_2 buffered solution for the pH 8 studies. Soil washing also helps to remove nonsettling microparticles and dissolved organic matter which can cause unreal (artifactual) hysteresis due to the solids concentration effect (Mackay and Powers, 1987; O'Connor and Connolly, 1980; Voice and Weber, 1985). That is, the K_p decreases with increasing solids concentration. Mixing at a faster speed (150 cycles/min) and centrifuging at a slower speed

(514g) than was used for the sorption and desorption studies (50 rpm-6315g) helps to increase the washing efficiency by removing more soil colloids (Gschwend and Wu, 1985). Many of the samples generated during the sorption studies were subsequently utilized in the desorption studies.

The low solubility and high sorption potential of the protonated PCP presented a problem in using a broad range of different initial concentrations (C_o). A low initial PCP concentration would leave an undetectable amount of PCP in solution. The result is a very narrow working PCP concentration range. One way to circumvent this problem is to use a lower solids mass. However, desorption studies require that enough PCP be sorbed in order to detect the desorption of the compound. Therefore, it would be necessary to vary our solids mass between experiments. Since the soil was washed, the solids concentration effect may not have been a problem. However, the decrease in K_p with increasing solids mass cannot always be accounted for by the solids concentration effect (DiVincenzo and Dentel, 1996). For this reason we chose to use the multiple spiking procedure rather than vary our solids mass. Furthermore, this might be indicative of a contaminated site which has repeated recharge of the pollutant.

Loss of PCP over the course of the experiments was negligible, with the soil-free controls containing 99% of the original PCP concentration. Mixing beyond the apparent equilibrium (2 days) had no effect on sorption (see Chapter 3).

4.4.1 Sorption Kinetics

Figure 4.1 shows the short-term sorption kinetics for the protonated (pH 4) form of PCP (C_o = 5.1 mg/L), at a pH of 4.1 ± 0.1, out to 7 days of sorption. Each point was the average of two replicates and one time (3.6 days) had seven replicates. At this pH, 82% of the PCP was in the protonated form. An apparent equilibrium was reached in about 42 hours (≈ 2 days). No analytically measurable statistically significant change in the aqueous phase PCP concentration occurred for 5 days following this apparent equilibrium. A line of apparent equilibrium has been superimposed on the graph as a visual aid.

The time frame in which there was no measurable change in the aqueous PCP concentration (statistically different than concentration at the apparent equilibrium for at least 90% confidence) was designated the apparent equilibrium plateau. The calculated partition coefficient (K_p) for the time with seven replicates (3.6 days) was 90

L/kg with a standard deviation of 7.60. The K_p was calculated by the method of difference:

$$\frac{(C_o - C_e) \cdot V}{M \cdot C_e} \qquad (4.1)$$

where C_o is the initial PCP concentration, C_e is the equilibrium aqueous PCP concentration, V is the total volume of solution, and M is the mass of soil.

It would be easy at this point to conclude that equilibrium had been established. However, when the kinetics were followed for an extended amount of time a slow sorption stage began to manifest itself. This effect is clearly demonstrated in Figures 4.2 and 4.3. The concentration at 14.1 days was statistically different than the concentration at the apparent equilibrium (Figure 4.2). This was determined by a comparison of means (see section 3.4.4, equations 3.4 and 3.5) between the seven replicates at 3.6 days and the two replicates at 14.1 days. A 95% confidence interval was used. The slow sorption continued to roughly 70 days. However, the change was less significant, as demonstrated by significance only occurring at 90% confidence between 14 and 70 days. This is analogous to the observation that the slow sorption stage was non-linear. The rate of change in the aqueous PCP concentration was slowing down.

The non-linear sorption is clearly demonstrated in Figure 4.3 in which the y-axis scale is expanded and the data from the apparent equilibrium (2 days) out to 70 days is shown. The seven replicates at 3.6 days are now represented as an average with an error bar for the standard deviation. It is clear in this figure that the rate of change in the aqueous PCP concentration is faster from the point of the apparent equilibrium out to 14 days. It then slows down after 14 days. The data suggest a leveling off between 20 and 40 days. However, this is based on only one data point. Furthermore, the change in concentration of PCP is approximately linear from 14 days out to 70 days.

Another interesting observation was that the apparent equilibrium plateau previously defined is simply due to analytical limitations. Although not statistically different there was clearly a slow continuous drop in the aqueous PCP concentration.

Sorption of HOCs is often biphasic; a slow sorption stage preceded by rapid sorption (1-3). The rapid sorption in this study was the sorption to the point of the apparent equilibrium. An extremely rapid initial stage resulted in 68% of the PCP being sorbed at the first sampling point (20 min). An additional 10% (total 78%) was then sorbed at the point of apparent equilibrium.

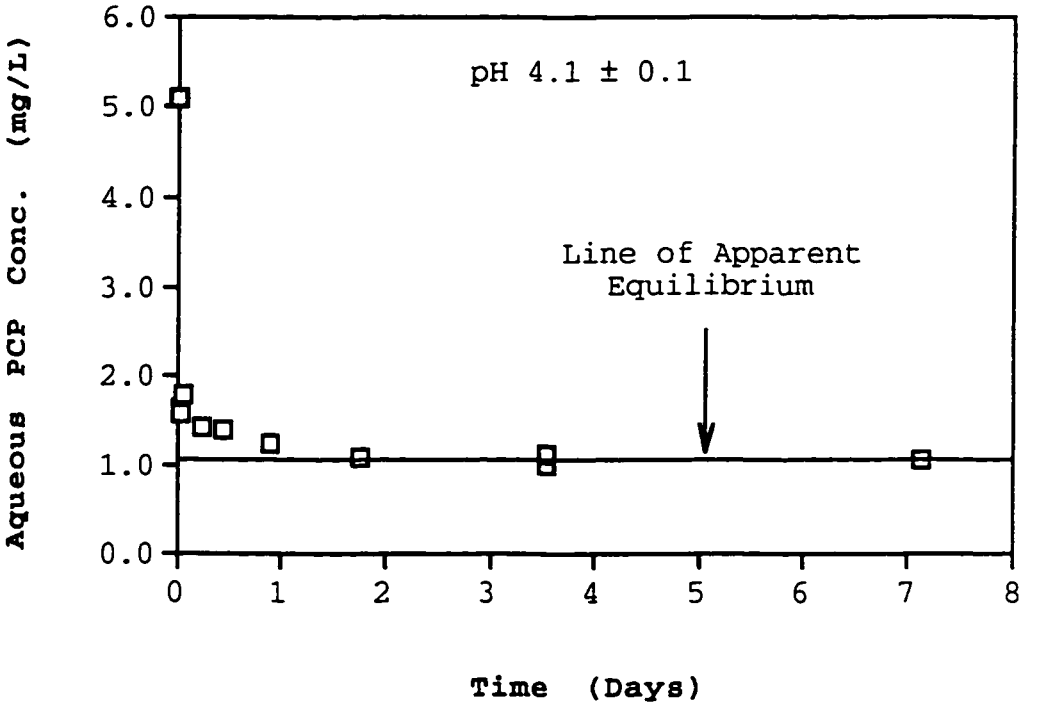

Figure 4.1 **Short-term sorption kinetics of PCP.** The pH was 4.1 ± 0.1. An apparent equilibrium occurred at about 42 h. A Line of Apparent Equilibrium has been superimposed for visual aid. Each point was the average of 2 replicates. There were 7 replicates at 3.6 days with a standard deviation 0.047.

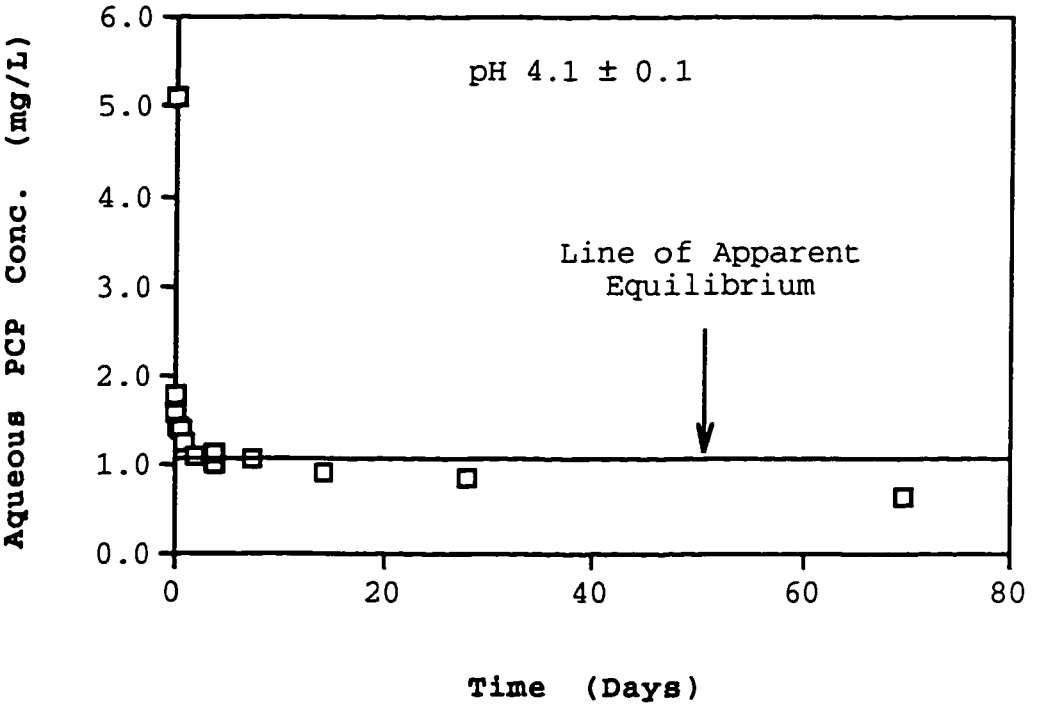

Figure 4.2 Slow sorption kinetics of PCP. The K_p for PCP at the apparent equilibrium was 90 L/kg with a standard deviation of 7.60.

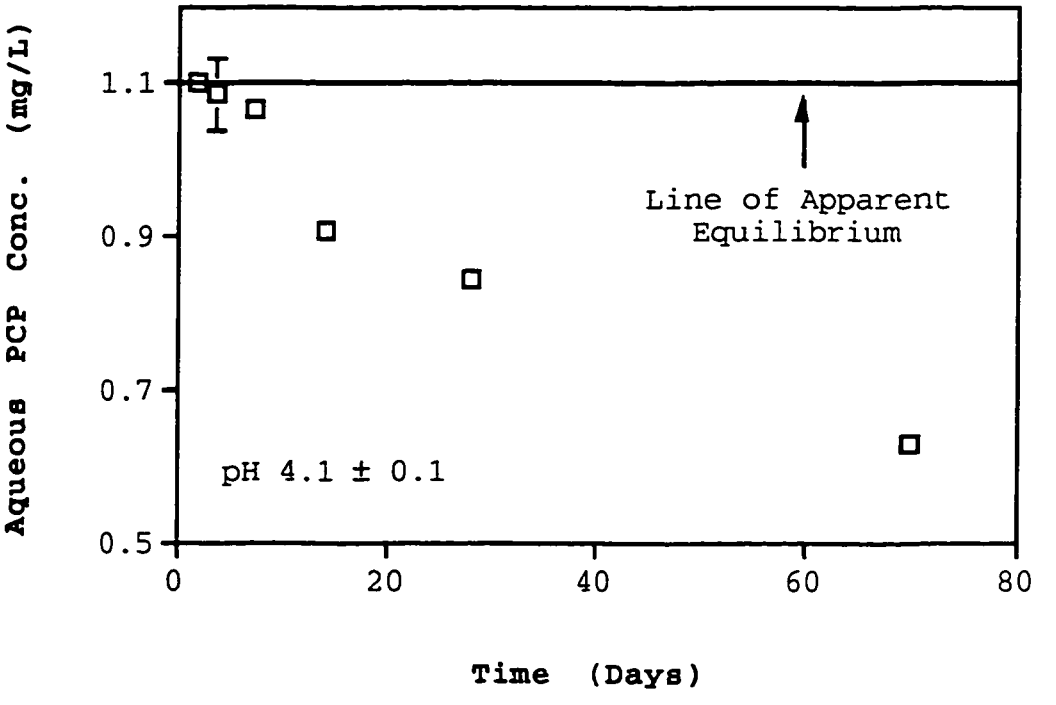

Figure 4.3 Expanded slow sorption kinetics of PCP. The error bar at 3.6 days was based on the standard deviation of 0.047 for 7 replicates.

Assuming that the apparent equilibrium was the true equilibrium these two phases could describe a biphasic relationship characterized by rapid and slow sorption. However, as the sorption continued there was an additional 6% (total 84%) sorbed by 28 days and a total of 88% sorbed by 70 days. This was the true slow sorption stage and the result was a biphasic relationship.

The ionized form of PCP did not show a significant change in the aqueous PCP concentration, beyond the apparent equilibrium, until 69 days (Figure 4.4). This may suggest that the ionized form was hindered from diffusing inward during the slow sorption stage due to a stronger more specific reaction with the surface. There were no sampling points between 27 and 69 days so the time at which there is a significant change in the aqueous PCP concentration is somewhat arbitrary. However, the level of confidence at 69 days (95%) was the same as the 14 day sampling point for the protonated species.

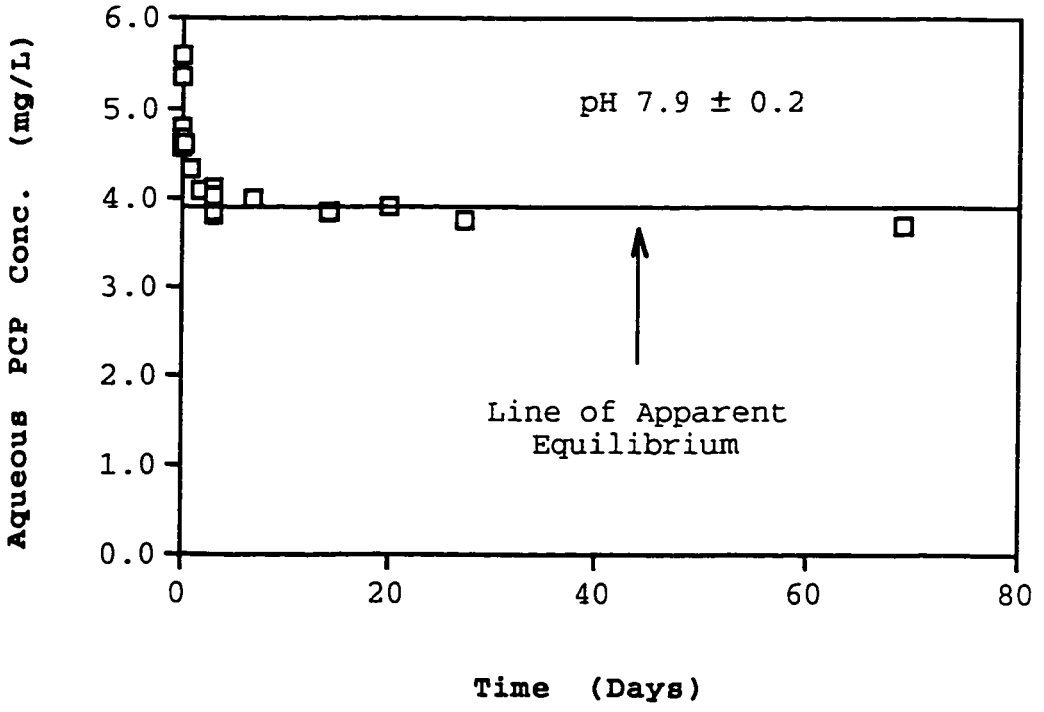

Figure 4.4 **Slow sorption kinetics of the ionized species of PCP.** The pH was 7.9 ± 0.2. An apparent equilibrium occurred at about 42 h. Each point was the average of 2 replicates. There were 7 replicates at 3.1 days with a standard deviation of 0.102.

The calculated partition coefficient (K_p) for the time with seven replicates (3.1 days) was 5.24 L/kg with a standard deviation of 0.46. At pH 7.9 there is less than 0.1% (see Equation 6.12) of the PCP in the neutral form; therefore, 5.24 L/kg can be considered the K_p for the anion. At pH 4.1, 18% of the PCP was in the anionic form. The K_p of 90 L/kg is the net K_p (K_p^{net}) not the K_p for the neutral form (K_p^n). Using a modification of the equation developed by Fontaine et al. (1991) one can calculate the K_p for the neutral species of PCP. This is given by

$$K_p^n = K_p^{net} + (K_p^{net})f - (K_p^a)f \qquad (4.2)$$

where

$$f = \frac{K_a M_a}{[H^+]M_n} \qquad (4.3)$$

K_p^a is the K_p for the anion, M_n and M_a are the molecular weights of the neutral and anion, respectively. Equation 4.2 gives the neutral K_p as a function of the net and anion K_ps, pH, and pK_a. This equation can then be used to solve for the net K_p at a given pH.

Using values of 90 L/kg for K_p^{net}, 5.24 L/kg for K_p^a, 1.778×10^{-5} for K_a, 7.94×10^{-5} for $[H^+]$, 266.33 and 265.34 for M_n and M_a, respectively, one obtains a value of 109.0 L/kg for K_p^n.

The initial rapid kinetics for both species of PCP showed similar results with equilibrium occurring in approximately 42 h. This rapid stage may be considered partitioning into the organic matter (see Sorption Isotherms below). The slow sorption stage has been postulated to be intraorganic matter (Brusseau and Rao, 1989; Brusseau and Rao, 1991) or intraparticle (Ball and Roberts, 1991; Steinberg et al., 1987) diffusion. However, diffusion into clay interlayers may also be a possibility. If diffusion into the clay interlayers is the cause of the slow sorption stage, then the negative charge of clay minerals might repel the ionized form of PCP, resulting in a hindered diffusion inward. The same reasoning could apply to the organic matter. The soil was preequilibrated to pH 8 and most of the functional groups will be negatively charged. It is also probable that there are two different mechanisms for the two different species. Since the ionized form is much more polar it may be able to displace water that has a strong dipole interaction with the clay. The protonated from may simply be diffusing into

the organic matter. The ionized PCP may be reacting more specifically with the surface.

If diffusion is the controlling mechanism for the slow sorption stage, then the concentration of the PCP could be very important. A higher concentration would result in a faster rate of diffusion. The initial concentration (C_o) of the two kinetic experiments was similar with C_o of the ionized form (5.56 mg/L) being higher than C_o for the protonated form (5.1 mg/L). However it might not be the initial concentration or even the bulk solution concentration of PCP that is important. If we consider a simple two site series model (Equation 2.8) in which partitioning takes place into site 1 and diffusion occurs from site 1 into site 2, then it is the concentration in site 1 that is important. This is depicted in the schematic shown in Figure 4.5. In a parallel model (Equation 2.7), diffusion into site 2 occurs from the bulk solution and it is the concentration of PCP in this phase that would be important.

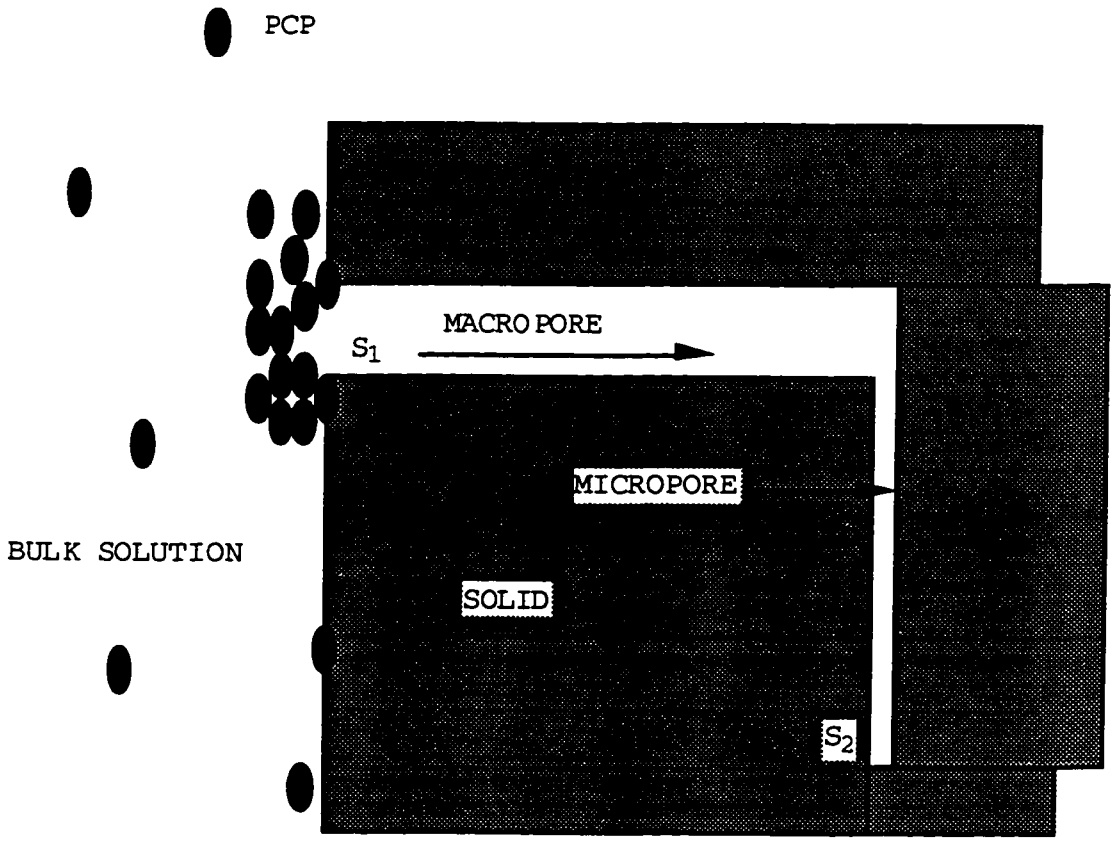

Figure 4.5 Schematic of series diffusion model.

