Sorption Kinetics and Mechanisms of Hydrophobic Ionizable Organic Compounds on Surfactant-Modified Clays

by

Michael G. Stapleton

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

May 1995

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"Take then good note of it. Nothing is too small I counsel you, put down in record even your doubts and surmises. Hereafter it may be of interest to you to see how true you guess. We learn from failure, not from success!"

Bram Stroker *Dracula* 1897.

ACKNOWLEDGMENTS

I would first like to thank my advisor, Donald L. Sparks, for his time, guidance, and support during the last several years. He has created a unique environment which offers many opportunities for students. This has directly resulted from his hard work and dedication to soil science. Students have been and continue to be the main focus of his activities at the University of Delaware. For the sake of future students, I hope this never changes.

I would also like to thank Steven K. Dentel for his collaboration, support, and the many discussions we have had. He never ceased to challenge me or present new ideas. In addition, I would like to thank the other members of my doctoral committee, Theodore H. Carski, Michael J. Duffy, and Noel C. Scrivner. My only regret is not taking greater advantage of their knowledge and expertise during my research. In the future, I hope they will allow me to consult them on problems and request advice.

I am deeply grateful to all the current and former students and post-docs with whom I have worked; especially Matthew J. Eick, Scott E. Fendorf, Paul R. Grossl, and Gerald J. Hendricks, for their technical expertise, sanity, patience, and humor. I would also like to thank Chaim Aharoni (Technion-Israel Institute of Technology) and

Diedrich Steffens (Justus Liebig University), visiting professors at the university, whose advice and guidance have been invaluable. In addition, I would like to thank the faculty and staff of the Plant and Soil Sciences Department and College of Agricultural Sciences at the University of Delaware, especially Caroline M. Golt and Elizabeth O. Mackenzie for their immeasurable assistance.

There are many people who have influenced me to pursue a college education, two I would particularly like to recognize: Karen Undeck and Henry Aaron. Ms. Undeck, my high school guidance counselor, suggested that I would probably never get into college, and if I insisted on applying I should select a school that had low admission standards. I ignored her advice and applied to a small private school; I was accepted and graduated in four years. It was during this time that I met Mr. Aaron. He grew up poor and black in a segregated country, but he had a dream as a child and achieved it as an adult. It was from him I learned the importance of a having a dream and refusing to accept limitations suggested by others.

I would especially like to thank my parents, Michael F. Stapleton and Jean L. Stapleton, for instilling in their children a strong work ethic and commitment to education. Without their support and encouragement, I would not have had the courage to start on this long journey in the first place.

Finally I would like to thank my wife, Sarah, and children, Luke and Emma, for their unconditional support during my studies. Words cannot describe my gratitude. Their love and encouragement made the long hours bearable.

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ABSTRACT

We investigated the kinetic and equilibrium sorption of pentachlorophenol (PCP) to a surfactant-modified clay and the solubility of PCP, as a function of pH and ionic strength. Pentachlorophenol is a hydrophobic ionizable organic compound (HIOC). Therefore, it can exist either as a protonated or deprotonated species. The objectives of this study were to determine differences in the sorption and solubility of the two species, and to model these properties as a function of pH.

The modifying surfactant was hexadecyltrimethylammonium cations (HDTMA). Large stable structures were observed on the external surface of the washed HDTMA-clay. Based on scanning force microscopy images and zeta potential measurements, we proposed that these structures were hemimicelles. They appeared to form when HDTMA replaces ≥ 70% of the clay's cation exchange capacity.

The PCP sorption was rapid and reversible, with equilibrium reached within 10 minutes. The sorption kinetics were characterized by a pseudo first-order model; there was not a significant difference in the rate of sorption between the two PCP species. Equilibrium sorption of the protonated species was significantly greater than the deprotonated species. The proposed model, represented by the summation of the sorption for the deprotonated species by a Langmuir isotherm and the protonated species by a linear isotherm, described the experimental data well. The solubility was strongly dependent upon the PCP speciation. A model for the maximum aqueous phase concentration of PCP, as a function of pH, was proposed. This model shows an exponential increase in the maximum PCP aqueous concentration, above the pK_a.

We concluded that the sorption and solubility of the two PCP species are significantly different. We believe that, to a varying degree, this is true for all HIOC. Therefore, when considering the environmental transport of HIOC speciation should be considered. We have presented a basic approach that may be used to estimate changes in the sorption and solubility of a HIOC as a function of pH.

Chapter 1

INTRODUCTION

The occurrence of anthropogenic organic compounds in surface and ground waters has raised significant concerns from a human and environmental health standpoint. Determination and prediction of the environmental fate and reactions of these compounds is now a major area of research. One group of compounds, hydrophobic ionizable organic compounds (HIOC), have the ability to ionize in the aqueous phase producing two or more species with significantly different sorptive properties. When ionization occurs in a pH region found in the natural environment, the speciation of the compound becomes critical in determining the environmental fate.

Public demand and more stringent regulatory requirements have focused attention on the removal and the treatment of these organic contaminants. Innovative treatment methods have been proposed to remove organic compounds from the aqueous phase. One method increases the sorption capacity of soils and clays by the addition of cationic surfactants. These surfactants, when exchanged with natural inorganic cations on the mineral surface, form a stable organic layer on the soil or clay. The resulting solids are referred to by several different names, i.e., modified-clays, surfactant modified clays, and organo-clays. Within the past ten years, the addition of surfactants to soils and clays has received increased attention. Surfactants have been used for the *in situ* modification of soils to increase the soil's ability to retain organic contaminants. In addition, modified-clays are being investigated as barriers to prevent the migration of contaminants and as sorbents for the removal of organic compounds from an aqueous phase. While there have been many studies to investigate the sorption of organic compounds to modified-clays, there is no research that has investigated the rate of sorption/desorption of organic compounds to these modified-clays. If these modified-clays are to be used as sorbents, then the rate of the sorption/desorption is critical to the engineering design.

In this research project, I studied the sorption of a HIOC to a modified-clay. The modified-clay provided a stable, high organic carbon content surface which allowed experiments to be conducted over a wide pH range to study sorption of HIOC. In addition, the changes in the clay surface with the addition of the modifying agent were evaluated. The objectives of this research were to:

- Investigate the short and long term sorption/desorption of pentachlorophenol (PCP) on a modified-clay in a pH range that would involve both the protonated and deprotonated species.
- Develop a model to describe the PCP sorption as a function of solution pH.

- Determine the kinetics of sorption/desorption of PCP on a modified-clay.

This research should provide information that will assist in better understanding the environmental fate and transport of HIOC and the role surfactant-modified clays play in their retention and mobility.

Chapter 2

LITERATURE REVIEW

2.1 Historical Perspective

Historically, the exchange of organic for inorganic cations has been studied for almost 80 years. In 1916 Lloyd noted that Fuller's earth adsorbed nicotine from aqueous solutions, especially when the alkaloid was in the salt form. In 1934 Smith reported that montmorillonite was capable of taking up hydrazine, ammonia, *n*-amylamine, piperidine, di-*n*-amylamine, nicotine, and strychnine cations from an aqueous solution. The adsorption process was essentially one of cation exchange since washing the clay complexes with water did not displace the organic cations. A one percent salt solution, however, released appreciable quantities of the sorbed species (1).

Ensminger and Gieseking (2) studied reactions between montmorillonite and organic compounds containing basic groups. Clays that have undergone exchange reactions with an organic cation are referred to as modified-clay complexes. They noted that the nitrogen in the tissues of animals and plants is in a basic form or a form that becomes basic upon hydrolysis. Organic matter derived from these sources will be capable of reacting like basic compounds, forming a cation in an aqueous solution. This should make possible a combination of the basic or "positive spots" of the organic matter and the acidic or "negative spots" on the crystal lattice of the clay (2).

Grim et al. (3) and Jordan (4) found that large aliphatic amines undergo exchange reactions on clay minerals with increasing ease as the size of the alkyl chain increases. Cowan and White (5) investigated the mechanism of exchange reactions between a homologous series of *n*-primary aliphatic amines -- from ethyl- (C_2) to tetradecyl-ammonium (C_{14}) -- on Na-montmorillonite. They found that sorption of an amine with less than eight carbon atoms did not exceed the cation exchange capacity (CEC) of the clay, although excess salt was in solution. However, when the length exceeded eight carbon atoms, adsorption occurred in excess of the CEC of the clay. Adsorption up to the CEC was characterized by electrostatic forces while adsorption in excess of the CEC was attributed to van der Waals forces. In addition, Cowan and White (5) noted that when the alkyl chain contained 12 carbon atoms, the hydrophobic character of the surface became quite apparent. Theng et al. (6) extended Cowan and White's (5) research with primary amines to also include secondary, tertiary, and quaternary amines but only for R groups (where R represents any alkyl group) that contained one to four carbon atoms. They found that sorption was of the Langmuir type, and the preference for adsorption increased with molecular weight.

Barrer and his co-workers (7-11) investigated the increased sorption capacity for nonpolar compounds by an amine-clay complex. The majority of this research was conducted in the gaseous phase at low temperature. Bayer (12) was the first to add a surfactant to a clay in order to change the sorption ability of the clay for an organic compound. He studied the effect of surfactants on the leachability of substituted urea herbicides in soil. Cationic, anionic, and nonionic surfactants were included in the test. The herbicides and the surfactants were mixed in an aqueous solution, added to soil columns, leached with simulated rainfall, and allowed to drain. Resistance of the herbicide to leaching was evaluated. While there was some variation in the results for the three surfactant groups, the cationic surfactants decreased leaching of the herbicides, the anionic surfactants had little impact on leaching, and the nonionic surfactants increased leaching.

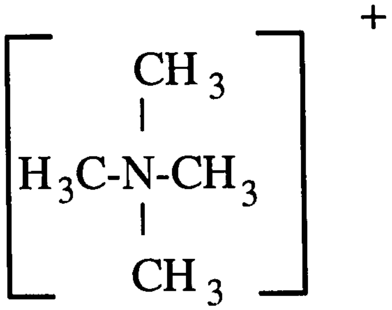
Smith and Bayer (13) investigated adsorption of diuron [3-(3,4-dichlorophenol)-1,1-dimethylurea] on soil as influenced by seven surfactants, five cationic compounds (quaternary amines) and two nonionic compounds. The objective of the study was to determine if adsorption of diuron could be enhanced so as to reduce its movement through the soil profile. Smith and Bayer (13) concluded that diuron sorption was greatly influenced by the molecular structure of the surfactant and the surfactant concentration in solution. The cationic surfactants increased the sorption on the soil; however, in the soil treated with the nonionic surfactants, there was no increase in diuron sorption. Sorption increased with the surfactant concentration and with the number and length of the R groups on the surfactant. The greatest sorption occurred when the surfactant contained two alkyl chains of twelve or more carbon atoms.

Diuron, which was adsorbed to the modified soil, was still available for plant root adsorption; thus, it was still chemically active as a herbicide.

2.2 Current Research

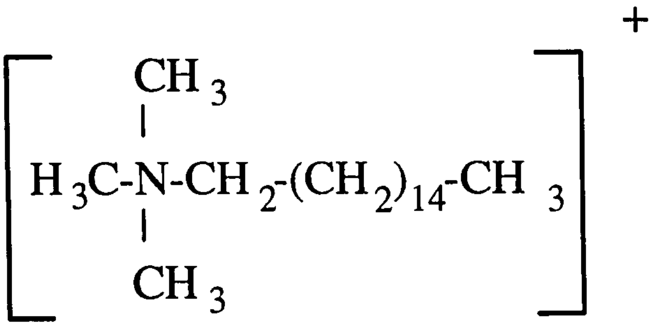
Recent research on organo-clays as sorbents for environmental applications has focused on the use of quaternary amines as the modifying cation, specifically, quaternary amines with the formula $[(CH_3)_3NR]^+$ with R representing a straight aliphatic carbon chain varying from C_1 to C_{16} in length. Research has mainly focused on the use of two quaternary amines, tetramethylammonium (TMA) and hexadecyltrimethylammonium (HDTMA), to modify the clay mineral (Figure 2.1).

The shorter chain organic cations are isolated from each other on the mineral surface (14-17). Therefore, part of the mineral surface is exposed and largely occupied by water (17-18). These water molecules, on the short chain organo-clay surface, serve to restrict access of large organic molecules to the interlamellar space. This leads to the size/shape selectivity found for organo-clays containing the shorter chain cations, especially TMA. However, the longer chain organic cations, such as HDTMA, have the ability to overlap their chains on the surface and form a uniform organic layer (19). This layer serves to remove water sorbed on the mineral surface resulting in a greater hydrophobic character on the surface.



$$\left[H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}}\text{-}CH_3 \right]^+$$

Tetramethylammonium
(TMA)



$$\left[H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}}\text{-}CH_2\text{-}(CH_2)_{14}\text{-}CH_3 \right]^+$$

Hexadecyltrimethylammonium
(HDTMA)

Figure 2.1 Structure of TMA and HDTMA cations

2.2.1 TMA-Clays

Mc Bride et al. (15) investigated the ability of a TMA-clay to sorb benzene, phenol, *o*-dichlorobenzene, and 1,2,4-trichlorobenzene from an aqueous solution. They found that only benzene and phenol were sorbed by the TMA organo-clay surface. The isotherms were nonlinear, and benzene was sorbed to a greater extent than phenol. The two chlorinated benzenes were not sorbed by the TMA organo-clay surface.

Mortland et al. (20) studied the sorption of phenol and a series of chlorinated phenols on a TMA-clay. Results were only presented for two of the four phenols studied: phenol and 3,4,5-trichlorophenol (345-TCP). The authors only presented graphical information, at a very low concentration, and did not provide any discussion of the results. Phenol was not sorbed and 345-TCP was only weakly sorbed. Boyd et al. (18) found that pentachlorophenol (PCP) was weakly sorbed by the TMA-clay.

Lee et al. (17) evaluated the ability of the TMA-clay surface to sorb a series of eight nonionic organic compounds (NOC) from the aqueous phase. They found the following degree of uptake for the compounds: benzene > toluene > xylene ≈ ethylbenzene > dichlorobenzene > trichlorobenzene > lindane. They noted that the isotherm shape changed from Type I for benzene to Type V for toluene, xylene, ethylbenzene, and dichlorobenzene. Linear sorption isotherms were found for 1,2,3-trichlorobenzene and lindane. Cadena (21) reported the following selectivity of organics for a TMA-clay: benzene >> toluene > *o*-xylene. The data were characterized using a Freundlich isotherm. Lee et al. (16) corroborated the findings of

Cadena (21). Research by Jaynes and Boyd (14) was consistent with the above findings: sorption of benzene was strong and characterized by a Type I isotherm. However, the sorption became weaker as the sorptive molecule became larger. Smith et al. (22) found that the sorption of tetrachloromethane to the TMA-clay could be characterized by a Langmuir-type isotherm.

While the same base clay was not used in the previous studies, there appears to be similarity in the order of uptake of NOC by the organo-clays. The ability of a TMA-clay surface to sorb NOC appears to be related to the molecular size of the sorptive molecule.

Competitive sorption effects between organic compounds and the TMA-clay were evaluated in two studies (16,22). Lee et al. (16) found that at equal relative concentrations toluene did not have an impact on the sorption of benzene; however, benzene did have an impact on the sorption of toluene. In addition, Smith et al. (22) found no competitive effect for tetrachloromethane sorption on a TMA-clay in the presence of trichloroethene. The authors indicated that all the NOC with the exception of toluene and xylene were sorbed on the interlamellar surfaces of the high charge TMA-smectite. There were some differences in the sorption isotherms of the organo-clays prepared from different base clays; this will be discussed in a later section.

2.2.2 HDTMA-Clays

Mortland et al. (20) and Boyd et al. (18) investigated the sorption of phenol and a series of chlorinated phenols on a HDTMA-clay. Based on the experimental data presented in these two papers, sorption decreased in the following order: pentachlorophenol (PCP) > 3,4,5-trichlorophenol (345-TCP) > 3,5-dichlorophenol (35-DCP) > 3-chlorophenol (3-MCP) > phenol. Sorption isotherms for the PCP, 345-TCP, and 35-DCP were nonlinear. Both PCP and 345-TCP sorption displayed a Type I isotherm, while the isotherm for 35-DCP sorption was characterized by a Type V isotherm. The isotherm for 3-MCP was relatively linear, and sorption of phenol on the HDTMA-clay surface was insignificant. There was not a discussion of the chlorophenol speciation in either paper and the pH for the sorption experiment was not reported in the Mortland et al. paper (20). Therefore, it is difficult to compare the sorption results without knowledge of the speciation of the organic sorptive.

Boyd et al. (19) found that the sorption isotherms for benzene and trichloroethene were linear and the organic matter partition coefficient [(K_{om}, kg solvent (kg OM)$^{-1}$)] values were comparable to the octanol/water partition coefficient [(K_{ow} , kg water (kg octanol) $^{-1}$)] values for the compounds. They evaluated the impact of changes in the quantity of HDTMA on the clay surface to determine if there was an effect on sorption of the NOC. Three different CEC percentage replacements by the organic cation were studied: 35, 70, and 100 percent. The data indicate that at the lowest HDTMA coverage the K_{om} values were significantly lower than the K_{om}

values for the two higher coverages. However, the decrease in sorption may have resulted from a change in the distribution of the type of organic carbon on the HDTMA-clay. The K_{om} value is based on the total organic carbon content of the sample: natural organic carbon ($\approx$1 percent) plus the added carbon from the surfactant (6-16 percent). Lee et al. (23) indicated that the HDTMA cation is approximately 10 to 30 times more effective on a weight basis than natural organic carbon in removing NOC from the aqueous phase. As the total organic carbon content decreases, resulting from a decrease in the percent CEC replacement by the organic cation, the relative percentage of the natural organic carbon increases. Therefore, based on the findings of Lee et al. (23) a decrease in the K_{om} values would be expected. This was not considered by Boyd et al. (19).

Lee et al. (23) evaluated the sorption of seven NOC, with aqueous solubilities ranging over two orders of magnitude, on a HDTMA-soil. Isotherms were linear and the K_{om} values were consistent with the K_{ow} values for the compounds. The degree of sorption was inversely related to the aqueous solubility of the compounds: benzene > trichloroethene > toluene > ethylbenzene > tetrachloroethene > *o*-dichlorobenzene > 1,2,4-trichlorobenzene. Smith et al. (22) found that the sorption of tetrachloromethane on the HDTMA-clay was characterized by a linear isotherm, relatively weak solute uptake, and noncompetitive sorption.

2.2.3 Other Organo-Clay Surfaces

Although the majority of the research on NOC sorption by organo-clays has involved TMA and HDTMA cations, there has been research with other quaternary ammonium cations. Smith et al. (22) studied the sorption of tetrachloromethane on ten organo-clays. Based on the sorption characteristics, these ten organo-clays could be classified into two groups depending on the chain length of the variable R group on the quaternary ammonium cation. When the alkyl functional group's chain length was two or fewer carbons, the sorption was characterized by a nonlinear isotherm, relatively strong solute uptake, and a competitive effect with trichloroethene. However, when the chain length was 12 or more carbons the sorption was characterized by a linear isotherm, relatively weak solute uptake, and a noncompetitive effect with trichloroethane. While only one sorptive was considered in the study, the general characteristics of the isotherms appear to be consistent with other research. Mortland et al. (20) noted that the sorption characteristics were similar between the members of the short chain group and also between members of the long chain group. Boyd et al. (18) also noted a similar trend in the sorption characteristics for the short and the long chain organo-clays.

Sorption isotherm characteristics for TMA-surfaces and TMPA-surfaces (trimethylphenylammonium) were similar. However, the TMPA-surface was a more effective sorbent as the molecular size of the sorptive increased. Sorption isotherm characteristics for dioctadecyldimethyl (DODMA), HDTMA, and hexadecylpyridinium

(HDPY) organo-clays were similar. As previously noted, the isotherms for PCP, 345-TCP, and 35-DCP on the HDTMA-clay were nonlinear. This was also true for sorption of these NOC on the HDPY and DODMA organo-clays. Lee et al. (23) found a linear isotherm and a general relationship between K_{om} and K_{ow} for the seven sorbates on dodecyltrimethylammonium (DTMA) and nonyltrimethylammonium (NTMA) organo-clays. Sorption on the NTMA-clay was not as intense as on the HDTMA and HDPY organo-clays.

Although Lee et al. (23) indicated that the sorption isotherm for the NTMA-clay was linear, there appeared to be a systematic deviation in the data. While there were some differences in the shapes of the isotherms, the general characteristics were similar. The difference in the isotherm characteristics, between the short and long chain clays, may be related to variation in the sorption mechanisms. This will be discussed in the next section.

Wolfe et al. (24, 25) studied the adsorption of 11 organic contaminants on three organo-clays. However, questions related to the experimental procedures section of these two papers raise some concerns about the interpretations and the validity of the data. Primary amines were used as the modifying cations in both studies. In general, amines are fairly strong bases, $pK_b \approx 4$ to 5 (26). Therefore, the cationic nature of the amine is a function of the solution pH. Neither paper reported the experimental pH nor if the pH was controlled during the reaction. Boyd et al. (18) also noted the pH problems that existed with these studies.

In Wolfe et al. (24), half of the tests were conducted above the solubility limit of the organic sorptives. In Wolfe et al. (25), the experimental procedure for the sorption isotherms resulted in the volatilization of the more volatile organic sorptives (benzene, chloroform, nitrobenzene, and toluene) from the aqueous phase. For example, of the original toluene that was lost during the equilibrium period, volatilization was responsible for 95% while sorption was responsible for the other 5% of the total toluene that was lost.

In addition, some of the results are counter to the research published to date. Based on the data presented in Wolfe et al. (25) benzene, butanol, chloroform, dimethylphthalate, nitrobenzene, phenol, and toluene are sorbed to a greater extent by the unmodified clay, than any of the organo-clays considered in the study. In contrast, McBride et al. (15) found insignificant sorption of benzene and phenol on the unmodified clay. Boyd et al. (19) found that sorption of benzene on the unmodified clay was insignificant. The results presented in Wolfe et al. (25) might be an artifact of the experimental procedure.

2.2.4 Sorption Mechanisms

There are two general sorption mechanisms responsible for the uptake of the NOC by organo-clays: adsorption and partition. These terms have been defined by Chiou (27). The term *sorption* is used to denote the uptake of a solute by a surface without reference to a specific mechanism. The term *adsorption* refers to the condensation of vapors or solutes (both being referred to as *adsorbates*) on a surface by physical or chemical bonding forces. The molecules that were not sorbed, i.e., remaining in solution, are refereed to as *sorptives* or *adsorptives*. In contrast to adsorption, the term *partition* or *partitioning* is used to denote an uptake in which the sorbed organic species permeates into the network of an organic structure. In general, adsorption can be considered a surface phenomenon with the adsorbate located only on the surface of the adsorbent; however, partitioning is the homogenous distribution of the sorbed material through the entire organic phase.

Smith et al. (22) studied the effects of the molecular structure of the modifying agent, i.e., the quaternary ammonium cation, on organo-clays' ability to sorb NOC. The study focused on the sorption of tetrachloromethane (carbon tetrachloride) to ten different organo-clays. Functional groups on the quaternary ammonium cations consisted of alkyl groups with variable chain lengths and/or aryl functional groups. The purpose of the study by Smith et al. (22) was to provide a better understanding of the mechanistic interactions of NOC and organic matter at the mineral surface.

Smith et al. (22) suggested either an adsorption or a partition mechanism for each of the ten organo-clays. Using the data from the sorption isotherms for tetrachloromethane, Smith et al. (22) separated the ten organo-clays into two groups based on the alkyl chain length. When the R group contained less than 12 carbon atoms, an adsorption type mechanism was proposed. These sorption isotherms were characterized by a nonlinear isotherm, relatively strong solute uptake, and a competitive effect with trichloroethene. When the R group contained 12 or more carbon atoms, a partition type mechanism appeared to be responsible for sorption. These sorption isotherms were characterized by a linear isotherm, relatively weak solute uptake, and a noncompetitive effect with trichloroethane. The two mechanisms could be identified based on the alkyl chain length of the modifying surfactant and could be characterized by TMA and HDTMA organo-clays. However, this dividing point, an R group with 12 carbon atoms, was somewhat arbitrary since there were no organic cations with R groups containing between 3 and 11 carbons that were included in the study; thus no comparison could be made. Smith et al. (22) noted that the difference in the sorption mechanism between the two groups of organo-clays appeared to be related to the alkyl-chain length rather than to the presence of an aryl functional group.

Lee et al. (23) investigated the sorption of benzene, toluene, and ethylbenzene on three organo-soils; NTMA, DTMA, and HDTMA. The log K_{om} values decreased in the order HDTMA ≈ DTMA > NTMA. They concluded that as the alkyl chain length decreased below C_{12}, the hydrocarbon moieties became more isolated and formed a less effective partition medium then when larger cations were present. However, they point out that the NTMA-soil was a more effective partition medium than natural organic carbon.

Cadena (21) stated that the adsorption of benzene by a TMA-clay was a "partitioning-like" reaction, based on his interpretation of Boyd et al. (19). However, Boyd et al. (19) investigated the sorption of benzene by a HDTMA-soil and concluded a partitioning mechanism was operational. While the base structure of the organic of the TMA and HDTMA cations is similar [$N(CH_3)_3R$], the difference in the R groups is significant: $R=CH_3$ [TMA] vs. $R=(CH_2)_{15}CH_3$ [HDTMA]. Lee et al. (17) pointed out that the mechanism for the uptake of NOC from water by TMA-smectite (i.e., adsorption) was distinctly different from that by HDTMA-smectite (i.e., partitioning). However, the isotherms were nonlinear for the sorption of benzene, toluene, and *o*-xylene on the TMA-clay.

2.2.4.1 Adsorption Mechanism

An adsorption mechanism has been invoked by a number of researchers to describe sorption of NOC by clay surfaces. McBride et al. (15) indicated that adsorption is the mechanism responsible for uptake of benzene by a TMA-clay. Based on infrared studies, they found that π-electron interactions with the silicate surface were the most significant adsorption process that occurred.

Mortland et al. (20) concluded that the sorption of phenol and chlorophenols on a TMA-clay was via an adsorption mechanism, but no clear reason(s) was given for this conclusion. However, the data presented in their paper appears to be consistent with this mechanism.

Boyd et al. (18) concluded that the TMA-clays and TMPA-clays behaved as a conventional mineral sorbent for the sorption of pentachlorophenol. They indicated that the organic moieties, such as the -CH_3 group, could not form an effective partition medium despite a significant carbon content. The authors concluded that no mechanism exists for significant uptake of PCP by these organo-clays, because PCP was not capable of displacing the water on the mineral surface.

Lee et al. (17) indicated that the sorption mechanism of NOC from an aqueous solution was adsorption. This conclusion was based on nonlinear isotherms and an inverse relationship between the preference of the surface for a compound and its water solubility.

Lee et al. (16) proposed an adsorption mechanism for the sorption of benzene, toluene, and xylene on a TMA-clay. This was based on nonlinear isotherms and a competitive effect between benzene and toluene for adsorption sites.

Smith et al. (22) indicated that the sorption of tetrachloromethane on TMA-, TEA-, benzyltrimethylammonium (BTMA)-, and benzyltrimethylammonium (BTEA)-clays could be described by an adsorption mechanism. This was based on nonlinear sorption isotherms, relatively strong solute uptake, and a competitive effect with trichloroethene. However, there were no competitive effects with the TMA-clays.

2.2.4.2 Partition Mechanism

A partition mechanism can be represented by the linear relationship of a contaminant species between two phases, e.g., concentration ratio between a solid and aqueous phase, kg aqueous phase (kg solid phase)$^{-1}$. For relatively water-insoluble organic solutes, a partition reaction has the following general characteristics related to the partition coefficient, K_p ; i) the partition coefficient for an organic solute is usually inversely related to the compound's water solubility, SW; ii) the partition coefficient is usually independent of the solute concentration, thus the sorption isotherm is linear over a large solute concentration range; and iii) the partition coefficient is not dependent on the presence of other solutes. Therefore, there is no sorption competition between the organic compounds in solution (27).

Boyd et al. (19) indicated that a partitioning like process was responsible for the sorption of benzene and trichloroethene by a HDTMA-clay. This mechanism was based on: linear isotherms (over a large relative concentration range), sorption depended on the organic carbon content of the organo-clay, and close agreement between the K_{om} and the K_{hw} (heptane-water partition coefficient) values.

Lee et al. (23) identified a partition mechanism for the sorption of benzene, toluene, and ethylbenzene by NTMA, HDTMA, and DTMA organo-clays.

Smith et al. (22) concluded that a partition mechanism was responsible for the sorption of tetrachloromethane onto HDTMA-, DTMA-, tetradecyltrimethylammonium (TTMA)-, benzyldimethylhexadecylammonium (BDHA)-, and dodecyldimethyl(2-

phenoxyethyl)-ammonium (DDPA)-clays. Sorption was characterized by linear isotherms, noncompetitive sorption, and relatively low solute uptake.

Jaynes and Boyd (28) indicated that the sorption of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and *t*-butylbenzene on a HDTMA-clay occurred by a partition mechanism. This observation was based on isotherm linearity and the close relationship between the log K_{ow} and log K_{om}.

Contrasting with these results are data from Mortland et al. (20) and Boyd et al. (18) for the sorption of phenol and chlorinated phenols. Mortland et al. (20) referred to the sorption of 3-monochlorophenol, 3,5-dichlorophenol, and 3,4,5-trichlorophenol on HDTMA and HDPY organo-clays as adsorption. The authors may be using adsorption as a general term, since they provide no discussion on the selection of the mechanism. However, the isotherms are distinctly nonlinear for the sorption of all of the above compounds. While this is consistent with an adsorption mechanism, it is not what one would expect based on other research with HDTMA and HPDY organo-clays.

In addition, Boyd et al. (18) indicated that the sorption of pentachlorophenol by HDTMA-clay occurs by a partition mechanism. This conclusion was based on a linear sorption isotherm for the PCP sorption. However, the data used to generate this linear isotherm represented a limited range of the sorption process. The linear isotherm occurred at a relative concentration [aqueous concentration (C_e) / aqueous solubility (SW)] between 0-0.02 (C_e / SW). However, other data presented in the paper included a larger relative concentration region, 0-0.2 (C_e / SW), and in this range the isotherm was nonlinear. Chiou (27) states that the observed isotherm linearity should extend over most of the relative concentration range. If the data are collected over a limited region of relative concentration, then the linear isotherm may only represent a portion of a nonlinear isotherm. It should not be mistaken for the linear portion of a nonlinear isotherm. The authors gave no explanation for the apparent inconsistency in the presentation of the data. However, the nonlinear isotherm could be explained based on the pH of the system. The pH appears to be in excess of the pK_a (4.74), therefore, the dominant aqueous species is the phenolate anion.

2.2.5 Aspects of the Mineral Surface

Several researchers have examined the importance of the type of the mineral surface on the sorption capability of the organo-clay (14,17,28). Specifically, they have evaluated the impact of the mineral layer charge on the sorption of NOC to the organo-clay.

Lee et al. (16) and Jaynes and Boyd (28) evaluated several smectite minerals to determine the impact of layer charge on the short chain organo-clays. TMPA and TMA organo-clays were prepared using a low and a high charge smectite. In both cases, the organo-clay with the lower base mineral charge density was a more effective sorbent. In the organo-clay with the greater charge density, Jaynes and Boyd (28) proposed that the closer packing of organic cations in the clay interlayers resulted in restricted access of the aromatic molecules to the interlamellar regions. In addition, Lee et al. (16) suggested that the hydration water may further occlude the interlamellar region, resulting in further restriction of the sorbate. Thus, for the short chain organo-clays, as the layer charge on the base mineral increases, the ability to sorb NOC from an aqueous solution decreases. This would be consistent with the adsorption mechanism proposed for the short chain organo-clays.

However, for the longer chain organo-clays, specifically HDTMA-clay, as the layer charge increases the sorption ability of the organo-clays also increases. Jaynes and Boyd (28) extensively investigated the impact of layer charge on the HDTMA-clay. They studied a series of seven clay minerals, ranging from KGa-2 kaolinite (charge, 0 mol/unit cell) to IMt-1 illite (charge, 1.44 mol/unit cell). The sorptives were a series of unsubstituted aromatic compounds (benzene, naphthalene, and biphenyl) and alkyl-aromatic compounds (toluene, ethylbenzene, propylbenzene, butylbenzene, and *t*-butylbenzene).

The authors found that when HDTMA was added, basal spacing of some clays increased. The greatest increase in spacing occurred with vermiculite followed by the high to low charged smectites; the basal spacings of illite and kaolinite were unchanged. Jaynes and Boyd (28), using the basal spacing of the organo-clays, proposed five potential geometric relationships between the organic cation and the clay surface. These were only proposed relationships; there is no physical evidence that the organic cations are found in any of these positions.

The HDTMA-exchanged vermiculite, illite, and smectite clays were effective sorbents. The organo-kaolinite did not significantly retain the organic sorptives. Jaynes and Boyd (28) also found that as the basal spacing increased, sorption of an organic molecule was facilitated. However as the organic sorptive molecule became larger, sorption was ultimately limited. This was true for all the clays. Comparing the experimental data for HDTMA-vermiculite and HDTMA-smectite (low charge) at similar HDTMA concentrations, Jaynes and Boyd (28) found that sorption isotherms for benzene on the two HDTMA-clays were similar; however, for alkyl benzene sorptives as progressively larger alkyl groups were added the HDTMA-vermiculite sorbed increasingly more of the alkyl-aromatic compounds than the smectites. This discrepancy was observed until the size of the sorbate molecule exceeded some critical value and then the isotherms of the two HDTMA-clays were similar.

In addition, Jaynes and Boyd (28) found that the sorption of the unsubstituted aromatic compounds was dependent upon the mass of adsorbed HDTMA and independent of the HDTMA surface geometry. This is in contrast to what was observed for the sorption of the alkyl-aromatic compounds, which was related to the HDTMA surface geometry and independent of the adsorbed HDTMA mass.

The geometric orientation of the organic cation in relation to the basal spacing is still not understood. The data indicated that there was a difference in the sorption characteristics between substituted and unsubstituted aromatic compounds. These are important findings. Part of the focus of the research of Jaynes and Boyd (28) was to identify parameters that are necessary for the use of a organo-soil as a barrier to the migration of organic contaminants. This data provided important information related to the evaluation of a soil or clay as a modified-surface.

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Chapter 3

CHARACTERIZATION OF THE HDTMA-CLAY.

3.1 Introduction

This chapter describes the basic structural properties and development of permanent negative surface charge on clay minerals, and the exchange reaction between natural inorganic cations on clay surfaces and organic cations to produce a modified-clay. In addition, characterization data on the HDTMA-clay is presented. These include analytical data to confirm that the exchange reaction occurred, and evidence is presented on changes that occurred in the surface properties of the clay after exchange with hexadecyltrimethylammonium cations (HDTMA).

3.2 Clay Mineral Structure and Development of Negative Surface Charge

Clay minerals are aluminosilicates that predominate in the clay fraction of soils at intermediate to advanced stages of weathering. These minerals are sandwiches of tetrahedral and octahedral sheet structures (Figure 3.1). The octahedral sheet is represented by an aluminum, iron, or magnesium atom in octahedral coordination

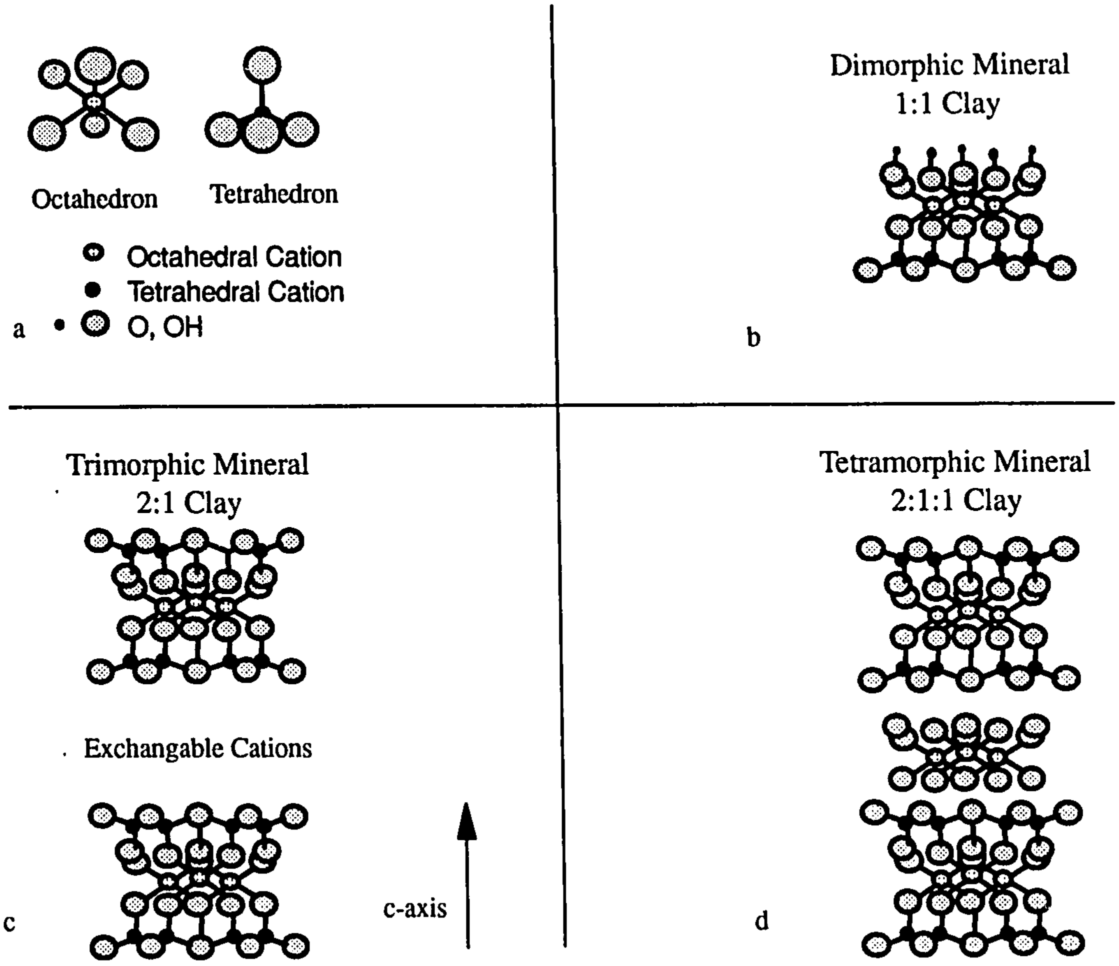

Figure 3.1 Ideal molecular structure of a) single tetrahedron and single octahedron, b) 1:1 clay mineral, c) 2:1 clay mineral, and d) 2:1:1 clay minerals

(Figure 3.1a) with six oxygen atoms i.e., $M_{2-3}(O,OH)_6$. When two of the three octahedral positions (M) are filled (Al^{3+}), the structure is referred to as dioctahedral. When all three positions are occupied (Mg^{2+}) the structure is referred to as triocthedral.

The tetrahedral sheet is composed of individual tetrahedra, SiO_4^{4-} , sharing three corner oxygen (basal oxygens) atoms with neighboring tetrahedra forming a hexagonal (only under ideal conditions, ditrigonal under normal conditions) mesh pattern in a continuous two dimensional sheet structure (Figure 3.1a). The fourth oxygen (apical oxygen) atom points normal to the tetrahedral sheet and is linked to the immediate adjacent octahedral sheet. This common plane consists of the shared apical oxygen and unshared OH (octahedral) groups that lie at the center of each tetrahedral six-fold ring at the same *z* -level as the apical oxygen (1).

There are three basic structural units that make up clay minerals based on the ratio of tetrahedral:octahedral sheets (Table 3.1): dimorphic minerals (1:1 ratio) (Figure 3.1b) , e.g., kaolinite is the best known example; trimorphic minerals (2:1 ratio), with the octahedral sheet sandwiched between two inward-facing tetrahedral sheets (the mica-type layer structure)(Figure 3.1c); tetramorphic minerals (2:1:1 ratio) with a trimorphic unit alternating with a octahedral sheet (Figure 3.1d) (chlorite is the best known example of a 2:1:1 clay mineral) (2).

Table 3.1 General classification of clay minerals.

Layer Type	Group	Layer Charge per Formula Unit
1:1	Kaolinite--Serpentine	0
2:1	Pyrophyllite--Talc	0
	Smectite	0.25-0.6
	Vermiculite	0.6-0.9
	Mica	1
	Brittle Mica	2
2:1:1	Chlorite	variable

Clay minerals vary widely in chemical composition and substitution of atoms in the structural unit usually occurs. The elemental substitution takes place during the mineral crystallization without changing the basic crystal structure. The resulting modification is permanent and is referred to as isomorphous substitution. This substitution is driven by ion size rather than ion valence. It occurs between ions differing by less than 10-15 % in the size of their ionic crystal radii (3). Common substitutions are Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+}, Fe^{3+}, or Fe^{2+} for the Al^{3+} (Mg^{2+}) in the octahedral sheet. Substitution of atoms with lower valence results in a positive charge deficit within the structural unit causing a permanent negative structural charge that must be balanced to maintain electroneutrality. This charge deficit may be compensated, to some extent, by internal substitution but for the most part electroneutrality is maintained by the electrostatic adsorption of cations.

In the natural environment, the cations that satisfy the negative charge on the clay are inorganic metals. These cations are surrounded, to a varying degree, by water molecules. The hydration of these exchangeable metal cations and the presence of Si-O groups in the clay mineral give the surface a hydrophilic character (4). This tends to prohibit nonionic organic compounds (NOC) from interacting with the mineral surface. As a result, the NOC cannot compete with water for adsorption sites on the mineral surface (5). Therefore, hydrophilic surfaces (i.e., low organic matter soils, clay, and aquifer materials) have only a limited sorption capacity for NOC.

Replacement of inorganic cations on the clay surfaces with organic cations will change the mineral surface to a more hydrophobic character and increase the sorption capacity for organic compounds. The resulting sorption characteristics of the modified clay are a function of the surfactant that has been added to the mineral surface.

3.3 Materials and Methods

3.3.1 Preparation of the Base Clay

Sodium-montmorillonite (SWy-1) from Crook County, Wyoming was obtained from the Source Clays Repository at the University of Missouri. The clay was fractionated by adding approximately one hundred grams of SWy-1 to one kg of deionized water (DI). Particles > 2μm in diameter were removed by sedimentation. The pH of the suspension was then reduced to 5 with dilute HCl, and the temperature of the suspension was increased to 333 K and maintained for three hours to remove any carbonates from the mineral surface. After cooling to room temperature, the clay was Na-saturated by increasing the Na^+ concentration, in the suspension, to $1m$ (molality) (using NaCl) and equilibrated for 24 hours. The suspension was then washed with DI, dialyzed, and freeze-dried. The pretreated clay, termed the base clay, was used for subsequent preparation of HDTMA-clay.

The cation exchange capacity (CEC) of the base clay, as measured by Ca-Mg exchange, was 90 cmol kg^{-1}. X-ray diffraction analysis of the clay did not reveal the presence of other minerals.

3.3.2 Preparation of the HDTMA-Clays

The $HDTMA^+$ cation will readily replace the Na^+ cation on the smectite surface, up to the CEC of the clay (6). In this research, three modified clays were prepared based on different percent replacements of the CEC by $HDTMA^+$; 35%, 70%, and 100%. The modified clays will be referred to as HDTMA(35%)-clay, HDTMA(70%)-clay, and HDTMA(100%)-clay.

The modified clays were prepared by the addition of an appropriate mass of hexadecyltrimethylammonium bromide (also referred to as cetrimonium bromide)(Aldrich) to a 750 mg kg^{-1} base clay suspension. Since the suspension flocculated instantly upon addition of the $HDTMA^+$, it was mixed by hand until the floc was broken down sufficiently to allow mixing with a magnetic stir bar. The suspension was mixed for 24 hours, washed four times to remove excess ions, and freeze-dried. The wash water was analyzed for $HDTMA^+$ using the methodology of Furlong and Elliker (7). Analysis did not reveal any $HDTMA^+$, indicating that the HDTMA cations were quantitatively taken up at exchange positions. This assumption is consistent with the data of Zhang et al. (6), who showed that $HDTMA^+$ replaced > 95% of the Na^+ on the SWy-1 clay.

3.4 Evaluation of the HDTMA-Clay

3.4.1 Total Carbon and Nitrogen Analysis

The total carbon and nitrogen analyses (Table 3.2) of the HDTMA-clays were conducted using a Leco CNS-2000 elemental analyzer. Experimental results were consistent with the anticipated values based on calculation of the mass of the $HDTMA^+$ cation initially added to the clay suspension.

3.4.2 X-ray Diffraction Analysis

X-ray diffraction analyses (Table 3.3) were conducted with a Philips diffractometer using an APD 3520 controller and a RW 1729 X-ray generator utilizing Cu radiation (λ=1.540Å). Samples were analyzed as both packed powder mounts and as suspensions dried on glass sides. Diffractograms were characterized by a single diffraction peak for each sample (Table 3.3) with the peak slightly broadening as the percent replacement of the CEC by the $HDTMA^+$ cation increased.

3.4.3 Scanning Force Microscopy (SFM)

Scanning force microscopic (SFM) analysis was performed with a Digital Instruments NANOSCOPE II, operating under conventional force conditions. A silicon nitrile cantilever with a 100μm long tip was used in all of the image analyses that are presented. Multiple tips were used to image each surface; this was conducted to verify

Table 3.2 Total carbon and nitrogen analyses of clays including both experimental and theoretical data.

Sample	Experimental Data		Theoretical Calculation	
	% Carbon	% Nitrogen	% Carbon	% Nitrogen
SWy-1	0.35	0.026	NA	NA
HDTMA(35%)-clay	10.2	0.631	6.75	0.41
HDTMA(70%)-clay	13.8	0.852	12.7	0.78
HDTMA(100%)-clay	17.4	1.11	17.3	1.06

Table 3.3 X-ray diffraction results.

Sample	*d*-spacing nm
SWy-1	1.25
HDTMA(35%)-clay	1.39
HDTMA(70%)-clay	1.65
HDTMA(100%)-clay	1.75

that artifacts of individual tip shapes were not introduced in the final image. The acquired images were not visually enhanced other than by a low pass filtering to reduce noise levels. Fourier filtering was not used in these images. Figures 3.2 to 3.5 present images for SWy-1, HDTMA(35%)-clay , HDTMA(70%)-clay , and HDTMA(100%)-clay.

3.5 Results and Discussion

The total carbon and nitrogen analyses indicated that the added HDTMA was retained by the mineral surface. The retained HDTMA was not removed by washing; it was assumed that the HDTMA$^+$ cations were electrostatically bound to the clay. This finding is consistent with the data of Zhang et al. (6), who showed that HDTMA$^+$ cations replaced > 95% of the Na$^+$ cations on the SWy-1 clay when the HDTMA was added in a mass equivalent to the CEC. The conclusions reached by Zhang et al. (6) were based on both the loss of HDTMA and the appearance of sodium in the aqueous phase during the exchange reaction.

Based on a 1:1 stoichiometric Na$^+$:HDTMA$^+$ exchange, it was assumed that the HDTMA$^+$ cations were uniformly distributed across the internal and external surface area of the clay. The addition of HDTMA to internal surfaces should result in an increase in the *d*-spacing of the clay to accommodate the organic cation in the interlayer. The expansion of the montmorillonite interlayer should occur in steps

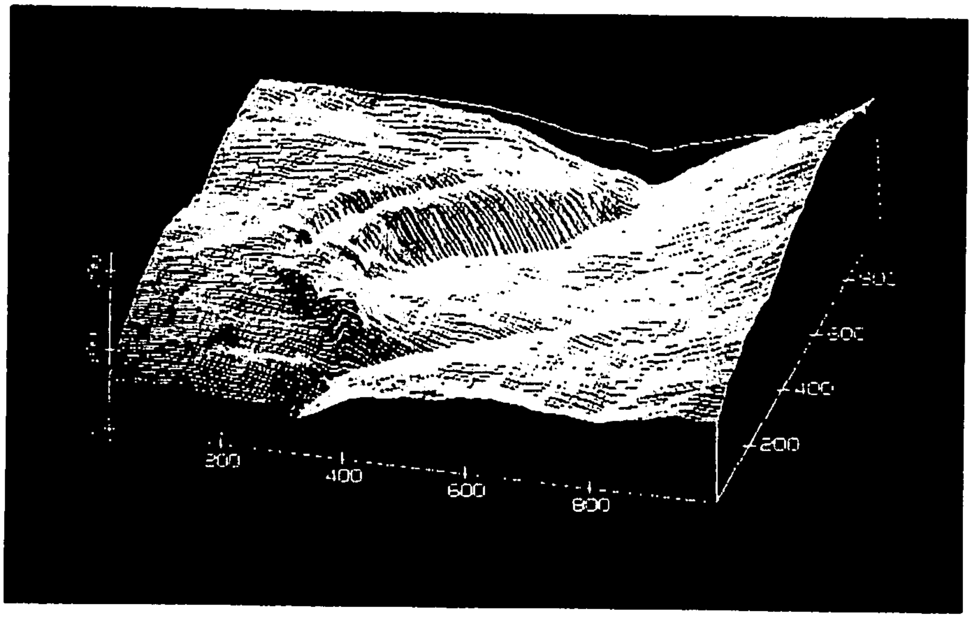

Figure 3.2 SFM image of the unmodified SWy-1 surface.

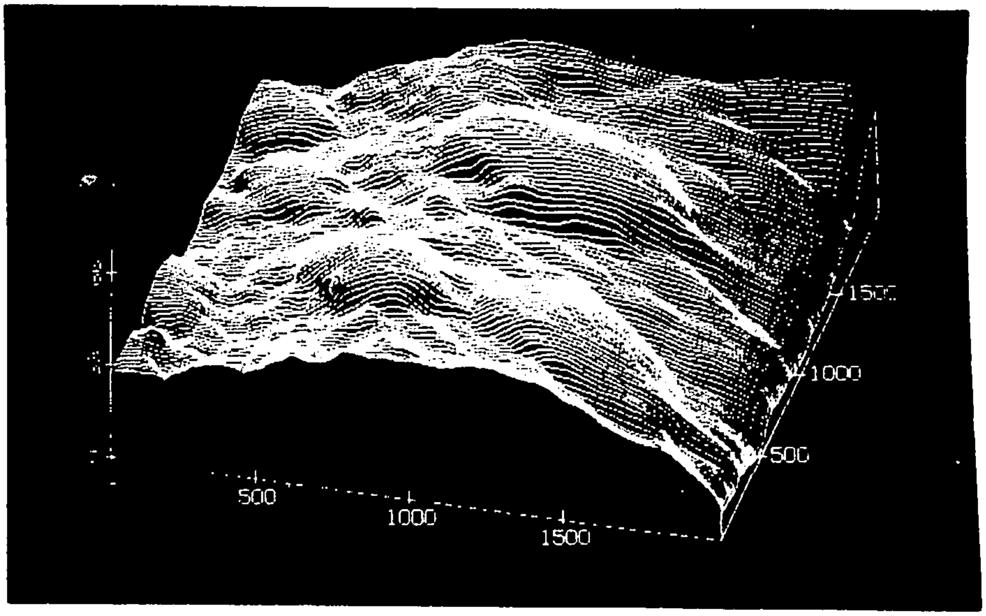

Figure 3.3 SFM image of the HDTMA(35%)-clay.

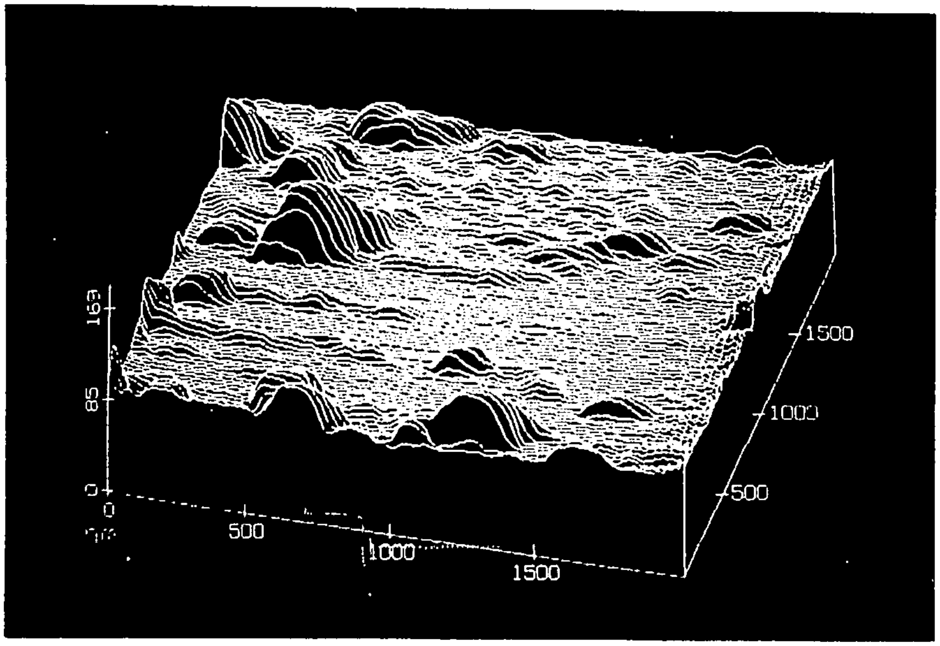

Figure 3.4 SFM image of the HDTMA(70%)-clay.

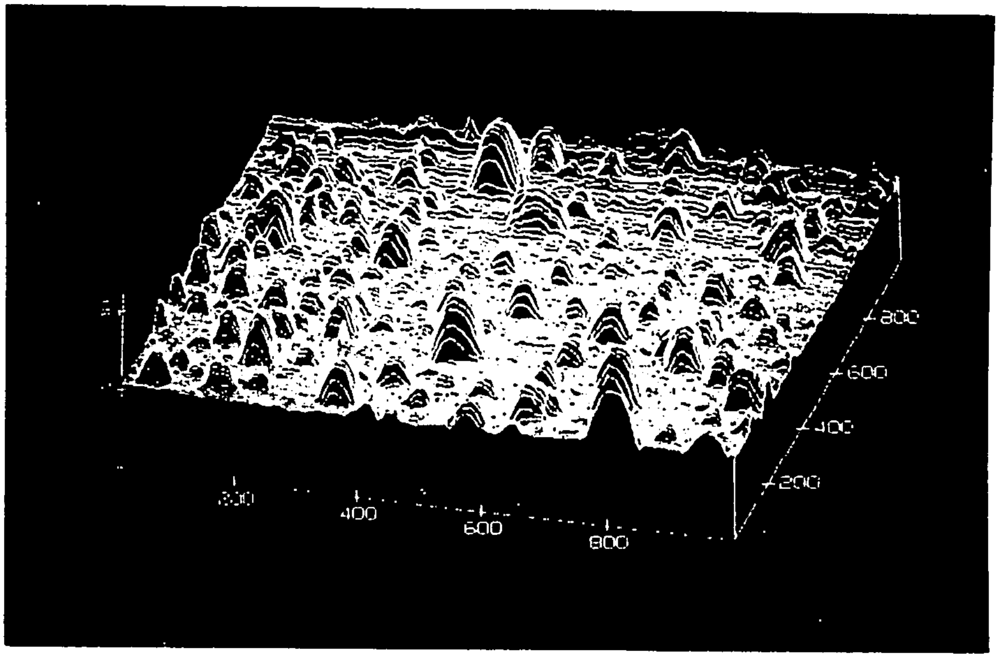

Figure 3.5 SFM image of the HDTMA(100%)-clay.

based on the van der Waal diameter of the HDTMA tail, ≈ 0.4 nm. When addition of HDTMA results in less than monolayer coverage (<60% CEC) the *d*-spacing should be approximately 1.35 nm, and with bilayer coverage, the *d*-spacing should increase to approximately 1.75 nm (Figure 3.6). The changes in the *d*-spacings of the modified-clay were consistent with the addition of the HDTMA to the interlayer, forming monolayer coverage in the HDTMA(35%)-clay and bilayer coverage in the HDTMA(70%)-clay and HDTMA(100%)-clay.

The SFM images (Figs. 3.2 - 3.5) show a signification alteration in the clay's external surface occurred with the addition of HDTMA. This indicates that in addition to HDTMA sorption on internal surfaces there is also sorption on external surfaces. The clay surface becomes very flat and "pancake" like structures (appears as a paraboloid in Figs. 3.2 - 3.5 due to vertical exaggeration) are found randomly on the surface. These features were found predominantly on the HDTMA(70%)-clay and HDTMA(100%)-clay samples.

Based on the images for the HDTMA(100%)-clay sample, the "pancake" like structures were approximately 15-18 nm in height, and they had a diameter of 100-150 nm. Given a qualitative estimate of the surface charge density of the clay as, 1.5 nm^2 $site^{-1}$, and a $HDTMA^+$ head surface area of ≈ 0.5 nm^2, the head group would cover ≈30% of the external surface area of the HDTMA(100%)-clay sample. This is similar

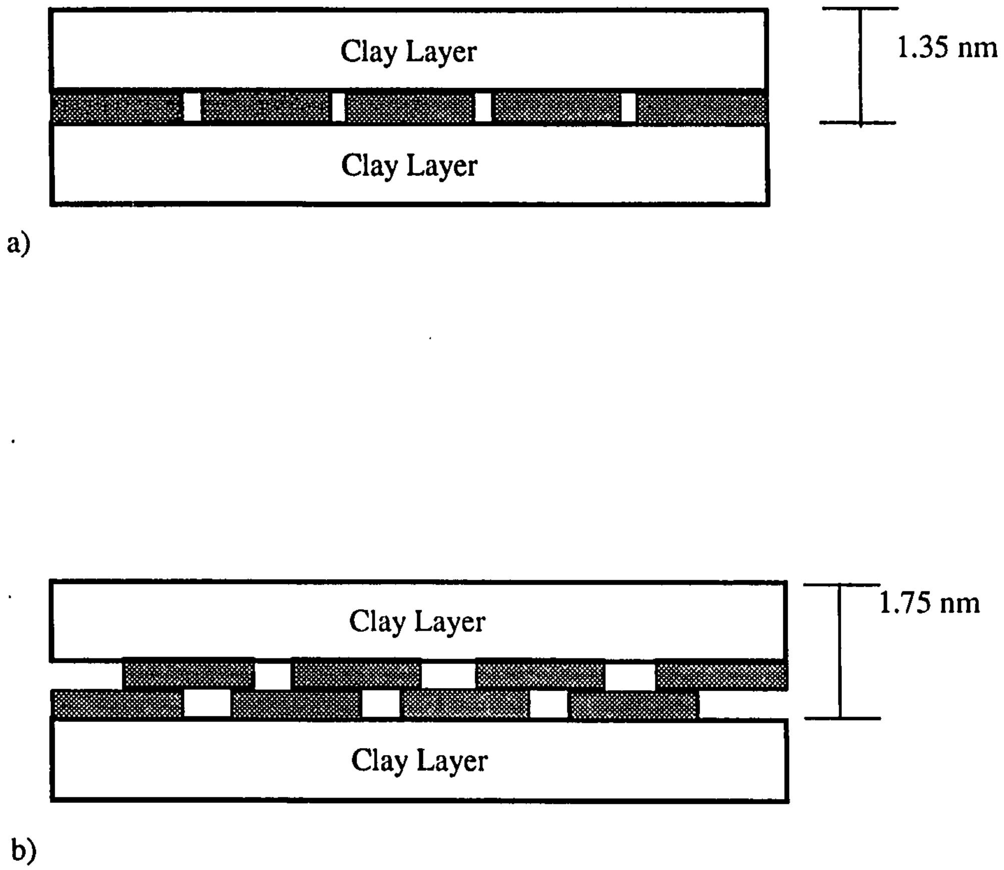

Figure 3.6 *d*-spacing of the modified-clay with a monolayer and bilayer of HDTMA.

to the observed "pancake" coverage determined from the SFM images. If the HDTMA$^+$ cations are at exchange positions on the external surfaces, the position of the hydrophobic tail must be considered. The tail, due to its hydrophobic nature, will not favor a position normal to the surface, pointing into the water. Therefore, either the tails are bound up very close to the surface or they are arranged as a hemimicelle. The hemimicelle structure is composed of a bilayer of the surfactant with the hydrophobic tail inside the hemimicelle and the polar head group sticking out into the aqueous phase (Figure 3.7). Thus, a portion of the sorbed HDTMA$^+$ cations would not be contributing to balancing the negative surface charge, and they would provide an apparent positive charge to the solid phase. Due to the large relative internal:external surface area ratio on montmorillonite (8), the amount of total HDTMA$^+$ cations needed to form the external hemimicelle structure is not significant in relation to the HDTMA$^+$ on the clay internal surface. In addition, this could account for the observed greater HDTMA$^+$ cation uptake than Na$^+$ release upon modification.

Assuming that the replacement of the Na$^+$ cation by the HDTMA$^+$ cation is stoichiometric, one would expect the zeta potential to be relatively constant with increasing HDTMA$^+$ replacement up to 100% CEC replacement. Once the Na$^+$ cations have been exchanged and the HDTMA$^+$ cations are in excess, there would be hydrophobic sorption of the HDTMA$^+$ cations. This will result in an increase in the

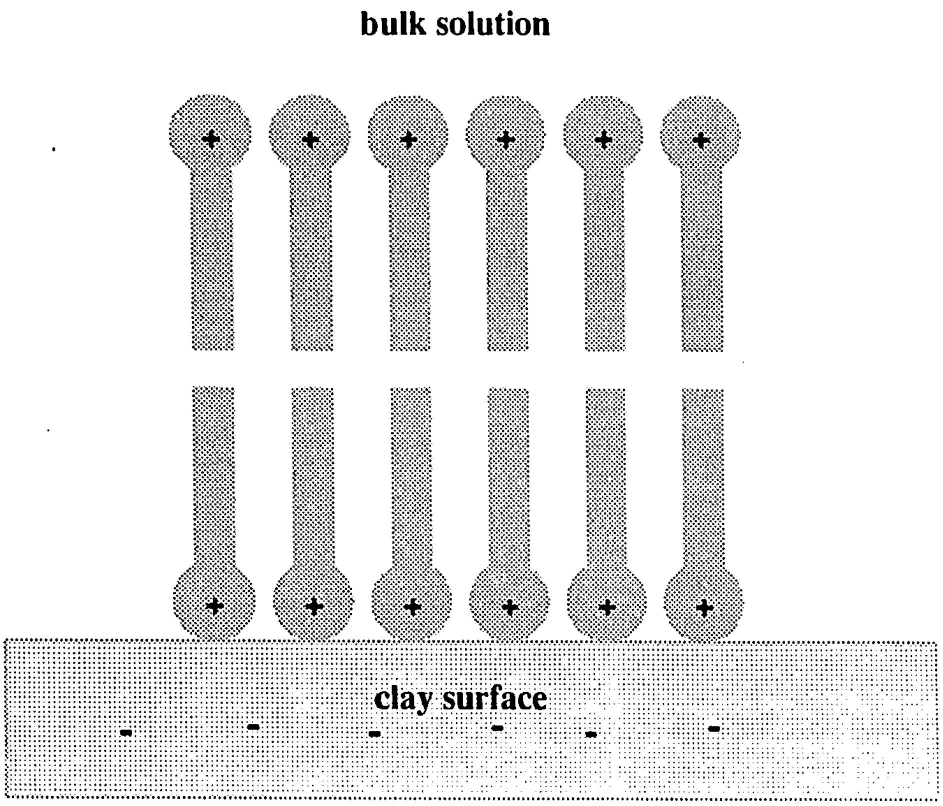

Figure 3.7 Hemimicelle bilayer structure.

zeta potential until the critical micelle concentration (cmc) of the surfactant is reached. The zeta potential would be reversed when the hydrophobically bound surfactant balances the exposed negative surface charge. However, if the zeta potential were to be reversed prior to complete sodium exchange, this would indicate hemimicelle formation.

Jamrah (9) determined the zeta potential for HDTMA-clay (SWy-1) at loadings from 0 - 500% $HDTMA^+$ replacement of the CEC (Figure 3.8). There was a reversal of the zeta potential at ≈ 60% CEC replacement. In addition, the work of Xu and Boyd (10) presents similar results for the sorption of HDTMA to a vermiculite. Therefore, the reversal of the zeta potential would provide evidence for the formation of a hemimicelle structure on the surface prior to complete exchange of the inorganic cations.