Perhaps the reason for the hindered slow sorption (assuming the series model is in action) is that the extent of sorption of PCP into site 1 for the ionized form is extremely low, and therefore there is a smaller concentration gradient when compared to the protonated form. The partition coefficient at the 2 day apparent equilibrium ($K_{p(apparent)}$) for the ionized form is approximately 5 L/kg and for the protonated form it is roughly 109 L/kg. See Figures 4.2 and 4.3.

To test this hypothesis a kinetic experiment was set up for the ionized form in which C_o was high enough (19.8 mg/L) to result in a sorbed concentration (82.5 mg/kg) in site 1 comparable to what it was for the protonated form (100.0 mg/kg) in Figure 4.2. The results are shown in Figure 4.6 as the change in K_p with time. The results from Figure 4.2 are also shown for comparison. Five replicates are shown for each time at pH 8.

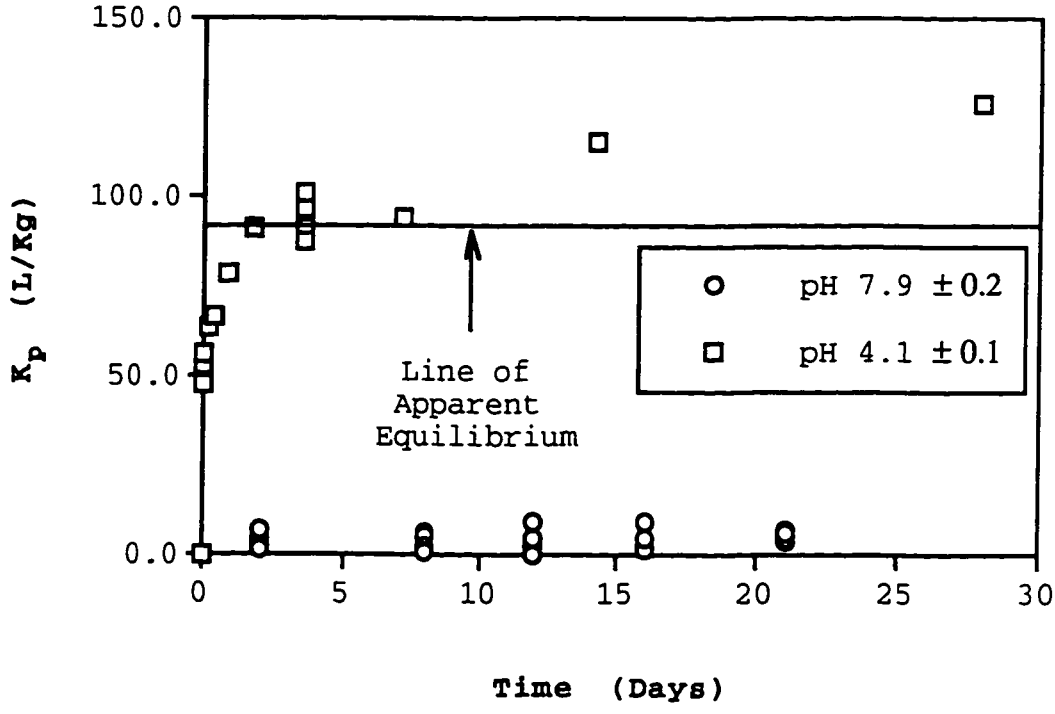

Figure 4.6 Slow sorption kinetics of ionized form of PCP at high initial concentration (19.8 mg/L). Depicted as the rate of increase in K_p with time. The amount of PCP sorbed (82.5 mg/kg), after the initial rapid sorption, approaches the amount sorbed (100 mg/kg) for the neutral species in Figure 4.2. These data are also shown here.

There is no statistically significant change in K_p for 21 days of sorption (95% C.I.), when compared to 2 days of sorption. This suggests that the differences in the slow sorption stage between the protonated and ionized forms are not entirely due to the concentration gradient created by differences in rapid sorption of the two forms. If this were the case, we would have expected to see a significant change in K_p, at this concentration (19.8 mg/L), for the ionized form.

4.4.2 Sorption Isotherms

At this point it appears that the reduced slow sorption of the ionized form is not a result of differences in rapidly sorbed concentrations. The ionized form is either repelled by the negatively charged surfaces, has a different slow sorption mechanism such as clay interlayer diffusion, and/or reacts more specifically with the surface resulting in a hindrance of the slow sorption stage. In order to explore the second and third possibilities we constructed comparative sorption isotherm experiments at pH 4 and 8.

Initially, three identical isotherms (pH 4) were incubated for three different residence times (2, 10, and 21 days). Due to the solubility limitations of PCP it was necessary to utilize the multiple spike methodology

discussed in the Methods section. This would allow for equilibrium aqueous concentrations (C_e) of PCP close to the solubility limit and would confirm a truly linear isotherm. If single spikes were used and all initial PCP concentrations were below the solubility limit, the highest attainable C_e for 1 g of soil (as mentioned previously, it is undesirable to vary the solids mass between experiments) would only be approximately 27% (2 mg/L) of the PCP solubility limit. In this case, the concentration range of C_e could represent the linear portion of a nonlinear isotherm.

The multiple spiking method employed (6 spikes) resulted in compounded errors that added more scattering to the data. All the isotherms, fit with the linear sorption model (Equation 2.1), appeared linear out to C_e values greater than 6 mg/L (Figure 4.7). This along with the good predictability of the organic matter distribution coefficient (K_{om}) from the octanol water partition coefficient (K_{ow}) would suggest a partitioning mechanism into the soil organic matter. The K_{om} is the K_p divided by the fraction of organic matter (f_{om}). Using the K_p from the kinetic study (90 L/kg) and f_{om} = 0.017 yields a value of 5294 L/kg. Using Chiou's equation (Chiou, 1989):

$$\log K_{om} = 0.904 \log K_{ow} - 0.779 \qquad (4.2)$$

with a log K_{ow} of PCP equal to 5.01 (Leo et al., 1971), yields a value of 5624 L/kg. There is only a 6% variation between these numbers.

There is a trend of increasing slope (K_p) with increasing residence time. The K_ps in order of increasing residence time are 57.4, 55.3, and 75.5 L/kg. The difference between 2 and 10 days is not significant (95% C.I.). This is analogous to the kinetic study in which there was no significant change in the aqueous PCP concentration for at least 5 days following the apparent equilibrium (2 days). The difference between 2 and 21 days is only significant at 80% confidence.

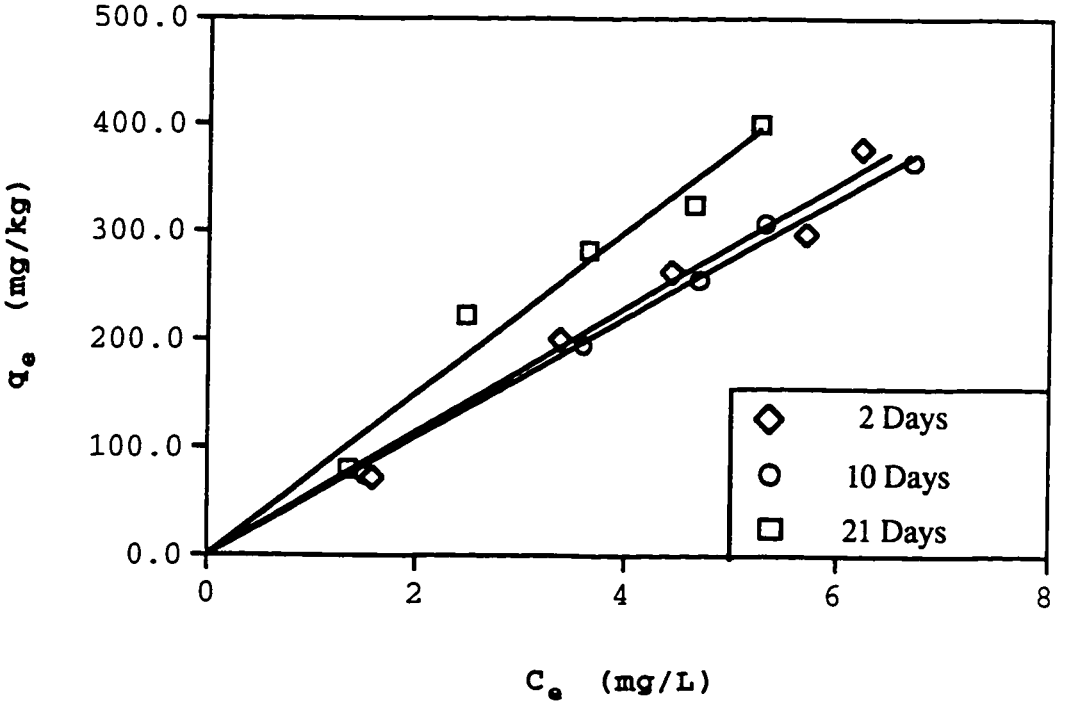

Figure 4.7 Sorption isotherms of PCP with increasing residence time. The pH was 4.1 ± 0.1. There was no significant difference between 2 and 10 days of sorption. The significance between 2 and 21 days of sorption is only 80%. Each point is the average of 3 replicates. Error bars are too small to be seen.

The trend of increasing sorption with increasing residence time, analogous to the kinetic study (Figure 4.2), was less significant for the isotherm study due to the scattering of the data. The increase in K_p from 2 days out to 21 days for both experiments was approximately 1.3 times. However, it was clear that the K_p at the apparent equilibrium (2 days) was much less for the isotherm experiment (57.4 L/kg) than for the kinetic study (90 L/kg).

The only difference in the methodology for the two experiments, besides the multiple spiking used for the isotherms, was that in the kinetic studies the samples were mixed continuously and were laid on their side for the entire time. The samples for the sorption isotherm studies were mixed for two days on their side and then stood upright without any mixing for the remaining incubation. As mentioned previously, mixing beyond the apparent equilibrium had no effect on sorption. Therefore, either the interfacial area between the aqueous and solid phases, which was greater in the kinetic study due to the tubes lying down, the spiking method, and/or the concentration differences had some effect on the system. The initial concentration of PCP in the kinetic study was 5.1 mg/L. The final concentrations for the isotherms, after spiking,

ranged from 4.5 to 21.4 mg/L. This point will be discussed further below.

Figure 4.8 shows two isotherms at pH 4 (10 day residence time) and 8 (6 days residence time). These samples were sorbed for between six and ten days and therefore do not represent any significant slow sorption. Each point is the average of three replicates. The pH 8 isotherm was fit with the Langmuir model (Equation 2.4). This was accomplished by using the linear form of the equation, $C_e/q_e = 1/bq_{max} + C_e/q_{max}$ and performing a regression on C_e/q_e vs. C_e. The constants q_{max} and b can then be calculated from the slope and intercept, respectively.

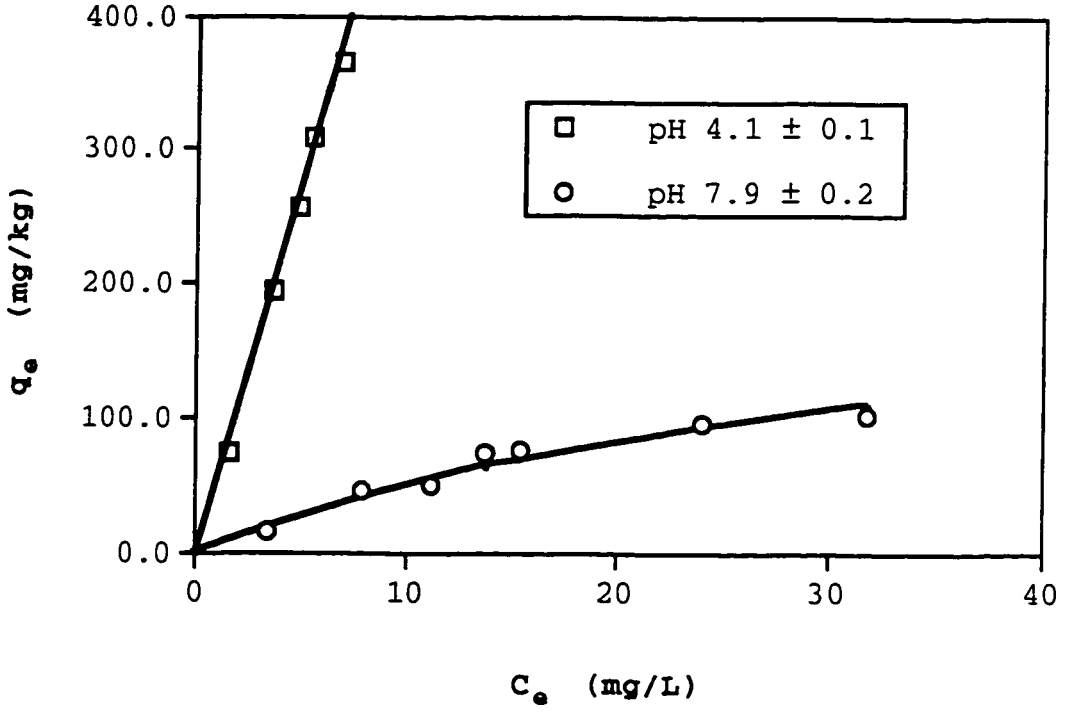

Figure 4.8 **Comparative PCP sorption isotherms.** Each data point is the average of three replicates. The data at pH 4.1 were fit with the linear sorption model and the data at 7.9 were fit with the Langmuir model.

The q_{max} calculated from the Langmuir equation was 250 mg/kg. One sees that not even half of the soil surface has been covered at pH 8. On the contrary, at pH 4 the coverage is well beyond the monolayer surface coverage. If we assume the surface coverage is roughly the same for the two species, then this further supports the supposition that the protonated form is partitioning into the organic matter of the soil. It is indeed a linear isotherm and not simply the linear portion of a nonlinear isotherm.

If the equilibrium aqueous concentration of PCP at pH 8 was comparable to what it was at pH 4 then the pH 8 isotherm would appear linear. One might have incorrectly hypothesized this to be a partitioning mechanism based on the isotherm. However, a true linear isotherm is linear out close to the solubility limit. At higher equilibrium solution concentration it becomes clear that the pH 8 isotherm is distinctly nonlinear when compared to the linear isotherm at pH 4.

This might suggest a difference in the rapid sorption mechanism that can be attributed to the ionized form reacting more specifically with the surface when compared to the protonated form. This more specific association with the surface could result in a hindrance of the PCP when it attempts to diffuse to sites deeper within the soil matrix.

4.4.3 Desorption Studies

Different sorption mechanisms may result in different desorption behavior. A contaminant which is more specifically sorbed may be more resistant to desorption. This will have profound implications for any attempted remediation strategies. To address this concern, comparative desorption studies were carried out on PCP for different sorption times and pH values.

Table 4.1 shows the results of an extended sorption-desorption study at both pH 4.1 and 7.9. The percent desorbed is based on the sorption equilibrium value. That is, it is not an indication of the total amount desorbed. Desorption was carried out once by simply removing 80% (20 ml) of the solution volume replacing it with PCP-free solution and desorbing for the required time interval. One hundred percent desorbed means that the PCP solution concentration after desorption was what would be predicted based on the apparent equilibrium sorption partition coefficient ($K_{p(apparent)}$). That is, the desorption K_p equaled the sorption K_p.

Table 4.1. **Percent PCP Desorbed.** Percent of equilibrium concentration desorbed for the protonated and ionized forms of pentachlorophenol.

Sorption Time (Days)	Desorption Time (Days)	% Desorbed* pH 4.1	% Desorbed* pH 7.9
		(± 9%)	(± 15%)
2	2	95	86
8	2	94	74
16	2	64	64
21	2	68	49
12	2	60	55
12	8	99	50
12	12	90	23
12	18	94	20

* Percent desorbed based on the predicted sorption equilibrium value.

It is clear that with increasing residence time there is a decrease in the amount of PCP desorbed for both species of PCP. This has been reported repeatedly in the literature (Di Toro and Horzempa, 1982; Hatzinger and Alexander, 1995; Horzempa and Di Toro, 1983; Kan et al., 1994; Pignatello, 1990; Pignatello et al., 1993; Pignatello and Huang, 1991). However, the mechanism causing this might differ for the two species.

Looking at the samples that were all sorbed for 12 days there is a distinct difference between the two species. The percent desorbed for the protonated form increases with increasing desorption time from 2 to 8 days. This implies that the PCP needs time to diffuse out of the soil matrix. However, longer sorption times might result in more resistant fractions. Furthermore, the size of the resistant fraction might be smaller than the equilibrium sorbed value. If this were the case one would not see the resistance to desorption except for repeated desorption steps. These possibilities will be explored further in Chapter 6.

The ionized form (pH 7.9) of PCP does not show this trend. The PCP seems to be more strongly sorbed to the surface and is therefore resistant to desorption. In fact there is actually a decrease in the amount desorbed with

increasing desorption time. The reason for this is unclear.

Making conclusions about field soils based on lab results may lead to grave mistakes. Short-term lab sorption-desorption equilibrium times may inaccurately estimate the distribution of the contaminant in the field. A pollutant that appears to be resistant to desorption may in fact be slowly diffusing outward. This results in a continued threat to our water resources.

4.5 Conclusions

Kinetic and equilibrium sorption-desorption studies of pentachlorophenol (PCP) on soil suggest that the two species of PCP have different sorption mechanisms. The ionized form of PCP shows a hindered slow sorption stage, a nonlinear isotherm, and a greater resistance to desorption when compared to the protonated form. Different sorption mechanisms for the two species of PCP may have profound implications for both remediation and predicting its environmental behavior. More work is needed to investigate the differences in the environmental fate among species of ionizable organic chemicals.

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Chapter 5

SOIL COMPONENTS

5.1 Introduction

Chapter 4 demonstrated a slow sorption stage for the protonated (neutral) species of pentachlorophenol (PCP) which was much more pronounced than for the ionized (charged) species. In addition, the sorption in general was much less for the ionized form, and a different sorption mechanism was implied by the different isotherms for the two species.

This difference in sorption may be explainable in terms of soil organic matter (SOM). The sorption of organic chemicals that is often so well correlated with the SOM holds true mainly for nonpolar uncharged compounds (Chiou, 1989). The solubility of PCP, which is an indication of its polarity, is a function of the pH and changes as a result of the predominance of a given species. At low pH values ($pH < pK_a$) the neutral species, which is very hydrophobic (log K_{ow} = 5.01 (Leo et al., 1971), predominates. The charged species dominates at pH values greater than the pK_a.

The solubility of PCP is given by the equation:

$$S_{PCP} = S_{HA}(1 + 10^{pH-pK_a}) \qquad (5.1)$$

where S_{PCP} is the total solubility of both species of PCP and S_{HA} is the solubility of the neutral species. Using this equation with S_{HA} = 28 μM (Stapleton et al., 1994), the solubility of PCP (S_{PCP}) at pH 4.1 is 34 μM. The solubility at pH 7.9 is 0.04 M. This is a three order of magnitude difference. Additionally, the log K_{ow} of PCP at a pH of 7.9 is roughly 3.20 (Kaiser and Valdmanis, 1982). This further demonstrates the difference in the polarity of the two PCP species.

The slow sorption stage of hydrophobic nonionizable organic chemicals (HNOC) has been postulated to be both intraorganic matter (Brusseau et al., 1991) or intraparticle (Ball and Roberts, 1991; Steinberg et al., 1987) diffusion. If the organic matter is indeed important for the neutral species of PCP then this might explain the differences in slow sorption seen for the two species. The charged species would be less soluble in the hydrophobic SOM.

The objectives of this research were to look at the slow sorption of the protonated species of PCP in the absence of the SOM. This was accomplished by removing the organic matter from the soil by chemical treatment. Additionally, the effect of the soil preequilibration step

used in Chapter 4 was evaluated in terms of removing SOM at different pH values.

5.2 Materials

Pentachlorophenol was purchased from Sigma (purity > 95%) and used as received. Hexane was HPLC grade. 2,4,5-trichlorophenol was used as an internal standard for GC analysis (Sigma, purity > 95%). All inorganic reagents used were analytical grade (Fisher Chemicals).