It is proposed the $HDTMA^+$ cations formed a hemimicelle structure on the HDTMA(70%)-clay and HDTMA(100%)-clay samples. The structure of the hemimicelle would be similar to a pancake, made up of a bilayer of $HDTMA^+$cations. While this bilayer would be 3-6 nm in thickness, it is proposed that the "pancake" would be potentially similar to a bubble and have water trapped between the mineral surface and the hemimicelle. This would allow it to rise ≈ 10 nm from the clay surface. If this were the case then the structure observed from the SFM imaging could be explained.

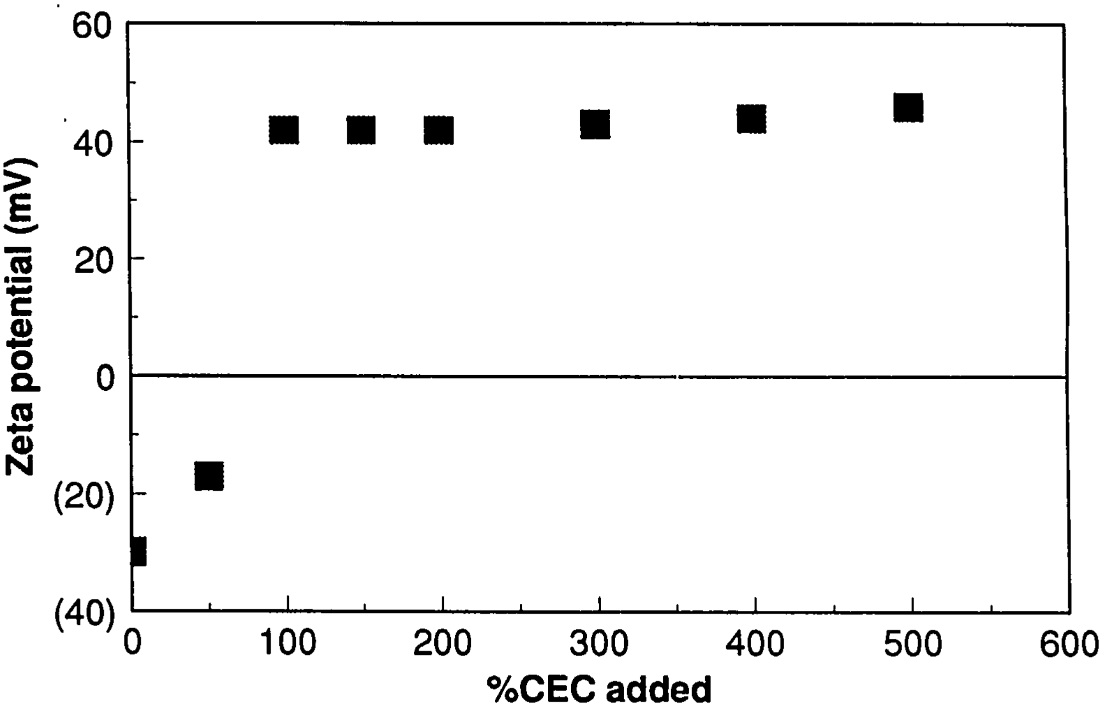

Figure 3.8 Zeta-potential of montmorillonite as affected by the amount of HDTMA$^+$ cation expressed as %CEC added. From Jamrah (1993)

3.6 Conclusions

1) The $HDTMA^+$ that was initially added to the SWy-1 clay was retained on the mineral surface.

2) The $HDTMA^+$ that was retained on the mineral surface was located at both internal and external mineral surfaces.

3) The formation of a hemimicelle surfactant structure on the external surface was proposed.

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Chapter 4

SORPTION OF PENTACHLOROPHENOL TO HDTMA-CLAY AS A FUNCTION OF IONIC STRENGTH AND pH

4.1 Introduction

The use of surfactant-modified clay as a sorbent for organic compounds from an aqueous phase has been an active area of research (1-19). The majority of this research has involved the use of quaternary ammonium compounds (surfactants) to modify smectitic clays. The addition of the surfactant to the clay, via an ion exchange reaction, produces a sorbent with an increased sorption capacity for organic compounds. The selectivity of the sorbent can be controlled, to a degree, by the surfactant that is used to modify the clay. Therefore, it is possible to produce a sorbent that can maximize the sorption of a specific class of compounds. Background information on the modification process was presented in Chapters 2 and 3 and will not be discussed here.

The majority of the research in this area has focused on the sorption of nonionic organic compounds (NOCs), while few studies (7) have investigated the sorption of ionizable organic compounds (IOCs). Ionizable organic compounds, in the aqueous phase, can exist either as a protonated or deprotonated species. They can be represented by organic acids and bases as shown in the following equilibrium relationship;

$$HA^{\circ} \rightleftharpoons A^{-}+H^{+} \qquad K_a=\frac{(A^{-})\,(H^{+})}{(HA^{\circ})} \qquad \textbf{(4.1)}$$

$$BH^{+} \rightleftharpoons B^{\circ}+H^{+} \qquad K_a=\frac{(B^{\circ})\,(H^{+})}{(BH^{+})} \qquad \textbf{(4.2)}$$

where,

HA° = the organic acid, protonated species

A^{-} = the conjugate base of the organic acid, deprotonated species

B° = the organic base, deprotonated species

BH^{+} = the conjugate acid of the organic base, protonated species

K_a = dissociation constant, $pK_a = -\log(K_a)$

The occurrence of the protonated and deprotonated species depends on the solution pH in relation to the pK_a of the compound. The protonated species are dominant when the $pH \ll pK_a$; the deprotonated species are dominant when the $pH \gg pK_a$. However, both the protonated and the deprotonated species are significant when the $pH \approx pK_a$.

One might anticipate that the chemical properties of the two species would be different. Therefore, it is important to consider differences in the chemical properties of the species when describing sorptive behavior. However, the sorption of an IOC on a surfactant-modified clay, over a pH range that would include both species, has not been systematically investigated to date. The pH range of surface and groundwater is approximately from 4 to 9. Therefore, IOCs with a pK_a in the same range are of special interest, because both the protonated and deprotonated species may be found in the aqueous phase. Several priority pollutants are IOCs and have pK_as that fall within the above range, such as chlorinated phenols, nitrophenols, and dinitrophenols. Most notable is the organic acid pentachlorophenol (PCP), with a pK_a of 4.75 (20).

Solubility and distribution ratios are two general properties of IOCs that can differ significantly with pH. For PCP, Valsaraj et al. (21) reported the solubility to range from 30 to >15 000 µM as the pH increased from 2.5 to 8. Kaiser and Valdmanis (22) found that the logarithm of the distribution ratio (log D) between octanol and water decreased from 4.8 to 1.3 when the pH increased from 4 to 10. Jafvert et al. (23) also reported an increase in the distribution ratio with a decrease in pH. In addition, the ionic strength and the background electrolyte have been shown to influence the distribution ratio of PCP between octanol and water at pH >8 (23).

It is important to differentiate between two terms to avoid confusion when discussing IOCs; a partition coefficient (K_p) which is the concentration ratio for a particular species (protonated or deprotonated) between two phases, and a distribution ratio (D) which is the ratio of the total analytical concentration (protonated and deprotonated) between these two phases. Westall and coworkers (23-26) determined distribution ratios of hydrophobic ionizable organic compounds (HIOCs) between octanol and water as a function of solution pH, and the nature and concentration of the background electrolyte. For such hydrophobic substances, these papers convincingly show that the ionic species of organic acids and bases enter the octanol phase. Four mechanisms for the distribution of an IOC between two phases were proposed (23-26), based on an organic acid (HA):

(I) Hydrophobic sorption of the protonated species

$$HA \rightleftharpoons \overline{HA} \qquad (4.3)$$

(II) Transfer of the deprotonated species, as an ion pair ($\overline{A}^- + \overline{M}^+$) or a free ion ($\overline{A}^-$), between two phases

$$A^- + M^+ \rightleftharpoons \overline{A^-M^+} \quad (\overline{A^-} + \overline{M^+}) \qquad (4.4)$$

(III) Sorption of the deprotonated species to a lipophilic surface with the counterion retained in the electric double layer

$$\overline{Y} + A^- + M^+ \rightleftharpoons \overline{Y\text{-}A^-} + M^+ \qquad (4.5)$$

(IV) Ion exchange of the deprotonated species with a surface group, such as hydroxide

$$\overline{XOH} + A^- \rightleftharpoons \overline{XA} + OH^- \qquad (4.6)$$

where,

M^+ = background cation,

$\bar{Y}$ = uncharged (lipophilic) surface site

$\bar{X}$ = positively charged (hydrophilic) surface site

The overbar indicates a nonaqueous phase.

These mechanisms have been used to describe the distribution of PCP between octanol and water, and a solid phase and water, and were considered for application to a water-PCP organo-clay system in the present study.

In this paper, we report on equilibrium batch isotherms conducted in order to investigate the sorption of PCP to a hexadecyltrimethylammonium-montmorillonite (HDTMA-clay) as a function of pH and ionic strength. The objectives were to describe the sorption mechanism(s) of an HIOC on a HDTMA-clay as a function of pH and ionic strength and tc present a model for the sorption of PCP on HDTMA-clay capable of describing data over a wide pH range.

4.2 Experimental Methods

4.2.1 Determination of PCP Solubility

When conducting sorption experiments, it is important to consider the solubility of the sorbate. The solubilities of IOCs are pH dependent, and for hydrophobic compounds they can be very low. However, there is a limited amount of information on PCP solubility in the literature, with considerable disagreement between reported values. Valsaraj et al. (21) suggested that the discrepancies could have resulted from inappropriate control of pH and temperature during the experiments. We, therefore, determined the solubility under our experimental conditions in the pH range 4 - 5.5 and at a temperature of 298 K. Experiments could then be designed to avoid the formation of a precipitate in the aqueous phase.

The solubility of PCP was determined in a pH range of 4-5.5 and at ionic strengths of 0.001 and 0.1 *m* with NaCl as the background electrolyte. A concentrated PCP solution (0.01 *m*) was added to the aqueous phase until precipitation occurred. The samples were placed on an orbital shaker and allowed to equilibrate for several months in an environmental chamber at 298 K until a constant aqueous phase concentration was achieved. The pH was manually adjusted, with dilute NaOH or HCl, as needed during this period.

4.2.2 Sorption Batch Studies

Preparation of the base clay and the HDTMA-clay was given in Section 3.3 (Materials and Methods). Three modified clays were prepared based on different percent replacements of the CEC by $HDTMA^+$: 35%, 70%, and 100%. They will be referred to as HDTMA(35%)-clay, HDTMA(70%)-clay, and HDTMA(100%)-clay. Batch studies were conducted over an aqueous concentration range of 3 to 200 μm (or up to the solubility limit at lower pH values), at background ionic strengths of 0.001, 0.01 and 0.1m (NaCl), and at pH 4 and 8.5 for all three HDTMA-clays. In addition, sorption isotherms were conducted, under the above conditions, at several pHs in the 4 to 8.5 range for the HDTMA(100%)-clay sample. The PCP sorption experiments, except those at pH greater than 7.5, were conducted in 25 ml Corex® centrifuge tubes with Teflon® cap liners or 125 ml Erlenmeyer flasks. Initially, the ionic strength of the DI was adjusted, the modified clay was added, and then the pH of the suspension was adjusted to the desired value. The solid/solution ratio was 100 mg modified-clay per kg solvent for all experiments. The suspension was mixed on either an orbital or reciprocating shaker for 24 hr. Then the PCP was added, as a concentrated solution (0.01m), to obtain the desired initial PCP concentration. The pH was automatically adjusted during the addition of the PCP using an autoburette with either dilute HCl or NaOH solutions. Once the pH was stabilized, the samples were placed in an environmental chamber (298 K) and gently mixed for 24 hr. Long term equilibrium studies have not shown a significant change in the sorption equilibrium between a 24 hr. and 6 month period. The pH was determined at the beginning and end of each experiment; pH variation was less than 0.2 units. The pH prior to sampling is reported in all tests. At the end of the equilibrium period, the samples were removed from the shaker and allowed to settle for a minimum of 2 hours. Samples (5-10 ml) of the clear supernatant were removed with a glass pipet for analysis. Analysis of the blanks in the experiment indicated that the loss of PCP from the aqueous phase was only due to sorption to the HDTMA-clay. The sorbed PCP concentration was determined based on the change in the aqueous phase PCP concentration over the test period.

Absorption of CO_2 (g) by the aqueous phase made the pH difficult to maintain above 7.5. Atmospheric CO_2 could not be successfully excluded from the headspace of the centrifuge tubes or Erlenmeyer flasks that were used. Therefore, the isotherms were conducted in a single, 500 ml three neck flask, with multiple additions of PCP. The system was closed to the atmosphere, with N_2 continually purged through the system, and the pH was automatically adjusted using an autoburette. This allowed for continual monitoring of the pH and automatic addition of titrant, maintaining the pH at the desired value. The PCP was added in 6 separate additions. After addition of a PCP aliquot, the system was allowed to equilibrate for a minimum of 2 hours before it was sampled, then the next aliquot of PCP was added to the system. Kinetic studies showed that the system was at equilibrium within 2 hours. All additions were made over a 24-hour period. During sampling, a 15-20 ml sample of the suspension was withdrawn. This sample was allowed to settle or was filtered and a subsample of the clear supernatant was analyzed to determine the PCP concentration. Experimental error was kept below 10% for all reported values.

4.2.3 Desorption Batch Studies

Batch desorption experiments were conducted by diluting equilibrated PCP/HDTMA-clay samples with 0.001*m* NaCl. There were two different initial equilibrium experimental conditions that were studied;

- pH = 4, equilibrium PCP conc.=30 u*m*, HDTMA-clay solid phase conc.=100mg kg^{-1}
- pH = 8, equilibrium PCP conc=30 u*m*, HDTMA-clay solid phase conc.=200mg kg^{-1}

Initially samples were equilibrated to each of the above conditions. The suspensions were stored in an environmental chamber at 298 K for the duration of the experiment. They will be referred to as the stock PCP/HDTMA-clay suspensions. The desorption experiments were conducted on a regular basis over a period of six months to determine if the length of equilibrium period had an effect on desorption.

The desorption experiments were conducted in 25 ml Corex® centrifuge tubes with Teflon® liners, and each tube contained a magnetic stir bar to aid in mixing during pH adjustment. The total aqueous phase mass for a sample was 25g. The following procedure was followed when a desorption cycle was initiated. The stock PCP/HDTMA-clay suspensions were well mixed to ensure a uniform suspension, a predetermined mass (0.5-25 g) of one stock PCP/HDTMA-clay suspension was transferred into a centrifuge tube and then the total suspension mass was increased to 25g by the addition of 0.001 *m* NaCl (pH adjusted). The pH of the resulting suspension was adjusted to the desired value (pH 4 or 8.5) with either dilute HCl or NaOH. When the sample pH was 8, nitrogen gas was used to purge the headspace of the centrifuge tube during sample preparation and pH adjustment. Once the pH was adjusted, the samples were capped, and the tubes were placed in an environmental chamber (298 K) on a shaker for 24 hrs. After the equilibrium period, the samples were centrifuged (5 min, 9000g) and a sample of the supernatant was removed for PCP analysis.

4.2.4 Analysis

Pentachlorophenol was quantified by its absorbance at 214 nm using a Hewlett-Packard HP 8452A Diode Array UV-Visible Spectrophometer. Five to ten ml samples of the clear supernatant were acidified with 0.1 - 0.2 ml of 2 M H_2SO_4. The addition of the acid ensured that the PCP was quantified as the protonated species. A five-point calibration curve (2-30 µ*m*) was run before and after each set of analyses. In this absorbance region, the standard curve was linear. Samples were diluted, prior to acidification, to keep absorbance within the standard's range. No interferences were observed in the analyses.

4.3 Results

4.3.1 Solubility Determination

The solubility of the PCP increased with pH (Table 4.1), above the pK_a. There was no difference in the solubility, at pH = 4, between the two ionic strengths. However, as the pH increased above the pK_a, the solubility increased with ionic strength. All experimental and calculated solubility data are presented in Appendix C.

4.3.2 Sorption Isotherms

Sorption was related to the percent replacement of the CEC by $HDTMA^+$ and inversely related to the pH. Sorption on the HDTMA-clay increased as the percent replacement of the CEC by $HDTMA^+$ increased. At pH ≈ 4, sorption was linear and not related to the ionic strength for the three HDTMA-clays (Figure 4.1). At pH 8.5, sorption was nonlinear and a function of ionic strength for the HDTMA(70%, 100%)-clays (Figure 4.2). The nonlinear isotherm could be described by a Langmuir equation. Sorption to the HDTMA(35%)-clay was slight and the isotherm shape or the impact of ionic strength could not be clearly determined.

Sorption in the pH 4-8.5 range for the HDTMA(100%)-clay sample showed a change from a linear to a nonlinear isotherm. There was a rapid decrease in sorption as the pH increased from 5 to 6 (Figure 4.3) and the isotherms became distinctly nonlinear. However, the data could not be represented by a simple isotherm equation

Table 4.1 Solubility of pentachlorophenol as a function of pH and ionic strength

pH	Ionic Strength (*m*) NaCl	Solubility (μ*m*)
4.08	0.001	34.1 ± 1.5
5.03	0.001	81.6 ± 3.7
5.71	0.001	447 ± 18
4.02	0.1	33.1 ± 1.5
5.03	0.1	101.9 ± 3.7
5.61	0.1	470 ± 18

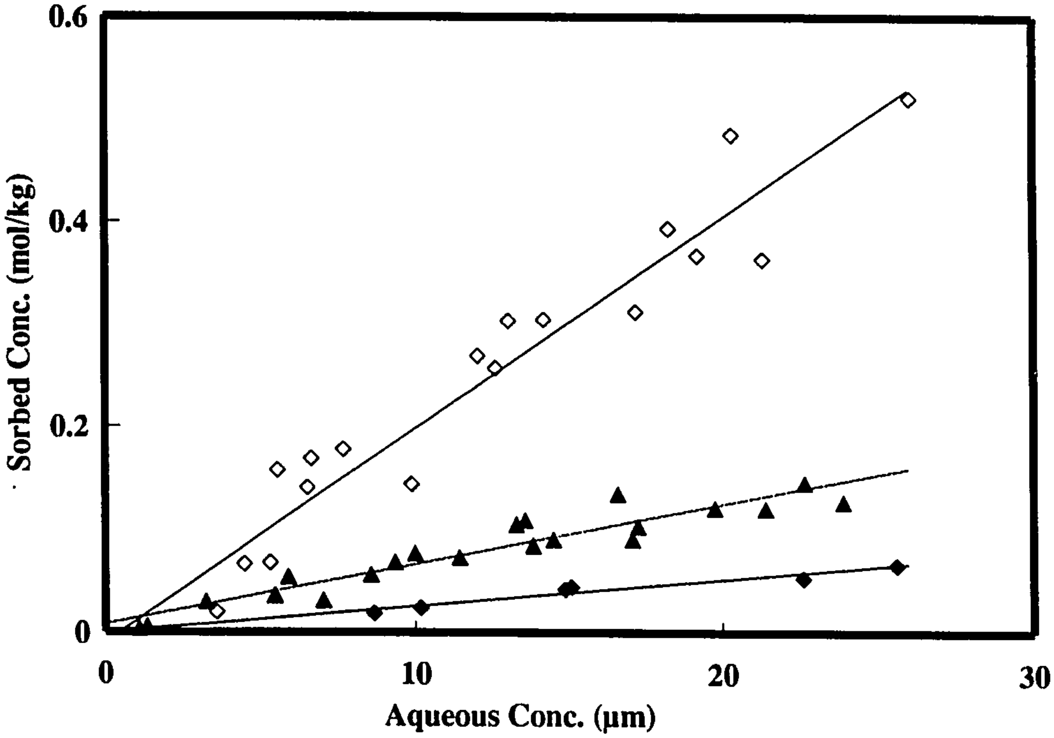

Figure 4.1 Sorption of pentachlorophenol vs. concentration at pH ≈4 for the three HDTMA-Clays, 0.001 *m* NaCl background electrolyte, HDTMA(35%)-Clay (◆), HDTMA(70%)-Clay (▲), and HDTMA(100%)-Clay (◇).

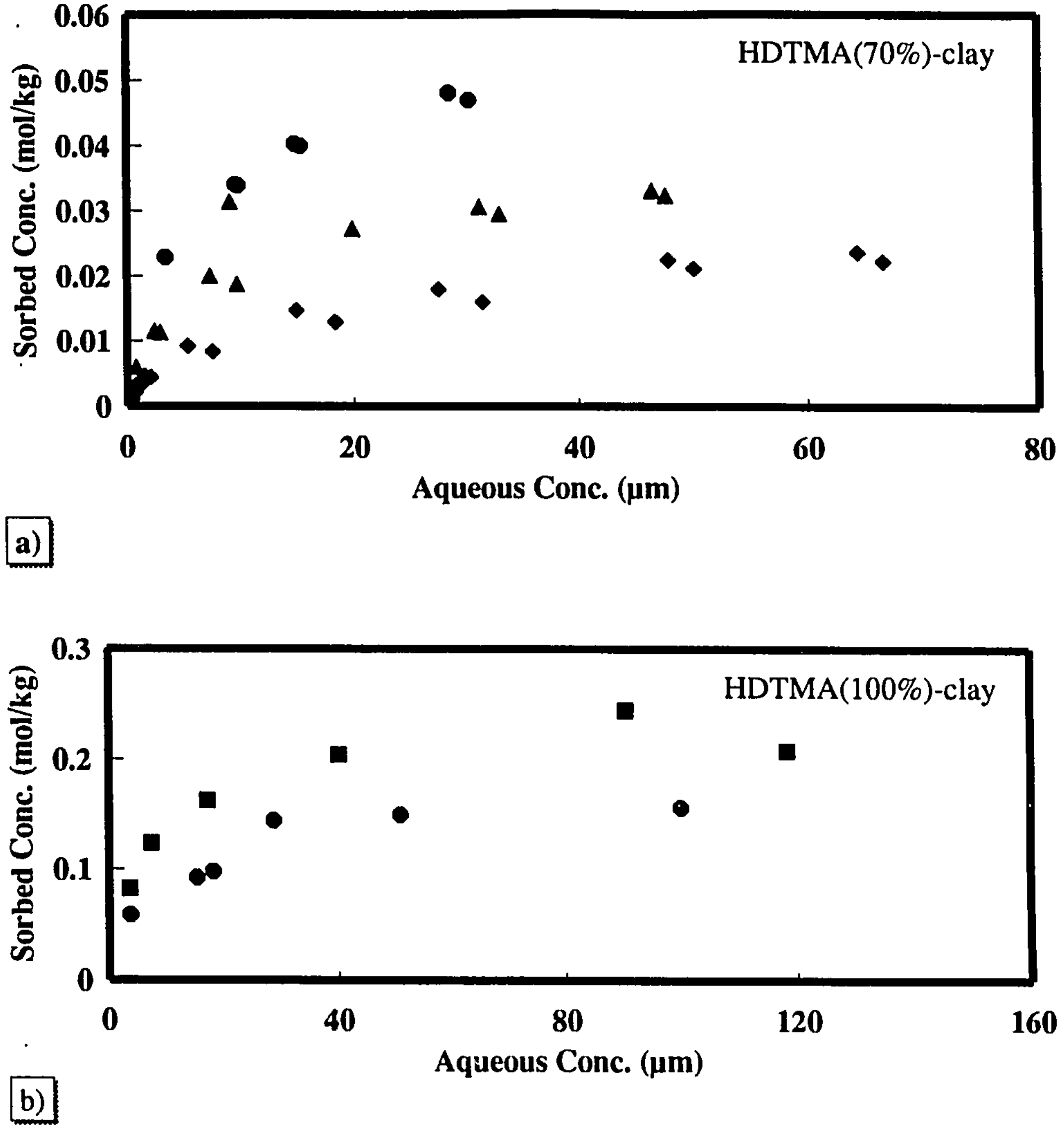

Figure 4.2 Sorption of pentachlorophenol vs. concentration at pH 8-8.5 as a function of ionic strength (NaCl) to HDTMA(70%)-clay and HDTMA(100%)-clay a) HDTMA(70%)-Clays; 0.001 *m* (◆), 0.01 *m* (▲), and 0.1 *m* (●). b) HDTMA(100%)-Clay; 0.001 *m* (●), and 0.1 *m* (■).

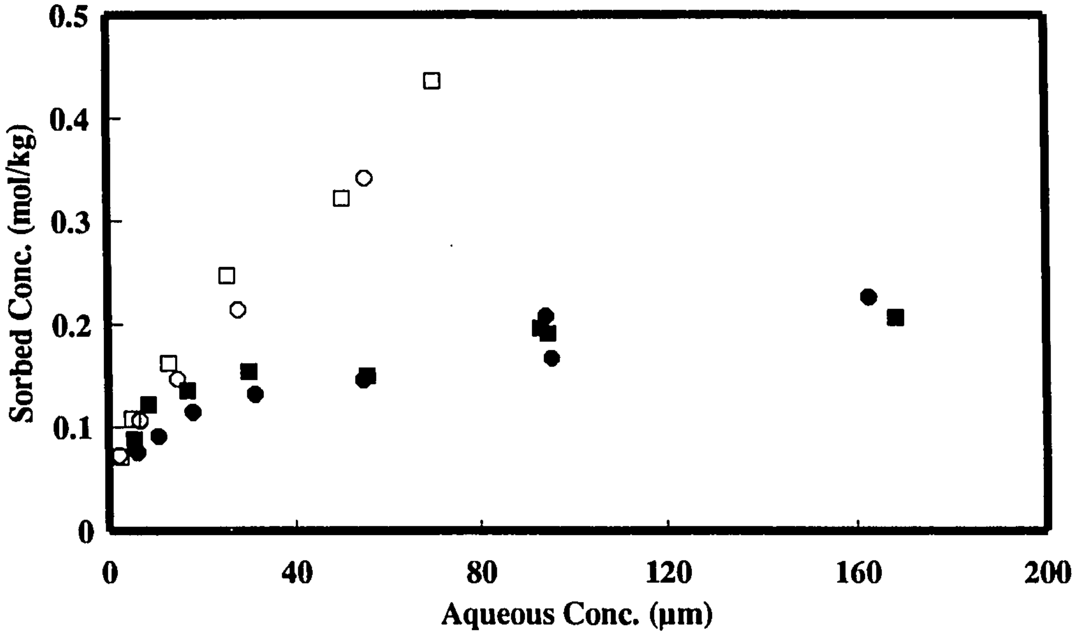

Figure 4.3 Sorption of pentachlorophenol vs. concentration at pH 5-6 for two ionic strengths, 0.001 *m* and 0.1 *m* (NaCl). (○) pH = 5.3, 0.001 *m*; (□) pH = 5.2, 0.1 *m*; (●) pH = 6.2, 0.001 *m*; (■) pH = 6.2, 0.1 *m*.

in this region. As the pH increased above 6, the nonlinear isotherms could be represented by a Langmuir equation. Sorption between pH 7 and pH 8.5 (Figure 4.4) was also described well by the Langmuir equation. There was a significant increase in the extent of sorption, with ionic strength, when the pH was greater than 8. All sorption data that appears in the figures are presented in Appendix D.

4.3.3 Desorption Isotherms

Desorption of PCP from the 100% CEC exchanged HDTMA-clay appeared to be reversible at both pH 4 and 8. The desorption characteristics of both species did not change with an increase in aging (Figure 4.5).

4.4 Discussion

4.4.1 Solubility Determination

The total pentachlorophenol concentration (PCP) in solution is the sum of the protonated (PCP°) and deprotonated (PCP⁻) species, represented by the following mass balance.

$$PCP = PCP^{\circ} + PCP^{-} \tag{4.7}$$

Given the dissociation of a proton,

$$PCP^{\circ} \rightleftharpoons PCP^{-} + H^{+} \tag{4.8}$$

The equilibrium relationship of the protonated (PCP°) and the deprotonated (PCP⁻)

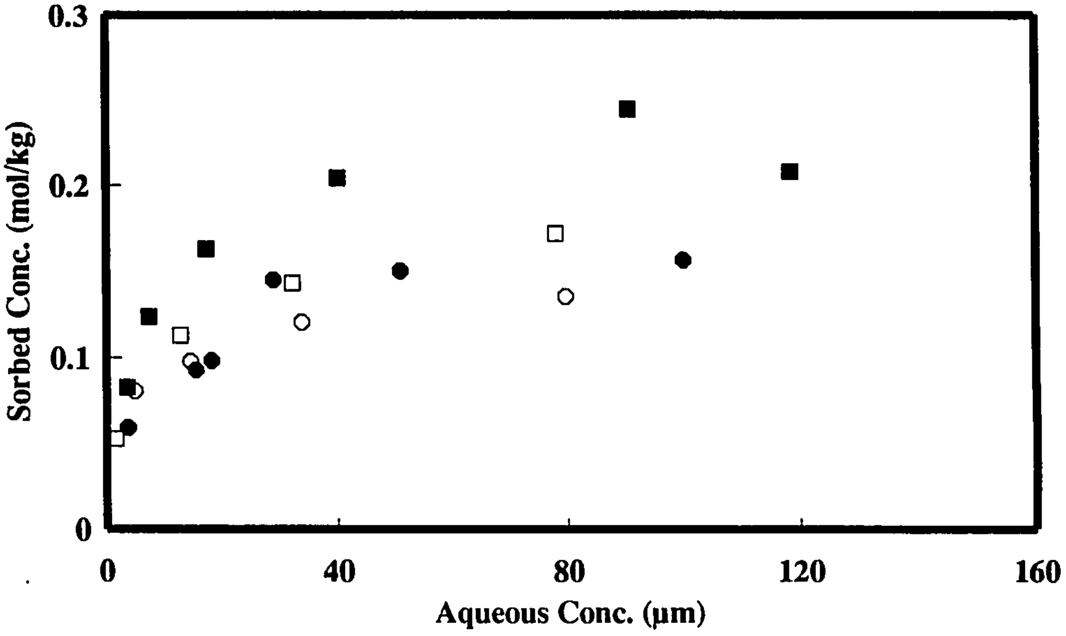

Figure 4.4 Sorption of pentachlorophenol vs. concentration at pH 7-8.5 for two ionic strengths, 0.001*m* and 0.1*m* (NaCl). (○) pH = 6.9, 0.001 *m*; (☐) pH = 6.7, 0.1 *m*; (●) pH = 8.5, 0.001 *m*; (■) pH = 8.5, 0.1 *m*

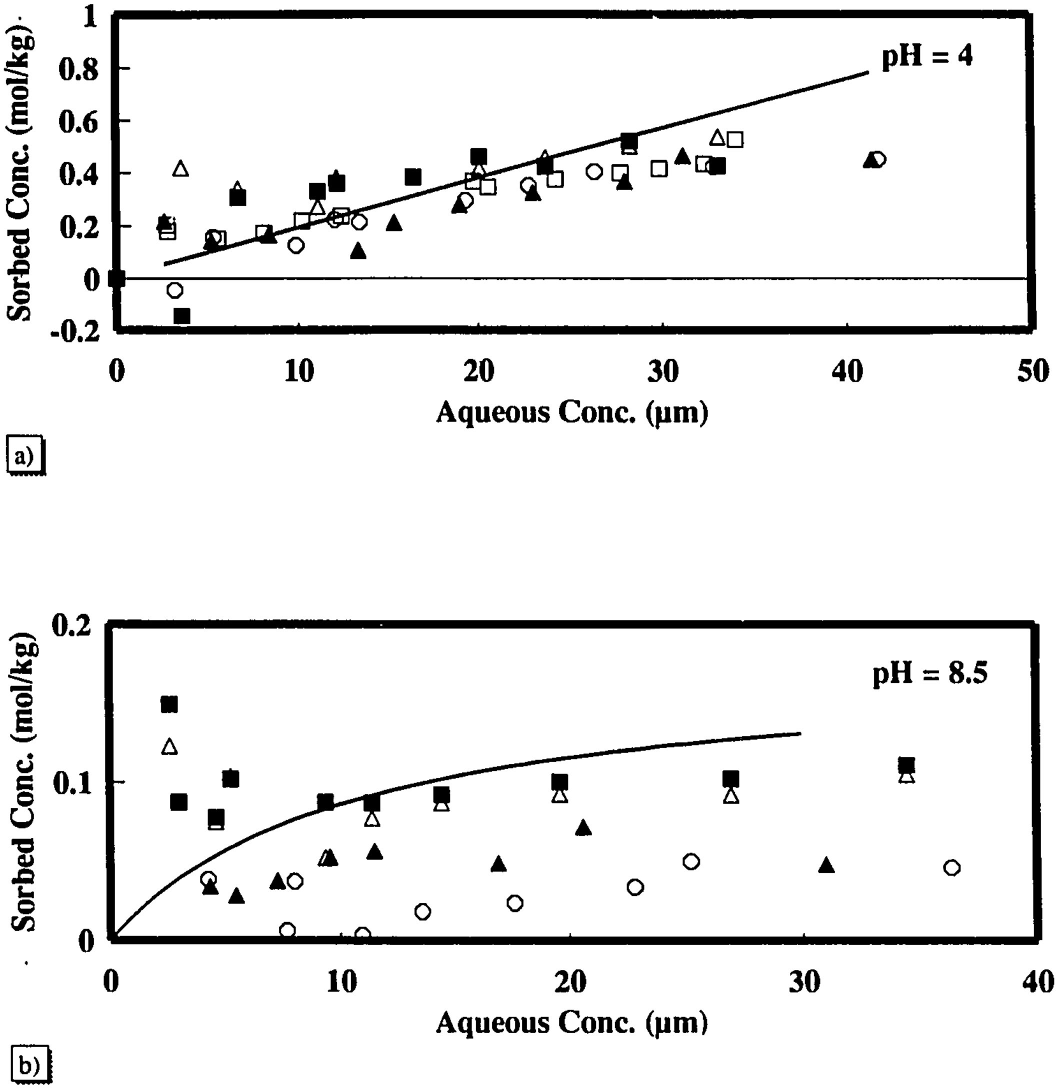

Figure 4.5 Desorption of the protonated and deprotonated PCP species from HDTMA(100%)-clay. Initial sorption 21 December 1993; Desorption (□) 29 December 1993, (▲) 7 February 1994, (○) 20 March 1994, (■) 20 April 1994, (△) 7 July 1994. a) pH = 4. b) pH=8.5.

species is a function of the solution pH given by;

$$K = \frac{(H^{+})\ \gamma [PCP^{-}]}{(PCP^{\circ})} \qquad (4.9)$$

Where the species activity is represented by ( ), the species concentration is represented by [ ], and γ is the activity coefficient with $(x) = \gamma [x]$. The activity coefficient for the protonated species was assumed to be unity based on the similar PCP solubilities at pH 4 between the two background ionic strengths samples, 0.001*m* and 0.1*m*.