The soil used was a surface (Ap) horizon of a Matapeake silt loam (Typic Hapludult). Physicochemical and mineralogical properties of the soil are as follows: pH = 6.1, cation exchange capacity (CEC), 5.02 cmol/kg, 1.7% organic matter, 29.6% sand, 58.6% silt, and 11.8% clay. The mineral suite of the < 2 μm clay fraction was kaolinite ≈ chloritized vermiculite > quartz > mica. A standard N_2/BET analysis yielded a surface area of 5.52 m^2/g.

5.3 Methods

5.3.1 Oxidation of Organic Matter

The organic matter of the soil was removed by oxidation using two different methods. The first method involved the use of hydrogen peroxide (H_2O_2) (Klute, 1986). For H_2O_2 treatment the soil requires an acidic medium. Since the pH of this soil is 6.1, removal of carbonates and

soluble salts, which impart an alkaline reaction, was not necessary. Furthermore, removal of these salts required the use of an organic solvent which could sorb to the soil and complicate the system.

For the first treatment, the soil was passed through a 2 mm sieve. Fifty grams of soil was placed into a 2 L beaker. Distilled water was added to yield approximately a 1:1.6 soil:water ratio. Three increments of 5 ml of 30% H_2O_2 were added. Frothing was observed. The sample was stirred with a glass rod and transferred to a hot plate at 65-70 °C. If the temperature rose above 70 °C it was quickly cooled down in a water bath. The sample was intermittently stirred and frothing eventually subsided to a minimum. The total time of the reaction was roughly 2 h. The sample was transferred with a funnel and wash bottle of distilled water to two 250 ml centrifuge bottles. Samples were centrifuged at 514g for 15 min. Since no clay remained suspended no $MgCl_2$ was added. The supernatant was discarded.

For the second treatment a sodium hypochlorite (NaOCl) method was employed (Omueti, 1979; Shuman, 1983). Twenty-five grams of 2 mm sieved soil was placed into each of two 250 ml centrifuge bottles. The pH of the NaOCl was adjusted to 8.5 with 3 M HCl. Fifty milliliters of the NaOCl was put into each bottle. Samples were placed in a

boiling water bath for 15 min and then spun down at 514g for 15 min. The supernatant was discarded. This was repeated twice more.

The samples from both treatments and two 25 g samples with no prior treatment, were all filled with 80 ml of water and shaken for 5 min on a reciprocating shaker at 150 cycles/min. The samples were then centrifuged at 514g. This was repeated again with 250 ml of water. This step was carried out to remove any residual NaOCl or H_2O_2. The untreated soil was included for consistency. All samples were then preequilibrated as described below.

5.3.2 Preequilibration of Soil

The natural soil pH was 6.1. The soil (20 g) was washed three times with a 250 ml solution (pH 4.0, pH 6.0 or pH 8.0) of 0.01 M $CaCl_2$, 0.02% NaN_3 (bacteriological inhibitor) by shaking at 150 cycles/min in 250 ml plastic screw capped bottles for 24, 48 and 48 h. The samples were spun down in between washes for 20 min at 514g. The washes were saved for analysis. The soil was then oven dried at 50 °C for approximately 48 h and screened to pass through a US standard No. 10 mesh (2 mm).

A modification of the procedure was necessary for the pH 8.0 studies. During the first wash it was necessary to repeatedly spike the suspensions with 4 M NaOH. This

was done every few hours over the course of 10 hours until the pH was stabilized at 8.0. The washing procedure was then carried out identical to that described above except that the entire process was performed in a glove box purged with nitrogen. This limited the presence of CO_2 so that an equilibrium pH of 8.0 could be obtained.

5.3.3 Sorption Kinetics

Sorption kinetic studies used 25 ml brown glass bottles with Teflon® lined screw caps. Samples were upright at all times. The bottles were removed from the shaker after two days of equilibrating and then allowed to incubate for additional times. Samples were collected and a portion of the liquid phase removed and saved for analysis. Five replicates were used at each time interval.

5.3.4 Analysis

An internal standard was added to all samples (2,4,5-trichlorophenol) and the samples were then diluted if necessary and acidified with 3 M HCl. A volume of hexane was added to all samples for extraction. Samples were often concentrated in hexane as deemed necessary.

After the addition of hexane the samples were vigorously vortexed. UV spectrophotometric analysis showed no detectable amount of PCP remaining in the aqueous phase (see Chapter 3). An aliquot of the hexane was then removed

and filtered through a 0.2 μm membrane filter. Each sample was then injected twice into a gas chromatograph equipped with an MS detector. Two qualifying ions for PCP were used in all cases. The integrity of the chromatography and the nonexistence of any aberrant peaks suggested the absence of any degradation.

5.4 Results and Discussion

The importance of intraorganic matter diffusion was explored by conducting sorption kinetic studies on soil in which the soil organic matter (SOM) was oxidized. The oxidation was carried out by both the H_2O_2 and NaOCl methods (see Methods). The importance of the organic matter in the sorption of organic chemicals is well documented (Chiou et al., 1979; Chiou et al., 1983; Rutherford et al., 1992). However, it is still unclear whether it is responsible for the slow sorption kinetics. If the slow sorption kinetics are still present in the absence of organic matter, then either the clay plays a part in the slow kinetics, or new surfaces, including clays, have been exposed that now play an important role.

The percent SOM was measured using furnace combustion at 800 °C. The NaOCl method resulted in approximately 80% reduction in the organic matter content. The H_2O_2 method only oxidized about 63% of the organic

matter. These reductions were based on comparisons to the original soil that had gone through the preequilibration (pH 4 wash) step, which was shown to reduce the organic matter content by 8.2%.

Figure 5.1 shows the results of the kinetic study at pH 4.2 ± 0.2 with three different soil treatments. The initial concentration (C_o) in this experiment, added in one spike, was 6.75 mg/L. There are 3-5 replicates at each time interval for each treatment. The slow sorption kinetics for the untreated and H_2O_2 treated soils were very evident for times beyond the two day apparent equilibrium. However, the NaOCl treated soil showed no significant change in K_p after 8 days of sorption. This was concluded by comparing the means at 8 and 20 days of sorption and noticing no significant difference at a 90% confidence interval.

Based on the rate of increase of K_p ($\Delta K_p/\Delta$time) for the untreated soil (≈ 3.3 K_p/day), we would expect values of K_p for the NaOCl treated soil to approach 65 L/kg. They only reached about 20 L/kg. This may suggest that in the absence of large amounts of SOM the slow sorption stage reaches equilibrium much sooner.

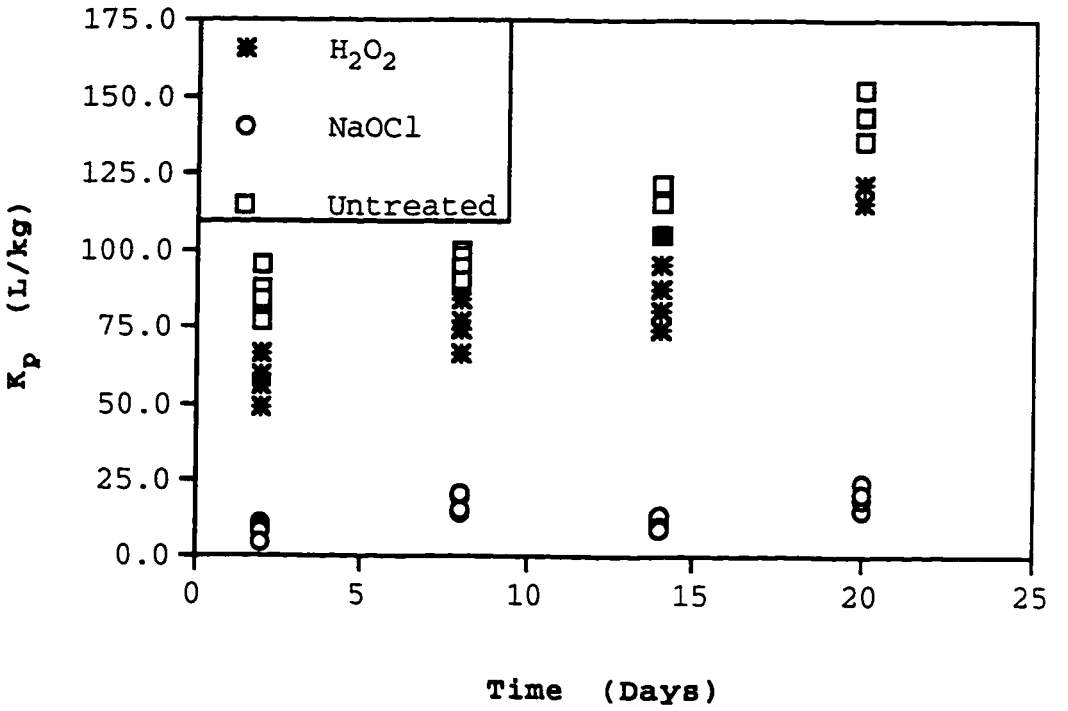

Figure 5.1 **Slow sorption kinetics of PCP on soil treated to remove the organic matter (OM).** H_2O_2 removed 63% of the OM. The NaOCl treatment removed 80% of the OM. After 8 days there was no significant change in the K_p with time for the NaOCl treated soil.

With these results in mind, an additional concern was that the preequilibration of the soil at pH 8, for the original slow sorption kinetic studies, would dissolve a substantially greater fraction of SOM when compared to the pH 4 preequilibration. If this were the case that could explain why the slow sorption stage was less evident at pH 8 (Figures 4.2 & 4.4). To address this concern we analyzed the supernatant of the washing solutions for organic carbon (OC) content after each wash.

The results are shown in Table 5.1 including a pH 6 washing solution. It is evident that the pH 8 solution removed twice as much organic carbon (14.2%) from the soil than the pH 4 wash (7.1%). When the amount of OC removed at pH 4 is compared to the furnace combustion mentioned above (8.2%), the numbers differ by 1.1%. However, furnace combustion is a quantification of organic matter and will always be greater than organic carbon. The difference might be considered the non-organic carbon content of the SOM.

Table 5.1 **Total Organic Carbon (TOC) Removal by Sequential Washes at Three Different pH Values.**

Sample[a]	TOC (mg)[b]	Total TOC (mg)[c]	% TOC[d]
pH 4-1	12.8		
pH 4-2	6.6		
pH 4-3	4.7	24.1	7.1
pH 6-1	12.4		
pH 6-2	7.2		
pH 6-3	4.5	24.1	7.1
pH 8-1	26.9		
pH 8-2	13.4		
pH 8-3	7.9	48.2	14.2

[a] The pH used in the washing procedure is followed by the number of the wash. [b] The total organic carbon (TOC) removed by each wash as measured by analysis of the supernatant in a carbon analyzer. [c] The TOC removed for the sum of the three washes for each procedure. [d] The % TOC removed in terms of the % SOM present. This is the sum of the three washes for each procedure.

The increased reduction in OC for the pH 8 solution can not account for the decrease in the slow sorption stage. The H_2O_2 treatment reduced the SOM content by 63%. If we assume that for every 8.2% of organic matter removed, 1.1% is non-organic carbon, that still results in a 54.5% reduction in OC for the H_2O_2 treated soil. This treatment still showed a substantial slow sorption stage (Figure 5.1). Therefore, the removal of 14.2% OC should have little to no effect on the slow sorption stage.

5.5 Conclusions

The soil organic matter (SOM) was largely responsible for the slow sorption of neutral PCP on soil. When 80% of the SOM was removed by sodium hypochlorite (NaOCl) the slow sorption stage was only detectable at early sorption times. Untreated soil and hydrogen peroxide (H_2O_2) treated soil, which oxidized 63% of the SOM, showed continued sorption at all sampling times. The amount of SOM removed by the soil preequilibration step at pH 8 was twice (14.2%) the amount for the pH 4 wash. Still, this was not substantial enough to account for the hindered slow sorption stage exhibited by the ionized PCP in comparison to the protonated PCP (see chapter 4).

5.6 References

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Chapter 6

CONCENTRATION EFFECTS

6.1 Introduction

The residence time of an organic chemical in the soil environment can greatly affect both the environmental fate and the removability of that compound from the soil. As the contact time increases, the organic compound could become more resistant to removal by a host of different soil remediation technologies. Bioremediation and soil washing may be much less effective for pollutants with long-term residence times in the field.

Hydrophobic organic compounds (HOCs) exhibit a slow sorption stage following an initial rapid sorption (Gilchrist et al., 1993; Karickhoff, 1984; Karickhoff and Morris, 1985). Both intraorganic matter diffusion (Brusseau et al., 1991; Brusseau and Rao, 1989) and intraparticle diffusion (Ball and Roberts, 1991b; McCall and Agin, 1985; Steinberg et al., 1987) have been postulated as the cause of this rate-limited sorption. This can often result in a slow or incomplete desorption

(Pignatello, 1990; Pignatello et al., 1993; Pignatello and Huang, 1991).

Many diffusion models attempt to describe both the slow sorption and desorption stages (Carroll et al., 1994; Connaughton et al., 1993; Pedit and Miller, 1995; Wu and Gschwend, 1986). However, there is a lack of long-term sorption kinetic data and a void in the understanding of the factors that control the slow sorption stage. The concentration gradient is inherent to all diffusion models; still, its effect on the slow sorption stage remains virtually unexplored. A complete understanding of the mechanisms which control the slow sorption of organic chemicals on soil is paramount to developing a useful kinetic model.

The objectives of this research were to investigate the long-term sorption kinetics for the protonated form of pentachlorophenol (PCP) on a silt loam soil. PCP is a hydrophobic ionizable organic compound (HIOC) with a pK_a of 4.75. In the protonated form, PCP can behave similarly to other hydrophobic nonionizable organic compounds (HNOCs). The effect of the concentration gradient on the slow sorption stage was investigated. In addition, the effect of both residence time and PCP concentration on the desorption of PCP was explored. Resistant PCP fractions were determined using hot methanol extracts.

6.2 Materials

Pentachlorophenol was purchased from Sigma (purity > 95%) and used as received. Hexane was HPLC grade. 2,4,5-trichlorophenol was used as an internal standard for GC analysis (Sigma, purity > 95%). All inorganic reagents used were analytical grade (Fisher Chemicals).

The soil used was a Matapeake silt loam (Typic Hapludult) from the Ap-horizon. Physicochemical and mineralogical properties of the soil are as follows: pH = 6.1, cation exchange capacity (CEC), 5.02 cmol/kg, 1.7% organic matter, 29.6% sand, 58.6% silt, and 11.8% clay. The mineral suite of the < 2 μm clay fraction was kaolinite ≈ chloritized vermiculite > quartz > mica. A standard N_2/BET analysis yielded a surface area of 5.52 m^2/g.

6.3 Methods

6.3.1 Preequilibration of Soil

The natural soil pH is 6.1. Due to the soil's relatively high buffering capacity it was necessary to preequilibrate the soil to the desired pH (4.0) of the experiment. This would allow for a constant pH over the course of the entire experiment. This was accomplished by washing the soil repeatedly. The soil (20 g) was washed three times with a 250 ml solution (pH 4.0) of 0.01 M $CaCl_2$, 0.02% NaN_3 (bacteriological inhibitor) by shaking at

150 cycles/min in 250 ml plastic screw capped bottles for 24, 48 and 48 h. The samples were spun down in between washes for 20 min at 514g. The soil was then oven dried at 50 °C for approximately 48 h and screened to pass through a US standard No. 10 mesh (2 mm).

6.3.2 Sorption Kinetic Studies

A solution of the same composition (to standardize pH and ionic strength) as used for the preequilibration of the soil, was used for the sorption studies (0.01 M $CaCl_2$, 0.02% NaN_3, pH 4.0). One gram of soil (determined to be appropriate in previous experiments) and 24.9 ml of solution were used in all experiments. All samples were spiked with aqueous PCP stocks (pH ~ 11.0, 1.275 mg/L) and then mixed on an orbital shaker at 50 rpm, in the dark (to prevent photolysis) at 25 ± 1 °C, for a minimum of 48 h. Additional mixing beyond this point proved to have no effect on sorption (see Chapter 3). In all experiments there was a minimum of 20% of the samples used as controls.

All *sorption kinetic studies* were mixed continuously at 50 rpm. Particle degradation was shown to be negligible as determined by N_2/BET analysis before and after mixing. Any percent change in surface area was less than the inherent error of the BET analysis. In these studies, 25 ml glass centrifuge tubes with Teflon® lined

screw caps were placed in a test tube rack lain on its side on the orbital shaker. This increased mixing efficiency and the contact area between the solution and solid phase. Samples were collected and centrifuged at 6315g for 15 min. A portion of the aqueous phase was then stored for analysis. All samples were conducted in duplicate and certain random times had multiple replicates. The *dual spike sorption kinetics* used the multiple spiking methodology discussed below.

Additional sorption kinetic studies used 25 ml brown glass bottles with Teflon® lined screw caps. Samples were upright at all times. The bottles were removed from the shaker after two days of equilibrating and then allowed to incubate for additional times. Samples were collected and a portion of the liquid phase removed and saved for analysis. Five replicates were used at each time interval.

6.3.3 Multiple Spiking

The solubility of the protonated form of PCP at 25 °C is 28 μM (7.46 mg/L) (Stapleton et al., 1994). In order to do sorption studies at higher concentrations than the solubility, we employed a multiple spiking approach. The samples for the dual spike kinetics were equilibrated for 3 days and then spiked again. The total concentration (C_T) of PCP added was 10.0 mg/L.

For sorption studies at even higher concentrations of PCP (~20 mg/L) the samples were spiked every two hours after the initial spike, for a total of 10 h (6 spikes). The concentrations of the spikes were calculated based on the kinetics, which showed substantial sorption after 2 h (~ 80% of the total amount sorbed). The aqueous PCP concentration never exceeded the solubility limit.

6.3.4 Desorption Studies

The *desorption kinetic studies* were conducted on samples that had sorbed PCP for 20 days. After 20 days the samples were centrifuged as described above. 80% of the solution volume was removed (20 ml) and replaced with PCP-free solution. Samples were then placed back on the orbital shaker at 50 rpm and collected over time. Aqueous samples were separated and stored following centrifugation. All samples were in duplicate with one sampling time having six replicates. Ten percent of all the samples were controls (no soil or no PCP).

Additional *desorption kinetic studies* were conducted on samples that had sorbed PCP for 12 days. The PCP was sorbed using the multiple spiking technique. After sorption 80% of the solution volume was removed (20 ml) and replaced with PCP-free solution. Samples were then placed back on the orbital shaker at 50 rpm for 2 days. The

samples were then removed from the shaker and collected over time. Aqueous samples were separated and stored. Five replicates were used at each time interval. Seventeen percent of all the samples were controls (no soil or no PCP).

Additional desorption studies were conducted on samples that had sorbed PCP for varying amounts of time. After sorption 80% of the solution volume was removed (20 ml) and replaced with PCP-free solution. Samples were then placed back on the orbital shaker at 50 rpm for 2 days. The samples were then removed from the shaker and collected over time. Aqueous samples were separated and stored. Five replicates were used at each time interval. Seventeen percent of all the samples were controls (no soil or no PCP).

6.3.5 Mass Balances

Samples that were set up for 100 days of sorption and 100 days of desorption were also used for mass balance purposes. The samples were originally sorbed for 100 days as described above. Twenty milliliters of solution was removed and replaced with an equal volume of PCP-free solution. After 2 days of desorption 5 ml of sample was removed and replaced with PCP-free solution. Desorption was then carried out for the remaining 98 days. At this

time 15 ml was removed and replaced with 10 ml of hot methanol (50 °C), resulting in a 1:1 aqueous:methanol ratio. The samples were vortexed vigorously for 30 s and then put on an orbital shaker at 150 rpm at 50 °C for 45 min. They were vortexed again for 15 s and allowed to stand (settle) for 12 h. The solution phase was then sampled and saved for analysis.

6.3.6 Analysis

An internal standard was added to all samples (2,4,5-trichlorophenol) and the samples were then acidified with 3 M HCl. A volume of hexane was added to all samples for extraction. The observation was made that the mass spectrometer (MS) analysis was most consistent within the concentration range of 0.5-2.5 mg/L of PCP. Therefore, the amount of hexane added varied depending on the predicted aqueous concentration of PCP. An attempt was made to have all the samples analyzed within this concentration range in order to reduce error. Hence, samples were often either diluted or concentrated in hexane as deemed necessary.

After the addition of hexane the samples were vigorously vortexed. UV spectrophotometric analysis showed no detectable amount of PCP remaining in the aqueous phase (see Chapter 3). An aliquot of the hexane was then removed and filtered through a 0.2 μm membrane filter. Each sample

was then injected twice into a gas chromatograph equipped with an MS detector. Two qualifying ions for PCP were used in all cases. The integrity of the chromatography and the nonexistence of any aberrant peaks suggested the absence of any degradation.

6.4 Results and Discussion

The soil preequilibration procedure stabilized the pH of the soil at 4.1 ± 0.1. This was the final pH in all studies. Soil washing also helps to remove nonsettling microparticles and dissolved organic matter which have been implicated in the solids concentration effect (Mackay and Powers, 1987; O'Connor and Connolly, 1980; Voice and Weber, 1985). Removal of these particles is important when conducting batch desorption studies.

During the desorption step the removal of a volume of solution containing these particles and replacing it with a particle-free solution results in a decrease in the suspended solids concentration. This can produce an artifactual hysteresis. Mixing at a faster speed (150 cycles/min) and centrifuging at a slower speed (514g) than was used for the sorption and desorption studies (50 rpm-6315g) helps to increase the washing efficiency (Gschwend and Wu, 1985).

The low solubility and high sorption potential of PCP presented a problem in using a broad range of different initial concentrations (C_o). A low initial PCP concentration would leave an undetectable amount of PCP in solution. The result is a very narrow working PCP concentration range.

One way to circumvent this problem is to use a lower solids mass. However, desorption studies require that enough PCP be sorbed in order to detect the desorption of the compound. Therefore, it would be necessary to vary our solids mass between experiments. Since the soil was washed, the solids concentration effect may not be a problem. However, the decrease in K_p with increasing solids mass cannot always be accounted for by the solids concentration effect (DiVincenzo and Dentel, 1996). For this reason we chose to use the multiple spiking procedure rather than vary our solids mass. Furthermore, this might be indicative of a contaminated site which has repeated recharge of the pollutant.

Loss of PCP over the course of the experiments was negligible, with the controls containing 99% of the original PCP concentration. Mixing beyond the apparent equilibrium (2 days) had no effect on sorption.

6.4.1 Concentration Gradient

The occurrence of a slow sorption stage is not surprising as it has been demonstrated repeatedly in the literature for a host of HOCs (Ball and Roberts, 1991a; Brusseau and Rao, 1991; Gilchrist et al., 1993; Karickhoff and Morris, 1985; Kookana et al., 1992). However, there is a deficiency in long-term sorption kinetic data. PCP in the protonated form would be expected to exhibit the same behavior as HNOCs. Diffusion into organic matter (Brusseau et al., 1991; Brusseau and Rao, 1989) or intraparticle diffusion (Ball and Roberts, 1991b; McCall and Agin, 1985; Steinberg et al., 1987) have been the most common postulated mechanisms for the slow sorption stage. Since diffusion is in part controlled by a concentration gradient one would expect the slow sorption stage to be concentration dependent.

The objective of the experiment was to repeat the sorption kinetics at a much higher PCP concentration. Due to the solubility limitations of PCP it was necessary to utilize the dual spike methodology discussed in the Methods section. After 3 days of equilibration the samples were spiked a second time with PCP. The concentration in the aqueous phase was raised close to the initial concentration of the first spike, resulting in a total PCP concentration (C_T) of 10.0 mg/L. The original sorption kinetic studies

(Figure 4.2) used an initial concentration of 5.1 mg/L. The kinetics for both spikes were followed by sampling, the same as for the original kinetics. The results are shown in Figure 6.1. The set of data points closest to the y-axis represents the kinetics of the initial spike. At a time of 3 days the remaining samples were removed from the shaker and spiked again. This is represented by a dashed line on the figure. The aqueous concentration of the remaining samples at 3 days was now 5.56 mg/L. The kinetics of these samples were then followed and are represented by the second set of data in Figure 6.1.

The initial spike followed closely the original kinetics (Figure 4.2) with 78% of the PCP sorbed at the time of apparent equilibrium. The calculated K_p for the five replicates at 3 days was 88 L/kg. This agreed with the original kinetics (Figure 4.2) whose K_p was 90 L/kg. The pooled standard deviation of these 12 samples (7 from original kinetics and 5 from first spike of dual spike kinetics) was 4.55 and therefore the difference in K_p values was not significant at 95% confidence (see Equations 3.4 and 3.5). This demonstrated the reproducibility of our system. It can now be assumed that if the samples of the first spike of the dual spike kinetics were sorbed for longer times, the results would be identical to the results of Figure 4.2.

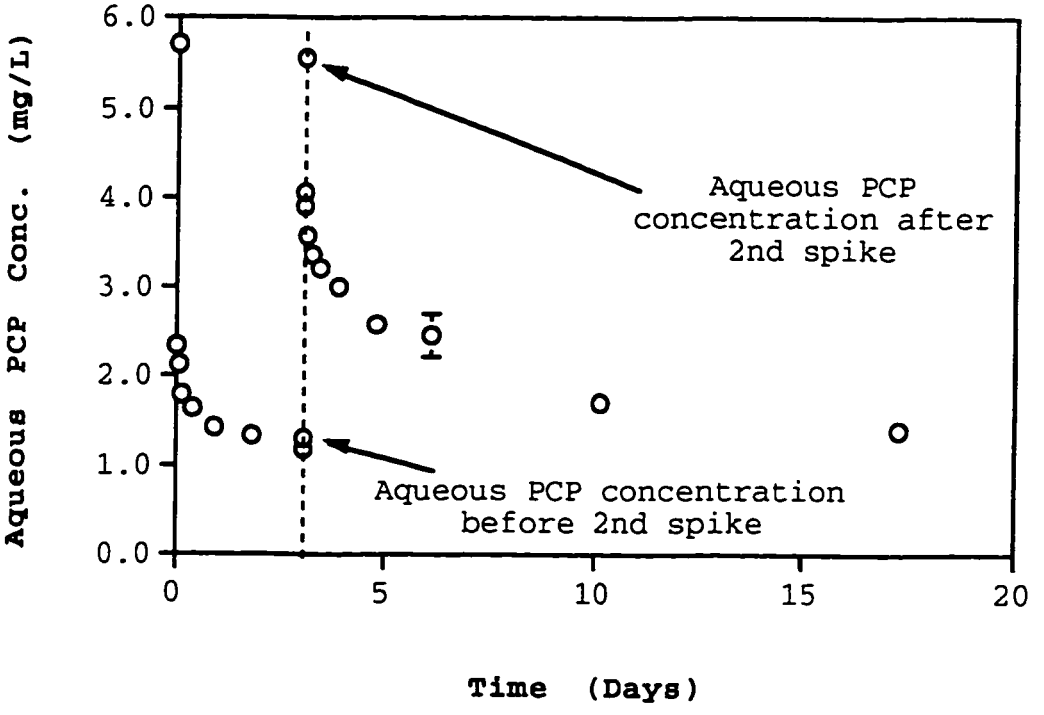


Figure 6.1 **Dual spike kinetics of PCP on soil.** The data closest to the y-axis represent samples collected after the first spike. At 3 days the remaining samples were removed from the incubator and spiked with additional PCP. This is represented by the dashed line. The second set of data represents the kinetics after the second spike. The first data point of the second spike represents the initial solution concentration of PCP for the second set of samples. The K_p for the samples at 3 days of the first spike is 88 L/kg. There are 5 replicates at 3 days with a standard deviation for K_p of 5.00.

Comparing the second spike (Figure 6.1) to the original kinetics (Figure 4.2) the apparent equilibrium plateau is much less evident for the second spike. The data point which has the error bar (based on standard deviation of 6 replicates) is at 6 days or 3 days from the time of the second spike. The preceding point is within one standard deviation of the replicates and cannot be considered significantly different. This appears to be the apparent equilibrium plateau previously identified. It was reached in roughly the same amount of time (42 h) as the original kinetics and the first spike of the dual spike kinetics. However, the slow sorption stage is much more pronounced.

A significant change in the aqueous phase PCP concentration was observed at the second data point beyond the apparent equilibrium. This is approximately 7 days after the second spike and roughly 10 days after the first spike. Furthermore, the K_p at the apparent equilibrium is depressed to 78 L/kg. This is significantly different than that calculated for both the first spike and the original kinetics (95% confidence) and is similar to what was observed for the isotherm studies.

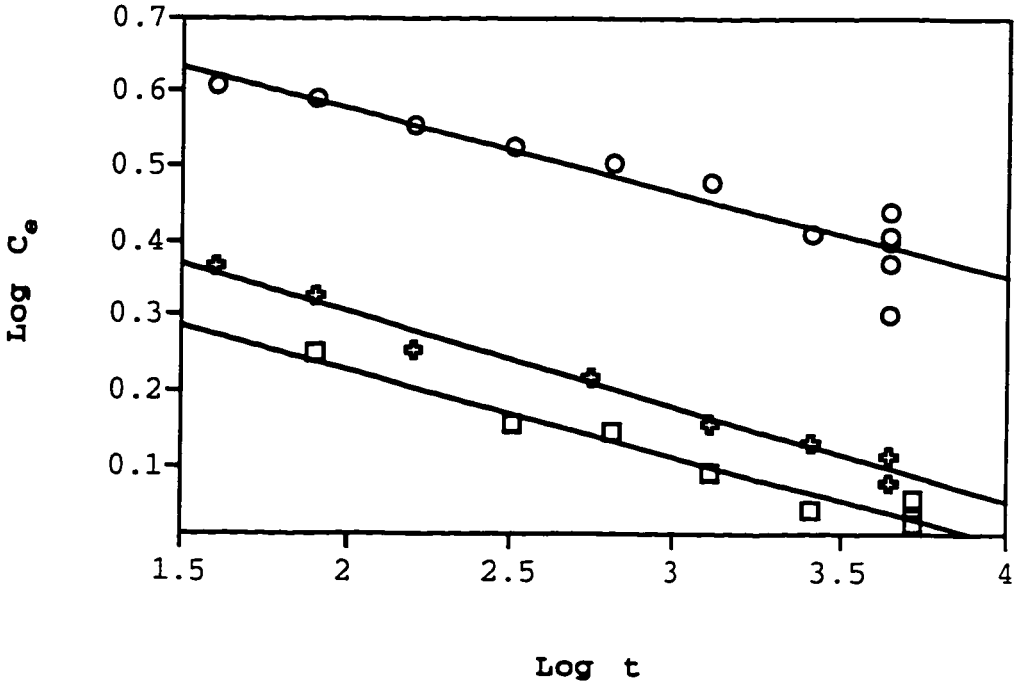
All three kinetic curves were linearized on a log log plot (Figure 6.2) in order to fit them to a simple power function model:

$$C_e = At^b \qquad (6.1)$$

where t is time in days, A and b are fitting parameters and C_e is as defined previously. This model is purely empirical and has no mechanistic basis but serves to give a qualitative description of the data. Attempts were also made to fit the data to first-and second-order rate equations. This was unsuccessful.

When only the data up to and including the apparent equilibrium was included (excluding the zero time point) in the linear plots, all slopes were identical within 90% confidence. The r^2 values for the original kinetics and the first spike of the dual kinetics were 0.95 and 0.98, respectively. Due to the compounded error of the dual spike method the second spike had a slightly lower r^2, 0.87. These results suggest that the initial rapid partitioning kinetics are independent of the initial PCP concentration or the presence of previously sorbed PCP.

When the data beyond the apparent equilibrium were included in the fits for the original and second spike kinetics, major differences were observed. The original kinetics fit the later data very well and gave an equation nearly identical to the equation including only the data up to the point of apparent equilibrium. However, the second spike kinetics did not fit the later data well.



□	Original Kinetics	y = -0.116x + 0.462	r^2 = 0.947
✤	1st Spike	y = -0.127x + 0.560	r^2 = 0.976
○	2nd Spike	y = -0.114x + 0.806	r^2 = 0.873

Figure 6.2 **Linearized kinetic plots.** The original kinetics and the dual spike kinetics were linearized to fit to the power function model (Equation 6.1).

The model fits (Equation 6.1) for the apparent equilibrium data along with all the data for the original (Figure 4.2) and the second spike kinetics are shown in Figure 6.3. The concentrations are the total concentrations of PCP. The original kinetics were added in one spike and the dual spike kinetics were added in two spikes. The initial concentration at time zero for the dual spike kinetics represents the concentration in the aqueous phase immediately after the second spike, not the total concentration.

The second spike data were time normalized and shifted to the y-axis, for comparison purposes. The low concentration kinetics (original) were described by the model exceptionally well out to 28 days. In fact, the data out to 70 days (not shown) were also described very well with the power function model. The high concentration kinetics (2nd spike) could not be described by the power function model beyond the point of apparent equilibrium.

Figure 6.4 shows the above data converted into changes in the partition coefficient with time. As diffusion models would predict, the increase in K_p is much greater at higher PCP concentrations. Diffusion is driven by a concentration gradient and therefore higher concentrations will result in a greater rate of diffusion. Also evident is the depression in the K_p at approximately 3

days (apparent equilibrium plateau) for the higher concentration of PCP. This is similar to the effect seen for the isotherm experiments and will be discussed further below.

One concern was the dual spike methodology used for the higher concentration kinetics. These results were compared to the original kinetics which were only spiked once. Perhaps the differences in the results were a result of the different methodologies. In order to address this an experiment was designed to compare the increase in K_p for three different concentrations. The multiple spiking methodology was used for all three concentration treatments (see Methods). Three different stock solutions were used so that the spiking volumes, number of spikes and time of spikes would all be identical. The results are shown in Figure 6.5.

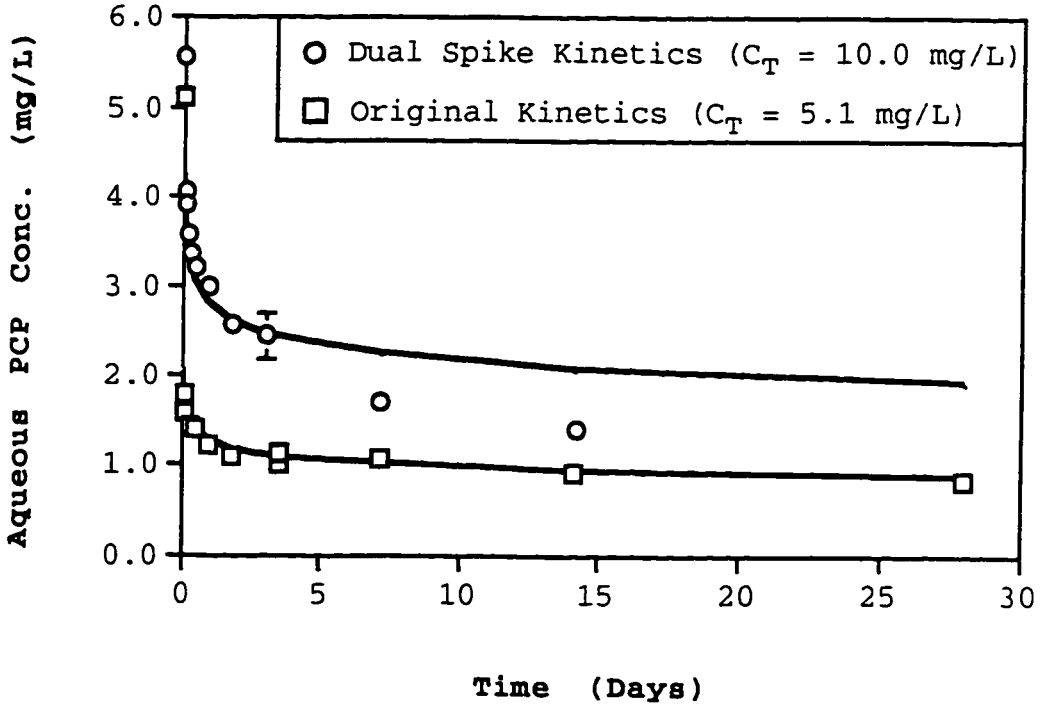


Figure 6.3 Power function model (Equation 6.1) kinetic fits. The data were linearized on log-log plots and fit only up to the apparent equilibrium. The onset of the slow sorption kinetics is much more abrupt for the higher concentration (dual spike) kinetics.

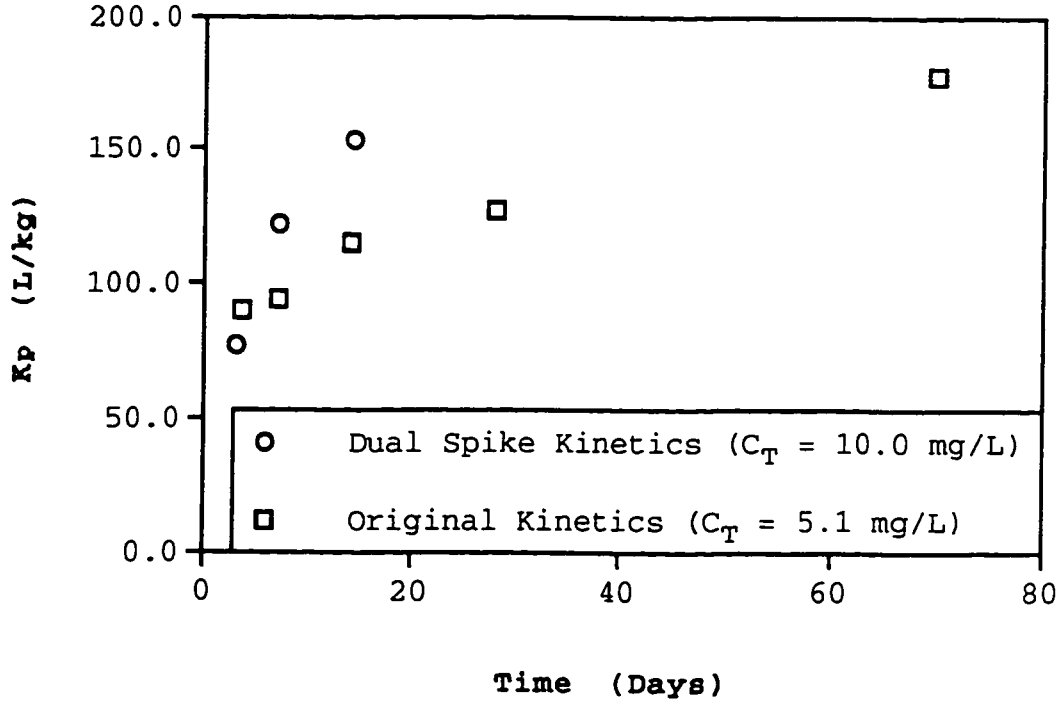


Figure 6.4 **Change in K_p with time.** The results from Figure 6.3 were converted into partition coefficients. The higher concentration kinetics show a much greater increase in K_p with time. The K_p at the apparent equilibrium, for the higher concentration samples, is depressed down to 78 L/kg.

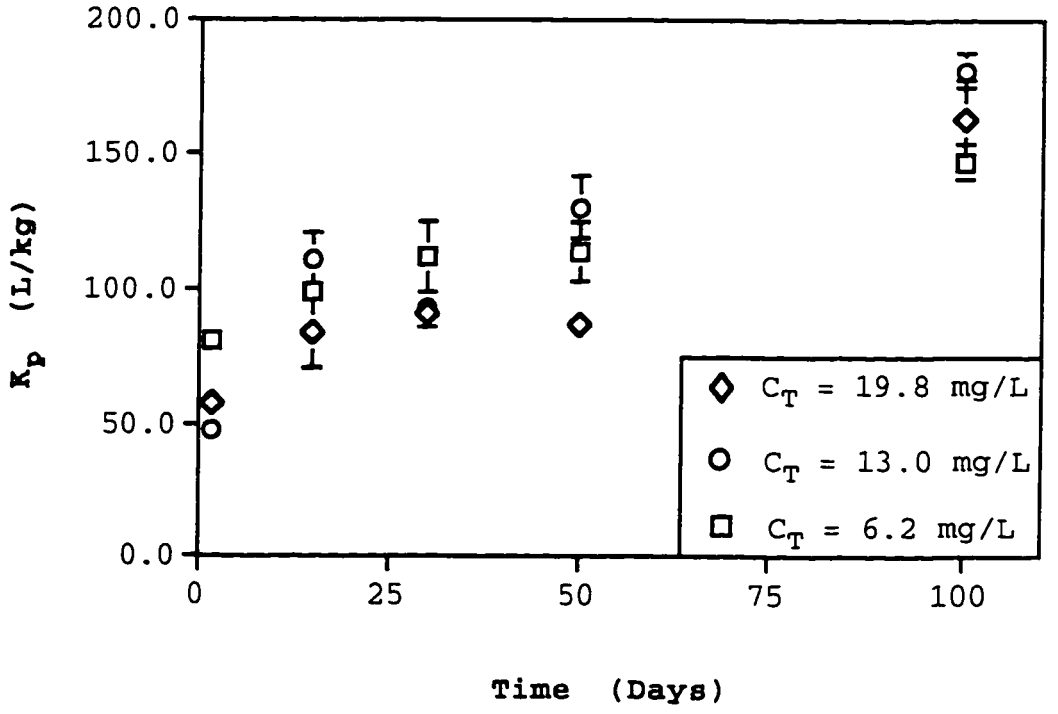


Figure 6.5 **Effect of PCP concentration on the slow sorption kinetics.** The multiple spiking methodology described in the Methods was used. Each concentration had 3-5 replicates at each time. The averages with error bars for the standard deviation are shown.

It was evident from these results that there was not a simple correlation between increasing concentration and the rate of increase in K_p. The intermediate concentration (13.0 mg/L) showed the greatest rate of increase in K_p between the apparent equilibrium (2 days) and 15 days ($\approx$ 4.8 K_p/day). It also had the largest K_p overall at 15 days, 50 days, and 100 days. The depression seen in the K_p at 30 days was both surprising and unexplainable.