The maximum aqueous phase PCP concentration (SW_{PCP}) can be related to the solubility of PCP° ($SW_{PCP^{\circ}}$), based on the mass balance (Equation 4.7) and equilibrium relationship (Equation 4.9) given $PCP^{\circ} = SW_{PCP^{\circ}}$ and $PCP = SW_{PCP}$;

$$SW_{PCP} = SW_{PCP}^{\circ} \left(1 + \frac{10^{pH-pK_a}}{\gamma}\right) \qquad (4.10)$$

Initially the pH 4-5.1 solubility data (Table 4.1) were used to determine $SW_{PCP^{\circ}}$ using Equation (4.10). Based on these data, $SW_{PCP^{\circ}}$ was determined to be 27.9±1.1 μ*m*. Using this $SW_{PCP^{\circ}}$ value, the maximum aqueous phase PCP concentration was calculated as a function of pH (Figure 4.6). The estimated maximum aqueous phase PCP concentration (Figure 4.6) is consistent with solubility data from the literature (considering only data in which pH and temperature are indicated) (21, 22, 27). Equation (4.10) will be valid until the precipitation of a phenolate salt occurs.

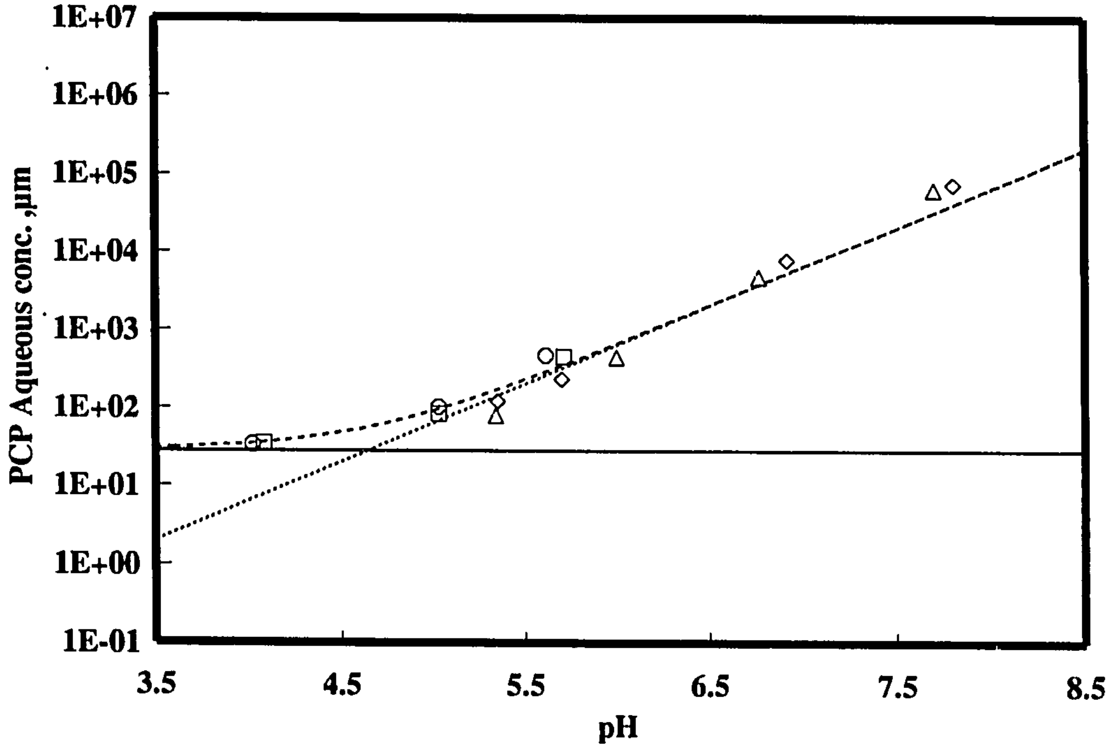

Figure 4.6 Solubility of pentachlorophenol vs. solution pH. Data points at 0.001*m* (□) and 0.1*m* (○) ionic strengths (NaCl) are shown. Lines are calculated (——) PCP°, (········) PCP^-, and total (------) PCP maximum aqueous concentrations, assuming I = 0.1 *m* NaCl (plus PCP^- and Na^+, contribution becomes significant at pH = 7), γ is taken from Equation (4.12), SW_{PCP° = 27.9µ*m*, and pK_a = 4.75. Solubility data for PCP in 0.0M (◇) and 0.1M (△) KCl were taken from reference (28).

Precipitation occurs when the activity product of PCP^- and a cation (M^{n+}) exceeds a salt's solubility product (K_{sp}).

$$K_{sp} = (M^{n+})(PCP^-) \tag{4.11}$$

The activity coefficient (γ) for the protonated species that was used in the above equations was based on the Davies equation (given $I < 0.5$ *m*).

$$\log\gamma = -0.5z^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \tag{4.12}$$

Where z is the charge on the deprotonated species (-1) and I is the ionic strength of the solution. Table 4.2 lists the activity coefficients (γ) for the deprotonated species for a range of ionic strengths.

Therefore, as the ionic strength increases above 0.001 *m* the activity correction becomes significant. The increase in the solubility with ionic strength (Table 4.1) results from the decrease in the activity coefficient as ionic strength increased. Appendix C presents the model and assumptions used to calculate the data in Figure 4.6 and SW_{PCP°

4.4.2 Sorption Isotherms

Tables 4.3 and 4.4 present the Langmuir constants for the sorption isotherms for the three HDTMA-clays at pH 4 and 8.5. Sorption of the protonated species was greater than the sorption of the deprotonated species for all three HDTMA-clays. In addition, sorption was related to the percent replacement of the CEC by $HDTMA^+$.

Table 4.2 Activity coefficients for PCP^- based on Davies Equation [Eq. (4.12)].

Ionic Strength (*m*) NaCl	Activity Coefficient γ
0	1.00
0.0001	0.99
0.001	0.97
0.01	0.90
0.05	0.82
0.1	0.79
0.5	0.74

Table 4.3 Linear isotherm equations for the three HDTMA-clays, pH ≈ 4.

HDTMA-Clay CEC Replacement	Regression slope (mol kg^{-1} μm^{-1})	Regression y-intercept (mol kg^{-1})	r^2
35%	2.60E-03	7.00E-04	0.9479
70%	5.81E-03	7.81E-03	0.9030
100%	2.07E-03	9.89E-03	0.9188

Table 4.4 Langmuir coefficients for the three HDTMA-clays, pH = 8.5.

HDTMA-Clay CEC Replacement	Ionic Strength	Langmuir Constant K † (kg/μm)	Langmuir Constant M † (mol/kg)	r^2
70%	0.001M	7.92E-02	2.64E-02	0.9666
	0.01M	2.05E-01	3.54E-02	0.8940
	0.1M	1.75E-01	5.58E-02	0.9768
100%	0.001M	4.58E-1	9.06E-2	0.9906
	0.01M	-----	-----	-----
	0.1M	2.04E-01	1.52E-01	0.7495

† Based on the Langmuir Equation, $q = KMC\ (1+KC)^{-1}$, where q is the amount of PCP sorbed, C is the aqueous phase PCP concentration, and Langmuir constants K and M (sorption capacity).

However, the degree of sorption for the protonated species was not directly related to the added carbon content of the surfactant. The ability of the surfactant cations (on a mass basis) to sorb PCP increased with the percent replacement of the CEC by the $HDTMA^+$. This would appear to indicate that the HDTMA cations are separated from each other on the surface at the lower replacements, reducing their ability to be an effective sorbent.

The significant change in the isotherm shape, for all HDTMA-clays, between pH 4 and 8.5 suggests that there are at least two sorption mechanisms. We hypothesize that the main difference in the isotherms is related to the sorption of the protonated vs. the deprotonated PCP species.

The change in the sorption near the pK_a is consistent with research reported by Schellenberg et al. (20) and Lee et al. (29) for the sorption of PCP by soil and sediments. Lee et al. (29) compiled data from the literature that shows a similar sorption trend as a function of the pH. However, a linear isotherm was used to describe the sorption of both the protonated and deprotonated species. The data presented in our paper differs from these previous results in that a distinctly nonlinear isotherm above the pK_a is observed. We believe the differences in our data compared to those of Schellenberg et al. (20) and Lee et al. (29) result either from the smaller aqueous equilibrium range in their studies (with data representing only the linear section of a nonlinear isotherm), or from different operative sorption mechanisms with organoclays than with soils and sediments. Boyd et al. (3) reported a nonlinear sorption isotherm for the sorption of PCP to a HDTMA-clay for two pHs, 5.5 and 10. The authors did not indicate that there was a difference in the sorption between the two pHs. However, the range for the aqueous concentration was only 0-15 μM, and a difference in the sorption may not be apparent in this range.

We believe the sorption mechanism for PCP° is partitioning between the hydrophobic section of the modified-clay and the aqueous phase. This conclusion is based on a linear isotherm over at least 90% of the compound's solubility and similarity between the K_{ow} and the distribution coefficient normalized for the organic carbon content, K_{oc}. This is consistent with a partition process (30). The first of the proposed mechanisms by Westall and coworkers (23-26), Equation (4.3), would represent this reaction.

The sorption mechanism for the phenolate species could be represented by either the second or third mechanism, Eqs. (4.4) and (4.5), proposed by Westall and coworkers (23-26). Respectively, these would be sorption in the three-dimensional lipophilic space (either as a neutral ion pair or as a free ion with a counter-ion to balance the charge), or sorption to the two-dimensional lipophilic surface with a counter-ion in the double layer. The latter of these would seem most likely to yield the nonlinear isotherm observed at high pH where PCP^- is predominant, since the extent of sorption is limited by the area of the exposed nonpolar surface. Similarity of the initial slopes of the PCP^- and PCP° isotherms may then be explained by similar affinities of the nonpolar portions of the respective molecules for the nonpolar phase.

The experimental results also suggest that there may be a modification in the sorption mechanism above pH 8 as ionic strength increases. These findings are similar to those of Westall et al. (25) who suggested the relationship between the ionic strength and log D (log of the distribution ratio) is related to the shift in the main species, in the octanol phase, from the protonated to the deprotonated form. However in our system, the shift from the protonated to the deprotonated sorbed species occurred at a pH < 6 in the equilibrium range under study. The potential modification in the sorption mechanism of PCP^- may involve an increase in the affinity between PCP^- and a counter ion.

Based on our experimental data, we propose a model that describes PCP sorption, in our system, as a function of pH at a background ionic strength of 0.001*m*. The model consists of the summation of the isotherms representing the independent sorption of the deprotonated and protonated species. The sorption of the deprotonated species (q_{PCP^-}) has been represented by a nonlinear isotherm (Equation 4.13a), and the sorption of the protonated species (q_{PCP°) has been represented by a linear isotherm (Equation 4.13b). Thus, the total sorption of PCP on HDTMA-clay (q_{PCP}), as a function of pH, can be represented by the following set of equations:

$$q_{PCP^-} = \frac{PCP^- * K_{PCP^-} * M_{PCP^-}}{1 + PCP^- * K_{PCP^-}} \qquad \textbf{(4.13a)}$$

$$q_{PCP^\circ} = PCP^\circ * m_{PCP^\circ} \qquad \textbf{(4.13b)}$$

$$q_{PCP} = q_{PCP^-} + q_{PCP^\circ} \qquad \textbf{(4.13c)}$$

where,

K_{PCP^-} = Langmuir equation constant for the sorption of the deprotonated species (μm^{-1})

M_{PCP^-} = Langmuir equation constant for the sorption of the deprotonated species (mol kg^{-1})

m_{PCP° = slope of the linear isotherm, for the sorption of the protonated species (mol kg^{-1} μm^{-1})

The two PCP species were determined, as a function of pH, based on Eqs. (4.7) and (4.9) for unit activity;

$$PCP^- = \frac{PCP}{1 + 10^{pK_a - pH}} \qquad \textbf{(4.14a)}$$

$$PCP^\circ = PCP - PCP^- \qquad \textbf{(4.14b)}$$

To describe q_{PCP} using Equation (4.13c), one must first determine K_{PCP^-}, M_{PCP^-}, and m_{PCP°. To do this without solving for all three values simultaneously, experimental results may be used from a pH region where the aqueous and sorbed concentrations of one species are insignificant. For example at pH 8.5, the aqueous concentration of the deprotonated species is four orders of magnitude greater than the protonated species. Therefore, it may be assumed that the sorption of PCP° is insignificant, allowing for the determination of K_{PCP^-} and M_{PCP^-}. The 0.001*m* data set, at pH 8.5, was therefore used to represent the sorption of PCP^-. The two Langmuir constants, in Equation (4.13a) were estimated using ISOTHERM, a nonlinear least square optimizing routine (31).

Due to the potential dissolution of the mineral surface, the lowest pH used in these experiments was 4.0. At this pH, 15% of the total PCP in solution was the deprotonated species (PCP^-), which represents a significant part of the total PCP sorption. Therefore, the sorption of the protonated species (q_{PCP°) could not be directly determined. Thus the sorption of the protonated species was back calculated from the total sorption. Accordingly, data between pH 4 - 4.4 were used to model the sorption of PCP°.

Based on a sample's pH, total aqueous phase PCP concentration (PCP) and total solid phase PCP (q_{PCP}) concentration, Eqs. (4.14a) and (4.14b) were used to determine the aqueous phase concentrations of the individual species, PCP° and PCP^-. Then using PCP^-, Equation (4.13a) was used to determine q_{PCP^-}. The sorption of the protonated species was determined using q_{PCP} and q_{PCP^-} with Equation (4.13c). These data, PCP° vs. q_{PCP°, were subjected to a least square regression with a forced fit through the origin. Final values determined for the three adsorption parameters and the regression coefficient, r^2, are presented in Table 4.5. Figures 4.7 and 4.8 contains plots of Equations (4.13a) and (4.13b) with experimental data for sorption of PCP^- and PCP° species.

Table 4.5: Model constants for the sorption of PCP on HDTMA-clay, using Equations (4.13a)[†] and (4.13b)[‡].

	Constant	Units	r^2
Linear Isotherm			0.918
$m_{PCP^{\circ}}$ †	$2.01*10^{-2} \pm 6.71*10^{-4}$	mol kg^{-1} μm^{-1}	
Langmuir Isotherm			0.899
$K_{PCP^{-}}$ ‡	$9.52*10^{-2} \pm 3.24*10^{-2}$	μm^{-1}	
$M_{PCP^{-}}$ ‡	$1.76*10^{-1} \pm 1.64*10^{-2}$	mol kg^{-1}	

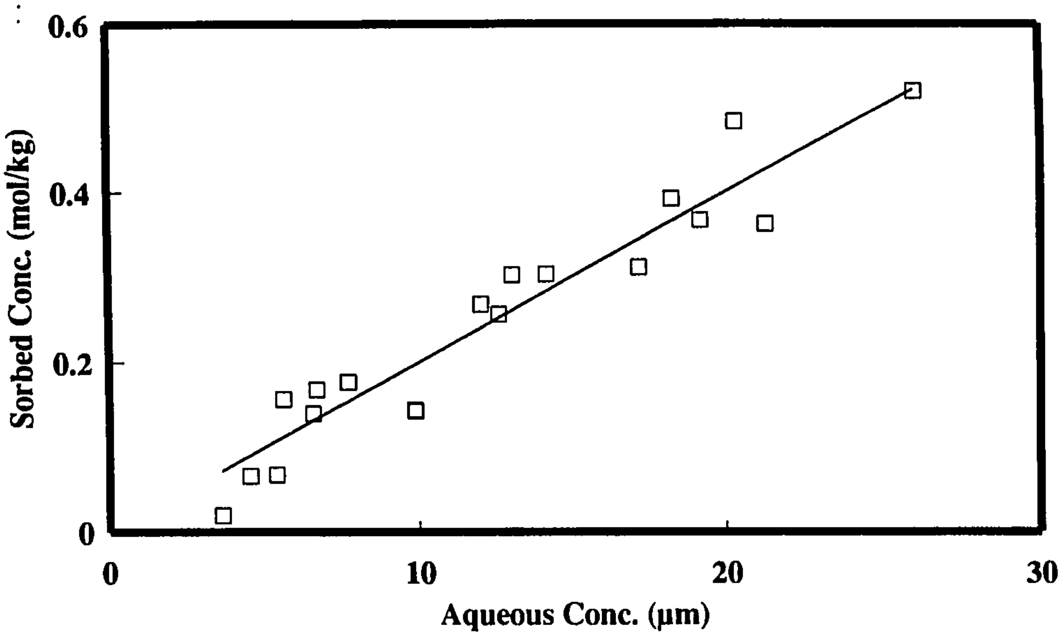

Figure 4.7 Plot of linear isotherms (pH = 4) based on Equation (4.13a) with experimental data. (——) model based on Eq. (4.13a), (□) experimental data.

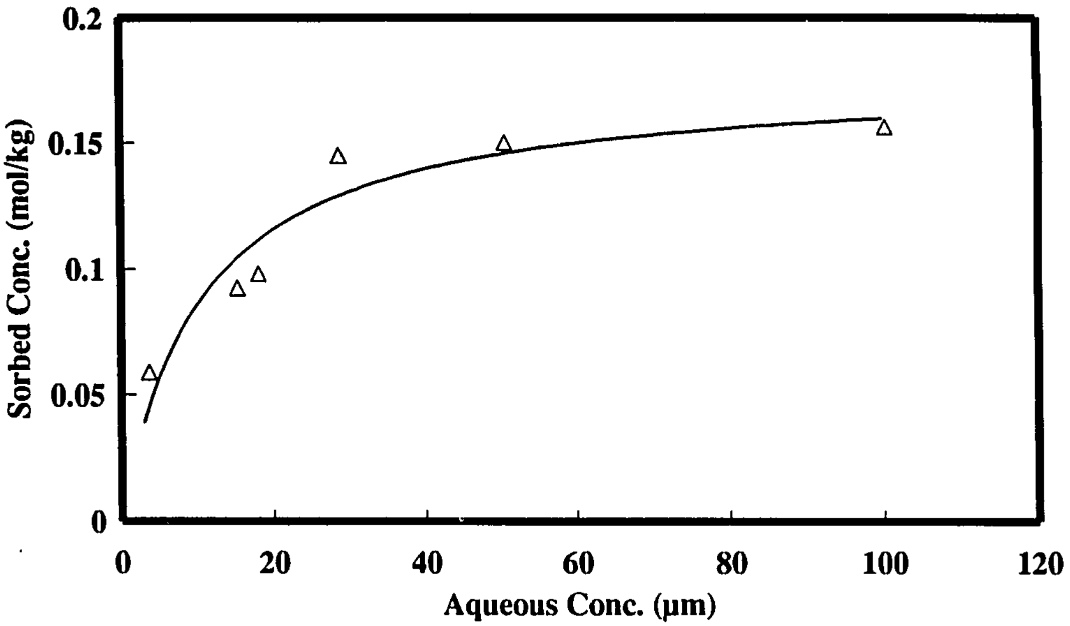

Figure 4.8 Plot of Langmuir isotherm based on Equation (4.13b) with experimental data. pH = 8.5, I = 0.001 *m* NaCl. (——) model based on Eq. (4.13b), (△) experimental data.

The Model, Equations (4.13a-4.13c), successfully described the sorption as a function of pH for an ionic strength of 0.001*m* (Figure 4.9). The experimental data plotted on the graph are consistent with the calculated isotherms, especially in the pH transition zone when the isotherms change from linear to nonlinear. The good fit of the data would indicate that the sorption of each species is independent of the other. The model does not predict the increase in sorption as a function of ionic strength that occurs in the experimental data when the pH is > 8.

Using the model, one can also predict the sorption of both PCP species as a function of the solution pH, given a constant total PCP concentration in solution (C_e)(Figure 4.10). At low C_e (1μ*m*), the sorption is uniform across the pH range. This results because the linear section of the Langmuir equation, for PCP^-, is similar to the linear isotherm, for PCP°. However, as C_e increases, sorption of the deprotonated species decreases relative to the linear increase in sorption of the protonated species. Therefore, there is greater sorption at pH 4 vs. pH 8.5 (Figure 4.11). Also as the C_e increases, the pH at which $q_{PCP^\circ} = q_{PCP^-}$ increases. When the $C_e > SW_{PCP^\circ}$, q_{PCP} will increase with pH until the C_e limits the concentration of PCP° and the dominant sorbed species shifts from q_{PCP° to q_{PCP^-}. The total PCP sorption is limited by the solubility of the protonated form at low pH and by the maximum sorption of the deprotonated form at high pH.

It is not known whether this model also applies to the sorption of IOCs to soils or sediments, but it would appear reasonable to expect limited sorption of ionized

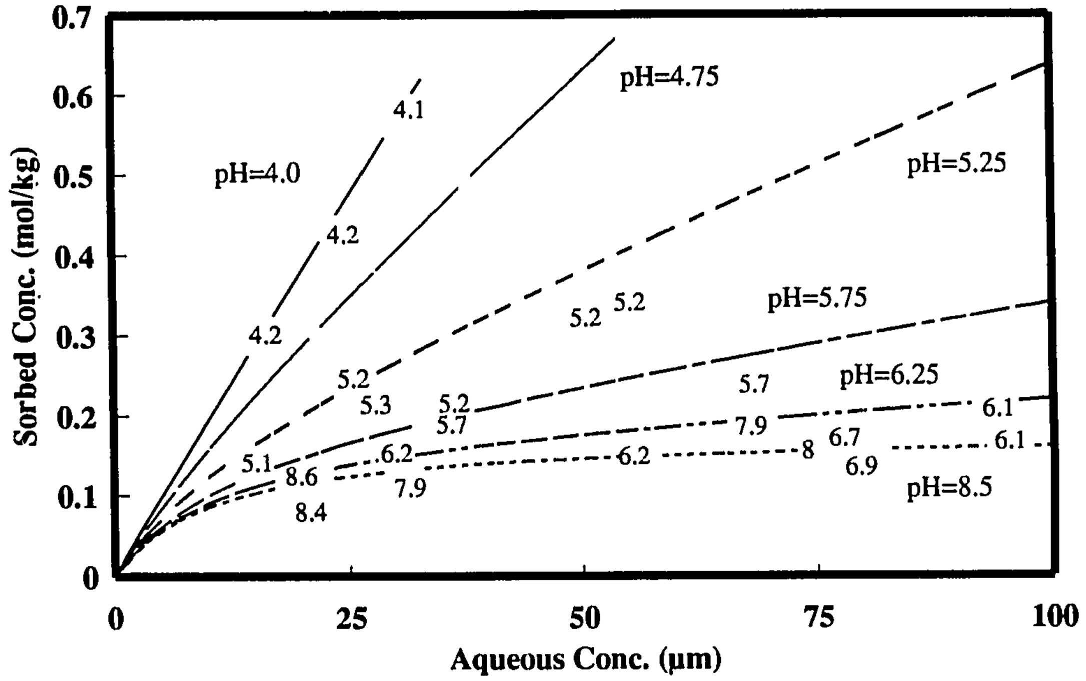

Figure 4.9 Pentachlorophenol sorption vs. concentration for 0.001*m* ionic strength (NaCl). Model calculated for indicated pH values based on Equations (4.13a-4.13c). Experimental data points shown by measured equilibrium pH values.

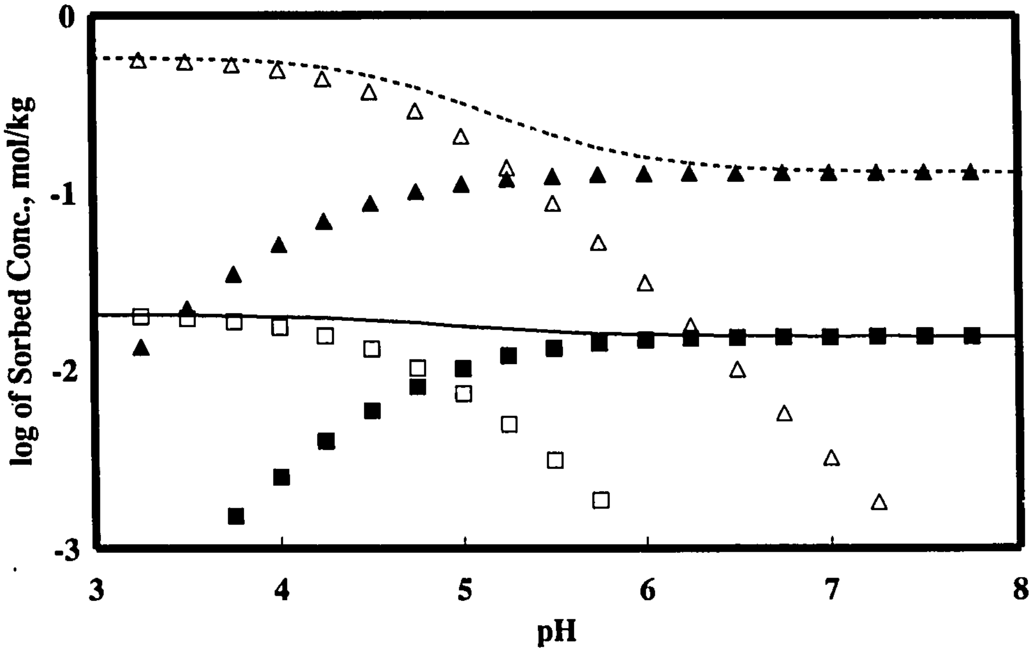

Figure 4.10 Plot of q_{PCP}, $q_{PCP^{o}}$, and $q_{PCP^{-}}$ for 1 and 28 μ*m* equilibrium PCP concentrations (C_e). (□) PCP° , 1 μ*m*; (■) PCP⁻, 1 μ*m*; (–) Total PCP, 1 μ*m*; (△) PCP° , 28 μ*m*; (▲) PCP⁻, 28 μ*m*; (– –) Total PCP, 28μ*m*.

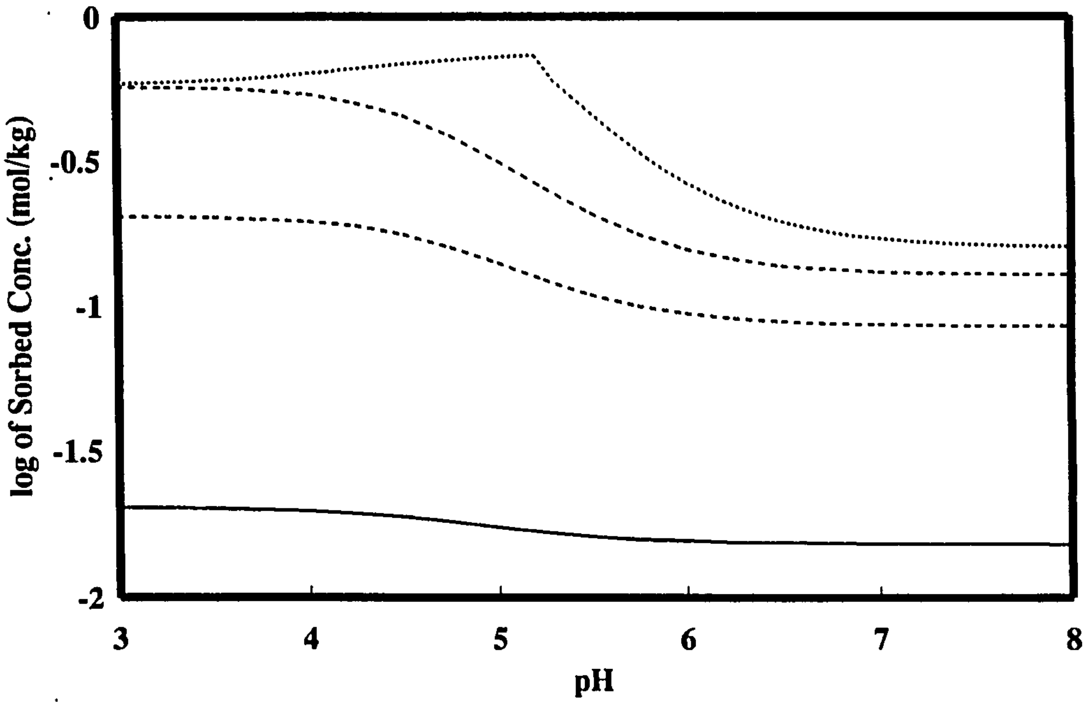

Figure 4.11 Total sorption of PCP as a function of pH for 1, 10, 28, and 100 μ*m* C_e. In the 100μ*m* line, precipitation of PCP occurs when the pH is < 5. Thus the concentration is represented by the maximum aqueous phase concentration, as given in Figure 4.6. All points were calculated based on Equations (4.13a - 4.13c). (–) 1 μ*m*; (– –) 10 μ*m*; (— — —) 28 μ*m*; (– – – –) 100 μ*m*.

species on such surfaces resulting in a nonlinear isotherm if characterized over a sufficient concentration range. The model would then predict that the environmental fates of ionized and nonionized species would be significantly different. We have shown that in a narrow pH range, $pK_a \pm 2$ pH units, both the sorption and solubility of an IOC can change dramatically. When this pH range is within that found in the aqueous environment both the protonated and deprotonated species will be found. Therefore, it is important that one understand how the speciation of an IOC such as PCP will affect its environmental fate and transport since a minor change in pH will allow PCP to exist as either a sorbed, insoluble compound or a soluble, mobile ion. Additional research should be completed to confirm the application of the general form of Equations (4.13a-4.13c) and to extend the results to solids and sediments based on organic carbon to better predict environmental transport of an IOC.

4.4.3 Desorption Isotherms

While desorption of PCP from the modified clay occurred at both pH 4 and 8, there were a number of experimental problems. The pH was difficult to control in the sample tubes in the pH = 4 sample set which resulted in a variation in the final sample pH between 3.9-5.6. Therefore, some of the sorbed equilibrium relationships that appear to be low have pH's that significantly exceeded 4. However, once the sorption was corrected for pH, the final sorption was within 90% of the expected equilibrium value. In addition, the equilibrium relationships for the 7 February 1994 and 20 March 1994 deprotonated desorption sample sets were too low. The reason for this could not be explained. The 20 April 1994 and 6 July 1994 sample sets and the initial equilibrium value were within expected limits based on the sorption data presented in the previous section. Thus, there appears to be some consistent determinant error in the 7 February 1994 and 20 March 1994 deprotonated data sets.

The indeterminate error for the calculation of the sorbed deprotonated species concentration increased significantly as the equilibrium aqueous PCP concentration decreased. This error became large when the PCP concentration was less than 5μm. The error arose from uncertainties in the mass of the modified-clay in the system as increasingly smaller fractions of the stock PCP/HDTMA-clay suspensions were diluted in the desorption experimental procedure. However, the sorption appears reversible for both the protonated and deprotonated PCP species, but further investigations should be conducted based on experimental designs to further reduce the errors involved in the experiments.

4.5 Conclusions

1) The solubility of pentachlorophenol increases with pH as a direct function of the speciation between the protonated and deprotonated species. The solubility changes by 4 orders of magnitude between pH 4 and 8.

2) The sorption of pentachlorophenol to the HDTMA-clay was a direct function of the percent replacement of the clay's CEC by the HDTMA cation.

3) The sorption of the protonated PCP species, to the HDTMA-clay, was significantly greater than the sorption of the deprotonated PCP species. Therefore, the sorption of PCP to the modified-clay decreased with an increase in the pH of the system as the dominant PCP species changed from the protonated to the deprotonated form. This change in sorption was modeled with a simple equation that was able to represent the experimental data over the pH 4-8.5 range.

4) Desorption of the both species from the modified-clay appeared to be reversible.

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Chapter 5

SORPTION/DESORPTION KINETICS OF PENTACHLOROPHENOL TO HDTMA-CLAY

5.1 Introduction

The presence of anthropogenic organic compounds in the environment has become a major concern to Federal, state, and local environmental officials, as well as the general population. The actual or potential human and environmental exposure to these compounds is now being quantified in an attempt to explain the cause of adverse health effects and to predict potential health effects from contaminant exposure. Mathematical modeling is often used to predict the movement of a contaminant from a source to a point of potential exposure. This movement via surface or groundwater involves the distribution of the contaminant between an aqueous and a solid phase. For simplicity it is often assumed that equilibrium exists between these two phases. This assumption is valid when the time of contact, of the two phases, is greater than the time required for the system to reach equilibrium. When the contact time is shorter than the equilibrium period, a condition of nonequilibrium exists and the resulting kinetic limitations should be considered.

The transfer of a contaminant between the two phases occurs in many different conditions, the most common is groundwater transport. When the rate of groundwater flow is slow, the problem is minimized. However, the kinetic limitations may become critical when there is a rapid infiltration of water into a soil, suspension of contaminated sediment in an aqueous phase, or settling of a contaminated solid phase in a quiescent body of water. In addition, treatment applications like "pump and treat" to reduce groundwater contamination or the removal of contaminants during wastewater treatment processes rely heavily on kinetic estimates for system design. Thus, an understanding of the reaction kinetics is important in predicting the environmental transport and remediation of contaminants.

As concern about the presence of these anthropogenic compounds has grown, the need for research investigating the sorption/desorption kinetics of organic compounds has been recognized. Until recently, the standard batch method was the main technique that was used to study these phenomena, but newer methods have been used (1,2). The gas purge and miscible-displacement techniques have been increasingly used to collect kinetic data related to the sorption and desorption of organic compounds with soils and sediments. The miscible-displacement technique has been primarily used to investigate sorption dynamics in subsurface systems, while the gas purge technique has been used to investigate sediment/water systems (2).

While the standard batch technique has many useful applications, there are several limitations. One of the most significant is the time required to remove an aliquot from the system and separate the solid phase. When this time becomes significant relative to the half-life of the reaction under study, the method is inappropriate for measuring the kinetics of the reaction.

The gas purge technique that was first used by Karickhoff (3) has been used by several researchers (see (4) and other references cited therein). It involves suspending a solid phase in an aqueous environment and nondestructively analyzing the sorptive gas phase concentration to monitor the reaction. This method is only applicable for chemicals whose Henry's constants are of sufficient magnitude to be detected in the gas phase. The gas purge method is useful for highly sorptive compounds and solid phases that contain a large percentage of either clay or organic material. (2).

The miscible-displacement technique has been used widely in chemical engineering, petroleum engineering, and soil science to investigate reactions in porous media. While the technique has mainly been used to evaluate the sorption kinetics of inorganic compounds, recently it has been used to successfully investigate the sorption of organic compounds (see (2) and other references cited therein). The technique involves packing a small column with a solid phase, running an aqueous sorptive through the column, and monitoring the loss of the sorptive across the column. The miscible-displacement technique is suited for low-sorptive systems and solid phases with a relatively high degree of permeability. Thus solid phases with a high clay or organic matter content cannot be used in this system.

While not widely used to monitor the sorption reaction of organic compounds, the stirred-flow chamber (SFC) has potential to investigate sorption/desorption reaction kinetics of organic compounds. The SFC was first proposed by Carski and Sparks (5) for studying the kinetics of adsorption/desorption phenomena on soils and soil components. Theoretical and experimental aspects of the SFC technique have been given by Seyfried et al. (6), Bar-Tar et al. (7), and Eick et al. (8). Seyfried et al. (6) determined the fastest reaction that could be measured with the SFC had a half-life of 3 minutes.

While all four of the above kinetic techniques have been successfully used with different experimental conditions, none of these techniques is able to monitor the sorption or desorption of a sorptive with a low Henry's constant and highly sorptive clay sized particles such as the PCP/HDTMA-clay system. The low Henry's constant of PCP makes the gas purge technique ineffective, because the gas phase concentration is below the level of detection required for the analysis. The low permeability of the HDTMA-clay eliminated the use of the miscible-displacement technique. In addition, preliminary data indicated that the kinetics of the PCP/HDTMA-clay system were too rapid to be measured with the standard batch technique, and the rate of the sorption was too fast to be measured with the SFC method .

Therefore, a continuous flow technique was developed for this study to monitor the sorption/desorption of PCP on HDTMA-clay. Kinetic data were collected in real time starting within 30 seconds of the initiation of the reaction and continuing until equilibrium was reached. The technique, while similar to the standard batch method, did not require the separation of the liquid and solid phase prior to analysis. The sorptive suspension concentration was continually monitored during the experiment by UV detection. This method could be used to investigate other sorptive/sorbent systems as long as the sorptive has an absorbance or florescence spectra unique to the system under study, and the sorbent has a large affinity for the sorptive.

The objective of this research was to measure the sorption and desorption kinetics of the PCP/HDTMA-clay system for both the protonated and deprotonated PCP species. The sorption of both species of PCP appeared to be characterized by two time stages. There was an apparent initial fast sorption followed by an approach to equilibrium within 10 minutes. The rate of the fast stage, which represented 15 to 30 % of the total PCP sorption, could not be kinetically measured. This research reports on the rate of the second stage in which equilibrium was achieved within 10 minutes.

5.2 Experimental Methods

The procedures for the preparation of the SWy-1 base clay and the HDTMA-clay are presented in Section 3.3 (Materials and Methods). The kinetic investigation focused only on the 100% CEC exchanged HDTMA-clay, HDTMA(100%)-clay.

5.2.1 Kinetic Studies

The kinetic studies were conducted using three different experimental methods that measured three time intervals; a rapid mix method was used to measure the sorption in the 2 - 120 sec. time interval, a continuous flow method was used during the 30 - 1 200 sec. time interval, and a standard batch method was used for times > 5 minutes. The selection of the experimental method was based on the time interval over which the kinetic experiment was conducted as will be described later.

The rapid mix method experiments were conducted in a 2.5 ml (10 mm, path length) quartz cuvette. The sorption was initiated by the simultaneous rapid addition, using two Rainin electronic pipetters, of an HDTMA(100%)-clay suspension and a PCP solution. The cuvette was located in a UV-VIS diode array spectrophotometer and the change in the aqueous PCP concentration was monitored by the UV absorbance of PCP at 218 nm. The sample was scanned every 2 sec. All experiments were conducted at room temperature (290-300 K).

The continuous flow method experiments were conducted using a batch reactor with continual monitoring of the suspension PCP concentration by the UV absorbance at 218 nm. The continuous flow experimental apparatus (Figure 5.1) consisted of a 300 ml, three neck, water jacketed flask, 1.5 ml quartz flow-through cuvette (5 mm path length), and a peristaltic pump connected in series. A magnetic stir bar was used to keep the sorbent in a uniform suspension in the reaction vessel. At t=0, the reaction was initiated by the addition of an aliquot of PCP (0.01 *m*) stock solution.

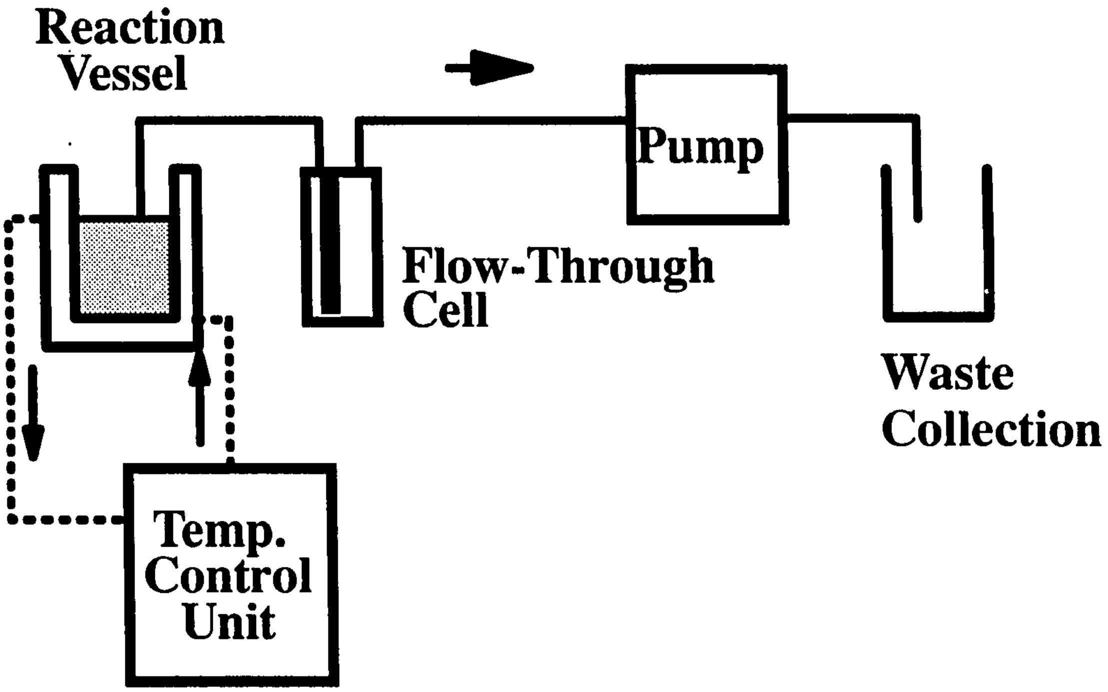

Figure 5.1 Experimental apparatus

The suspension was allowed to mix for 5 seconds, then the PCP/HDTMA(100%)-clay suspension was continually pumped from the reaction vessel through the cuvette that was contained in the UV spectrophotometer. The suspension was withdrawn from the reaction vessel through Teflon tubing using a peristaltic pump at a flow rate of 6.5 to 13 ml min^{-1}. The flow rate did not have an effect on the PCP absorbance, and there was not a build up of solids in either the reaction vessel or the flow cell during the experiment. Temperature in the reaction vessel was maintained to ±0.2 K using a constant temperature water bath to circulate water through the reaction vessel's water jacket at 20 L min^{-1}.

When the pH of the suspension was greater than 7, the reaction vessel was closed and an Ascarite (sodium hydroxide coated silica) trap was used to remove CO_2 (g) from the atmosphere of the reaction vessel. This prevented the absorption of CO_2 (g) by the suspension, which would result in a pH decrease. Once the suspension was placed into the reaction vessel, air was drawn into the reaction vessel through the Ascarite trap, purging CO_2 (g) from the gas phase above the sample.

A standard batch method was used to collect data when the time region was greater than 5 min. The reactions were conducted in either a batch reactor or in a series of identical 25 ml centrifuge tubes over an extended period from several days to several months. The sorption was initiated by the injection of a PCP solution into the reaction vessel containing the HDTMA(100%)-clay suspension at t=0. In order to monitor the progress of the sorption a sample was removed from the batch reactor or a centrifuge tube replicate was sacrificed. The sample was centrifuged at 3 000 g for 10 min. Then a portion of the clear supernatant was removed using a glass pipet, and the UV-absorbance of PCP was determined at 214nm. The temperature for these experiments was 298 K.

The majority of the experiments were conducted using the continuous flow method. This was the only method that was able to record data over the entire second stage of the sorption reactions. The other two methods were only able to measure limited portions of the reaction, thus providing only supplemental information. The rapid mix method provided data only during the first 2 minutes after the initiation of the reaction. This method was also limited by inability to control the reaction temperature and the lack of mixing after the turbulence of the initial addition. The standard batch method was employed to gather preliminary kinetic data and was useful in the development of the continuous flow method.

5.2.2 Experimental Conditions

Experimental conditions that were employed for the sorption study using the continuous flow method were:

- pH, 4 (protonated species) and 8 (deprotonated species)
- initial PCP concentrations, 15, 30, and 60 μm,
- HDTMA(100%)-clay suspension concentrations, 100, 200, and 300 mg (kg solvent)$^{-1}$.

The above treatments result in nine different experimental conditions per pH level. Blanks for the three suspension concentrations, three PCP initial concentrations, and the background electrolyte (0.001*m*. NaCl) were also run. The reactions were studied at 298 K. In addition, studies at each pH were conducted to investigate the effect of temperature on the sorption rate; pH=4, C_i = 30μm, Solid conc.= 100 mg/kg; pH=8, C_i =15μm, Solid conc. = 200 mg/kg. Four temperatures were investigated in addition to 298 K: 283, 313, 323, and 343 K. All reactions were conducted in a background electrolyte of 0.001 *m* NaCl.

5.2.3 PCP Analysis

Pentachlorophenol was quantified by UV absorbance using a Hewlett-Packard HP 8452A Diode Array UV-Visible Spectrophometer. The spectrophotometer was interfaced with a personal computer running software (Hewlett-Packard, HP 89532K UV-visible kinetic software) that enabled the collection and storage of the spectral data for the experimental runs. Each reported spectral analysis consisted of the UV spectrum between 190-320 nm (2 nm increments) signal averaged over 1 sec. The cuvette was scanned every 5 seconds during the continuous flow experiments.

The UV-absorbance spectra of protonated and deprotonated species of PCP are different (Figure 5.2). Absorbance maximums were determined at 214 and 224nm, respectively, for the protonated and deprotonated species. Thus the UV spectra of a PCP solution, in the spectral range under study, is a function of the solution pH. Due

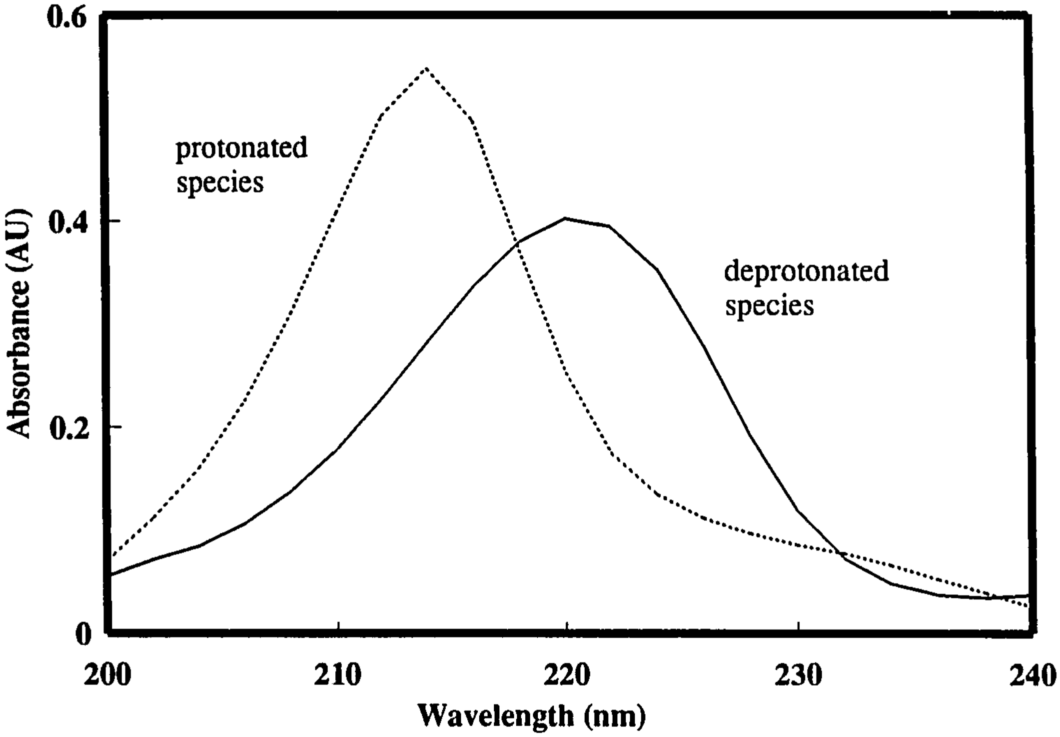

Figure 5.2 UV spectra of the protonated and deprotonated species of pentachlorophenol.

to greater sensitivity of the protonated species, PCP is most accurately quantified at 214 nm, but this requires the reduction of the solution pH to < 3. Therefore, the solid and aqueous phases must be separated prior to analysis. If these phases cannot be separated prior to analysis, the analysis must be conducted at a wavelength where the absorbance is not a function of pH, i.e., 218 nm. Therefore, the PCP analysis for the standard batch method was conducted at 214 nm while analysis for the rapid mix and continuous flow methods was conducted at 218nm. Pentachlorophenol aqueous concentration was determined based on the linear relationship of absorbance vs concentration in the 2-25µ*m* region at 214 nm and in the 2-60µ*m* region at 218 nm with a 5 point standard curve in both cases. The absorbance response of the instrument was relatively constant during the three year experimental period.

5.3 Results and Discussion

Initially the standard batch kinetic experiments indicated that sorption of the protonated and deprotonated species reached equilibrium within 20 min (Figure 5.3). Based on these results, the kinetic investigations focused on the change in the aqueous PCP concentration during the first 20 minutes of the experiment.

The sorption of organic compounds to soils and sediments is regularly observed as a two step phenomenon (3,9-15). It is characterized by an initial rapid sorption followed by a slower sorption in which the system reaches equilibrium. The initial sorption usually occurs over a time period of minutes to hours. The slower sorption

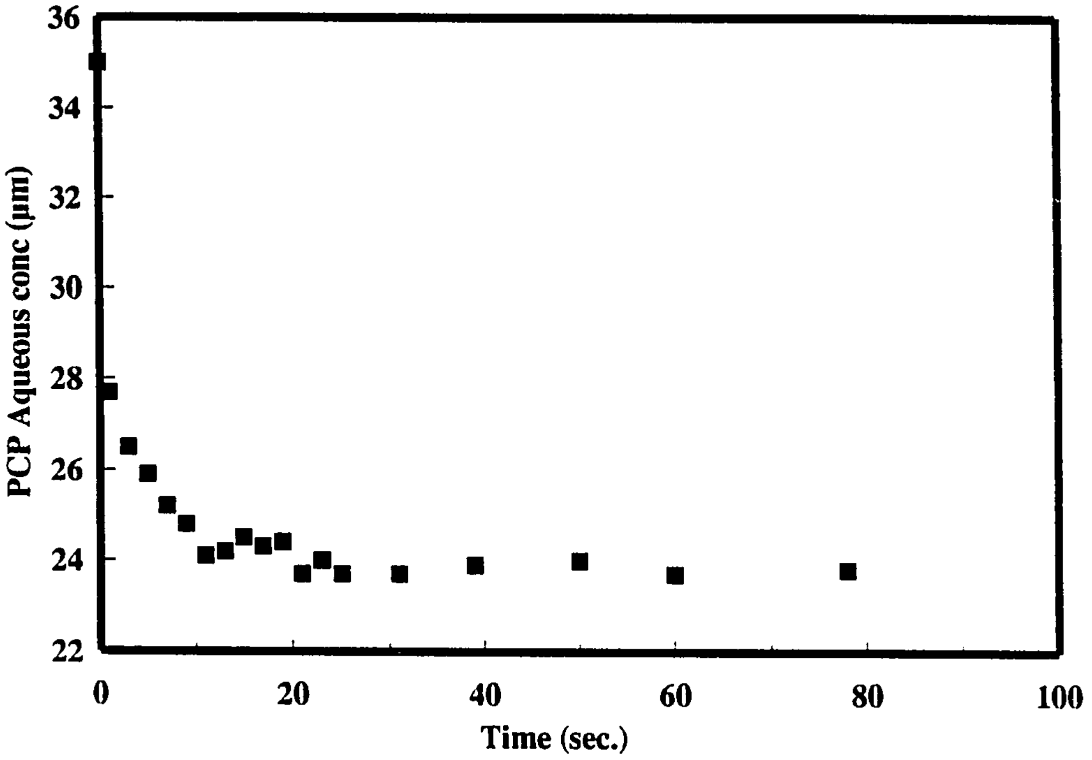

Figure 5.3 Plot of the aqueous phase pentachlorophenol concentration vs. time for the sorption of PCP by HDTMA(100%)-clay, using a standard batch method for data collection.

step occurs over a period of days to months. However, these time periods vary between different systems.

Similarly for the data in this study, the sorption of both PCP species appeared to be characterized by two stages. There was an apparent initial rapid sorption followed by a reaction that reached equilibrium within 600 sec. or 10 minutes (Figure 5.4). These two stages were observed in all sorption experiments. The first stage was characterized as an instantaneous reaction (15-30 % of the total reaction) based on the initial data points collected, using both the rapid mix and continuous flow method. These data were significantly less than the initial sorptive concentration (t=0). Being unable to measure the sorption in the first stage, the research focused on the sorption in the second reaction stage, which accounted for 70-85% of the total sorption. The kinetics of this stage were measured using the continuous flow method.

Researchers agree that the rate-limiting mechanism for the sorption of organic compounds is diffusion. Evidence has been given for both interparticle diffusion and interorganic matter diffusion. Interparticle diffusion assumes the sorptive moves through a fixed series of pores instantaneously sorbing to the organic matter on the pore walls, while interorganic matter diffusion assumes the sorptive diffuses through the organic material as if it were represented by a flexible polymeric-type structure. However, there is much disagreement about how best to model the diffusion controlled sorption data. Some researchers have recommended the use of a specific diffusion based model, while others advocate a general mass transfer based model.

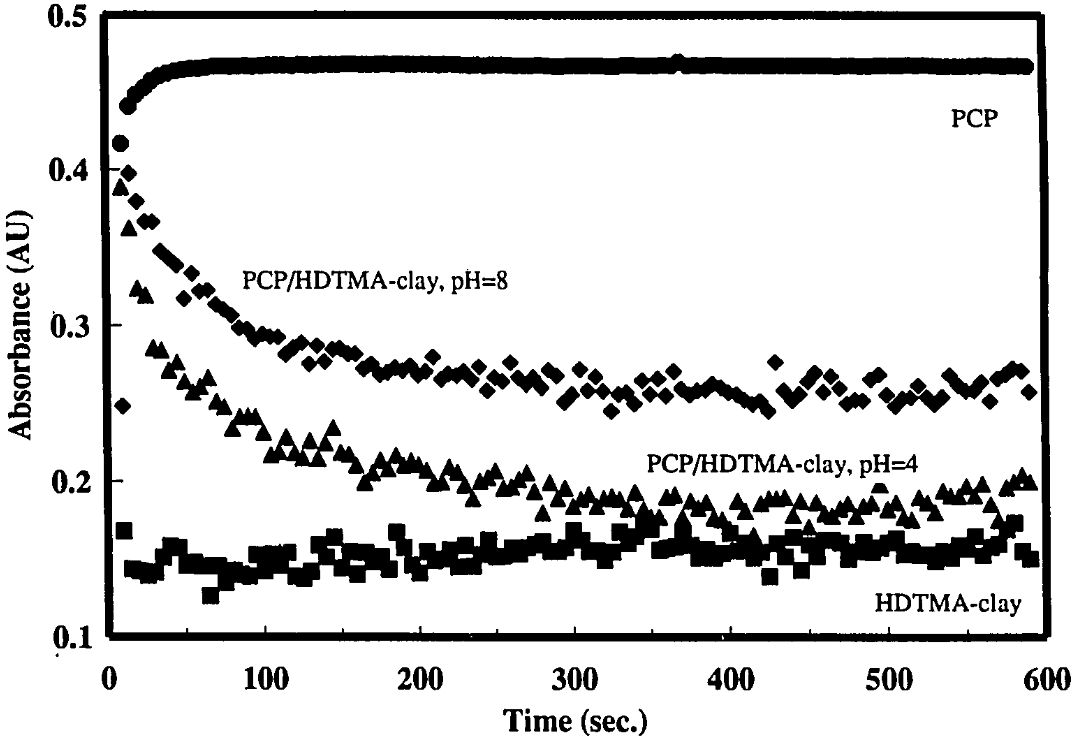

Figure 5.4 Plot of the absorbance at 218 nm vs.time for the sorption of PCP by HDTMA(100%)-clay using a continuous flow method for data collection.

The use of a specific diffusion based model requires a detailed description of the internal geometry of the porous media. In addition, if sorption is a two stage process a description of the initial rapid sorption stage must be included. Use of a diffusion based model also requires a commitment to a particular mechanism. If both of these can be accomplished then a specific diffusion based model can describe the data with fewer adjustable parameters than a general mass transfer based model. However, in many cases, sufficient data do not exist to define the geometric relationships of the solid phase and the complete sorption mechanism. When this occurs general mass transfer based models are more desirable (4).

One mass transfer model, the radial diffusion model has been used to describe the sorption of organic compounds to soils and sediments (14,15). Other researchers have used a pseudo first-order mass transfer model (2-4,16,17) to represent sorption. Brusseau and Rao (16) used a first-order bicontinum mass transfer model to successfully describe the sorption of an organic sorptive by soils, as given below,

$$A \rightleftharpoons B_{fast} \rightleftharpoons B \qquad (5.1)$$

Where A is the aqueous phase solute concentration, B_{fast} is the sorbed-phase concentration in the equilibrium domain, and B is the sorbed-phase concentration in the kinetically-limited domain. When the first reaction ($A \rightleftharpoons B_{fast}$) is in instantaneous equilibrium, a simple first-order reaction can be used to describe the second reaction ($A \rightleftharpoons B$) regardless of whether the reaction occurs in series or in parallel with the first reaction.

Since a specific mechanism for the sorption of PCP on HDTMA-clay was unproven, the experimental kinetic data in this study were modeled using a similar approach to Brusseau and Rao (17). The sorption and desorption reactions were modeled based on a pseudo first-order reversible reaction, given the first stage is in equilibrium and the solid phase is in excess:

$$\ln\left(\frac{[PCP_e]-[PCP_o]}{[PCP_e]-[PCP_t]}\right)=-(k_f+k_r)\,t=-k_s\ t. \qquad (5.2)$$

Where $[PCP_o]$, $[PCP_t]$, and $[PCP_e]$ are the aqueous PCP concentrations at the initial time, at time=t, and at equilibrium respectively, k_f is the sorption rate coefficient, and k_r is the desorption rate coefficient. The experimental data were plotted based on the left hand side of Equation 5.2 vs. time (Figure 5.5). The slope of a linear regression of this plot will give k_s which is the sum of the sorption and desorption rate coefficients.

The calculated rate coefficients (Table 5.1), based on the sorption data, did not change significantly (95% confidence interval) with an increase in the initial sorptive concentration within a given HDTMA(100%)-clay mass loading in the system at pH 4 and 8. There was a significant increase (95% confidence interval) in the rate coefficients from the low HDTMA(100%)-clay mass loading (100 mg/kg) to the two higher HDTMA(100%)-clay mass loadings (200 and 300 mg/kg). While this represented only a 20-30 percent increase in the rate coefficient between the 100 and 200 mg/kg HDTMA(100%)-clay mass loadings, it was significant and consistent for

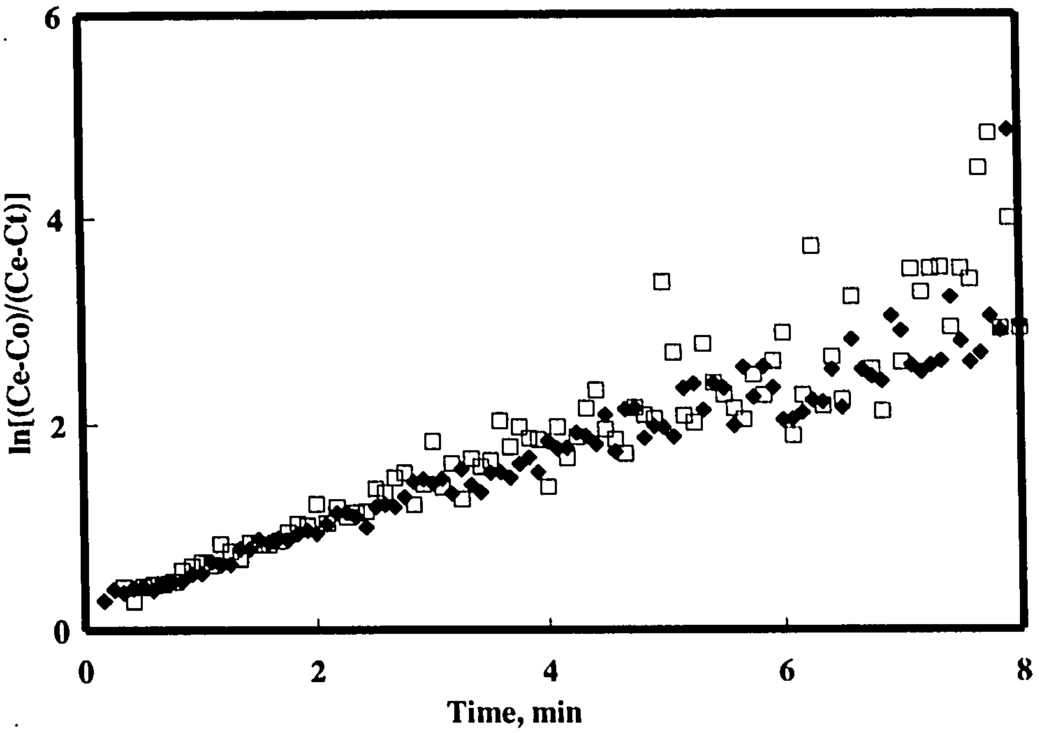

Figure 5.5 Linear plot of pseudo first-order reaction model [Eq. (5.2)] for sorption data. (◆) data for sample pH = 4, I = 0.001 *m*, HDTMA(100%)-clay = 100 mg/kg, C_i = 15 μ*m*; (□) data for sample pH = 8, I = 0.001 *m*, HDTMA(100%)-clay = 100 mg/kg, C_i = 15 μ*m*.