However, when the dual spike kinetics (Figure 6.1) were followed for longer times, the aqueous PCP concentration increased between 14 and 28 days. This is analogous to the K_p decreasing between 15 and 30 days for the intermediate concentration in Figure 6.5. The total concentration (C_T) of PCP in the dual spike study was 10.0 mg/L. This is comparable to the intermediate concentration (13.0 mg/L) in Figure 6.5.

All the data in Figure 6.5 followed the same general trend. There appeared to be a leveling off between 30 and 50 days, but then there was again an increase up to 100 days. This increase between 50 and 100 days may be attributable to another possible phenomenon. The effectiveness of the bacteriological inhibitor (NaN_3) was not tested as a function of time. It is possible that at long time periods it is no longer effective and the

increase in K_p might be attributable to degradation. Furthermore, with diffusion to a localized region, it is possible that the solubility is being exceeded and precipitation is occurring.

When the multiple spiking samples with the lowest concentration are compared to the original kinetics (Figure 4.2) the only effect appears to be a slight diffusing of the PCP front. That is, the steepness of the kinetic curve was lessened (rate of increase in K_p was not as rapid). Otherwise, the trend of the kinetic curve is roughly the same. The dual spike kinetics did not show this effect but they were spiked three days apart as compared to every two hours.

The highest concentration samples in Figure 6.5 (19.8 mg/L) had the lowest K_p at all time intervals except at the apparent equilibrium (99% C.I.). This suggested that more than just diffusion was responsible for the increase in K_p during the slow sorption stage. There could be balancing factors in effect. For instance, the samples with the highest concentration had a lower K_p due to a decrease in the polarity of the aqueous phase which resulted in less favorable sorption. This could explain the depression, observed here and previously, in the K_p at the apparent equilibrium for the higher concentration samples. Another possibility was that we were seeing the

saturation of site 1 if one considered a simple 2-site model. However, if partitioning was the mechanism of sorption on site 1 this seemed less likely. Furthermore, this can not account for the intermediate concentration having the greater K_p at most of the sampling times.

One further explanation was that the PCP was inducing the release of soil organics and/or colloids. Galil and Novak (Galil and Novak, 1995) showed that as the initial PCP concentration is increased the amount of total organic carbon (TOC) in solution increased. This would decrease the K_p by increasing the amount of PCP associated with TOC in solution. However, this effect was minimal at pH values below 5.5. Still, the highest concentration used in their experiments was 10 mg/L.

Collective results from several different experiments are shown in Table 6.1. The K_p values are the values after 2-4 days of equilibration (apparent equilibrium plateau). The trend of decreasing K_p with increasing C_T is very evident. The standard deviations for each set of data are also shown. The data are also graphed in Figure 6.6. There is a good linear correlation (r^2 = 0.913) for all data except for the C_T = 13.0 mg/L sample. These data were not fit to the regression. These were also the same concentration data in Figure 6.5 that showed the

largest K_p at 15 days of sorption and the depression at 30 days of sorption.

The data for the 2-day sorption isotherm are also shown using the average concentration (14.0 mg/L) of the entire isotherm. It falls within the same region as the C_T = 13.0 mg/L samples. This might explain why the K_p for the 2-day isotherm was so depressed.

The trend beyond C_T = 10 mg/L is unclear. A more realistic explanation might be that beyond C_T = 10 mg/L the effect is no longer seen. This would explain the apparent outlyers at C_T = 13.0 mg/L and the isotherm point.

Table 6.1. **The Effect of Total PCP Concentration (C_T) on the Apparent Equilibrium Partition Coefficient ($K_{p(apparent)}$).**

C_T (mg/L)	$K_{p(apparent)}$[a]	Standard Deviation
5.10	90.51	7.60
5.70	88.27	5.00
6.20	80.87	5.43
6.75	84.93	7.05
10.00	78.06	11.83
13.00	47.98	3.26
14.00[b]	55.64	6.37
19.80	57.28	1.04
19.80	54.22	1.80
19.80	66.84	9.33
21.40	60.78	4.93

[a] The partition coefficient is the K_p (L/kg) at 2-4 days of equilibration (apparent equilibrium plateau). [b] This is the average concentration for all the isotherm tubes for 2-days residence time.

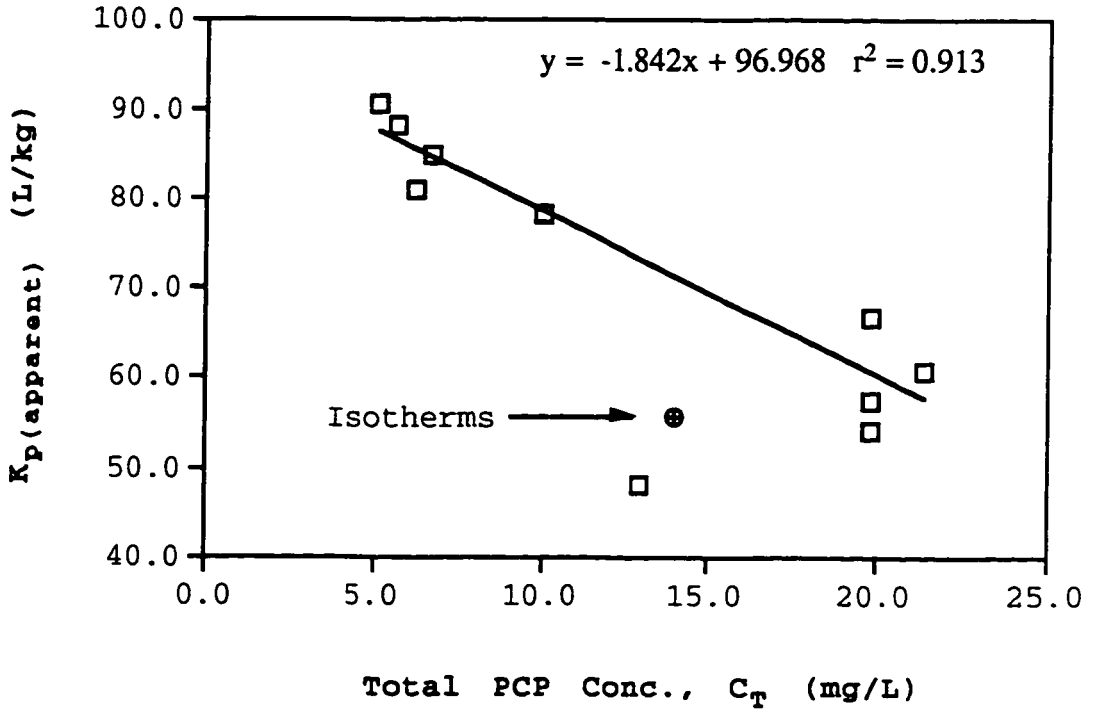


Figure 6.6 **Effect of total PCP concentration on the apparent equilibrium K_p.** Graphical depiction of data in Table 6.1. The data at 13.0 mg/L were not included in the regression. The average concentration (14.0 mg/L) for the 2-day sorption isotherm is also included.

In summary, it appears that as the concentration of PCP is increased the K_p at the apparent equilibrium decreases. However, as the concentration increases there is a greater rate of increase in the K_p beyond the apparent equilibrium (slow sorption stage). The result is K_p being greater at some time beyond the apparent equilibrium even though the K_p at the apparent equilibrium is less. This trend reverses at some point beyond C_T = 13.0 mg/L. At these higher concentrations, the rate of increase in K_p is comparable to the rate at lower concentrations.

The preceding results might explain why the isotherm at 21 days was still linear. If the K_p increases faster for higher concentration samples this would result in a nonlinear isotherm for longer incubated samples. However, the trend is not consistent. Some of the higher concentration samples increase at a slower rate than the intermediate samples. There might be a balancing effect on the isotherm, decrease in K_p due to conentration effect (Figure 6.6) and increase in K_p due to greater rate of diffusion (Figure 6.5), and this might in fact account for some of the scattering of the data. Perhaps longer incubation times would result in nonlinear isotherms.

Additionally, the two day isotherm would be expected to be nonlinear with downward curvature. This is a result of the higher concentration samples having a lower

K_p at the 2-day apparent equilibrium. However, all but the lowest concentration point on the isotherm had PCP concentrations greater than 10.0 mg/L. In this region there is no clear correlation of decreasing K_p with increasing C_T (Figure 6.6).

6.4.2 Desorption Studies

The *desorption kinetics* of PCP followed the same general trend as the sorption kinetics (Figure 6.7). These samples were sorbed for 20 days with an initial PCP concentration of 6.12 mg/L. The first sampling point (40 min) represents 74% of the total desorption. The apparent equilibrium was reached in roughly the same time as it was reached for the sorption kinetics (42 h). The equilibrium concentration reached was what would be predicted based on the sorption K_p at 20 days. No slow desorption stage was detectable, even for 20 days of desorption (results not shown), due to the small concentration change between the first samples and the final samples. Only 15% of the total amount sorbed (123 mg/kg) was desorbed. Any change in the solution concentration would not be detectable by our analysis.

In order to look closer at the desorption kinetics and attempt to identify a slow desorption stage beyond 42 h (≈ 2 days), it was necessary to increase the sorbed

concentration of PCP. This was accomplished by repeatedly spiking the sorption experiment with PCP (see Methods section).

The results clearly show desorption beyond the 2-day sampling time (Figure 6.8). These samples were sorbed for 12 days. Most of the desorption occurs within 2 days and then there is continued desorption up to 8 days. The aqueous concentration reached is the concentration that would be predicted based on the sorption equilibrium. That is, there was no hysteresis. However, it is important to note that the residence time of PCP on the soil was only 12 days. Longer sorption times might have resulted in hysteresis.

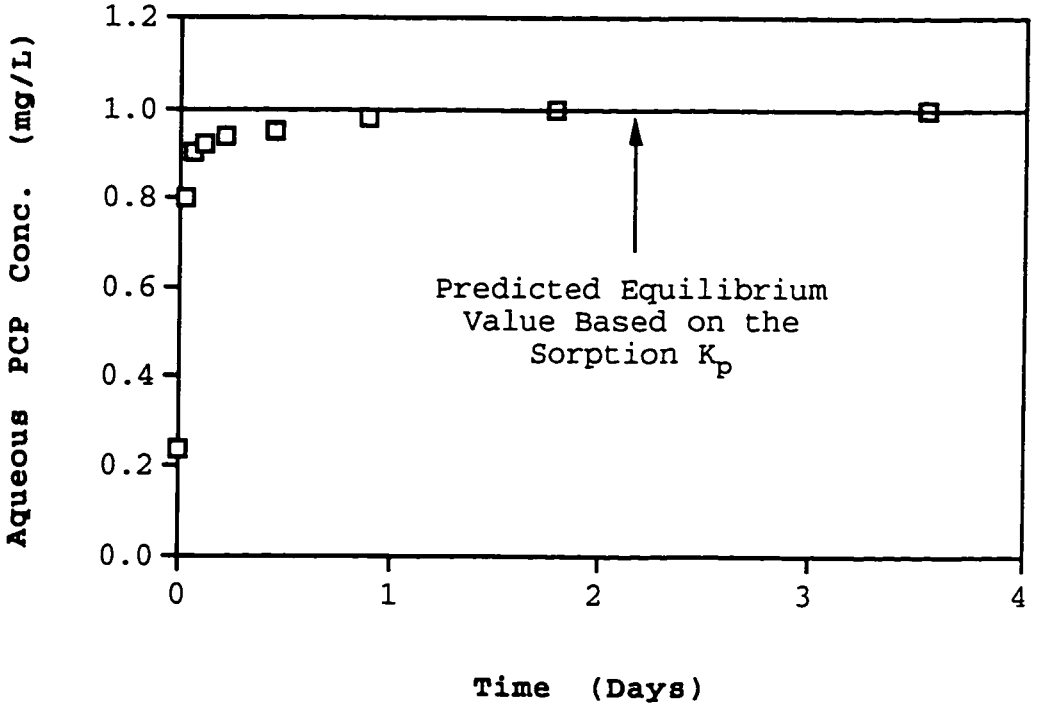


Figure 6.7 **Desorption kinetics of PCP from soil.** The samples were sorbed for 20 days, centrifuged and then 80% of the solution (20 ml) was replaced with PCP-free solution. The pH was 4.1 ± 0.1. The equilibrium aqueous PCP concentration was what would be predicted based on the sorption K_p at 20 days.

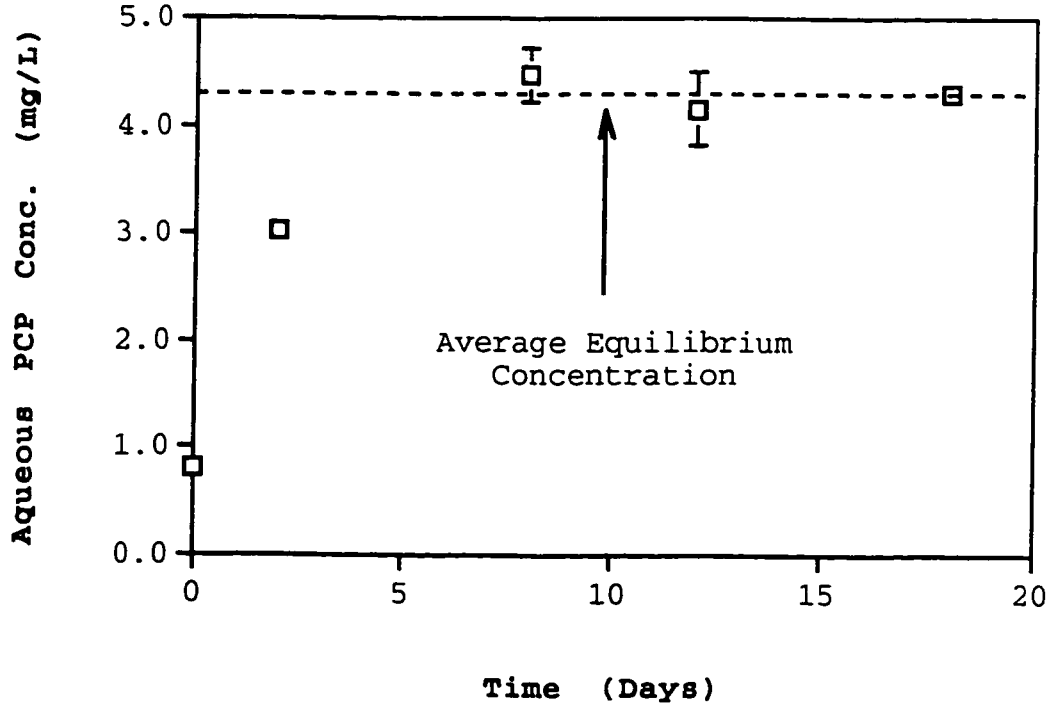


Figure 6.8 **Desorption kinetics of an elevated sorbed PCP concentration.** The samples were sorbed for 12 days and then 80% of the solution (20 ml) was replaced with PCP-free solution. The pH was 4.1 ± 0.1. There were five replicates for each time. The average concentrations are plotted with error bars for the standard deviation. The average equilibrium concentration is the average for all 8, 12, and 18 day samples.

Hysteresis can be defined as a lag in response exhibited by a system in reacting to changes in forces or chemical conditions. In the context of this system one is referring to the distribution of PCP between the solid and solution phases. PCP is allowed to sorb to the solid phase until equilibrium or an apparent (pseudo) equilibrium has been achieved. The K_p is a measure of the distribution of the PCP between the two phases at equilibrium. The chemical conditions are altered by removing a portion of the bulk solution containing PCP and replacing it with PCP-free solution. The system responds by adjusting the distribution of PCP between the two phases (desorption).

If the K_p for the desorption is the same as for the sorption then there is no hysteresis. If it is greater than the sorption K_p, then there is hysteresis. Assuming the hysteresis is not an artifact of the lab technique, the lag in response may have two probable causes. One possibility is slow desorption kinetics resulting from the slow sorption kinetics. That is, the PCP needs time to diffuse out of the soil matrix into the bulk solution. The other possibility is that the PCP has become strongly sorbed to the surface; such that, it is resistant to desorption.

This is what was seen in Table 5.1. The percent desorbed was the hysteresis reported as a whole number.

The hysteresis of the protonated species of PCP (pH 4.1) disappeared when the desorption times approached the sorption times, suggesting that the hysteresis was kinetically controlled. On the other hand the ionized species (pH 7.9) showed no reversal in the hysteresis, suggesting that it was more strongly bound to the surface.

At this point two types of hysteresis will be defined. Apparent hysteresis is defined as follows:

$$\frac{K_{p(apparent)}}{K_{p(desorbed)}} \qquad (6.2)$$

where $K_{p(apparent)}$ is the sorption partition coefficient at the apparent equilibrium and $K_{p(desorbed)}$ is the partition coefficient for the desorption. This would be analogous to measuring the hysteresis of a field contaminated soil, whose initial PCP concentration and actual K_p is unknown. The apparent equilibrium (2 days) of the laboratory measured K_p is assumed to be the true equilibrium.

The second type of hysteresis is probable hysteresis. This is defined as follows:

$$\frac{K_{p(actual)}}{K_{p(desorbed)}} \qquad (6.3)$$

where $K_{p(actual)}$ is the true partition coefficient at a given sorption time. This takes into account the slow sorption stage.

The following experiments were designed to examine the hysteresis of the protonated PCP more closely. Longer sorption-desorption times were employed in addition to varying PCP concentrations.

The bar graphs in Figure 6.9 show the results of a two day desorption study at pH 4.1 for three different concentrations (6.2, 13.0, 19.8 mg/L). There were five replicates for each time and treatment. All three treatments were treated identically with respect to the number, times, and volumes of PCP spikes. This was accomplished by using three different stock solutions. The samples were sorbed for varying amounts of time.

The y-axis in Figure 6.9a represents the K_p at the apparent equilibrium (2 days) divided by the subsequent desorption K_p. Values of one indicate desorption to the point of equilibrium predicted by the apparent sorption K_p. That is, the sorption K_p is equal to the desorption K_p. Values less than one can be considered hysteretic. Propagation of error results in significance (± 2 standard deviations, 95% confidence) occurring at ± 0.14. Therefore, values of 0.86 or greater are non-hysteretic.

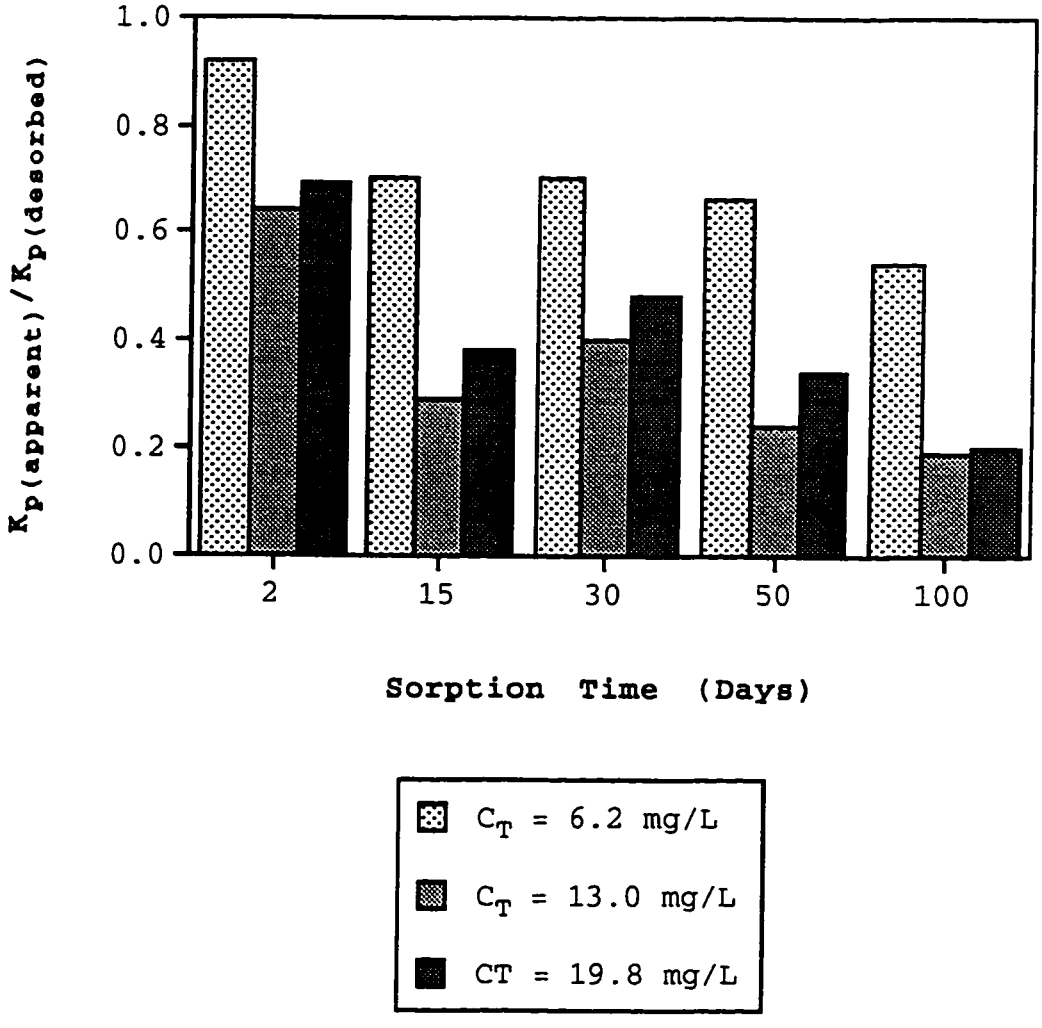


Figure 6.9a Apparent hysteresis for 2-day desorption of PCP from soil. Each bar represents the average of 5 replicates. pH = 4.1 ± 0.1.