Table 5.1 Rate coefficients for the sorption of pentachlorophenol to HDTMA(100%)-clay at 298 K for all experimental conditions

pH	HDTMA(100%)-clay Loading (mg/kg)	Rate Coefficient, k_s (sec^{-1})
4	100	7.20E-03 ± 1.07E-03
4	200	9.70E-03 ± 8.08E-04
4	300	9.85E-03 ± 1.61E-03
8	100	7.91E-03 ± 1.61E-03
8	200	9.26E-03 ± 1.71E-03
8	300	9.70E-03 ± 3.66E-03

the sorption of both species. However, an increase in the rate coefficient with HDTMA(100%)-clay mass loading was not indicated when the data for the 200 and 300 mg/kg were compared. If the rate coefficient was dependent upon the HDTMA(100%)-clay mass loading, then the increase should have been consistent across all HDTMA(100%)-clay mass loading rates. In addition, there was not a significant difference (95% confidence interval) between the protonated and deprotonated species for similar experimental conditions.

As the temperature increased, the percentage of the total sorption that was instantaneous also increased. Therefore, the sorption reaction became more difficult to monitor as the change in the measured aqueous phase concentration became small. At 323 K, no change in the PCP concentration could be detected. Thus, only data at 283, 298, and 313 K were used to evaluated the change in the rate coefficient as a function of temperature based on Equation (5.3), the Arrhenius equation,

$$k_s = Ae^{-E_a/RT} \tag{5.3}$$

Where E_a is the energy of activation , k_s is the rate coefficient, R is the universal gas constant and T is temperature (K). The E_a for the sorption of the protonated and deprotonated species were 9.0 and 11.2 kJ/mol based on a linear plot of Equation 5.3 (Figure 5.6). The similarity of the rate coefficients for the protonated and deprotonated PCP species indicates that the sorption mechanism may be similar. This is consistent with the conclusions of the equilibrium study that proposed similar mechanisms of sorption based on hydrophobic interactions. The rate limiting

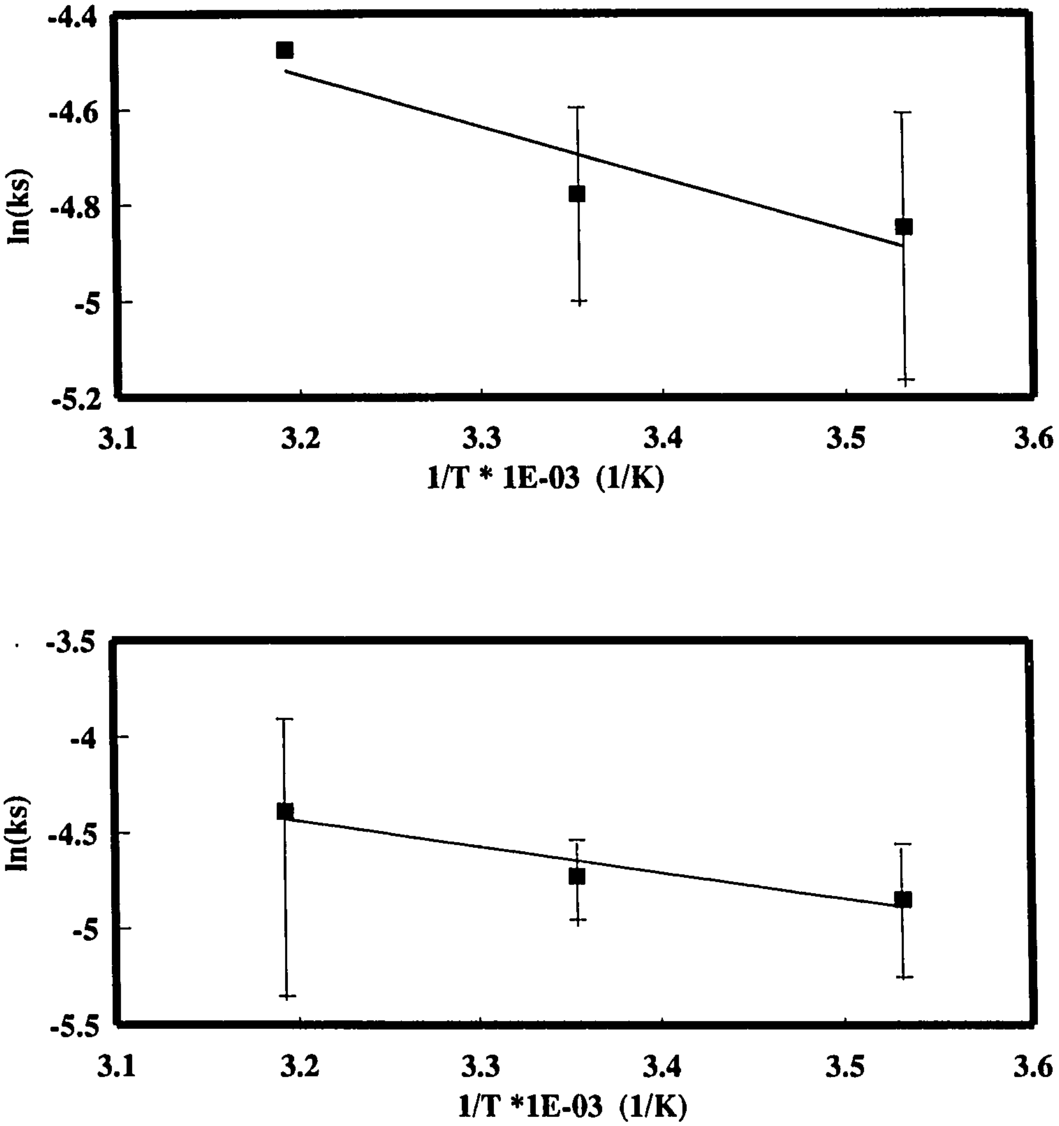

Figure 5.6 Arrhenius plot of the change in the rate coefficients as a function of temperature.

mechanism could be similar for both PCP species based on the similar rate of sorption and the low energy of activation (E_a) for both species and is consistent with a hydrophobic sorption interaction and a diffusion-limited mechanism.

5.4 Conclusions

1) The sorption of the protonated and deprotonated species of PCP was characterized by two stages; a first stage in which there was an instantaneous sorption followed by a second stage that reached equilibrium within 10 minutes.

2) The sorption reaction that occurred in the first stage could not be measured with the experimental apparatus. However, the sorption of both the PCP species in the second stage, could be characterized by a pseudo first-order reversible reaction.

3) The energy of activation for the sorption reaction of both PCP species was low. This is consistent with the proposed hydrophobic sorption mechanism and a diffusion limited mechanism.

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Chapter 6

SUMMARY AND CONCLUSIONS

The main objective of my doctoral research was to study the sorption and solubility of pentachlorophenol (PCP) over a pH range that included both the protonated and deprotonated PCP species. We used the data collected from this study to propose models that described the sorption of PCP to a surfactant modified-clay and the aqueous phase PCP solubility as a function of pH. The modified-clay was prepared by the addition of HDTMA cations, via an ion exchange reaction, to a montmorillonite clay. This produced a hydrophobic sorbent with a high organic carbon content that was very stable. The HDTMA-clay served as an excellent sorbent that provided no experimental interferences during either the equilibrium or kinetic experiments.

The first research task that I undertook was to determine the aqueous phase solubility of PCP between pH 4 and 6. These data were very important because they were used to determine the maximum equilibrium concentration that could be employed in the sorption experiments without causing precipitation of PCP. The data showed an increase in the PCP solubility with pH and, above the pK_a, an increase in

PCP solubility with ionic strength. The solubility of the protonated species was 28 µ*m*. When this concentration was exceeded a white precipitate formed. The precipitation kinetics were slow, and sometimes a precipitate would form overnight. In the 4-6 pH range, we did not observe the precipitation of a phenolate salt. Therefore, the maximum aqueous phase concentration of the deprotonated species was a function of the pH and the solubility of the protonated species. A model for the maximum aqueous phase concentration of PCP, as a function of pH, was proposed based on the mass balance and the equilibrium relationship for the two PCP species. This model shows an exponential increase in the maximum PCP aqueous concentration, above the pK_a. The proposed model is consistent with solubility data from the literature. In the 4-8 pH range, the maximum aqueous concentration of PCP increases by a factor of 10 000.

The sorption of both PCP species, by the HDTMA-clay, was rapid and appeared reversible. The sorption appeared to occur in two stages, an initial instantaneous stage followed by a rapid second stage with equilibrium being reached within 10 minutes. The rate of sorption, in the second stage, was described by a pseudo first-order reaction. There was not a significant difference in the rate of sorption between the two PCP species, and sorption was characterized by a low energy of activation.

Equilibrium sorption of the protonated species was significantly greater than the deprotoanted species with linear sorption over the solubility range. Therefore, a partition mechanism was proposed for the sorption of the protonated species by the HDTMA-clay. Sorption of the deprotonated species was distinctly nonlinear and was represented by a Langmuir equation. We proposed that the sorption mechanism of the deprotonated species was as a neutral pair, with the phenolate anion in association with a cation from the background electrolyte. However, our data have suggested that hemimicelle formation occurred, on the external surface, when the HDTMA cation replaces ≥ 70% of the CEC. If the hemimicelles are present, the electrostatic sorption of the deprotonated species would also have to be considered as a potential sorption mechanism.

The difference in the sorption of the two species leads to a significant change in sorption between pH 5 and 7. We could successfully model this change, as a function of pH, by the combination of a linear isotherm for the protonated species and a Langmuir isotherm for the deprotonated species.

This research has conclusively shown that there are significant differences in the sorption and the solubility between the protonated and deprotonated PCP species, and we have provided models that will estimate these properties as a function of pH. However, there is still much research to be done. We have laid out a basic relationship between the speciation and the sorption of PCP to HDTMA-clay. This relationship needs to be tested to see if the approach is applicable for the sorption of

PCP to unmodified soils and for application to other HIOC. In addition, linear sorption of the deprotoanted species occurred when the PCP aqueous phase concentration was less than 5 μm and the slope is similar to the sorption of the protonated species. There were only a few data points in this region, due to the detection limit of the PCP analysis. More research should be conducted to better define the comparative sorption between the two species in this low concentration range, possibly using ^{14}C as a tracer.

While the modified clay was a secondary focus of the research, several important conclusions can be drawn from the data. First, aging of the samples did not affect the reversibility of PCP sorption. Thus modified soils, in the natural environment , should not be considered a permanent sink for the sorbed contaminants. Once the aqueous phase sorptive concentration is less than the aqueous equilibrium concentration, desorption will occur and the modified surface will serve as a contaminant source. While the reversibility may present some difficulties it should not rule out the consideration of soil modification by surfactants. However, the impact of the reversibility should be considered. Second, with the sorptive characteristics of the modified-clay a direct function of the surfactant and with the sorption being rapid and reversible, the modified-clay could serve as a sorbent in a treatment system for the selective removal of a contaminant from an aqueous waste stream. The use of modified-clay as a selective sorbent for treatment applications should be investigated further.

In addition, several other interesting observations should be investigated further. The proposed hemimicelle formation has never been reported in the literature for clay that was modified at $\leq$ 100% exchange of the CEC. The hemimicelles appear stable, not removed by washing, and zeta potential measurements are consistent with their formation. Additional experiments should be conducted confirming the hemimicelle formation. If these structures are present, the anion exchange capacity (AEC) of the modified-clay should be determined. Also, experiments should be conducted to determine if hemimicelle formation occurs with other surfactants.

While, it may have seemed sophomoric conducting a study to find if the sorption and solubility of hydrophobic ionizable organic compounds (HIOC) are a function of pH. Occasionally, research results are published in which the speciation of HIOC are not reported and may not have been considered. In addition, outside the research community there is a trend to simplify complex environmental chemical behavior. All too often, this results in assumptions that describe the chemical and physical properties of a HIOC considering only one species. If both species are present, in the aqueous phase, a significant error could result. This research has provided a mechanism to estimate the sorption of PCP, as a function of pH, to HDTMA-clay and the aqueous phase PCP solubility . We hope this will serve as the basis for other models and will emphasize the importance of speciation when estimating the environmental fate and transport of an ionizable compound.

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Appendix A

GLOSSARY

γ	activity coefficient, based on Davies equation
3-MCP	3-monochlorophenol
345-TCP	3,4,5-trichlorophenol
35-DCP	3,5-dichlorophenol
A^-	conjugate base of acid, HA°, (anion)
BDHA	benzyldimethylhexadecylammonium
BH^+	conjugate acid of base, B° , (cation)
BTEA	benzyltrimethylammonium
BTMA	benzyltrimethylammonium cation
B°	base (neutral species)
C_e	aqueous phase equilibrium concentration μm
CEC	cation exchange capacity (cmol kg^{-1})
cmc	critical micelle concentration
D	distribution coefficient
DDPA	dodecyldimethyl(2-phenoxyethyl)-ammonium cation
DI	distilled water
DODMA	dioctadecyldimethyl cation
DTMA	dodecyltrimethylammonium cation
E_a	energy of activation (kJ)
HA°	acid (neutral species)
HDPY	hexadecylpyridinium cation
HDTMA	hexadecyltrimethylammonium cation
HIOC	hydrophobic ionizable compound
IMt	illite, Silver Hill, Montana
IOC	ionizable organic compound
KGa	kaolinite, Warren County, Georgia
K_{hw}	heptane/water partition coefficient
K_{oc}	organic carbon partition coefficient

K_{om}	organic matter partition coefficient
K_{ow}	octanol/water partition coefficient
K_p	partition coefficient
k_s	pseudo first-order rate coefficient (sec^{-1})
M^+	general cation
NOC	nonionic organic compound
NTMA	nonyltrimethylammonium cation
OM	organic matter
PCP	pentachlorophenol
PCP°	protonated PCP species
PCP^-	deprotoanted species
pK_a	- log (K_a), where K_a is the acid dissociation constant
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R-group	any alkyl group, general formula $C_n H_{2n+1}$
Saz	high-montmorillonite, Apache County, Arizona
SFM	scanning force microscopy
SWy-1	low-montmorillonite, Cook County, Wyoming
T	temperature (K)
TMA	tetramethylammonium cation
TMPA	trimethylphenylammonium cation
TTMA	tetradecyltrimethylammonium cation

Appendix B

PREPARATION OF BASE CLAY

Pretreatment Procedure for Base Clay

I. Removal of $CaCO_3$.
  - A. Weight out ≈100 grams of clay, add 4 L deionized water, stir well, and let stand overnight.
  - B. Determine the pH of the suspension. If the pH is > 8.0, then treat to remove carbonates. Decrease the pH of the suspension to < 7. Initially, determine the volume of 0.05M HCl to reduce the suspension pH. Add required volume of 0.05 M HCl to neutralize the clay suspension and place in a water bath at 60°C for 2 to 3 hours. Cool sample before continuing.

II. Particle size separation, < 2 μm.
  - A. Transfer the clay suspension into 16 centrifuge bottles (250 mls).
  - B. Centrifuge at 1500 rpm (380 g) for 10 minutes, pour out and save the top 2/3 of the clay suspension.
  - D. Fill centrifuge tube with deionized water, shake well, centrifuge at 1500 rpm (380 g) for 10 minutes, pour out and save the top 2/3 of the clay suspension.
  - E. Repeat Step D.
  - F. Collect the saved suspension and discard the separated solids.

II. Homoionic saturation.
  - A. Increase the salt concentration in the saved suspension to desired value [1.0 M (NaCl, KCl) or 0.5 M ($CaCl_2$, $MgCl_2$)], shake well, centrifuge at 1500 rpm (380 g) for 10 minutes, and discard the clear supernatant.
  - C. Fill centrifuge tube with salt solution [1.0 M (NaCl, KCl) or 0.5 M ($CaCl_2$, $MgCl_2$)], shake well, centrifuge at 1500 rpm (380 g) for 10 minutes,
  - D. Decant supernatant, add salt solution, shake well, and centrifuge at 1500 rpm (380 g) for 10 minutes, and discard the clear supernatant.

III. Removal of free salt.
  - A. Place the remaining clay suspension in dialysis tubes, and put tubes into a sufficient volume of deionized water for 2 days. Change wash water twice a day.
  - B. Dialyze in 10^{-4} M solution (of saturating ion), change the solution once a day until the conductance measurement does not differ from the original solution. Freeze clay suspension in ice cube trays then freeze dry.

Appendix C
SOLUBILITY DATA

Variable and Rule Sheets for the calculation of the PCP speciation for the PCP solubility data. Calculations completed in TK Solver.

```
•••••••••••••••••••• VARIABLE SHEET •••••••••••••••••••• For Academic Use Only
St Input•••• Name••• Output••• Unit••••• Comment•••••••••••••••••••••••••••••••
L  3.44E1    PCP               μm        Total pentachlorophenol conc.
L            PCPp    2.82E1    μm        Protonated pentachlorophenol conc.
L            PCPd    6.23E0    μm        Deprotonated pentachlorophenol conc.
L  4.08      pH
   4.75      pKa
L            ac      .97                 Activity Coefficient for PCPd
L            I       .001      m         Ionic strength
L  .001      NaCl              m         Background NaCl conc.
```

```
•••••••••••••••••••• RULE SHEET ••••••••••••••••••••••• For Academic Use Only
S Rule•••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••••
* PCP=PCPp+PCPd
* PCPd=10^(pH-pKa)*PCPp/ac
* ac=10^(-0.5*(sqrt(I)/(1+sqrt(I))-0.3*I))
* I=NaCl+PCPd
```

Solubility data input into TK Solver model (PCP, pH, NaCl) to calculate the deprotonated species (PCPp).

```
•••••••••••••••••••• TABLE: b ••••••••••••••••••••••••• For Academic Use Only
Title:
Element PCP••••••• pH••••••••• NaCl•••••• PCPp•••••• ••••••• ••••••• •••••••
1       34.39      4.08        .001       28.1556924
2       82.4       5.03        .001       27.6973933
3       33.44      4.02        .1         27.0286098
4       101.9      5.03        .1         29.7306381
```

	PCP	pH	I	PCPp		
1	34.39	4.08	0.001	28.1556924		
2	82.4	5.03	0.001	27.6973933		
3	33.44	4.02	0.1	27.0286098		
4	101.9	5.03	0.1	29.7306381		
		avg		<u>28.1530834</u>	<u>+/-</u>	<u>1.149026</u> μm

TK Solver model output for total PCP concentration as a function of pH, 0.001 m NaCl background electrolyte.

		Total PCP	Deprotonated PCP	Davies Activity Coefficient (gamma)	Ionic Strength
		(µm)	(µm)		(m)
Run #	pH	PCP	PCPd	ac	I
1	3	2.87E+01	5.18E-01	0.97	0.001
2	3.2	2.90E+01	8.22E-01	0.97	0.001
3	3.4	2.95E+01	1.30E+00	0.97	0.001
4	3.6	3.02E+01	2.06E+00	0.97	0.001
5	3.8	3.14E+01	3.27E+00	0.97	0.001
6	4	3.33E+01	5.18E+00	0.97	0.001
7	4.2	3.64E+01	8.22E+00	0.97	0.001
8	4.4	4.12E+01	1.30E+01	0.97	0.001
9	4.6	4.88E+01	2.06E+01	0.97	0.001
10	4.8	6.09E+01	3.27E+01	0.97	0.001
11	5	8.00E+01	5.19E+01	0.96	0.001
12	5.2	1.10E+02	8.23E+01	0.96	0.001
13	5.4	1.59E+02	1.31E+02	0.96	0.001
14	5.6	2.35E+02	2.07E+02	0.96	0.001
15	5.8	3.57E+02	3.29E+02	0.96	0.001
16	6	5.51E+02	5.22E+02	0.96	0.002
17	6.2	8.59E+02	8.31E+02	0.95	0.002
18	6.4	1.35E+03	1.32E+03	0.95	0.002
19	6.6	2.14E+03	2.12E+03	0.94	0.003
20	6.8	3.42E+03	3.39E+03	0.93	0.004
21	7	5.47E+03	5.44E+03	0.92	0.006
22	7.2	8.80E+03	8.77E+03	0.90	0.010
23	7.4	1.42E+04	1.42E+04	0.89	0.015
24	7.6	2.31E+04	2.31E+04	0.86	0.024
25	7.8	3.77E+04	3.77E+04	0.84	0.039
26	8	6.17E+04	6.17E+04	0.81	0.063
27	8.2	1.01E+05	1.01E+05	0.78	0.102
28	8.4	1.66E+05	1.66E+05	0.76	0.167
29	8.6	2.69E+05	2.69E+05	0.74	0.270
30	8.8	4.30E+05	4.30E+05	0.74	0.431
31	9	6.67E+05	6.67E+05	0.75	0.668
32	9.2	9.99E+05	9.99E+05	0.79	1.000
33	9.4	1.43E+06	1.43E+06	0.88	1.436
34	9.6	1.97E+06	1.97E+06	1.01	1.975
35	9.8	2.61E+06	2.61E+06	1.21	2.611
36	10	3.33E+06	3.33E+06	1.50	3.333

TK Solver model output for total PCP concentration as a function of pH, 0.1 m NaCl background electrolyte.

		Total PCP	Deprotonated PCP	Davies Activity Coefficient (gamma)	Ionic Strength
		(µm)	(µm)		(m)
Run #	pH	PCP	PCPd	ac	I
1	3	2.88E+01	6.38E-01	0.79	0.1
2	3.2	2.92E+01	1.01E+00	0.79	0.1
3	3.4	2.98E+01	1.60E+00	0.79	0.1
4	3.6	3.07E+01	2.54E+00	0.79	0.1
5	3.8	3.22E+01	4.02E+00	0.79	0.1
6	4	3.45E+01	6.38E+00	0.79	0.1
7	4.2	3.83E+01	1.01E+01	0.79	0.1
8	4.4	4.42E+01	1.60E+01	0.78	0.1
9	4.6	5.35E+01	2.54E+01	0.78	0.1
10	4.8	6.84E+01	4.02E+01	0.78	0.1
11	5	9.19E+01	6.38E+01	0.78	0.1
12	5.2	1.29E+02	1.01E+02	0.78	0.1
13	5.4	1.88E+02	1.60E+02	0.78	0.1
14	5.6	2.82E+02	2.54E+02	0.78	0.1
15	5.8	4.31E+02	4.03E+02	0.78	0.1
16	6	6.66E+02	6.38E+02	0.78	0.1
17	6.2	1.04E+03	1.01E+03	0.78	0.1
18	6.4	1.63E+03	1.60E+03	0.78	0.1
19	6.6	2.57E+03	2.54E+03	0.78	0.1
20	6.8	4.06E+03	4.04E+03	0.78	0.1
21	7	6.43E+03	6.41E+03	0.78	0.1
22	7.2	1.02E+04	1.02E+04	0.78	0.1
23	7.4	1.62E+04	1.62E+04	0.78	0.1
24	7.6	2.58E+04	2.58E+04	0.77	0.1
25	7.8	4.12E+04	4.12E+04	0.77	0.1
26	8	6.60E+04	6.60E+04	0.76	0.2
27	8.2	1.06E+05	1.06E+05	0.75	0.2
28	8.4	1.70E+05	1.70E+05	0.74	0.3
29	8.6	2.71E+05	2.71E+05	0.74	0.4
30	8.8	4.27E+05	4.27E+05	0.74	0.5
31	9	6.58E+05	6.58E+05	0.76	0.8
32	9.2	9.82E+05	9.82E+05	0.81	1.1
33	9.4	1.41E+06	1.41E+06	0.89	1.5
34	9.6	1.94E+06	1.94E+06	1.03	2.0
35	9.8	2.57E+06	2.57E+06	1.23	2.7
36	10	3.28E+06	3.28E+06	1.53	3.4

Appendix D
SORPTION DATA

Data for Figure 4.1

	===35%==	====70%==	====100%==
PCP Equili Conc µm	SURFACE CONC mol/kg	SURFACE CONC mol/kg	SURFACE CONC mol/kg
8.7	1.83E-02		
10.2	2.40E-02		
15.1	4.41E-02		
14.9	4.20E-02		
22.6	5.35E-02		
25.6	6.61E-02		
7.1		3.13E-02	
5.5		3.60E-02	
13.6		1.09E-01	
10.0		7.67E-02	
13.3		1.05E-01	
16.6		1.34E-01	
1.1		3.62E-03	
3.3		2.97E-02	
5.9		5.38E-02	
9.4		6.85E-02	
13.8		8.46E-02	
17.1		9.07E-02	
19.8		1.21E-01	
23.9		1.27E-01	
1.3		6.03E-03	
5.5		3.61E-02	
8.6		5.65E-02	
11.5		7.27E-02	
14.5		9.05E-02	
17.3		1.03E-01	
21.4		1.20E-01	
22.6		1.45E-01	
4.51			6.62E-02
9.88			1.44E-01
17.2			3.12E-01
3.6			1.99E-02
5.36			6.76E-02
9.91			1.43E-01
7.7			1.77E-01
13.06			3.03E-01
20.32			4.84E-01
6.69			1.68E-01
14.19			3.04E-01
18.27			3.93E-01
5.6			1.57E-01
12.05			2.69E-01
19.19			3.67E-01
6.57			1.40E-01
12.63			2.57E-01
21.3			3.63E-01
26.03			5.20E-01

Data for Figure 4.2a

EQUIL. CONC. µm	0.001M SURFACE CONC 70%CEC mol/kg	0.01M SURFACE CONC 70%CEC mol/kg	0.1M SURFACE CONC 70%CEC mol/kg
0.417	1.09E-03		
0.683	2.14E-03		
1.049	3.14E-03		
1.443	3.81E-03		
2.068	4.43E-03		
7.503	8.35E-03		
18.374	1.29E-02		
31.422	1.60E-02		
50.174	2.12E-02		
66.537	2.24E-02		
0.754	3.25E-03		
1.265	3.87E-03		
1.526	4.62E-03		
5.326	9.21E-03		
14.918	1.47E-02		
27.486	1.80E-02		
47.941	2.25E-02		
64.354	2.37E-02		
0.743		5.98E-03	
2.886		1.13E-02	
9.630		1.88E-02	
9.044		3.13E-02	
32.955		2.95E-02	
46.490		3.32E-02	
2.375		1.16E-02	
7.272		2.00E-02	
19.884		2.73E-02	
31.103		3.06E-02	
47.690		3.24E-02	
3.378			2.29E-02
9.571			3.40E-02
15.301			3.99E-02
30.267			4.70E-02
9.782			3.39E-02
14.851			4.02E-02
28.484			4.81E-02

Data for Figure 4.2b

pH	EQUIL CONC. µm	0.001M SURFACE CONC 100% mol/kg	0.1M SURFACE CONC 100% mol/kg
8.5	3.67	5.88E-02	
8.5	15.32	9.25E-02	
8.5	18.07	9.81E-02	
8.5	28.75	1.45E-01	
8.5	50.83	1.50E-01	
8.5	100.18	1.56E-01	
8.5	3.56		8.26E-02
8.5	7.31		1.24E-01
8.5	17.16		1.63E-01
8.5	40.06		2.04E-01
8.5	90.66		2.44E-01
8.5	118.40		2.08E-01

Data for Figure 4.3

EQUIL CONC. µm	pH	SURFACE CONC 0.001M mol/kg A	SURFACE CONC 0.1M mol/kg B	SURFACE CONC 0.001M mol/kg C	SURFACE CONC 0.1M mol/kg D
2.30	5.39	7.28E-02			
6.59	5.35	1.07E-01			
14.71	5.32	1.47E-01			
27.81	5.27	2.15E-01			
55.18	5.25	3.42E-01			
6.62	5.24	1.06E-01			
2.48	5.25		7.16E-02		
5.08	5.16		1.08E-01		
12.93	5.2		1.63E-01		
25.50	5.18		2.47E-01		
50.46	5.15		3.22E-01		
70.18	5.17		4.36E-01		
6.14	6.37			7.54E-02	
10.71	6.25			9.12E-02	
18.15	6.18			1.14E-01	
31.42	6.07			1.32E-01	
54.69	6.13			1.45E-01	
94.28	6.08			2.08E-01	
162.73	6.12			2.26E-01	
95.47	6.08			1.67E-01	
5.44	6.1				8.81E-02
8.46	6.09				1.22E-01
16.82	6.16				1.35E-01
55.52	6.2				1.50E-01
30.01	6.19				1.54E-01
94.73	6.11				1.91E-01
168.27	6.2				2.06E-01
93.13	6.16				1.97E-01

Data for Figure 4.4

pH	EQUIL CONC. (μm)	SURFACE CONC 0.001M mol/kg	SURFACE CONC 0.1M mol/kg	SURFACE CONC 0.001M mol/kg	SURFACE CONC 0.1M mol/kg
6.9	4.87	8.06E-02			
6.9	14.36	9.76E-02			
6.9	33.75	1.20E-01			
6.9	79.68	1.36E-01			
6.7	1.53		5.25E-02		
6.7	12.67		1.13E-01		
6.6	32.10		1.43E-01		
6.7	77.97		1.72E-01		
8.5	3.67			5.88E-02	
8.5	15.32			9.25E-02	
8.5	18.07			9.81E-02	
8.5	28.75			1.45E-01	
8.5	50.83			1.50E-01	
8.5	100.18			1.56E-01	
8.5	3.56				8.26E-02
8.5	7.31				1.24E-01
8.5	17.16				1.63E-01
8.5	40.06				2.04E-01
8.5	90.66				2.44E-01
8.5	118.40				2.08E-01

Data for Figure 4.5a

Date		29-DEC-94	07-Feb-94	20-Mar-94	20-April-94	
pH		4	4	4	4	4
	EQUIL CONC.	SURFACE CONC	SURFACE CONC	SURFACE CONC	SURFACE CONC	SURFACE CONC
	um	mol/kg	mol/kg	mol/kg	mol/kg	mol/kg
	34.0	5.26E-01				
	32.3	4.32E-01				
	27.8	3.98E-01				
	29.9	4.14E-01				
	24.3	3.74E-01				
	20.6	3.46E-01				
	19.8	3.67E-01				
	12.4	2.36E-01				
	10.2	2.18E-01				
	8.1	1.72E-01				
	5.6	1.51E-01				
	2.8	1.79E-01				
	2.8	2.01E-01				
	41.4		4.48E-01			
	31.2		4.62E-01			
	28.0		3.64E-01			
	23.0		3.24E-01			
	19.0		2.77E-01			
	15.3		2.12E-01			
	13.3		1.06E-01			
	8.4		1.63E-01			
	5.2		1.40E-01			
	2.6		2.17E-01			
	41.7			4.48E-01		
	32.8			4.20E-01		
	26.4			4.02E-01		
	22.8			3.50E-01		
	19.3			2.94E-01		
	13.4			2.12E-01		
	12.1			2.23E-01		
	9.9			1.24E-01		
	5.4			1.55E-01		
	3.2			-4.49E-02		
	33.1				4.25E-01	
	28.3				5.19E-01	
	23.7				4.22E-01	
	20.1				4.59E-01	
	16.4				3.82E-01	
	12.2				3.60E-01	
	11.1				3.31E-01	
	6.7				3.07E-01	
	3.6				-1.45E-01	
	33.1					5.36E-01
	28.3					4.99E-01
	23.7					4.55E-01
	20.1					4.17E-01
	16.4					3.84E-01
	12.2					3.81E-01
	11.1					2.70E-01
	6.7					3.38E-01
	3.6					4.19E-01

Data for Figure 4.5b

Date		07-Feb-94	20-Mar-94	20-April-94	07-Jul-94
pH		8	8	8	8
	EQUIL CONC.	SURFACE CONC	SURFACE CONC	SURFACE CONC	SURFACE CONC
	um	mol/kg	mol/kg	mol/kg	mol/kg
	41.0	6.84E-02			
	31.0	4.79E-02			
	20.6	7.18E-02			
	16.9	4.90E-02			
	11.5	5.68E-02			
	9.6	5.29E-02			
	7.3	3.77E-02			
	5.5	2.81E-02			
	4.3	3.40E-02			
	3.4	-7.64E-03			
	36.3		4.63E-02		
	25.2		5.02E-02		
	22.8		3.35E-02		
	17.6		2.33E-02		
	13.6		1.79E-02		
	11.0		3.26E-03		
	7.7		6.05E-03		
	8.0		3.72E-02		
	4.3		3.81E-02		
	3.5		-3.59E-04		
	34.5			1.11E-01	
	27.0			1.02E-01	
	19.6			1.01E-01	
	14.5			9.22E-02	
	11.4			8.71E-02	
	9.4			8.75E-02	
	5.3			1.02E-01	
	4.6			7.77E-02	
	2.6			1.49E-01	
	3.0			8.77E-02	
	34.5				1.05E-01
	27.0				9.22E-02
	19.6				9.26E-02
	14.5				8.70E-02
	11.4				7.74E-02
	9.4				5.26E-02
	5.3				1.04E-01
	4.6				7.49E-02
	2.6				1.23E-01