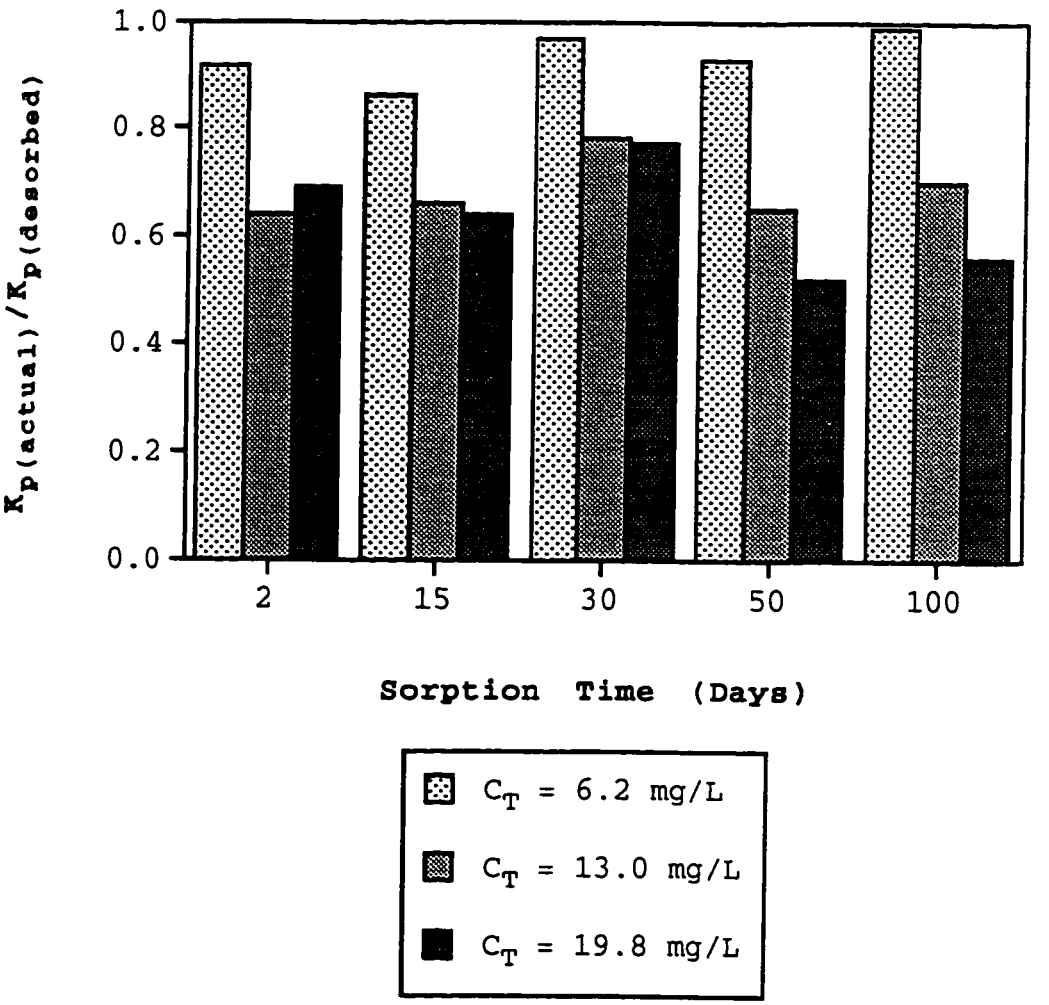


Figure 6.9b Probable hysteresis for 2-day desorption of PCP from soil. Each bar represents the average of 5 replicates. pH = 4.1 ± 0.1.

The only samples which were nonhysteretic were the 2 day samples for the lowest concentration (6.2 mg/L). There was a clear concentration effect as was seen for the sorption studies (Figure 6.5). At each time interval the hysteresis for the 6.2 mg/L samples was the least and the intermediate concentration (13.0 mg/L) showed the most hysteresis. Again, as with the sorption, there was no clear correlation between concentration and desorption.

There was also a slight decrease in the hysteresis (increase in ratio) from 15 to 30 days. This represents the same points in Figure 6.5 in which there was a drop in the K_p. All three concentrations show this effect and it is outside of two standard deviations from what can be considered a linear drop from 2 to 100 days. This might suggest that the effect is real and not an artifact. Comparing Figure 6.5, 2 to 15 days represents the region in which the rate of change in K_p is the greatest. Therefore, initiating desorption at time in the sorption profile when the K_p is rapidly changing (15 days) might induce more hysteresis.

Figure 6.9b shows the results for the probable hysteresis values. Again there was a concentration dependence. Here we see that there was absolutely no hysteresis for the low concentration samples (> 0.86). The hysteresis was also reduced for the other samples.

However, now there appears to be a direct correlation between concentration and hysteresis. The higher the concentration of PCP, the greater the hysteresis. This is true at all sampling times except at 2 days.

This would suggest that the hysteresis was at least partially controlled by the sorption kinetics. When the slow increase in K_p is accounted for, much of the hysteresis disappears. The extent of hysteresis will probably depend on where the true sorption equilibrium lies. If the onset of desorption was initiated at a time in the sorption profile when the K_p was rapidly changing, then substantial hysteresis can be expected. This is what was seen at 15 days for the apparent hysteresis. However, this effect disappeared for the probable hysteresis. Suggesting that when the actual sorption K_p is known and accounted for then much of the hysteresis disappears.

This importance of the sorption kinetics is supported by comparing Figure 6.5 and 6.9. The intermediate concentration shows the greatest rate of increase in K_p, and as a result the most apparent hysteresis. Once the increase in K_p is accounted for (probable hysteresis) the highest concentration samples show the most hysteresis. This might be a result of the concentration gradient. Since true equilibrium has not been reached, the gradient is still driving inward. The

higher concentration samples have a larger gradient inward, and therefore might exhibit a greater resistance to desorption.

A field contaminated soil that shows substantial hysteresis might simply be the result of not knowing the initial concentration and the true sorption K_p. An additional concern is not allowing sufficient time for the contaminant to diffuse outward. This will be addressed below (Figure 6.10).

Another apparent trend is the increase in hysteresis with increasing residence time. This is a common occurrence and has been reported extensively (Di Toro and Horzempa, 1982; Hatzinger and Alexander, 1995; Horzempa and Di Toro, 1983; Kan et al., 1994; Pignatello, 1990; Pignatello et al., 1993; Pignatello and Huang, 1991). However it does not imply that the PCP is irreversibly bound. It is important to point out that the samples were only desorbed for two days. Extended desorption times might result in a disappearance of the hysteresis. The bar graphs in Figure 6.10 address this concern.

The bar graphs in Figure 6.10 show the results of an extended desorption study at pH 4.1 for three different concentrations (6.2, 13.0, 19.8 mg/L) All samples were treated identical to that described above for the 2-day desorption study. The samples were sorbed for varying

amounts of time and then desorbed for the same amount of time as in the sorption step.

The intentions were to demonstrate whether the hysteresis could be accounted for based on desorption time. As mentioned above, these samples showed increasing apparent hysteresis with increasing sorption time. However, the desorption was only carried out for the apparent equilibrium time (2 days). Diffusion of the PCP outward may require times approaching the sorption time.

If this is the case then the hysteresis is simply a kinetic phenomenon. Values of one indicate desorption to the point of equilibrium predicted by the apparent sorption K_p. Values less than one can be considered hysteretic. Propagation of error results in significance (± 2 standard deviations, 95% confidence) occurring at ± 0.15. Therefore, values of 0.85 or greater are non-hysteretic.

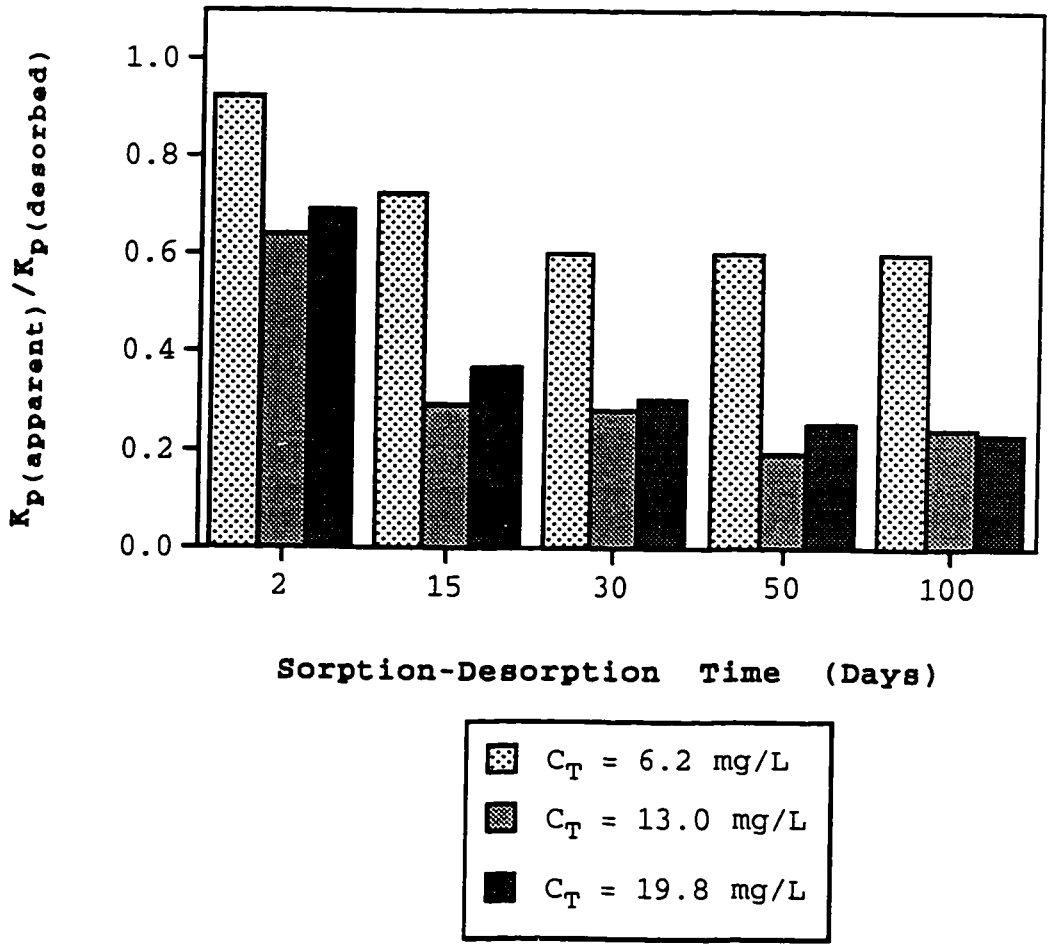


Figure 6.10a Apparent hysteresis for extended desorption of PCP from soil. Each bar represents the average of 5 replicates. pH = 4.1 ± 0.1.

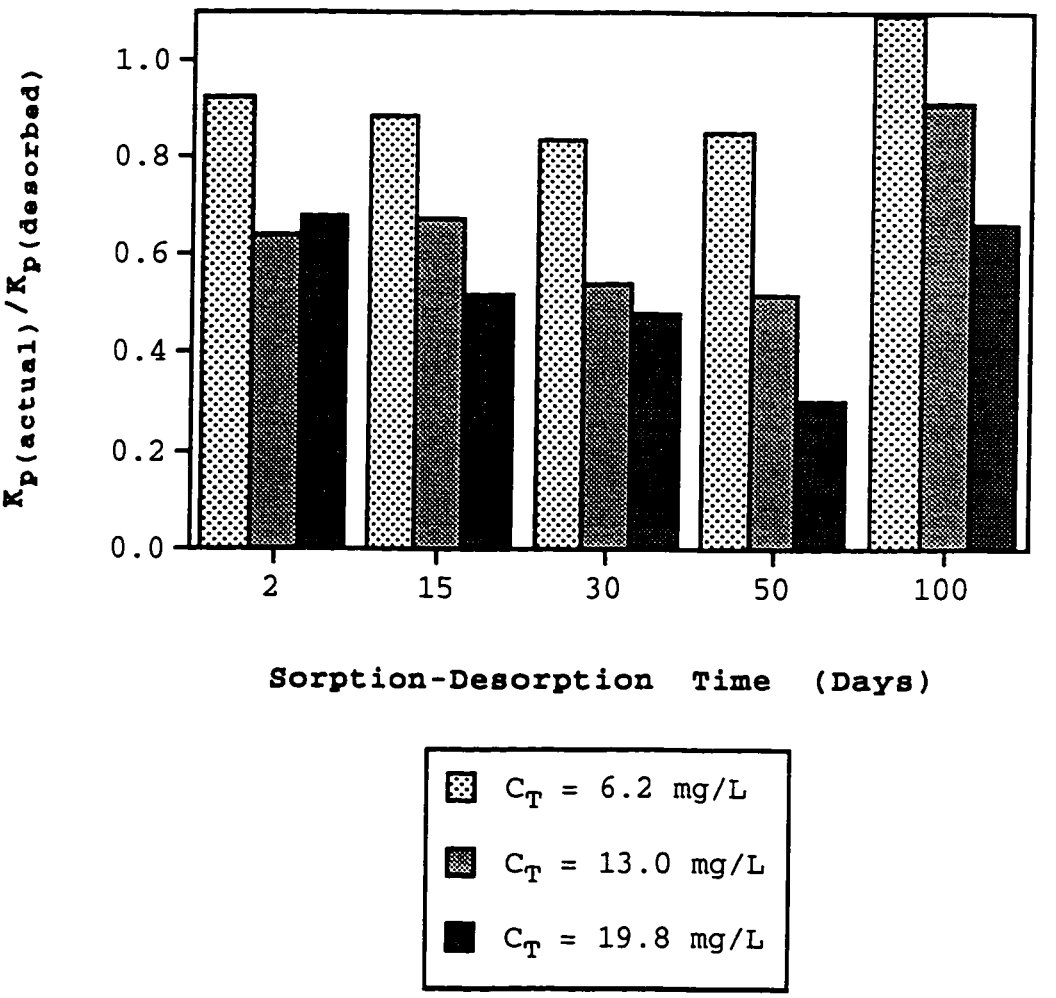


Figure 6.10b Probable hysteresis for extended desorption of PCP from soil. Each bar represents the average of 5 replicates. pH = 4.1 ± 0.1.

Again the intermediate concentration showed the most apparent hysteresis (Figure 6.10a). There is also the general trend of increasing hysteresis with increasing sorption-desorption time. However, there is no significant change beyond 30 days. This might suggest that any additional sorption after a given time period is easily removed and no more hysteresis results. Since there is still hysteresis even with long desorption times, one can conclude that either the desorption kinetics are slower than the sorption kinetics, or there is a resistant fraction forming, or both. One might hypothesize that there are a finite number of sites which bind PCP irreversibly and the remaining PCP simply needs time to diffuse outward.

All three treatments showed the same general trend in which probable hysteresis increased up to 30-50 days and then decreased from 50-100 days (Figure 6.10b). The lowest concentration sample (6.2 mg/L) showed no significant probable hysteresis at any sorption-desorption time (Figure 6.10b). This suggests that when the slow sorption kinetics are accounted for there is no hysteresis. The intermediate concentration (13.0 mg/L) showed no hysteresis at 100 days but the highest concentration (19.8 mg/L) still showed some hysteresis. This might suggest that the hysteresis is concentration dependent. Assuming the mechanism is the

same at any concentration, we would expect the highest concentration sample to eventually show values of one for the probable hysteresis. As mentioned previously, true equilibrium has not been reached. The higher concentration samples have a larger inward gradient, and therefore might exhibit a greater resistance to desorption and consequently more hysteresis.

The sorption profile changes with concentration. The point at which desorption is initiated could determine the extent of hysteresis. However, desorption is only carried out twice. Additional sequential desorptions could disclose a resistant fraction. Furthermore, in addition to slow sorption, field soil experiences an "aging" which includes wetting and drying of the soil resulting in cracking and restructuring of soil pores. Entrapment in soil micropores may be much more important for a field soil.

The fact that apparent hysteresis values do not converge to one (Figure 6.10a) would suggest that either there is a resistant fraction forming, the desorption kinetics are slower than the sorption kinetics, or desorption is initiated at a time in the sorption profile in which PCP is still readily sorbing. After a desorption time equal to that of the sorption time, the K_p for all concentrations was still greater than the apparent sorption

K_p. To address this concern we decided to conduct some mass balances and attempt to determine the size of the resistant fraction.

6.4.3 Mass Balances

Mass balances were conducted on the 100 day sorbed-desorbed samples using hot methanol extracts (see Methods). The results are shown in Table 6.2. Although there was a large range of recovery the average recovery for the two higher masses was 92 and 94%. Some of the error can be attributed to repeated sampling, for analysis purposes, of the solution phase and removal and addition of solution phases for desorption.

Table 6.2. **Mass Balances.** Pentachlorophenol (PCP) recovered from soil by hot methanol extracts for three different total PCP masses (M_T)[a].

	% Recovered		
	M_T = 402.8 µg	M_T = 263.1 µg	M_T = 116.4 µg
	94.0	82.5	86.6
	87.4	107.8	73.8
	103.2	81.1	78.1
	86.0	105.8	76.0
	88.3	-	65.3
Average ± S.D.[b]	92 ± 7	94 ± 14	76 ± 8
Resistant Fraction (µg)[c]	32.2	15.8	27.9

[a] PCP recovered from soil after 100 days of sorption and 100 days of desorption. See Experimental Procedures for the extraction method. [b] Average of the 4-5 replicates ± one standard deviation. [c] Determined based on M_T - average recovery.

Assuming what remains on the soil is the resistant fraction, then the average concentration of the resistant fraction might be considered to be somewhere between the resistant fractions calculated for the high and intermediate masses. These were 32.2 and 15.8 µg, respectively. The low recovery of the 116.4 µg treatment can be accounted for based on the size of the resistant fraction. It falls within the range of the other two masses (27.9 µg). However, this represents a much larger fraction of the total PCP mass and therefore the recovery is correspondingly lower.

The size of these resistant fractions can now be compared to the size of the resistant (hysteretic) fractions for the apparent hysteresis samples in Figure 6.10a. If they are the same than we can say that the hysteresis is due to the formation of a resistant fraction.

This was accomplished by comparing the sorbed fraction after desorption to the predicted sorbed fraction based on the sorption K_p. This can be considered the resistant fraction for the hysteresis samples. Equations 6.13 and 6.14 below can be used for this purpose.

Accounting for the solution removal, the initial concentration of PCP for the 116.4 µg samples was 5.32 mg/L. From this C_e and q_e can be calculated yielding a sorbed fraction of 101.5 µg. The actual sorbed average

value is 112.25 ± 1.4, where 1.4 is the standard deviation. The difference between these two (10.75 μg) is the resistant fraction. Similar calculations were carried out for the other two masses. The calculated values for the intermediate and upper mass samples were 189.75 and 302.75 μg, respectively. The actual sorbed values were 256.75 ± 3.01 and 394.75 ± 3.58, respectively. The mass balance resistant fractions are substantially less for all masses (> 10 standard deviations).

This would suggest that the kinetics are also important and not just the formation of resistant fractions. It also implies that a true chemical equilibrium may never have been established. Desorption initiated before sorption equilibrium is reached will yield hysteretic values. Furthermore, contaminants that exhibit hysteresis in the field may only be partially due to resistant fractions, and may actually be diffusing out of the soil matrix slowly over time.

One cause for concern was the speciation of PCP at a pH of 4.1. A substantial amount of PCP is in the ionized form. Results presented so far suggest that the ionized PCP might be more specifically adsorbed and more resistant to desorption than the protonated PCP. The resistant fraction formed might be a result of the ionized form of

PCP strongly sorbing. Calculations were carried out to determine if this could explain the resistant fraction.

The Henderson-Hasselbach equation is defined as:

$$pH = pK_a + \log([A^-]/[HA]) \quad (6.1)$$

where $[A^-]$ and [HA] are the concentrations of the ionized and protonated forms of PCP, respectively, and pK_a is the -log K_a where K_a is the acid dissociation constant.

Given the following mass balance:

$$PCP = HA + A^- \quad (6.2)$$

where PCP is the total concentration of both PCP species, the degree of protonation can be solved for with the following steps:

$$\log([HA]/[A^-]) = pK_a - pH \quad (6.3)$$

$$HA/(PCP - HA) = 10^{pK_a-pH} \quad (6.4)$$

$$\frac{1}{\frac{PCP}{HA} - 1} = 10^{pK_a-pH} \quad (6.5)$$

$$\frac{PCP}{HA} = \frac{1}{10^{pK_a-pH}} + 1 \quad (6.6)$$

multiplying through by HA yields;

$$PCP = \frac{HA}{10^{pK_a-pH}} + HA \quad (6.7)$$

since

$$10^{pK_a-pH} = 10^{-\log K_a+\log H} \quad (6.8)$$

and

$$10^{pK_a-pH} = 10^{(\log(H/K_a))} \qquad (6.9)$$

one obtains

$$PCP = \frac{[HA]K_a}{[H]} + [HA] \qquad (6.10)$$

which yields

$$PCP = \left[\frac{K_a}{H} + 1\right]HA \qquad (6.11)$$

and finally the degree of protonation is given by,

$$\frac{HA}{PCP} = \frac{1}{1+\frac{K_a}{H}} \qquad (6.12)$$

At a pH of 4.1, H = 7.943×10^{-5} M. The K_a of PCP is 1.778×10^{-5}. Using these values in Equation 6.12 yields a degree of protonation of 0.82. Eighteen percent of the PCP is in the ionized form.

Taking into account the solution removal for the desorption steps, the initial concentration of PCP for the 402.8 µg samples is 17.4 mg/L. Eighteen percent of this (3.13 mg/L) is in the ionized form. Using the K_p of 5 L/kg from Chapter 4 and the equation

$$q_e = \frac{(C_o - C_e) \cdot V}{M} \qquad (6.13)$$

one can calculate the amount of ionized PCP sorbed to the surface. Solving Equation 4.1 for C_e one obtains

$$C_e = \frac{C_o \cdot V}{V + MK_p} \qquad (6.14)$$

With M equal to 0.001 kg and V equal to 0.0249 L, and using 3.13 mg/L one obtains 2.61 mg/L for a value of C_e. Using this value in Equation 6.13 yields a value of 12.95 µg. The intermediate mass yields a value of 8.65 µg. The low mass (116.4 µg) yields a value of 3.99 µg. These are substantially less then the values calculated from the methanol extracts. This might suggest that the resistant fraction is only partially a result of the ionized form of PCP.

These results and previous results would suggest that the ionized form is only partially responsible for the formation of resistant fractions. Since there does not appear to be a clear trend between concentration and the size of the resistant fraction, the actual fraction might be somewhere near the average of the three treatments (25.3 µg). One explanation is that there is a different set of finite sites within the soil which are responsible for the formation of the resistant fraction. For all three masses these sites would be saturated.

6.5 Conclusions

The slow sorption kinetics of neutral pentachlorophenol on soil were concentration dependent. At higher PCP concentrations the slow sorption kinetics were much more rapid and the onset was sooner. However, there

was not a clear definable trend in which concentration could be correlated to K_p. Desorption studies demonstrated that the extent of hysteresis was also concentration dependent. At higher PCP concentrations, a smaller percent of the sorbed PCP at equilibrium was desorbed. Desorption and methanol extraction studies demonstrated that hysteresis of the neutral PCP is mainly a kinetic phenomenon but residual fractions do form. The hysteresis also increased with increasing residence time and was greater for higher concentration samples.

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Appendix A

GLOSSARY

A^-	anion of acid HA (charged species)
b	Langmuir sorption constant
C.I.	confidence interval
C_e	aqueous phase equilibrium concentration (mg/L)
C_o	initial concentration (mg/L)
C_T	total concentration (mg/L)
DOM	dissolved organic matter
f_{oc}	fraction of organic carbon
f_{om}	fraction of organic matter
HA	acid (neutral species)
HOC	hydrophobic organic compound
HIOC	hydrophobic ionizable organic compound
HNOC	hydrophobic nonionizable organic compound
K_a	acid dissociation constant
K_{oc}	organic carbon partition coefficient
K_{om}	organic matter partition coefficient
K_{ow}	octanol/water partition coefficient
K_p	partition coefficient (L/kg)
$K_{p(actual)}$	actual partition coefficient
$K_{p(apparent)}$	apparent partition coefficient
$K_{p(desorbed)}$	desorption stage partition coefficient
K_p^a	partition coefficient of anionic species
K_p^n	partition coefficient of neutral species
K_p^{net}	partition coefficient of both species
M	mass of sorbent (kg)

M_a	molecular weight of anionic species
M_n	molecular weight of neutral species
M_T	total PCP mass (μg)
P	pressure of nitrogen
P_o	saturated vapor pressure of nitrogen
pK_a	- log (K_a)
q_e	sorbed phase equilibrium concentration (mg/kg)
q_{max}	Langmuir adsorption maximum
S_1	labile (fast) sorbed concentration
S_2	nonlabile (slow) sorbed concentration
S_{HA}	solubility of neutral PCP
S_{PCP}	total PCP solubility
S_p	pooled standard deviation
SOM	soil organic matter
TOC	total organic carbon
V	volume of solution (L)

Appendix B

SURFACE AREA DATA

Data for Figure 3.2

BET N2 ADSORPTION

Sample Name:	Matapeake	Flowrate (cm3/min):	7
Degas T (C):	100	Bridge Current (amp):	150
Room T (K):	293	Sensitivity:	32
Atm. P (mmHg):	760	Sat. VP(mmHg)Po:	775
Sample wt. (g):	0.81171	Degas Time (hr):	48

N2	He	A	Vcal (ml)	Acal	C (N2)	P	Wt. of Ads. (X)	P/Po	y-axis
3	17	1424	1	981	0.15	114.0	0.00169	0.147	101.95
3	17	1397	1	978	0.15	114.0	0.00166	0.147	103.60
4	16	1620	1	1076	0.20	152.0	0.00175	0.196	139.05
4	16	1559	1	1042	0.20	152.0	0.00174	0.196	139.93
5	15	1643	1	1034	0.25	190.0	0.00185	0.245	175.39
5	15	1715	1	1132	0.25	190.0	0.00177	0.245	183.95
6	14	1724	1	1060	0.30	228.0	0.00190	0.294	219.91
6	14	1681	1	1022	0.30	228.0	0.00192	0.294	217.45

Xm = 0.00128752
St = 4.48376327
S = 5.52384875 m^2/g

Regression Statistics

Multiple R	0.99846778
R Square	0.99693791
Adjusted R Square	0.99642757
Standard Error	2.7752601
Observations	8

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1	15045.598	15045.598	1953.44897	8.9826E-09
Residual	6	46.2124118	7.70206863		
Total	7	15091.8104			

	Coefficients	Standard Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	-14.39522	4.06933011	-3.5374913	0.00950179	-24.352519	-4.4379206
P/Po	791.084423	17.8987127	44.197839	7.9275E-10	747.287819	834.881028

Appendix C

SOLIDS CONCENTRATION

Data for Figure 3.3

PCP Solids Concentration

Sample #	soil (g)	Solution (g)	Solids Conc (g /Kg)	Ce (mg/L)	qe (mg/kg)	Kp (L/kg)
1	0.1	24.76	4.04	1.8	49.52	27.51
2	0.1	24.94	4.01	1.7	74.82	44.01
3*	0.1	24.96	4.01	1.7	74.88	44.05
3	0.1	24.96	4.01	1.7	74.88	44.05
4	0.3	25.00	12.00	1.5	41.67	27.78
5	0.3	25.00	12.00	1.5	41.67	27.78
6	0.3	24.9	12.05	1.7	24.90	14.65
7	0.5	25.01	19.99	1.5	25.01	16.67
8	0.5	25.00	20.00	1.4	30.00	21.43
9	0.5	24.95	20.04	1.4	29.94	21.39
10	0.7	24.98	28.02	1.3	24.98	19.22
11	0.7	24.93	28.08	1.3	24.93	19.18
12	0.7	25.05	27.94	1.5	17.89	11.93
13	0.9	24.92	36.12	1.4	16.61	11.87
14	0.9	24.93	36.10	1.3	19.39	14.92
15	0.9	24.89	36.16	1.2	22.12	18.44
16	1.1	24.92	44.14	1.3	15.86	12.20
17	1.1	24.94	44.11	1.2	18.14	15.12
18	1.1	24.95	44.09	1.2	18.15	15.12
19	1.3	25.00	52.00	1.1	17.31	15.73
20	1.3	24.91	52.19	1.2	15.33	12.77
21	1.3	24.90	52.21	1.3	13.41	10.31
22	1.5	24.95	60.12	1.1	14.97	13.61
23	1.5	24.96	60.10	1.1	14.98	13.61
24	1.5	24.90	60.24	0.7	21.58	30.83
25	1.7	25.00	68.00	1.1	13.24	12.03
26	1.7	24.90	68.27	1.2	11.72	9.76
27	1.7	24.95	68.14	1.1	13.21	12.01
28	1.9	24.95	76.15	1.0	13.13	13.13
29	1.9	24.96	76.12	1.2	10.51	8.76
30	1.9	24.96	76.12	1.3	9.20	7.07
31	2.1	25.00	84.00	1.3	8.33	6.41
32	2.1	24.99	84.03	1.3	8.33	6.41
33	2.1	24.93	84.24	1.1	10.68	9.71
34	0.0	24.94	0.00	1.9	-	
35	0.0	24.87	0.00	2.1	-	
36	0.0	24.99	0.00	1.8	-	

Appendix D

KINETICS

Data for Figure 4.6 (pH 7.9)

Ce (mg/L)*	Time (Days)	qe (mg/Kg)	Kp (L/Kg)
4.00	2	80.00	4.82
4.40	2	38.50	2.11
4.15	2	64.44	3.74
3.70	2	111.12	7.24
4.45	2	33.31	1.80
3.80	8	100.75	6.39
4.05	8	74.81	4.45
3.95	8	85.19	5.20
4.30	8	48.87	2.74
4.65	8	12.56	0.65
3.45	12	137.06	9.57
4.30	12	48.87	2.74
4.05	12	74.81	4.45
4.75	12	2.19	0.11
4.70	12	7.37	0.38
3.45	16	137.06	9.57
4.05	16	74.81	4.45
4.35	16	43.69	2.42
4.50	16	28.13	1.51
4.00	16	80.00	4.82
4.10	21	69.63	4.09
3.90	21	90.37	5.58
4.00	21	80.00	4.82
3.75	21	105.94	6.81
3.80	21	100.75	6.39

* Concentration after a 1/4.15 dilutiion.

Data for Figure 4.6 (pH 4.1)

Time (days)	C_e (mg/L)	q_e (mg/kg)	K_p (L/kg)
0	5.1	0.000	0.000
0.014	1.635	86.625	52.982
0.0278	1.575	88.125	55.952
0.0556	1.782	84.300	47.306
0.111			
0.222	1.441	91.475	63.480
0.444	1.398	92.550	66.202
0.889	1.234	96.650	78.323
1.778	1.099	100.025	91.015
3.556	1.084	100.400	92.620
3.556	1.097	100.075	91.226
3.556	1.129	99.275	87.932
3.556	1.051	101.225	96.313
3.556	1.012	102.200	100.988
3.556	1.134	99.150	87.434
7.111	1.066	100.850	94.606
14.139	0.908	104.800	115.419
28	0.843	106.425	126.246
70	0.629	111.775	177.703

Appendix E

ISOTHERM DATA

Data for Figures 4.7 and 4.8 (pH 4.1)

Average Ce (mg/L)			Average qe (mg/kg)		
2 days	10 days	21 days	2 days	10 days	21 days
1.58	1.50	1.35	72.60	74.70	78.44
3.35	3.58	2.47	200.40	194.84	222.44
4.43	4.70	3.63	263.10	256.47	283.03
5.70	5.30	4.65	298.80	308.76	324.94
6.23	6.73	5.25	377.60	365.20	402.13

Kp = 57.4 L/kg (2 days)

Kp = 55.3 L/kg (10 days)

Kp = 75.5 L/kg (21 days)

Data for Figure 4.8 (pH 7.9)

Average Ce (mg/L)	Average qe (mg/kg)	Ce/qe	Cebqmax	bCe	1 + bCe	Cebqmax/(1+bCe)
3.28	15.21	0.216	20.026	0.080	1.08	18.54
7.80	45.00	0.173	47.580	0.190	1.19	39.97
11.08	48.96	0.226	67.606	0.270	1.27	53.22
13.75	73.75	0.186	83.875	0.336	1.34	62.80
15.38	75.32	0.204	93.788	0.375	1.38	68.20
24.10	95.00	0.254	147.010	0.588	1.59	92.57
31.88	101.57	0.314	194.438	0.778	1.78	109.37

slope =	0.004
intercept =	0.164
b =	0.024
qmax =	250.000

Appendix F

DESORPTION DATA

Data for Table 4.1 (pH 4.1)

Sample	Co (mg/L)	Ce (mg/L)	qe (mg/Kg)	Kp (L/Kg)	Avg Kp	% desorbrd*
SB2-S						
1	19.80	6.10	341.13	55.92		
2	19.80	5.95	344.87	57.96		
3	19.80	5.20	363.54	69.91	66.84	
4	19.80	4.95	369.77	74.70		
5	19.80	4.90	371.01	75.72		
control	4.50	4.50				
SB2-S/D						95%
1	15.39	3.60	293.58	81.55		
2	15.39	3.65	292.34	80.09		
3	15.39	3.85	287.36	74.64	70.39	
4	15.39	4.00	283.62	70.91		
5	15.39	5.50	246.27	44.78		
control	4.50	4.60				
SB8-S						
1	19.80	5.80	348.60	60.10		
2	19.80	4.80	373.50	77.81		
3	19.80	4.95	369.77	74.70	72.26	
4	19.80	5.40	358.56	66.40		
5	19.80	4.60	378.48	82.28		
control	4.50	4.45				
SB8-S/D						94%
1	15.67	3.50	303.07	86.59		
2	15.67	4.70	273.19	58.13		
3	15.67	3.85	294.36	76.46	71.11	
4	15.67	3.60	300.58	83.49		
5	15.67	5.15	261.99	50.87		
control	4.50	4.15				
SB16-S						
1	19.80	4.40	383.46	87.15		
2	19.80	3.90	395.91	101.52		
3	19.80	3.45	407.12	118.00	101.95	
4	19.80	3.85	397.16	103.16		
5	19.80	3.95	394.67	99.92		
control	4.50	4.35				
SB16-S/D						64%
1	16.64	3.30	332.25	100.68		
2	16.64	3.00	339.72	113.24		
3	16.64	3.25	333.50	102.61	105.20	
4	16.64	3.30	332.25	100.68		
5	16.64	3.10	337.23	108.78		
control	4.50	4.55				
SB21-S						
1	19.80	4.10	390.93	95.35		
2	19.80	4.15	389.69	93.90		
3	19.80	4.05	392.18	96.83	101.33	
4	19.80	3.75	399.65	106.57		
5	19.80	3.55	404.63	113.98		
control	4.50	4.65				
SB21-S/D						68%
1	16.65	3.70	322.49	87.16		
2	16.65	3.40	329.96	97.05		
3	16.65	3.40	329.96	97.05	97.74	
4	16.65	3.30	332.45	100.74		
5	16.65	3.15	336.19	106.73		
control	4.50	4.30				

Table continued on next page.

Sample	Co (mg/L)	Time (Days)	Ce (mg/L)	qe (mg/Kg)	Kp (L/Kg)	Avg. Kp	% desorbed
DB12-S							
1	19.80		4.10	390.93	95.35		
2	19.80		3.55	404.63	113.98		
3	19.80		3.75	399.65	106.57	98.30	
4	19.80		4.40	383.46	87.15		
5	19.80		4.35	384.71	88.44		
control	4.50		4.65				
DB2-D							60%
1	16.56	2	2.90	340.21	117.31		
2	16.56	2	3.10	335.23	108.14		
3	16.56	2	2.90	340.21	117.31	112.24	
4	16.56	2	3.10	335.23	108.14		
5	16.56	2	3.05	336.48	110.32		
control	4.50		4.65				
DB8-D							99%
1	16.56	8	4.55	299.13	65.74		
2	16.56	8	4.55	299.13	65.74		
3	16.56	8	4.55	299.13	65.74	67.40	
4	16.56	8	4.70	295.39	62.85		
5	16.56	8	4.05	311.58	76.93		
control	4.50		4.70				
DB12-D							90%
1	16.56	12	4.45	301.62	67.78		
2	16.56	12	4.45	301.62	67.78		
3	16.56	12	3.95	314.07	79.51	74.67	
4	16.56	12	3.80	317.80	83.63		
5	16.56	12					
control	4.50		4.55				
DB18-D							94%
1	16.56	18	4.20	307.84	73.30		
2	16.56	18	4.40	302.86	68.83		
3	16.56	18	4.35	304.11	69.91	71.10	
4	16.56	18	4.45	301.62	67.78		
5	16.56	18	4.10	310.33	75.69		

* % of 2-day equilibrium sorbed value. That is 100 x $K_{p(apparent)}/K_{p(desorbed)}$.

Codes: SB = sorption bottle
DB = desorption bottle
S = sorption
D = desorption

Data for Table 4.1 (pH 7.9).

Ce (mg/L)	Sorb,desorb	qe (mg/Kg)	Kp (L/Kg)	Cdesorb	qe (mg/kg)	Kp (L/kg)	% desorbed
4.00	2,2	80.00	4.82	5.45	15.25	2.80	
4.40	2,2	38.50	2.11	5.25	20.25	3.86	
4.15	2,2	64.44	3.74	4.60	36.50	7.93	86%
3.70	2,2	111.12	7.24	4.60	36.50	7.93	
4.45	2,2	33.31	1.80				
3.80	8,8	100.75	6.39	5.30	18.00	3.40	
4.05	8,8	74.81	4.45	5.05	24.25	4.80	
3.95	8,8	85.19	5.20	4.45	39.25	8.82	74%
4.30	8,8	48.87	2.74	4.65	34.25	7.37	
	8,8						
3.45	12,2	137.06					
4.30	12,2	48.87	2.74	5.25	11.00	8.76	
4.05	12,2	74.81	4.45	4.45	31.00	6.97	55%
4.75	12,2	2.19	0.11	4.55	28.50	6.26	
4.70	12,2	7.37	0.38				
3.45	16,2	137.06	9.57	5.25	26.00	4.95	
4.05	16,2	74.81	4.45	5.20	27.25	5.24	
4.35	16,2	43.69	2.42	4.80	37.25	7.76	64%
4.50	16,2	28.13	1.51	4.75	38.50	8.11	
4.00	16,2	80.00	4.82				
4.10	21,2	69.63	4.09	5.70	28.00	4.91	
3.90	21,2	90.37	5.58	5.30	38.00	7.17	
4.00	21,2	80.00	4.82	4.35	61.75	14.20	49%
3.75	21,2	105.94	6.81	4.45	59.25	13.31	
3.80	21,2	100.75	6.39	5.30	38.00	7.17	

Appendix G

SOIL ORGANIC MATTER OXIDATION DATA

Data for Figure 5.1

Ce (mg/L)				qe (mg/Kg)			Kp (L/Kg)		
H2O2	NaOCl	Untreated	Time (Days)	H2O2	NaOCl	Untreated	H2O2	NaOCl	Untreated
2.00	4.75	1.40	2	118.75	50.00	133.75	59.38	10.53	95.54
2.10	5.00	1.60	2	116.25	43.75	128.75	55.36	8.75	80.47
2.00	4.90	1.50	2	118.75	46.25	131.25	59.38	9.44	87.50
1.85	5.05	1.55	2	122.50	42.50	130.00	66.22	8.42	83.87
2.30	5.65	1.65	2	111.25	27.50	127.50	48.37	4.87	77.27
1.65	4.30	1.35	8	127.50	61.25	135.00	77.27	14.24	100.00
1.70	3.75	1.38	8	126.25	75.00	134.25	74.26	20.00	97.28
1.55	4.20	1.42	8	130.00	63.75	133.25	83.87	15.18	93.84
1.65		1.48	8	127.50		131.75	77.27		89.02
1.85	3.70	1.46	8	122.50	76.25	132.25	66.22	20.61	90.58
1.60	4.65	1.15	14	128.75	52.50	140.00	80.47	11.29	121.74
1.40	4.35	1.15	14	133.75	60.00	140.00	95.54	13.79	121.74
1.30	4.80	1.15	14	136.25	48.75	140.00	104.81	10.16	121.74
1.50	4.85	1.20	14	131.25	47.50	138.75	87.50	9.79	115.63
1.70	5.00	1.30	14	126.25	43.75	136.25	74.26	8.75	104.81
1.45	3.70	1.25	20	132.50	76.25	137.50	91.38	20.61	110.00
1.15	4.20	1.05	20	140.00	63.75	142.50	121.74	15.18	135.71
1.20	3.85	1.00	20	138.75	72.50	143.75	115.63	18.83	143.75
1.15	3.45	1.00	20	140.00	82.50	143.75	121.74	23.91	143.75
1.20	3.70	0.95	20	138.75	76.25	145.00	115.63	20.61	152.63

Appendix H

TOTAL ORGANIC CARBON DATA

Data for Table 5.1

Conc(mg/L)	Response	Treatment	Response	Correction	Conc(mg/L)	mg TOC	Total TOC	% removed	% OM
0.00	0.00	pH 4-1	65.00	68.14	51.20	12.80			
18.80	23.00	pH 4-2	32.00	35.14	26.40	6.60			
37.60	50.00	pH 4-3	22.00	25.14	18.89	4.72	24.10	7.10	1.58
53.10	70.00	pH 6-1	63.00	66.14	49.69	12.42			
		pH 6-2	35.00	38.14	28.66	7.16			
		pH 6-3	21.00	24.14	18.14	4.53	24.10	7.10	1.58
		pH 8-1	140.00	143.14	107.54	26.89			
		pH 8-2	68.00	71.14	53.45	13.36			
		pH 8-3	39.00	42.14	31.66	7.92	48.20	14.20	1.46