Data for Figure 4.7

EQUIL CONC. (μm)	SURFACE CONC mol/kg
4.51	6.62E-02
9.88	1.44E-01
17.2	3.12E-01
3.6	1.99E-02
5.36	6.76E-02
9.91	1.43E-01
7.7	1.77E-01
13.06	3.03E-01
20.32	4.84E-01
6.69	1.68E-01
14.19	3.04E-01
18.27	3.93E-01
5.6	1.57E-01
12.05	2.69E-01
19.19	3.67E-01
6.57	1.40E-01
12.63	2.57E-01
21.3	3.63E-01
26.03	5.20E-01

Data for Figure 4.8

EQUIL CONC. (μm)	SURFACE CONC 0.001M mol/kg
3.67	5.88E-02
15.32	9.25E-02
18.07	9.81E-02
28.75	1.45E-01
50.83	1.50E-01
100.18	1.56E-01

Data for Figure 4.9

	Ct µm	Q	mol/kg					
pH		4	4.75	5.25	5.75	6.25	8	9
alapha-0		0.85	0.50	0.24	0.09	0.03	0.00	0.00
alapha-1		0.15	0.50	0.76	0.91	0.97	1.00	1.00
	0.00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	3.40	6.62E-02	5.87E-02	5.12E-02	4.62E-02	4.41E-02	4.31E-02	4.30E-02
	6.80	1.32E-01	1.11E-01	9.09E-02	7.76E-02	7.20E-02	6.92E-02	6.92E-02
	10.20	1.97E-01	1.60E-01	1.24E-01	1.01E-01	9.16E-02	8.68E-02	8.67E-02
	13.00	2.50E-01	1.98E-01	1.48E-01	1.17E-01	1.04E-01	9.75E-02	9.74E-02
	14.30	2.74E-01	2.15E-01			1.09E-01	1.02E-01	1.01E-01
	15.00		2.24E-01	1.64E-01		1.11E-01	1.04E-01	1.04E-01
	17.00	3.25E-01	2.50E-01	1.79E-01	1.36E-01	1.18E-01	1.09E-01	1.09E-01
	22.00	4.18E-01	3.11E-01	2.14E-01	1.56E-01			1.19E-01
	23.40		3.28E-01	2.24E-01	1.61E-01	1.35E-01	1.22E-01	1.21E-01
	23.80	4.51E-01	3.33E-01		1.62E-01	1.36E-01	1.22E-01	1.22E-01
	28.00	5.28E-01	3.82E-01	2.53E-01	1.76E-01	1.44E-01	1.28E-01	1.28E-01
	29.00	5.47E-01	3.94E-01	2.59E-01	1.79E-01		1.30E-01	1.29E-01
	32.00		4.28E-01	2.77E-01	1.88E-01	1.51E-01		1.33E-01
	32.00	6.02E-01	4.28E-01	2.77E-01	1.88E-01	1.51E-01		1.33E-01
	33.00	6.20E-01	4.39E-01	2.83E-01		1.53E-01	1.34E-01	1.34E-01
	38.50		5.01E-01	3.15E-01	2.06E-01	1.61E-01	1.39E-01	1.38E-01
	40.80		5.26E-01	3.28E-01	2.12E-01	1.64E-01	1.40E-01	1.40E-01
	44.20		5.64E-01	3.48E-01	2.20E-01	1.69E-01	1.43E-01	1.42E-01
	47.60		6.00E-01	3.66E-01	2.29E-01	1.73E-01	1.45E-01	1.44E-01
	51.00		6.37E-01	3.85E-01	2.37E-01	1.77E-01	1.47E-01	1.46E-01
	54.00		6.69E-01	4.01E-01	2.44E-01	1.80E-01	1.48E-01	1.47E-01
	57.80			4.21E-01	2.52E-01	1.84E-01		1.49E-01
	58.60			4.25E-01	2.54E-01	1.85E-01	1.50E-01	1.49E-01
	64.60			4.57E-01	2.67E-01	1.91E-01	1.52E-01	1.51E-01
	65.50			4.62E-01	2.69E-01	1.91E-01	1.52E-01	1.52E-01
	68.00			4.75E-01	2.75E-01		1.53E-01	1.53E-01
	71.00			4.90E-01	2.81E-01	1.96E-01	1.54E-01	1.53E-01
	73.00			5.00E-01	2.85E-01	1.98E-01	1.55E-01	1.54E-01
	81.60			5.45E-01	3.03E-01	2.06E-01		1.56E-01
	83.00			5.52E-01	3.06E-01	2.07E-01	1.57E-01	1.56E-01
	88.40			5.79E-01	3.17E-01	2.11E-01	1.58E-01	1.57E-01
	91.50			5.95E-01	3.23E-01	2.14E-01	1.59E-01	1.58E-01
	93.00			6.02E-01	3.26E-01		1.59E-01	1.58E-01
	96.50			6.20E-01	3.34E-01	2.18E-01		1.59E-01
	98.00			6.27E-01	3.37E-01	2.19E-01	1.60E-01	1.59E-01
	100.00			6.38E-01	3.40E-01	2.20E-01	1.60E-01	1.59E-01

Data for Figures 4.10 and 4.11

	1 μm			10 μm		
pH	log(Q1)	log(Q2)	log(Total Q)	log(Q1)	log(Q2)	log(Total Q)
3	-1.69897	-3.53462	-1.69268	-0.69897	-2.54061	-0.69276
8	-4.9393	-1.81531	-1.81498	-3.9393	-1.06651	-1.06593
2	-1.69037	-4.52724	-1.68974	-0.69037	-3.52724	-0.68974
2.25	-1.6925	-4.27737	-1.69138	-0.6925	-3.27819	-0.69138
2.5	-1.6925	-4.02872	-1.69051	-0.6925	-3.03058	-0.69051
2.75	-1.69465	-3.77989	-1.69109	-0.69465	-2.78516	-0.69114
3			-1.69268	-0.69897	-2.54061	-0.69276
3.25	-1.70333	-3.29073	-1.69225	-0.70333	-2.3019	-0.69253
3.5	-1.71444	-3.05159	-1.69491	-0.71444	-2.07109	-0.69575
3.75	-1.73283	-2.82102	-1.69875	-0.73283	-1.85387	-0.70115
4	-1.76195	-2.6038	-1.70355	-0.76195	-1.65561	-0.70974
4.25	-1.80967	-2.4045	-1.7113	-0.80967	-1.48413	-0.7263
4.5	-1.88273	-2.23433	-1.72285	-0.88273	-1.34775	-0.75473
4.75	-1.9914	-2.09691	-1.73993	-0.9914	-1.24565	-0.79915
5	-2.1343	-1.99568	-1.75845	-1.1343	-1.17653	-0.85387
5.25	-2.3098	-1.92445	-1.77469	-1.3098	-1.13136	-0.91045
5.5	-2.51145	-1.87943	-1.78835	-1.51145	-1.10403	-0.96059
5.75	-2.73283	-1.85387	-1.79997	-1.73283	-1.08778	-0.99913
6	-2.96257	-1.83565	-1.80438	-1.96257	-1.07883	-1.02549
6.25	-3.20412	-1.82681	-1.80897	-2.20412	-1.07314	-1.04215
6.5	-3.44855	-1.82102	-1.8109	-2.44855	-1.07007	-1.05227
6.75	-3.69465	-1.81816	-1.81242	-2.69465	-1.06854	-1.05839
7	-3.9431	-1.81816	-1.81491	-2.9431	-1.06753	-1.06178
7.25	-4.19179	-1.81531	-1.81349	-3.19179	-1.06702	-1.06377
7.5	-4.44129	-1.81531	-1.81428	-3.44129	-1.06651	-1.06468
7.75	-4.69037	-1.81531	-1.81473	-3.69037	-1.06651	-1.06548
8			-1.81498	-3.9393	-1.06651	-1.06593
8.25	-5.19044	-1.81531	-1.81513	-4.19044	-1.06651	-1.06619
8.5	-5.44009	-1.81531	-1.81521	-4.44009	-1.06651	-1.06633
8.75	-5.69037	-1.81531	-1.81525	-4.69037	-1.06651	-1.06641
9	-5.9393	-1.81531	-1.81528	-4.9393	-1.06651	-1.06645

Data for Figures 4.10 and 4.11

	28.3μm			100μm		
				Based on solubility limit		0.25
pH	log(Q1)	log(Q2)	log(Total Q)	log(Q1)	log(Q2)	log(Total Q)
3	-0.25104	-2.10624	-0.24502	-0.23958	-2.09528	-0.23356
8	-3.49349	-0.89279	-0.8917	-2.9393	-0.7986	-0.79547
2	-0.24413	-3.08145	-0.24349	-0.23958	-3.07676	-0.23895
2.25	-0.24489	-2.83268	-0.24377	-0.23958	-2.82974	-0.23846
2.5	-0.24565	-2.58838	-0.24368	-0.23958	-2.5817	-0.23761
2.75	-0.24718	-2.3439	-0.24372	-0.23958	-2.3363	-0.23612
3			-0.24502	-0.23958	-2.09528	-0.23356
3.25	-0.25649	-1.87615	-0.24619	-0.23958	-1.86012	-0.2293
3.5	-0.2668	-1.65956	-0.24957	-0.23958	-1.63639	-0.2225
3.75	-0.28483	-1.46471	-0.25704	-0.23958	-1.42829	-0.21233
4	-0.31426	-1.29671	-0.27124	-0.23958	-1.24489	-0.19866
4.25	-0.36251	-1.16304	-0.29869	-0.23958	-1.09205	-0.1825
4.5	-0.43652	-1.06449	-0.34467	-0.23958	-0.97469	-0.16622
4.75	-0.54363	-0.99568	-0.41229	-0.23958	-0.89279	-0.15243
5	-0.68613	-0.95468	-0.49894	-0.23958	-0.83565	-0.14146
5.25	-0.86328	-0.92812	-0.59346	-0.3098	-0.80967	-0.19044
5.5	-1.06449	-0.91364	-0.68152	-0.51145	-0.8041	-0.33255
5.75	-1.28483	-0.90309	-0.75227	-0.73283	-0.80134	-0.46471
6	-1.51713	-0.89963	-0.80576	-0.96257	-0.80134	-0.57349
6.25	-1.75696	-0.8962	-0.84013	-1.20412	-0.7986	-0.65463
6.5	-2.00087	-0.8962	-0.86334	-1.44855	-0.7986	-0.71086
6.75	-2.24718	-0.89279	-0.874	-1.69465	-0.7986	-0.74666
7	-2.49621	-0.89279	-0.8821	-1.9431	-0.7986	-0.76853
7.25	-2.74473	-0.89279	-0.88673	-2.19179	-0.7986	-0.78139
7.5	-2.99568	-0.89279	-0.88938	-2.44129	-0.7986	-0.78883
7.75	-3.24336	-0.89279	-0.89086	-2.69037	-0.7986	-0.79307
8			-0.8917	-2.9393	-0.7986	-0.79547
8.25	-3.74232	-0.89279	-0.89218	-3.19044	-0.7986	-0.79684
8.5	-3.9914	-0.89279	-0.89244	-3.44009	-0.7986	-0.79761
8.75	-4.24336	-0.89279	-0.8926	-3.69037	-0.7986	-0.79805
9	-4.49349	-0.89279	-0.89268	-3.9393	-0.7986	-0.79829

Appendix E
KINETIC DATA

Table units μmolal

RUN #	43	47	72	44	45	66	75	62
pH:	4	4	4	4	4	4	4	4
Initial conc. (μm)	15.0	15.0	15.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	200	200	100	100	100	200	100
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
30	12.469	9.430	9.002	26.716	25.762	27.097	21.234	53.578
35	12.640	8.800	8.525	25.991	25.952	27.034	20.609	53.597
40	12.338	8.372	8.534	25.612	25.517	27.137	19.945	53.096
45	12.260	8.234	8.634	25.559	25.754	26.668	18.487	52.578
50	12.244	8.484	7.755	25.300	25.419	26.291	18.595	51.919
55	11.922	8.262	7.971	25.001	24.899	26.015	18.020	51.264
60	11.908	7.704	7.356	24.681	24.501	25.562	16.952	50.652
65	11.450	7.571	7.264	24.193	24.516	25.743	17.262	50.407
70	11.559	8.034	6.773	24.008	23.826	25.225	16.295	49.919
75	11.533	6.828	7.275	23.483	23.629	25.018	15.736	49.903
80	10.989	7.155	6.753	23.328	23.328	24.881	15.193	49.738
85	10.988	6.687	6.490	23.038	23.193	24.524	15.307	48.893
90	10.701	6.457	6.045	22.644	23.382	24.094	14.490	48.234
95	10.789	6.208	5.923	22.483	22.971	24.092	14.378	48.029
100	10.674	6.346	6.108	22.497	22.630	24.005	13.826	47.495
105	10.722	6.045	6.000	22.260	22.445	23.527	13.999	47.232
110	10.540	5.874	5.927	22.016	22.225	23.340	13.915	46.707
115	10.441	5.914	5.575	21.655	22.191	23.207	13.339	46.531
120	10.523	5.560	5.677	21.703	22.146	23.087	13.396	46.060
125	10.273	5.518	5.732	21.368	21.776	22.974	12.857	45.894
130	9.998	5.285	5.474	21.436	21.603	22.716	12.990	45.427
135	9.996	5.659	4.999	21.208	21.212	22.538	12.669	45.245
140	10.093	5.042	4.900	21.025	21.136	22.345	12.165	44.940
145	10.351	5.051	5.045	20.734	21.013	22.238	12.238	44.561
150	9.862	5.087	5.313	20.646	21.008	22.139	12.372	44.639
155	9.810	4.844	5.076	20.594	20.841	22.057	11.701	44.406
160	9.865	5.068	5.303	20.421	20.937	22.080	12.341	44.101
165	9.667	5.021	4.867	20.411	20.397	21.792	11.842	43.842
170	9.377	4.719	5.336	20.158	20.648	21.648	11.518	43.435
175	9.343	4.700	4.978	20.171	20.060	21.446	11.416	43.072
180	9.412	4.426	4.900	20.184	20.260	21.558	11.561	43.199
185	9.332	4.007	4.779	20.102	19.782	21.039	11.276	42.664
190	9.596	4.484	4.965	20.116	19.865	21.208	10.975	42.475
195	9.174	4.161	4.463	19.881	19.558	21.205	11.707	42.360
200	9.431	4.617	4.487	19.675	19.951	21.085	11.129	42.263
205	9.567	4.509	4.753	19.639	19.573	21.090	10.392	42.109
210	9.233	4.334	4.773	19.363	19.467	21.103	10.597	42.134
215	9.216	3.888	4.949	19.056	19.257	20.724	11.181	41.953
220	9.304	4.169	4.382	19.142	19.455	20.660	10.610	41.537
225	9.098	3.755	4.667	19.292	19.148	20.530	10.477	41.662
230	9.006	4.169	4.937	19.236	19.136	20.495	10.708	41.194
235	9.220	3.781	4.174	19.041	19.205	20.480	10.491	41.387
240	8.812	3.847	4.049	18.786	18.889	20.363	10.354	41.027
245	8.900	3.834	4.067	18.869	18.909	20.583	10.015	41.290
250	8.891	3.887	4.162	18.824	18.958	20.290	10.057	43.579
255	8.719	4.022	4.480	18.635	18.522	20.393	10.061	40.816
260	8.756	3.604	4.422	18.796	18.551	20.215	10.233	40.604
265	8.846	3.746	3.990	18.741	18.683	20.012	9.741	40.363
270	8.551	3.695	4.262	18.501	18.605	19.868	9.571	40.345
275	8.935	3.729	4.478	18.518	18.364	19.940	10.187	40.171
280	8.501	3.631	4.478	18.205	18.433	19.820	9.640	40.368
285	8.489	4.035	4.423	18.513	18.212	19.761	9.603	40.099
290	8.773	3.919	4.456	18.339	18.126	19.738	9.823	39.871
295	8.654	3.870	3.983	18.285	18.258	19.654	9.783	39.899
300	8.663	3.604	4.419	18.163	18.308	19.383	9.831	39.837
305	8.764	3.820	4.514	18.178	17.887	19.473	9.384	40.084
310	8.341	3.853	4.205	18.306	18.126	19.473	9.174	39.652
315	8.315	3.716	4.032	18.063	18.083	19.419	9.978	39.517
320	8.509	4.048	3.555	18.471	18.011	19.516	9.635	39.353

Table units µmolal

RUN #	43	47	72	44	45	66	75	62
pH:	4	4	4	4	4	4	4	4
Initial conc. (µm)	15.0	15.0	15.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	200	200	100	100	100	200	100
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
325	8.311	3.526	3.822	18.602	18.125	19.343	9.917	39.518
330	8.342	3.921	3.811	18.562	17.886	18.972	9.407	39.090
335	8.650	3.244	3.833	18.551	17.857	19.300	9.105	39.260
340	8.212	3.827	3.687	18.408	17.876	19.250	9.288	39.007
345	8.403	3.455	3.716	18.453	17.714	19.432	9.016	38.761
350	8.207	3.869	3.885	18.323	17.868	19.285	9.203	39.074
355	8.337	3.259	4.031	18.449	17.818	19.036	9.580	38.679
360	8.598	3.498	3.900	18.333	17.600	18.934	9.065	38.826
365	8.589	3.043	4.047	18.483	17.573	19.256	8.793	38.870
370	8.527	3.295	3.862	18.102	17.575	18.922	8.893	38.517
375	8.426	3.513	3.546	18.035	17.316	19.150	8.969	38.410
380	8.441	3.251	4.007	18.140	17.343	18.811	9.168	38.500
385	8.228	3.543	3.849	18.307	17.186	18.797	8.799	38.258
390	8.486	3.226	3.765	17.920	17.337	18.699	9.219	38.686
395	8.077	3.602	3.509	18.006	17.408	18.944	8.855	38.438
400	8.227	3.587	3.564	17.886	17.120	18.754	9.130	38.220
405	8.266	3.049	3.373	17.903	17.130	18.714	9.063	37.970
410	8.297	3.407	3.213	18.030	17.218	18.685	8.832	38.018
415	7.988	3.178	3.763	17.828	17.105	18.731	8.894	38.058
420	8.043	2.757	4.256	18.219	17.065	18.937	9.066	37.963
425	8.202	3.390	3.750	17.873	17.139	18.548	8.820	37.905
430	8.242	3.048	3.789	18.201	17.119	18.698	8.874	38.331
435	8.203	3.574	4.313	17.955	16.942	18.575	8.808	37.741
440	8.179	3.314	3.731	17.943	17.162	18.321	9.591	37.559
445	7.929	3.657	3.684	17.642	17.020	18.350	9.412	37.752
450	8.087	3.416	3.904	17.601	17.140	18.613	8.871	37.645
455	8.185	3.736	3.730	17.847	17.008	18.611	8.851	37.954
460	8.139	3.418	3.963	17.718	16.804	18.425	8.514	37.599
465	7.988	3.096	3.309	17.498	16.980	18.333	8.267	37.680
470	8.041	3.484	3.708	17.535	17.213	18.579	8.209	37.808
475	7.697	3.360	4.248	17.553	16.786	18.292	8.336	38.112
480	8.016	3.261	3.815	17.542	16.745	18.504	8.933	37.969
485	7.894	3.492	3.860	17.800	16.783	18.333	8.690	37.758
490	7.856	3.287	3.838	17.683	16.847	18.197	8.303	37.990
495	8.035	3.063	3.914	17.594	16.787	18.292	8.541	37.366
500	7.988	3.746	3.735	17.748	16.548	18.499	8.369	37.507
505	8.118	3.677	3.279	17.535	16.487	18.287	8.588	37.463
510	8.104	3.562	3.417	17.587	16.818	18.652	9.106	37.116
515	7.831	3.493	3.279	17.144	16.943	18.300	8.672	37.326
520	8.198	3.750	3.657	17.505	16.568	18.367	8.484	37.679
525	8.159	3.317	3.742	17.622	16.461	18.112	8.429	37.965
530	7.641	3.299	3.945	17.237	16.656	18.201	8.346	37.370
535	8.110	3.243	4.153	17.338	16.673	18.324	9.096	37.041
540	8.280	3.309	3.468	17.304	16.410	18.178	8.416	37.162
545	8.044	3.416	3.391	17.082	16.726	18.200	8.946	36.922
550	7.812	3.265	3.453	17.678	16.703	18.412	8.329	36.957
555	7.896	3.172	3.597	17.701	16.268	18.488	8.642	37.112
560	8.063	3.514	3.244	17.659	16.512	18.361	8.403	36.952
565	7.969	3.128	3.667	17.934	16.185	18.350	8.831	36.978
570	7.692	3.318	3.331	17.584	16.318	18.442	8.632	36.852
575	7.987	3.671	3.365	17.741	16.677	18.356	8.334	36.870
580	7.888	3.317	3.529	17.549	16.256	18.415	8.430	36.975
585	7.909	3.562	3.619	17.555	16.156	18.305	8.325	36.971
590	8.230	3.215	3.585	17.450	16.522	18.341	8.743	36.718
595	7.830	3.651	3.366	17.575	16.548	18.559	8.480	36.786
600	8.031	3.048	3.735	17.673	16.406	18.641	8.825	36.962
605	7.742	3.490	3.567	17.467	16.476	18.645	8.455	36.858
610	7.719	3.297	3.784	17.569	16.477	18.352	8.621	37.102
615	7.712	3.771	3.902	17.333	16.264	18.351	8.415	36.733

Table units µmolal

RUN #	43	47	72	44	45	66	75	62
pH:	4	4	4	4	4	4	4	4
Initial conc. (µm)	15.0	15.0	15.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	200	200	100	100	100	200	100
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
620	7.877	3.513	3.722	17.444	16.550	18.761	8.461	36.470
625	8.179	3.265	3.851	17.659	16.209	18.391	8.509	36.944
630	7.936	3.402	3.983	17.364	16.738	18.481	8.143	36.523
635	7.784	3.347	3.666	17.419	16.753	18.552	8.791	36.655
640	8.135	3.204	3.870	17.584	16.525	18.570	8.268	36.325
645	7.906	3.050	4.149	17.643	16.233	18.822	8.311	36.586
650	7.768	3.192	4.220	17.412	16.296	18.363	8.026	36.588
655	8.021	3.255	3.749	17.510	16.531	17.999	8.252	36.618
660	7.874	3.437	3.757	17.376	16.119	18.176	8.871	36.363
665	7.924	3.605	4.162	17.240	16.332	18.649	8.304	36.139
670	7.699	3.203	4.029	17.383	16.114	18.164	8.238	36.173
675	7.681	3.763	4.016	17.337	16.364	18.547	8.461	36.156
680	7.908	3.678	4.050	17.419	16.295	18.360	8.439	36.597
685	7.723	3.490	4.146	17.235	16.300	18.550	8.480	36.338
690	7.947	3.404	4.257	17.408	16.209	18.385	8.048	36.515
695	7.940	3.485	4.668	17.533	16.344	18.283	8.723	36.407
700	7.869	3.396	3.965	17.295	16.089	18.030	8.878	36.443
705	7.833	2.805	6.050	17.161	16.173	18.253	8.164	36.476
710	8.242	3.533	4.609	17.318	16.237	18.181	8.859	36.291
715	7.577	3.632	4.518	17.284	16.138	18.072	8.940	36.174
720	7.824	3.383	4.506	17.577	16.462	18.561	8.645	35.693
725	7.799	3.509	4.386	17.350	16.231	18.176	8.409	36.054
730	7.815	3.653	4.347	17.389	16.156	18.151	8.394	36.131
735	7.837	4.007	4.774	17.113	16.182	18.615	8.546	36.260
740	7.874	4.213	4.691	17.259	16.068	18.585	8.638	36.371
745	8.025	3.640	5.001	17.318	16.151	18.116	8.590	35.944
750	7.860	3.913	4.947	17.675	16.223	17.911	8.580	36.229
755	7.665	3.791	4.745	17.494	16.017	18.314	8.948	35.872
760	7.988	3.856	5.306	17.330	15.946	18.226	8.529	35.827
765	7.960	4.174	4.979	17.211	16.163	18.425	8.591	36.191
770	7.760	4.149	5.287	17.240	16.144	18.266	8.403	35.878
775	7.957	4.008	4.981	17.594	16.593	18.248	8.659	36.296
780	7.895	4.096	5.210	17.620	16.136	18.521	8.669	36.019
785	7.930	3.893	5.399	17.288	16.279	18.415	8.145	35.996
790	7.977	3.971	5.017	17.416	16.185	18.125	8.492	36.153
795	8.036	3.978	5.005	17.453	15.833	18.154	8.630	35.999
800	7.919	4.344	4.890	17.371	16.395	18.291	8.619	36.388
805	7.541	4.574	5.112	17.143	16.010	18.463	8.716	35.932
810	7.891	4.275	4.962	17.307	16.057	18.594	8.654	35.929
815	7.619	4.321	5.320	17.406	16.094	18.114	8.522	35.504
820	7.816	4.224	5.177	17.462	16.189	18.199	8.452	36.219
825	7.856	4.293	4.983	17.710	16.101	17.930	8.824	35.886
830	7.727	4.431	5.371	17.409	16.402	18.113	8.017	35.713
835	8.028	4.269	5.639	17.570	15.970	18.278	8.408	35.889
840	8.303	4.371	5.430	17.377	16.212	17.932	8.489	36.116
845	7.947	4.360	5.545	17.607	16.175	18.425	8.701	35.941
850	7.510	4.435	5.667	17.346	16.000	18.466	8.340	35.770
855	7.800	4.394	5.550	17.587	16.058	18.074	9.046	35.594
860	8.125	4.605	5.704	17.496	15.856	18.233	8.926	35.655
865	7.744	4.174	5.533	17.446	15.665	18.106	8.820	35.579
870	7.755	4.326	5.772	17.156	16.398	18.037	8.896	35.527
875	7.597	4.006	5.938	17.219	15.658	17.996	8.857	35.734
880	7.901	3.691	5.402	17.537	16.062	18.109	8.845	35.705
885	8.243	3.960	5.707	17.203	15.897	18.047	8.477	35.570
890	7.852	4.187	5.702	17.461	15.962	18.501	8.953	35.712
895	7.643	4.665	5.936	17.650	15.756	18.176	9.425	35.735
900	7.562	3.873	5.686	17.412	15.821	18.293	8.767	35.608
905	7.838	4.352	5.976	17.484	16.135	18.213	9.100	35.045
910	7.747	4.417	6.010	17.431	15.865	18.095	9.006	35.493

Table units μmolal

RUN #	43	47	72	44	45	66	75	62
pH:	4	4	4	4	4	4	4	4
Initial conc. (μm)	15.0	15.0	15.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	200	200	100	100	100	200	100
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
915	8.111	4.200	5.734	17.418	15.761	17.952	9.019	35.288
920	7.748	4.103	5.870	17.314	15.853	18.133	8.686	35.388
925	7.660	4.338	5.852	17.560	15.818	17.959	9.105	35.382
930	7.843	4.499	5.888	17.428	15.886	18.343	9.172	35.446
935	7.847	4.256	5.772	17.555	15.996	18.049	8.708	35.526
940	7.683	4.134	5.593	17.344	16.380	18.115	8.485	35.520
945	7.480	4.353	5.588	17.261	15.839	18.345	8.492	35.482
950	7.655	4.062	5.912	17.463	15.965	18.072	8.880	35.377
955	7.618	4.267	5.454	17.478	15.821	18.083	9.198	35.525
960	7.579	4.682	5.821	17.230	15.941	18.182	9.215	35.384
965	7.545	4.303	5.652	17.426	15.756	18.003	9.020	35.452
970	7.544	4.437	5.415	17.716	15.921	17.994	9.257	35.473
975	7.629	4.348	5.494	17.491	15.674	18.005	8.422	35.504
980	8.012	4.587	5.799	17.408	15.965	18.096	9.257	35.201
985	7.814	4.501	5.322	17.617	15.737	18.340	9.161	35.683
990	7.894	4.236	5.362	17.778	16.375	18.259	9.520	35.654
995	8.005	4.805	5.506	17.390	15.824	18.255	9.158	35.307
1000	7.720	5.375	5.485	17.661	15.889	18.143	8.766	35.430
1005	7.620	4.370	5.331	17.460	15.804	17.810	8.873	35.104
1010	7.614	4.921	5.793	17.646	15.722	18.224	9.422	35.319
1015	7.781	4.505	5.573	17.570	15.591	17.972	9.212	35.252
1020	7.335	4.491	5.292	17.466	15.595	18.274	9.568	35.158
1025	7.696	4.482	5.502	17.394	15.886	17.883	9.662	35.207
1030	7.833	4.602	5.410	17.584	15.793	18.116	9.592	35.537
1035	7.785	4.726	5.288	17.402	16.092	18.140	9.033	35.376
1040	7.707	4.826	5.306	17.310	15.813	18.120	8.837	35.096
1045	7.568	5.039	5.256	17.426	15.911	18.177	9.258	35.172
1050	7.800	4.888	5.236	17.591	15.718	18.223	9.893	35.468
1055	7.525	4.924	5.181	17.487	15.571	18.298	9.356	35.264
1060	7.564	4.640	5.323	17.566	15.945	18.250	9.817	35.257
1065	7.458	4.999	5.463	17.666	15.272	18.126	8.674	35.245
1070	7.749	5.274	5.699	17.904	15.604	17.984	8.943	35.141
1075	7.781	4.442	5.148	17.580	15.718	18.381	8.989	35.272
1080	7.883	4.818	5.278	17.748	15.544	18.050	9.633	35.231
1085	7.469	4.994	5.481	17.536	15.656	17.944	9.733	35.228
1090	7.551	5.045	5.173	17.814	15.647	18.283	9.727	34.989
1095	7.677	5.032	5.465	17.454	15.670	18.106	10.322	35.298
1100	7.783	4.822	5.585	17.607	15.660	17.668	9.615	35.472
1105	7.959	4.725	5.313	17.907	15.591	17.863	8.683	35.210
1110	7.479	4.966	5.505	17.455	15.591	17.965	9.879	35.012
1115	7.478	4.925	5.797	17.577	15.914	18.023	9.992	35.412
1120	7.392	5.031	5.412	17.656	15.769	17.939	9.174	35.205
1125	7.667	4.931	5.780	17.507	15.872	18.054	9.615	35.383
1130	7.445	5.062	5.706	17.328	15.670	17.599	10.015	34.837
1135	7.638	4.501	5.377	17.569	15.523	17.753	9.146	35.117
1140	7.743	4.722	5.939	17.828	15.564	17.762	9.069	35.588
1145	7.403	4.661	5.979	17.419	15.711	17.838	9.534	35.047
1150	7.472	5.203	6.113	17.888	15.690	17.853	10.430	34.956
1155	7.511	5.003	6.383	17.871	15.842	17.663	9.741	34.941
1160	7.565	5.387	6.464	17.440	15.740	17.950	10.137	35.006
1165	7.384	5.244	6.563	17.636	15.944	17.699	9.623	35.169
1170	7.392	4.797	6.615	18.059	15.838	17.677	9.682	35.073
1175	7.520	4.791	6.920	17.893	16.059	17.515	10.141	35.174
1180	7.509	4.916	7.120	17.391	15.662	17.540	10.459	35.166
1185	7.500	4.549	7.223	17.600	15.837	17.781	10.215	34.884
1190	7.331	4.842	7.731	17.556	15.633	17.666	10.080	35.246
1195	7.402	4.890	7.577	17.709	15.678	17.334	10.019	34.944