Regression Statistics

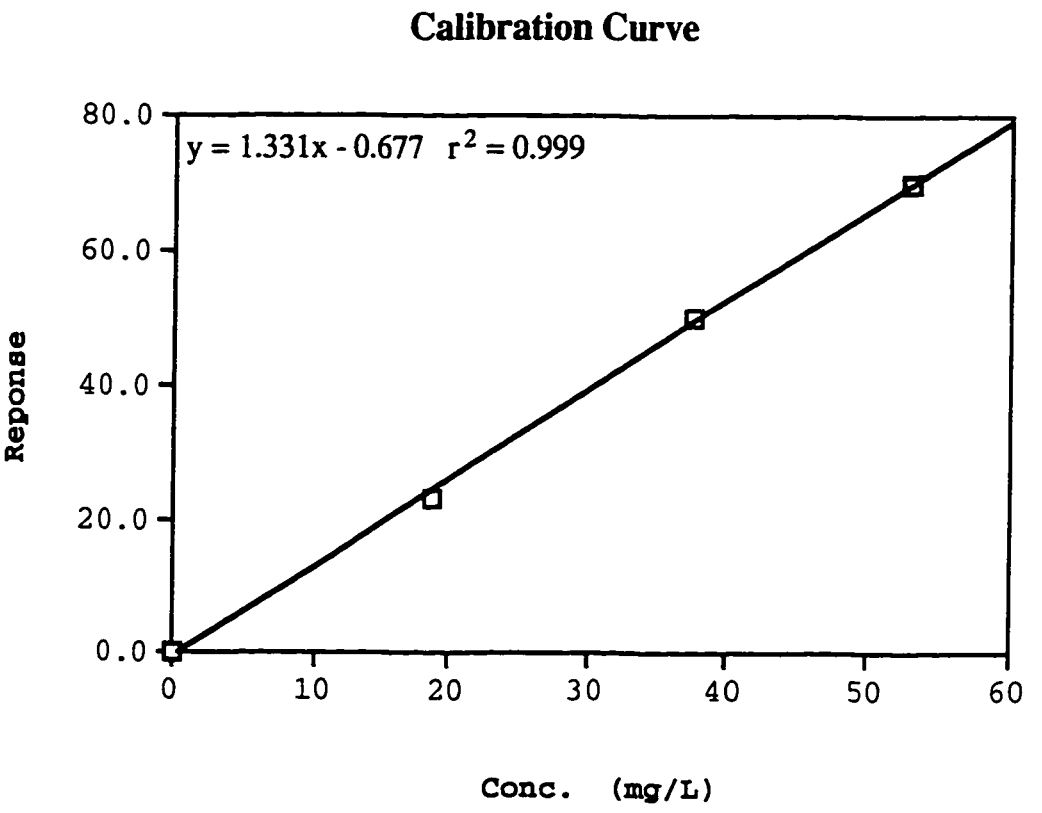
Multiple R	1.00
R Square	1.00
Adjusted R Square	1.00
Standard Error	1.15
Observations	4.00

Analysis of Variance

	df	Sum of Squares	Mean Square	F	Significance F
Regression	1.00	2814.08	2814.08	2109.76	0.00
Residual	2.00	2.67	1.33		
Total	3.00	2816.75			

	Coefficients	Standard Error	t Statistic	P-value	Lower 95%	Upper 95%
Intercept	-0.68	0.98	-0.69	0.54	-4.90	3.54
x1	1.33	0.03	45.93	0.00	1.21	1.46

Calibration curve for data in Table 5.1.



Appendix I

DUAL SPIKE KINETICS

Data for Figures 6.1, 6.2 and 6.3 (Dual Spike Kinetics).

Spike 1 of Dual Spike Kinetics

Time (Days)	Ce (mg/L)	log Ce	log t(min)	t^b	At^b
0.000	5.70				
0.028	2.33	0.367	1.602	0.626	2.273
0.056	2.13	0.328	1.903	0.573	2.081
0.111	1.80	0.255	2.204	0.525	1.906
0.222				0.481	1.745
0.382	1.65	0.217	2.740	0.449	1.629
0.889	1.43	0.155	3.107	0.403	1.464
1.778	1.35	0.130	3.408	0.369	1.340
3.056	1.30	0.114	3.643	0.345	1.251
3.056	1.20	0.079	3.643	0.345	1.251
3.056	1.30	0.114	3.643	0.345	1.251
3.056	1.20	0.079	3.643	0.345	1.251
3.056	1.30	0.114	3.643	0.345	1.251
3.056	5.56				
3.056	4.05		4.010	0.310	1.126
3.111	3.90		4.311	0.283	1.028
3.167	3.58				
3.278	3.35				
3.500	3.20				
3.944	3.00				
4.833	2.58				
6.111	2.45				

Spike 2 of Dual Spike Kinetics

Time (Days)	Ce (mg/L)	log Ce	log t(min)	t^b	At^b
0.000	5.56				
0.028	4.05	0.607	1.602	0.657	4.201
0.056	3.90	0.591	1.903	0.607	3.882
0.111	3.58	0.554	2.204	0.561	3.587
0.222	3.35	0.525	2.505	0.518	3.314
0.444	3.20	0.505	2.806	0.479	3.062
0.889	3.00	0.477	3.107	0.442	2.830
1.778	2.58	0.412	3.408	0.409	2.615
3.056		0.407	3.643	0.384	2.458
3.056		0.439	3.643	0.384	2.458
3.056	2.45	0.371	3.643	0.384	2.458
3.056		0.398	3.643	0.384	2.458
3.056		0.407	3.643	0.384	2.458
3.056		0.301	3.643	0.384	2.458
7.111	1.70	0.230	4.010	0.349	2.233
14.222	1.40	0.146	4.311	0.322	2.060
28.000			4.606	0.299	1.910

Data for Figures 6.2 and 6.3 (Original Kinetics).

			Original Kinetics		
Time (Days)	Ce (mg/L)	log t(min)	log Ce	t^b	At^b
0.000	5.100				
0.014	1.635			0.711	2.035
0.028	1.575			0.657	1.881
0.056	1.782	1.903	0.251	0.607	1.738
0.111				0.561	1.606
0.222	1.441	2.505	0.159	0.518	1.484
0.444	1.398	2.806	0.146	0.479	1.371
0.889	1.234	3.107	0.091	0.442	1.267
1.778	1.099	3.408	0.041	0.409	1.171
3.556	1.084	3.709	0.035	0.378	1.082
3.556	1.097	3.709	0.040	0.378	1.082
3.556	1.129	3.709	0.053	0.378	1.082
3.556	1.051	3.709	0.022	0.378	1.082
3.556	1.012	3.709	0.005	0.378	1.082
3.556	1.134	3.709	0.055	0.378	1.082
7.111	1.066	4.010	0.028	0.349	1.000
14.139	0.908	4.309	-0.042	0.323	0.924
28.000	0.843	4.606	-0.074	0.299	0.855
70.000	0.629			0.269	0.770

Appendix J

CONCENTRATION GRADIENT

Data for Figure 6.4

Time (Days)	C_e1 (mg/L)	C_e2 (mg/L)	q_e1 (mg/Kg)	q_e2 (mg/Kg)	K_p1 (L/Kg)	K_p2 (L/Kg)
3.06		2.45		220.25		89.90
3.56	1.11		99.75		89.86	
7.11	1.07	1.70	100.75	239.00	94.16	140.59
14.14	0.91		104.75		115.11	
14.22		1.40		246.50		176.07
28.00	0.84		106.50		126.79	
70.00	0.63		111.75		177.38	

Codes: 1 refers to the low concentration (original) kinetics.
2 refers to the high concentration (dual spike) kinetics.

Appendix K

CONCENTRATION EFFECTS

Data for Figure 6.5

Ce (mg/L)				qe (mg/Kg)			Kp (L/Kg)		
Co = 19.8	Co = 13.0	Co = 6.2	Time (Days)	Co = 19.8	Co = 13.0	Co = 6.2	Co = 19.8	Co = 13.0	Co = 6.2
6.10	4.60	1.40	2	342.50	210.00	120.00	56.15	45.65	85.71
5.95	4.45	1.45	2	346.25	213.75	118.75	58.19	48.03	81.90
6.00	4.20	1.55	2	345.00	220.00	116.25	57.50	52.38	75.00
	4.70		2		207.50			44.15	
	4.35		2		216.25			49.71	
4.80	2.35	1.30	15	375.00	266.25	122.50	78.13	113.30	94.23
5.00	2.60	1.20	15	370.00	260.00	125.00	74.00	100.00	104.17
3.90	2.55	1.25	15	397.50	261.25	123.75	101.92	102.45	99.00
4.75	2.20	1.25	15	376.25	270.00	123.75	79.21	122.73	99.00
2.85	2.30	1.25	15	423.75	267.50	123.75		116.30	99.00
4.40	2.60	1.20	30	385.00	260.00	125.00	87.50	100.00	104.17
4.45	2.85	1.20	3'	383.75	253.75	125.00	86.24	89.04	104.17
4.20	2.65	1.05	30	390.00	258.75	128.75	92.86	97.64	122.62
4.00	2.75	1.25	30	395.00	256.25	123.75	98.75	93.18	99.00
4.40	3.00	1.00	30	385.00	250.00	130.00	87.50	83.33	130.00
4.50	2.05	1.20	50	382.50	273.75	125.00	85.00	133.54	104.17
4.45	2.15	1.10	50	383.75	271.25	127.50	86.24	126.16	115.91
4.65	2.35	1.20	50	378.75	266.25	125.00	81.45	113.30	104.17
	1.95	1.10	50		276.25	127.50		141.67	115.91
4.15	2.00	1.00	50	391.25	275.00	130.00	94.28	137.50	130.00
2.70	1.55	0.90	100	427.50	286.25	132.50	158.33	184.68	147.22
2.80	1.55	0.95	100	425.00	286.25	131.25	151.79	184.68	138.16
2.90	1.55	0.90	100	422.50	286.25	132.50	145.69	184.68	147.22
2.45		0.90	100	433.75	325.00	132.50	177.04		147.22
2.40	1.65	0.85	100	435.00	283.75	133.75	181.25	171.97	157.35

Data for Figure 6.9 (2-day desorption).

Days Sorbed	Kd1	Co	Ce-1	qe-1	Kd-1	Kd1/Kd-1	Avg	Apparent	Avg
2	56.15	14.98	3.50	287.00	82.00	0.68		0.70	
2	58.19	14.98	3.40	289.50	85.15	0.68		0.67	
2	57.50	14.98					0.69		0.69
2		14.98							
2		14.98							
2	45.65	9.43	1.65	194.50	117.88	0.39		0.41	
2	48.03	9.43	2.80	165.75	59.20	0.81		0.81	
2	52.38	9.43	2.25	179.50	79.78	0.66	0.64	0.60	0.64
2	44.15	9.43	2.65	169.50	63.96	0.69		0.75	
2	49.71	9.43	2.35	177.00	75.32	0.66		0.64	
2	85.71	5.02	1.00	100.50	100.50	0.85		0.80	
2	81.90	5.02	1.00	100.50	100.50	0.81		0.80	
2	75.00	5.02	1.20	95.50	79.58	0.94	0.92	1.02	0.92
2		5.02	1.10	98.00	89.09			0.91	
2		5.02	1.25	94.25	75.40			1.07	
15	78.13	15.92	2.35	339.25	144.36	0.54		0.40	
15	74.00	15.92	2.30	340.50	148.04	0.50		0.39	
15	101.92	15.92	2.20	343.00	155.91	0.65	0.64	0.37	0.38
15	79.21	15.92	2.05	346.75	169.15	0.47		0.34	
15	148.68	15.92	2.40	338.00	140.83	1.06		0.41	
15	113.30	11.08	1.40	242.00	172.86	0.66		0.28	
15	100.00	11.08	1.40	242.00	172.86	0.58		0.28	
15	102.45	11.08	1.50	239.50	159.67	0.64	0.66	0.30	0.29
15	122.73	11.08	1.40	242.00	172.86	0.71		0.28	
15	116.30	11.08	1.50	239.50	159.67	0.73		0.30	
15	94.23	5.20	0.90	107.50	119.44	0.79		0.68	
15	104.17	5.20	0.90	107.50	119.44	0.87		0.68	
15	99.00	5.20	1.00	105.00	105.00	0.94	0.86	0.77	0.70
15	99.00	5.20	0.90	107.50	119.44	0.83		0.68	
15	99.00	5.20	0.95	106.25	111.84	0.89		0.72	
30	87.50	16.37	2.40	349.25	145.52	0.60		0.39	
30	86.24	16.37	2.45	348.00	142.04	0.61		0.40	
30	92.86	16.37	2.55	345.50	135.49	0.69	0.77	0.42	0.48
30	98.75	16.37	3.45	323.00	93.62	1.05		0.61	
30	87.50	16.37	3.30	326.75	99.02	0.88		0.58	
30	100.00	10.78	1.60	229.50	143.44	0.70		0.33	
30	89.04	10.78	1.65	228.25	138.33	0.64		0.35	
30	97.64	10.78	1.80	224.50	124.72	0.78	0.78	0.38	0.40
30	93.18	10.78	2.20	214.50	97.50	0.96		0.49	
30	83.33	10.78	2.10	217.00	103.33	0.81		0.46	
30	104.17	5.29	0.90	109.75	121.94	0.85		0.66	
30	104.17	5.29	0.95	108.50	114.21	0.91		0.71	
30	122.62	5.29	0.90	109.75	121.94	1.01	0.97	0.66	0.70
30	99.00	5.29	1.00	107.25	107.25	0.92		0.75	
30	130.00	5.29	0.95	108.50	114.21	1.14		0.71	
50	85.00	16.25	1.90	358.75	188.82	0.45		0.30	
50	86.24	16.25	1.90	358.75	188.82	0.46		0.30	
50	81.45	16.25	2.00	356.25	178.13	0.46	0.52	0.32	0.34
50		16.25	2.20	351.25	159.66			0.36	
50	94.28	16.25	2.55	342.50	134.31	0.70		0.43	
50	133.54	11.32	1.20	253.00	210.83	0.63		0.23	
50	126.16	11.32	1.20	253.00	210.83	0.60		0.23	
50	113.30	11.32	1.25	251.75	201.40	0.56	0.65	0.24	0.24
50	141.67	11.32	1.25	251.75	201.40	0.70		0.24	
50	137.50	11.32	1.40	248.00	177.14	0.78		0.27	
50	104.17	5.30	0.90	110.00	122.22	0.85		0.66	
50	115.91	5.30	0.90	110.00	122.22	0.95		0.66	
50	104.17	5.30	0.90	110.00	122.22	0.85	0.93	0.66	0.66
50	115.91	5.30	0.90	110.00	122.22	0.95		0.66	
50	130.00	5.30	0.90	110.00	122.22	1.06		0.66	
100	158.33	17.68	1.45	405.75	279.83	0.57		0.20	
100	151.79	17.68	1.20	412.00	343.33	0.44		0.17	
100	145.69	17.68	1.30	409.50	315.00	0.46	0.56	0.18	0.20
100	177.04	17.68	1.45	405.75	279.83	0.63		0.20	
100	181.25	17.68	1.60	402.00	251.25	0.72		0.23	
100	184.68	11.74	1.10	266.00	241.82	0.76		0.20	
100	184.68	11.74	1.05	267.25	254.52	0.73		0.19	
100	184.68	11.74	0.95	269.75	283.95	0.65	0.70	0.17	0.19
100		11.74	0.90	271.00	301.11				
100	171.97	11.74	1.05	267.25	254.52	0.68		0.19	
100	147.22	5.48	0.80	117.00	146.25	1.01		0.55	
100	138.16	5.48	0.80	117.00	146.25	0.94		0.55	
100	147.22	5.48	0.80	117.00	146.25	1.01	0.99	0.55	0.54
100	147.22	5.48	0.75	118.25	157.67	0.93		0.51	
100	157.35	5.48	0.80	117.00	146.25	1.08		0.55	

Data for Figure 6.10.

Ce			Sorp/Des	qe		
Co=19.8	Co=13.0	Co=6.2	Time	Co=19.8	Co=13.0	Co=6.2
3.50	1.65	1.00	2	287.00	194.50	100.50
3.40	2.80	1.00	2	289.50	165.75	100.50
	2.25	1.20	2		179.50	95.50
	2.65	1.10	2		169.50	98.00
	2.35	1.25	2		177.00	94.25
2.20	1.20	0.85	15	331.75	239.75	104.00
2.00	1.50	1.00	15	336.75	232.25	100.25
2.15	1.45	0.90	15	333.00	233.50	102.75
2.05	1.50	0.90	15	335.50	232.25	102.75
2.35	1.45	0.90	15	328.00	233.50	102.75
1.90	1.25	0.80	30	347.50	229.00	107.50
1.80	1.30	0.80	30	350.00	227.75	107.50
1.75	1.30	0.80	30	351.25	227.75	107.50
1.95	1.30	0.80	30	346.25	227.75	107.50
1.75	1.45	0.80	30	351.25	224.00	107.50
1.80	1.00	0.80	50	350.75	251.75	108.00
1.50	1.00	0.80	50	358.25	251.75	108.00
1.45	1.00	0.75	50	359.50	251.75	109.25
1.50	1.05	0.80	50	358.25	250.50	108.00
1.50	0.95	0.85	50	358.25	253.00	106.75
1.80	1.20	0.85	100	390.00	258.50	111.75
1.60	1.40	0.90	100	395.00	253.50	110.50
1.60	1.40	0.85	100	395.00	253.50	111.75
1.40	1.20	0.80	100	400.00	258.50	113.00
1.65	1.15	0.75	100	393.75	259.75	114.25

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	Kdes			Kads			Probable
Co=19.8	Co=13.0	Co=6.2	Co=19.8	Co=13.0	Co=6.2	Co=19.8	Co=13.0
82.00	117.88	100.50	56.15	45.65	85.71	0.68	0.39
85.15	59.20	100.50	58.19	48.03	81.90	0.68	0.81
	79.78	79.58	57.50	52.38	75.00		0.66
	63.96	89.09		44.15			0.69
	75.32	75.40		49.71			0.66
150.80	199.79	122.35	78.13	113.30	94.23	0.52	0.57
168.38	154.83	100.25	74.00	100.00	104.17	0.44	0.65
154.88	161.03	114.17	101.92	102.45	99.00	0.66	0.64
163.66	154.83	114.17	79.21	122.73	99.00	0.48	0.79
139.57	161.03	114.17		116.30	99.00		0.72
182.89	183.20	134.38	87.50	100.00	104.17	0.48	0.55
194.44	175.19	134.38	86.24	89.04	104.17	0.44	0.51
200.71	175.19	134.38	92.86	97.64	122.62	0.46	0.56
177.56	175.19	134.38	98.75	93.18	99.00	0.56	0.53
200.71	154.48	134.38	87.50	83.33	130.00	0.44	0.54
194.86	251.75	135.00	85.00	133.54	104.17	0.44	0.53
238.83	251.75	135.00	86.24	126.16	115.91	0.36	0.50
247.93	251.75	145.67	81.45	113.30	104.17	0.33	0.45
238.83	238.57	135.00		141.67	115.91	0.00	0.59
238.83	266.32	125.59	94.28	137.50	130.00	0.39	0.52
216.67	215.42	131.47	158.33	184.68	147.22	0.73	0.86
246.88	181.07	122.78	151.79	184.68	138.16	0.61	1.02
246.88	181.07	131.47	145.69	184.68	147.22	0.59	1.02
285.71	215.42	141.25	177.04		147.22	0.62	
238.64	225.87	152.33	181.25	171.97	157.35	0.76	0.76

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Co=19.8	Apparent Co=13.0	Co=6.2	Co=19.8	Avg. App. Co=13.0	Co=6.2	Co=19.8	Avg. Prob. Co=13.0
0.70	0.41	0.80					
0.67	0.81	0.80					
	0.60	1.02	0.69	0.64	0.92	0.68	0.64
	0.75	0.91					
	0.64	1.07					
0.38	0.24	0.66					
0.34	0.31	0.81					
0.37	0.30	0.71	0.37	0.29	0.72	0.52	0.67
0.35	0.31	0.71					
0.41	0.30	0.71					
0.31	0.26	0.60					
0.29	0.27	0.60					
0.29	0.27	0.60	0.30	0.28	0.60	0.48	0.54
0.32	0.27	0.60					
0.29	0.31	0.60					
0.29	0.19	0.60					
0.24	0.19	0.60					
0.23	0.19	0.56	0.25	0.19	0.60	0.30	0.52
0.24	0.20	0.60					
0.24	0.18	0.64					
0.26	0.22	0.62					
0.23	0.26	0.66					
0.23	0.26	0.62	0.23	0.24	0.60	0.66	0.91
0.20	0.22	0.57					
0.24	0.21	0.53					