Table units µmolal

RUN #	63	64	76	49	50	53	67	77
pH:	4	4	4	8	8	8	8	8
Initial conc. (µm)	60.0	60.0	60.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	100	100	200	100	100	100	100	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
30	50.957	49.883	41.542	13.567	13.065	13.361	15.684	12.374
35	50.759	49.271	41.035	13.509	12.976	13.306	15.701	11.229
40	50.243	48.955	40.117	13.268	12.664	13.291	15.536	11.090
45	49.889	48.797	38.802	13.448	12.546	13.219	15.794	11.030
50	49.256	48.408	37.699	13.340	12.505	12.900	15.508	11.023
55	48.665	47.641	36.568	12.995	12.421	12.800	15.644	11.238
60	48.234	47.189	35.422	12.913	12.461	12.711	15.329	10.181
65	47.839	46.725	34.318	13.197	12.230	12.770	15.265	10.133
70	47.004	46.389	33.431	13.333	12.384	12.289	15.102	10.401
75	46.629	46.059	33.279	12.991	11.960	12.445	14.840	9.855
80	45.862	45.918	33.027	12.653	11.999	12.612	14.866	9.367
85	45.528	45.433	31.585	12.861	11.986	12.266	14.658	10.071
90	45.009	44.951	31.431	12.877	11.698	12.303	14.979	9.182
95	44.733	44.557	31.052	12.992	12.021	12.308	14.659	9.276
100	44.451	44.018	30.297	12.684	11.848	12.238	15.038	9.390
105	44.252	43.733	29.485	12.468	11.868	12.071	14.557	9.302
110	43.573	43.699	29.153	12.478	11.647	11.918	14.635	8.866
115	43.311	43.451	29.075	12.444	11.725	11.952	14.634	9.192
120	43.121	42.589	28.341	12.201	11.786	11.627	14.365	9.164
125	42.944	42.301	28.318	12.607	11.391	11.908	14.244	8.572
130	42.461	42.102	27.312	12.406	11.492	11.663	14.265	9.075
135	41.989	42.025	26.887	12.645	11.252	11.812	14.646	8.495
140	42.077	41.840	27.073	12.368	11.350	11.747	14.323	9.078
145	41.534	41.486	26.431	12.561	11.553	11.732	14.069	8.782
150	41.223	41.439	25.801	12.301	11.393	11.426	14.143	8.321
155	41.067	41.069	26.274	12.401	11.384	11.475	14.065	8.553
160	40.686	40.589	25.623	12.214	11.161	11.304	14.196	8.947
165	40.386	40.692	24.852	12.186	11.156	11.255	14.148	8.012
170	40.529	40.443	25.012	12.043	11.092	11.635	13.979	8.253
175	40.177	40.522	25.123	12.064	11.140	11.377	14.081	8.211
180	40.109	40.102	24.923	12.155	10.893	10.980	13.997	8.118
185	39.873	39.715	24.721	11.981	11.145	11.411	13.884	8.575
190	39.638	39.781	24.350	11.949	11.090	11.162	13.837	8.452
195	39.475	39.308	23.984	11.942	11.217	11.561	13.933	8.035
200	39.656	39.435	24.148	12.108	10.881	11.119	13.835	8.223
205	39.328	38.992	23.876	12.371	10.978	11.193	13.993	8.470
210	39.115	39.096	23.679	11.681	11.131	11.137	13.624	8.139
215	38.904	38.737	23.520	11.711	11.209	10.845	13.846	8.212
220	38.950	38.775	23.340	11.584	10.777	11.023	13.706	8.221
225	38.758	38.509	23.360	11.699	10.838	10.882	13.997	7.922
230	38.928	38.806	23.172	11.640	11.047	10.959	13.750	8.089
235	38.488	38.418	22.631	11.730	10.886	10.968	13.975	7.666
240	38.329	38.208	22.503	11.821	11.038	11.407	13.768	8.229
245	37.961	38.046	22.674	11.664	10.890	10.884	13.804	7.996
250	37.857	37.745	22.031	11.742	10.698	11.115	13.770	8.076
255	37.771	37.760	22.481	11.571	10.798	10.949	13.674	7.970
260	37.555	37.623	22.004	11.766	10.896	10.775	13.608	7.930
265	37.784	37.517	21.717	11.647	10.654	10.685	13.434	7.487
270	37.995	37.221	22.058	11.605	11.003	10.897	13.867	7.430
275	37.562	37.306	21.667	11.903	10.970	10.966	13.677	7.702
280	37.298	37.360	22.203	11.608	10.825	11.079	13.642	7.237
285	37.272	37.069	21.327	11.422	10.736	10.771	13.494	7.817
290	37.172	37.263	21.407	11.859	10.709	10.812	13.558	7.731
295	37.374	37.085	21.083	11.619	10.757	10.831	13.678	7.302
300	37.312	36.700	21.430	11.493	10.642	10.382	13.403	7.824
305	37.063	36.844	22.051	11.700	10.557	10.541	13.399	7.637
310	37.013	36.885	21.633	11.671	10.499	10.814	13.441	7.670
315	37.097	36.841	21.084	11.564	10.458	10.856	13.775	7.429
320	36.383	36.532	21.103	11.499	10.746	10.516	13.402	8.036

Table units µmolal

RUN #	63	64	76	49	50	53	67	77
pH:	4	4	4	8	8	8	8	8
Initial conc. (µm)	60.0	60.0	60.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	100	100	200	100	100	100	100	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
325	36.690	36.470	20.672	11.421	10.829	10.653	13.375	7.411
330	36.649	36.110	20.609	12.131	10.560	10.705	13.680	7.563
335	36.775	36.274	20.512	11.405	10.686	10.772	13.449	7.993
340	36.355	36.391	20.624	11.665	10.611	10.837	13.640	7.364
345	36.306	36.303	20.185	11.733	10.631	10.620	13.549	7.804
350	36.243	36.210	20.850	11.643	10.557	10.709	13.518	7.661
355	36.430	35.886	20.158	11.429	10.654	10.571	13.516	7.830
360	36.306	35.698	20.361	11.609	10.780	10.486	13.356	7.778
365	36.192	36.182	19.958	11.462	10.409	10.939	13.428	7.696
370	36.236	36.018	20.350	11.798	10.482	10.709	13.539	7.433
375	35.996	35.810	20.664	11.271	10.509	10.335	13.663	7.305
380	36.122	36.085	20.808	11.592	10.546	10.760	13.356	7.996
385	36.294	35.597	20.598	11.599	10.388	10.557	13.506	7.447
390	35.841	35.405	20.164	11.196	10.353	10.729	13.352	7.433
395	35.724	35.427	19.983	11.300	10.534	10.406	13.584	7.819
400	35.657	35.530	19.681	11.545	10.269	10.232	13.304	7.722
405	35.631	35.394	20.024	11.395	10.616	10.599	13.374	7.560
410	35.479	35.278	20.076	11.516	10.555	10.791	13.209	7.412
415	35.360	34.928	19.925	11.386	10.551	10.204	13.454	7.675
420	35.903	35.103	19.894	11.386	10.683	10.575	13.413	7.910
425	35.165	35.643	20.077	11.346	10.497	10.363	13.380	7.447
430	35.554	35.510	19.811	11.600	10.296	10.399	13.405	7.558
435	35.067	34.931	19.714	11.554	10.388	10.362	13.292	7.697
440	35.375	34.964	20.042	11.771	10.410	10.361	13.194	7.302
445	35.254	34.896	19.475	11.303	10.362	10.472	13.609	7.230
450	35.273	34.884	19.595	11.310	10.417	10.362	13.404	7.338
455	35.240	34.473	19.667	11.568	10.195	10.378	13.368	7.833
460	35.451	34.714	19.876	11.148	10.478	10.274	13.598	7.182
465	35.133	34.663	19.249	11.241	10.340	10.259	13.558	7.780
470	35.074	34.554	19.544	11.307	10.298	10.475	13.320	7.237
475	35.417	34.247	19.686	11.322	10.548	10.307	13.356	7.692
480	34.973	34.756	19.532	11.606	10.255	10.474	13.299	7.530
485	34.814	34.975	20.237	11.817	10.462	10.664	13.326	7.353
490	34.973	34.686	18.849	11.436	10.432	10.432	13.182	7.805
495	34.849	34.542	19.074	11.410	10.386	10.491	13.362	7.448
500	34.756	34.580	19.177	11.324	10.176	10.450	13.078	7.854
505	35.487	34.322	19.329	11.118	10.327	10.369	13.285	7.973
510	35.054	34.180	19.561	11.392	10.252	10.262	13.214	7.759
515	34.693	34.278	18.956	11.413	10.455	10.471	13.137	7.711
520	34.691	34.380	19.059	11.422	10.242	10.450	13.290	7.548
525	34.590	33.908	18.918	11.293	10.176	10.252	13.299	7.941
530	34.652	33.920	19.087	11.273	10.368	10.616	13.339	7.142
535	34.494	33.958	19.055	11.763	10.516	10.739	13.161	7.295
540	34.539	34.045	18.923	11.349	10.357	10.221	13.265	7.423
545	34.412	34.195	19.381	11.354	10.490	10.478	13.523	7.618
550	34.481	34.133	19.043	11.515	10.074	10.423	13.342	7.533
555	34.331	34.023	18.981	11.339	10.377	10.544	13.093	7.432
560	34.735	34.144	18.989	11.293	10.298	10.767	13.107	7.521
565	34.387	33.735	18.919	11.157	10.161	10.674	13.131	7.495
570	34.324	33.944	19.069	11.458	10.557	10.878	13.203	7.414
575	34.433	33.872	19.438	11.276	10.604	10.502	13.260	7.469
580	34.401	33.556	19.179	11.222	10.469	10.514	13.340	7.421
585	34.425	33.762	19.277	11.312	10.564	10.886	13.395	8.127
590	34.419	33.815	18.788	11.135	10.443	10.748	13.133	7.461
595	34.328	33.645	18.695	11.374	10.121	10.863	13.169	7.468
600	34.736	33.738	18.448	11.319	10.308	10.863	13.588	7.741
605	34.486	33.494	18.339	11.237	10.568	10.454	13.294	6.907
610	34.371	33.714	18.707	11.225	10.640	10.629	12.963	7.309
615	34.188	33.744	18.620	11.128	10.529	11.011	13.134	7.715

Table units µmolal

RUN #	63	64	76	49	50	53	67	77
pH:	4	4	4	8	8	8	8	8
Initial.conc. (µm)	60.0	60.0	60.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	100	100	200	100	100	100	100	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
620	34.274	33.561	18.789	11.007	10.927	10.531	13.182	6.962
625	34.230	33.391	18.555	11.096	10.627	11.138	13.309	7.459
630	34.398	33.240	18.973	11.004	10.980	11.087	13.423	7.226
635	34.558	33.608	19.063	11.334	10.640	10.986	13.241	7.583
640	34.445	33.437	18.989	11.013	10.793	10.932	13.264	7.226
645	34.281	33.744	18.767	11.133	10.866	10.878	13.104	7.675
650	34.292	33.662	18.917	11.408	10.911	10.608	13.385	7.115
655	34.372	33.580	18.636	11.399	11.036	11.358	13.122	7.285
660	34.385	33.284	18.851	11.272	10.782	11.310	13.205	7.299
665	34.349	33.144	18.964	11.545	10.825	11.495	13.240	7.257
670	34.373	33.103	18.788	11.012	10.769	11.602	13.204	6.953
675	34.288	33.473	18.534	11.252	10.850	11.465	13.055	7.459
680	34.127	33.412	18.665	11.399	10.868	11.609	13.125	7.433
685	34.237	33.359	18.411	11.166	10.789	11.657	13.223	7.229
690	34.016	33.395	18.770	10.971	11.116	11.528	13.001	7.278
695	34.231	33.137	18.969	11.038	11.115	11.254	13.269	7.526
700	34.180	33.248	18.529	11.383	11.130	11.341	12.945	7.318
705	34.058	33.144	19.033	11.063	10.943	11.434	13.097	7.323
710	34.237	33.200	18.722	11.321	11.074	11.605	13.112	7.151
715	34.412	33.235	18.789	10.922	10.784	11.758	13.314	7.093
720	34.247	33.174	18.852	11.217	10.705	11.595	13.087	7.401
725	33.986	33.382	18.657	11.057	10.796	11.307	13.099	7.078
730	34.197	33.002	18.251	11.121	11.113	11.887	13.181	6.914
735	34.062	33.082	18.247	11.166	10.886	11.911	13.285	6.889
740	34.249	33.161	18.067	11.254	10.908	11.853	13.019	7.174
745	34.096	33.254	18.157	11.122	10.688	11.161	13.152	7.428
750	34.395	33.073	18.325	11.131	11.169	11.849	12.964	7.252
755	33.714	33.082	18.475	11.145	10.937	11.513	13.066	7.409
760	33.948	33.138	18.697	10.929	11.145	11.789	13.017	7.437
765	34.281	33.144	18.599	11.169	11.047	11.845	13.258	7.986
770	33.894	33.017	19.022	11.166	11.039	11.931	13.381	7.737
775	33.942	32.950	18.860	11.132	11.643	11.733	13.085	7.513
780	33.952	33.140	18.980	11.164	10.882	11.786	13.171	7.799
785	33.973	32.965	18.541	11.162	11.014	11.596	13.066	7.616
790	34.137	33.109	18.476	11.231	11.079	11.884	13.453	7.448
795	34.044	33.085	18.718	11.179	11.439	12.204	13.270	7.789
800	33.944	32.975	18.338	11.043	11.078	11.792	12.972	7.360
805	33.796	33.175	18.310	11.301	11.310	11.911	13.245	7.948
810	33.811	33.130	18.221	11.213	10.779	11.764	12.949	7.505
815	33.822	32.890	18.452	11.035	11.115	11.725	12.916	7.690
820	33.807	33.057	18.434	11.141	11.360	11.718	12.983	8.083
825	33.475	32.897	18.021	11.108	11.298	12.051	13.352	7.935
830	33.852	32.818	18.166	11.131	10.876	11.732	12.894	7.848
835	33.817	32.794	18.646	11.424	11.438	11.509	12.932	7.528
840	33.609	33.359	18.343	11.129	11.357	11.394	13.120	8.093
845	33.724	33.058	18.354	11.008	11.149	11.499	12.924	7.737
850	33.759	32.541	18.374	11.374	11.290	11.435	12.888	8.382
855	33.900	32.809	18.987	11.011	11.200	11.394	12.915	8.404
860	33.536	32.641	18.520	11.289	11.425	11.586	12.967	8.021
865	33.587	33.057	18.343	11.090	11.371	11.447	12.976	7.587
870	33.423	32.890	18.017	11.094	11.403	11.672	13.012	8.192
875	33.619	33.021	18.279	11.627	11.250	11.675	12.935	8.030
880	33.556	32.907	17.978	11.650	11.290	11.340	12.898	8.429
885	33.594	33.000	18.227	11.214	11.456	11.548	12.870	8.327
890	33.971	32.876	18.070	11.317	11.370	11.719	13.193	8.455
895	33.891	32.913	18.464	10.973	11.476	11.712	13.178	8.099
900	33.617	32.679	18.401	11.133	11.158	11.746	13.017	8.311
905	33.552	32.901	18.204	10.969	11.200	12.128	13.268	8.484
910	33.646	32.585	18.630	10.989	11.444	11.949	12.900	8.157

Table units μmolal

RUN #	63	64	76	49	50	53	67	77
pH:	4	4	4	8	8	8	8	8
Initial conc. (μm)	60.0	60.0	60.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	100	100	200	100	100	100	100	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
915	33.704	32.759	18.388	11.194	11.504	11.678	13.002	8.577
920	33.365	32.955	18.439	11.126	11.350	11.908	13.076	8.523
925	33.402	32.888	18.258	11.375	11.749	11.550	12.934	9.023
930	33.718	32.711	18.591	11.413	11.552	12.021	12.825	8.771
935	33.450	32.716	18.359	11.182	11.330	12.047	13.047	8.394
940	33.379	32.911	18.635	11.312	11.336	11.701	13.198	8.804
945	33.399	32.809	18.006	11.194	11.628	11.687	12.959	8.595
950	33.593	32.503	18.085	11.248	11.669	11.797	13.097	8.456
955	33.464	32.758	18.118	11.115	11.571	12.149	13.210	9.244
960	33.706	33.015	18.675	11.241	11.640	11.753	13.045	8.590
965	33.708	32.656	18.599	11.387	11.505	12.620	12.899	8.611
970	33.369	32.453	18.262	10.980	11.372	12.011	13.114	9.164
975	33.548	32.660	18.168	11.187	11.513	11.857	13.313	8.402
980	33.545	32.620	18.257	11.116	11.556	11.806	13.154	8.570
985	33.433	32.763	18.711	11.336	11.873	11.770	12.952	9.287
990	34.076	32.826	18.210	11.403	11.508	11.629	12.753	8.776
995	33.328	32.878	18.820	11.301	11.430	11.677	12.737	8.799
1000	33.472	32.527	17.991	11.166	11.548	11.745	12.893	9.003
1005	33.491	32.589	18.300	11.455	11.491	12.130	12.830	8.773
1010	33.475	32.546	18.329	11.132	11.307	11.674	13.107	8.693
1015	33.416	32.446	18.118	11.087	11.275	11.975	13.324	9.198
1020	33.416	32.731	18.362	11.150	11.590	11.918	12.842	9.114
1025	33.541	32.618	18.435	11.337	11.427	11.775	12.877	9.824
1030	33.363	32.512	18.513	11.152	11.209	11.888	13.137	9.426
1035	33.290	32.357	18.783	11.202	11.809	11.690	13.271	8.493
1040	33.331	32.522	18.319	11.108	11.138	11.648	13.091	9.374
1045	33.289	32.551	18.433	11.224	11.458	11.451	13.192	10.609
1050	33.569	32.512	18.886	11.194	11.269	11.769	13.136	9.082
1055	33.253	32.835	18.176	11.155	11.320	11.842	13.079	8.786
1060	33.228	32.371	18.487	11.169	11.348	11.835	13.260	8.913
1065	33.406	32.491	18.236	11.406	11.294	11.754	13.118	9.255
1070	33.172	32.539	18.250	11.526	11.534	11.509	13.329	9.161
1075	33.532	32.561	18.421	11.193	11.249	11.415	13.302	9.759
1080	33.216	32.766	18.018	11.351	11.433	11.616	13.008	9.362
1085	33.130	32.346	18.620	11.282	11.035	11.646	13.252	9.220
1090	33.247	32.597	18.216	11.374	11.474	11.707	13.127	9.026
1095	33.149	32.462	18.643	11.573	11.454	11.634	13.024	9.733
1100	33.144	32.208	18.987	11.344	11.645	11.673	12.895	9.389
1105	32.893	32.626	19.125	11.656	11.783	12.214	13.017	9.100
1110	33.415	32.550	18.959	11.478	11.555	11.739	12.910	9.292
1115	33.086	32.431	19.207	11.540	11.236	11.376	13.154	9.463
1120	33.144	32.484	18.983	11.710	11.201	11.734	13.289	9.441
1125	33.162	32.502	18.931	11.822	11.381	11.754	13.199	9.617
1130	33.120	32.299	19.048	12.206	11.533	11.862	13.349	9.596
1135	32.910	32.538	19.342	11.502	11.300	11.919	13.268	9.505
1140	32.935	32.317	18.720	11.753	11.193	11.949	13.588	9.814
1145	32.772	32.570	18.441	11.804	11.179	11.729	13.353	9.567
1150	32.967	32.310	18.791	11.772	11.637	11.952	13.249	9.662
1155	33.106	32.642	18.859	12.001	11.169	11.774	13.380	9.844
1160	32.621	32.526	18.932	11.812	11.380	11.827	13.699	9.767
1165	32.554	32.321	19.564	11.960	11.258	11.582	13.130	9.291
1170	32.640	32.285	19.598	11.960	11.169	12.138	13.511	9.923
1175	32.647	32.424	19.385	12.165	10.949	11.921	13.256	9.669
1180	32.450	32.190	19.303	12.008	11.980	11.601	13.123	10.117
1185	32.658	31.955	19.095	12.207	11.138	11.740	13.177	10.529
1190	32.739	32.240	19.005	12.249	11.206	12.066	13.460	9.992
1195	32.569	32.181	19.018	12.117	11.277	11.839	13.206	9.387

Table units μmolal

RUN #	51	52	68	78	69	70	79
pH:	8	8	8	8	8	8	8
Initial conc. (μm)	30.0	30.0	30.0	30.0	60.0	60.0	60.0
solid conc. (mg/kg)	100	100	100	200	100	100	200
Temp: (C°)	25	25	25	25	25	25	25
Time (sec.)							
30	30.370	28.469	31.054	25.264	62.649	62.136	59.261
35	30.487	28.531	30.779	25.211	62.642	62.181	59.065
40	30.076	27.860	30.693	25.499	62.588	61.758	58.947
45	29.832	27.833	30.676	25.501	62.191	61.582	58.708
50	30.019	27.806	30.393	25.137	61.953	61.626	57.899
55	29.770	27.390	30.167	25.107	62.106	61.335	57.851
60	29.610	27.563	30.037	24.639	61.971	61.221	57.371
65	29.681	27.265	30.421	24.717	61.829	61.116	57.085
70	29.519	27.101	29.714	23.928	61.743	61.130	56.849
75	29.436	27.299	29.623	24.148	61.631	61.156	57.010
80	29.804	27.143	29.474	23.808	61.417	60.828	56.917
85	29.131	27.024	29.729	23.714	61.550	60.960	56.694
90	29.507	26.984	29.564	23.553	61.615	60.709	56.516
95	29.057	27.158	29.405	23.055	61.623	60.930	56.490
100	28.985	27.100	29.501	23.182	61.659	60.547	56.034
105	28.767	26.775	29.430	22.961	61.276	60.657	55.981
110	28.835	27.039	29.156	22.819	61.217	60.635	55.684
115	28.966	26.403	29.223	22.758	61.326	60.416	55.533
120	28.784	26.585	29.090	22.881	61.483	60.442	55.375
125	28.698	26.529	29.037	22.657	61.296	60.538	56.005
130	28.667	26.290	29.293	22.570	61.094	60.605	55.323
135	28.659	26.322	28.891	22.395	61.018	60.163	55.234
140	28.619	26.656	28.817	22.804	60.880	60.332	55.188
145	28.890	26.657	28.650	22.516	60.544	60.293	54.658
150	28.796	26.448	28.603	22.495	60.877	60.334	54.995
155	28.786	26.616	28.973	23.004	60.665	60.042	54.433
160	28.650	26.472	28.544	22.268	61.066	60.180	54.539
165	28.574	26.380	28.593	22.962	60.668	60.143	54.557
170	28.793	25.994	28.578	22.346	60.855	60.114	53.980
175		26.106	28.516	22.357	60.846	60.281	54.100
180	28.723	26.183	28.566	22.045	60.801	59.980	54.202
185	28.721	26.003	28.674	22.347	60.778	60.082	54.016
190	28.607	25.997	28.542	21.891	60.650	59.888	54.225
195	28.560	25.938	28.395	21.994	60.692	59.956	54.212
200	28.708	25.926	28.512	22.048	60.815	60.116	53.548
205	28.512	25.893	28.348	21.948	60.960	60.125	53.973
210	28.626	25.850	28.461	22.307	60.606	59.972	53.841
215	28.430	26.015	28.580	22.216	60.477	59.969	53.791
220	28.592	26.049	28.323	21.729	60.680	59.674	54.456
225	28.633	26.079	28.298	22.256	60.733	59.898	53.794
230	28.805	25.580	28.300	22.026	60.383	59.708	53.730
235	28.648	25.819	28.261	22.103	60.622	59.725	53.412
240	28.646	25.614	28.246	21.586	60.353	59.737	53.760
245	28.544	25.836	27.997	22.007	60.397	59.783	53.227
250	28.554	25.537	28.070	21.683	60.554	60.010	53.233
255	28.637	25.921	28.010	22.147	60.284	59.764	52.953
260	28.660	26.052	28.047	21.621	60.061	59.740	53.302
265	28.719	25.929	28.034	21.673	60.361	59.937	52.889
270	28.745	25.596	27.978	21.713	60.488	59.573	53.351
275	28.406	25.668	28.122	21.675	60.419	59.692	52.885
280	28.422	25.757	27.925	21.464	60.496	59.833	53.323
285	28.588	25.480	28.090	22.089	60.413	59.698	52.638
290	28.681	25.658	27.961	21.532	59.824	59.785	52.817
295	28.367	25.595	27.941	22.285	60.143	59.653	52.710
300	28.403	25.556	28.124	21.576	60.385	59.730	52.997
305	27.946	25.661	27.970	22.124	60.291	59.664	52.897
310	28.245	25.400	28.001	21.732	60.305	59.868	53.262
315	28.793	25.569	28.169	21.651	60.052	59.944	53.155
320	28.590	25.606	28.104	21.866	60.427	59.791	52.783

Table units μmolal

RUN #	51	52	68	78	69	70	79
pH:	8	8	8	8	8	8	8
Initial conc. (μm)	30.0	30.0	30.0	30.0	60.0	60.0	60.0
solid conc. (mg/kg)	100	100	100	200	100	100	200
Temp: (C°)	25	25	25	25	25	25	25
Time (sec.)							
325	28.539	25.888	27.862	21.863	60.308	59.746	53.417
330	28.815	25.883	28.076	21.495	60.195	59.818	52.569
335	28.480	25.452	27.807	21.694	59.943	59.463	52.817
340	28.747	25.449	28.107	21.671	60.155	59.423	53.179
345	28.335	25.713	27.814	21.670	60.434	59.853	52.658
350	28.603	25.548	27.923	21.667	60.461	59.727	52.663
355	28.607	25.339	27.964	21.823	60.288	59.497	52.527
360	28.595	25.216	28.068	21.550	60.145	59.471	52.671
365	28.295	25.279	28.029	21.564	60.255	59.561	52.870
370	28.433	25.489	27.811	21.593	60.222	59.863	52.588
375	28.485	25.130	28.018	21.605	59.915	59.874	52.526
380	28.704	25.204	27.833	21.597	60.138	59.658	52.591
385	28.805	25.718	27.667	22.163	60.031	59.684	52.860
390	28.457	25.379	27.856	21.351	60.245	59.287	52.413
395	28.563	25.441	27.650	21.694	60.365	59.538	52.887
400	28.133	25.441	28.100	21.278	60.272	59.393	52.475
405	28.185	25.501	27.891	21.787	60.061	59.445	52.401
410	28.303	25.451	27.791	21.674	60.011	59.565	52.363
415	28.606	25.211	27.811	21.766	60.108	59.251	52.755
420	28.123	25.311	27.870	21.462	60.037	59.757	52.443
425	28.420	25.063	27.903	21.790	60.167	59.682	52.901
430	28.533	25.387	27.771	21.440	60.211	59.703	52.141
435	28.707	25.411	27.880	21.842	60.034	59.963	52.755
440	28.479	25.125	27.811	21.537	60.079	59.774	53.086
445	28.560	25.592	27.839	21.679	60.145	59.750	52.555
450	28.527	25.389	27.902	21.429	60.032	59.653	52.444
455	28.465	25.460	27.696	21.395	60.118	59.709	52.801
460	28.650	25.331	27.643	21.542	60.356	59.475	52.327
465	28.246	25.252	27.980	21.516	60.203	59.801	52.365
470	28.217	25.154	27.808	21.729	60.022	59.592	52.323
475	28.437	25.160	27.830	21.430	60.194	59.798	52.356
480	28.592	25.230	27.663	21.451	59.903	59.674	52.519
485	29.153	25.156	27.985	21.743	59.995	60.010	52.585
490	28.186	25.304	27.682	21.604	59.884	59.755	52.058
495	28.550	25.180	28.053	21.436	60.079	59.541	51.878
500	28.398	25.225	28.028	21.337	59.757	59.687	52.435
505	28.437	25.336	28.052	21.536	60.186	59.451	52.625
510	28.328	25.120	28.064	21.773	59.982	59.407	52.536
515	28.399	25.223	27.969	21.522	60.098	59.520	52.258
520	28.269	25.298	28.109	21.485	60.104	59.766	52.035
525	28.533	25.101	27.905	21.374	60.206	59.580	52.714
530	28.702	25.198	27.956	21.716	60.171	59.630	52.593
535	28.810	25.060	27.940	21.223	59.876	59.750	52.265
540	28.502	25.116	27.867	21.306	60.076	59.442	52.570
545	28.455	25.393	28.093	22.030	59.876	59.489	52.740
550	28.547	24.984	28.010	21.666	60.246	59.987	52.002
555	28.450	25.267	28.127	21.994	59.948	59.766	52.832
560	28.653	25.529	28.103	21.823	60.065	59.741	52.306
565	28.358	25.282	27.993	21.875	59.652	59.822	52.557
570	28.443	25.160	28.249	21.750	59.911	59.565	52.941
575	28.459	25.273	28.258	22.286	60.045	59.432	52.304
580	28.388	24.946	27.992	21.595	59.943	59.702	52.196
585	28.651	25.317	28.076	22.157	60.294	59.565	52.456
590	28.598	25.293	28.112	21.629	59.989	59.568	52.575
595	28.482	25.079	28.300	21.562	59.903	59.684	52.523
600	28.537	25.330	28.412	21.504	13.588	59.628	52.470
605	28.646	25.116	28.350	21.756	13.294	59.798	52.536
610	28.714	24.737	28.358	21.756	12.963	59.706	52.931
615	28.722	25.296	28.554	21.754	13.134	59.764	52.386

Table units μmolal

RUN #	51	52	68	78	69	70	79
pH:	8	8	8	8	8	8	8
Initial conc. (μm)	30.0	30.0	30.0	30.0	60.0	60.0	60.0
solid conc. (mg/kg)	100	100	100	200	100	100	200
Temp: (C°)	25	25	25	25	25	25	25
Time (sec.)							
620	28.925	25.231	28.518	21.930	13.182	59.722	52.623
625	28.647	25.132	28.747	22.003	13.309	59.960	52.502
630	28.450	25.377	28.660	21.516	13.423	60.143	52.130
635	28.470	25.382	28.372	22.292	13.241	59.825	52.128
640	28.678	25.120	28.682	21.934	13.264	60.146	52.729
645	28.481	25.026	28.405	22.502	13.104	60.085	52.248
650	28.629	25.069	28.748	22.089	13.385	59.760	52.846
655	28.588	25.135	28.988	21.942	13.122	60.035	52.791
660	28.654	25.175	28.875	21.855	13.205	59.549	52.717
665	28.380	25.548	28.942	22.433	13.240	60.004	52.631
670	28.585	25.253	28.809	21.882	13.204	59.503	52.537
675	28.603	25.140	28.884	21.966	13.055	59.972	52.704
680	28.856	25.305	29.079	21.688	13.125	60.204	52.461
685	29.005	25.113	29.086	21.875	13.223	59.627	52.895
690	28.755	25.033	29.006	22.391	13.001	59.975	52.700
695	28.568	25.198	29.166	21.986	13.269	59.791	52.671
700	28.396	25.212	28.993	22.522	12.945	59.670	53.099
705	28.719	25.143	29.173	21.946	13.097	60.128	52.777
710	28.599	24.830	28.978	22.242	13.112	59.985	52.736
715	28.621	25.106	29.306	22.174	13.314	60.200	53.052
720	28.277	25.406	29.261	22.024	13.087	59.737	52.618
725	28.491	25.317	29.575	22.031	13.099	59.826	53.093
730	28.333	24.974	28.976	21.935	13.181	60.170	52.671
735	28.754	25.443	29.728	21.911	13.285	59.942	52.671
740	28.423	25.105	29.448	21.895	13.019	59.932	53.545
745	28.439	25.175	29.361	21.975	13.152	59.813	52.618
750	28.611	25.462	29.684	22.766	12.964	59.737	52.795
755	28.488	25.187	29.526	22.478	13.066	59.958	53.123
760	28.489	25.074	29.569	22.350	13.017	59.866	52.990
765	28.324	24.916	30.727	22.104	13.258	59.903	53.011
770	28.526	25.149	29.622	22.069	13.381	59.929	53.368
775	28.639	24.961	29.315	22.185	13.085	59.843	53.080
780	28.601	25.246	29.686	21.894	13.171	59.762	52.950
785	28.352	25.070	29.852	21.973	13.066	59.840	53.622
790	28.594	25.125	29.321	22.093	13.453	59.776	53.865
795	28.172	25.201	29.511	22.344	13.270	59.788	53.144
800	28.493	25.585	29.481	22.428	12.972	60.022	53.904
805	28.550	25.396	29.547	22.308	13.245	59.767	53.362
810	28.331	25.239	29.667	22.830	12.949	60.065	53.439
815	28.398	25.345	29.564	22.190	12.916	59.638	54.072
820	28.377	25.227	29.677	22.378	12.983	59.697	53.898
825	28.664	25.118	29.798	21.966	13.352	60.208	53.193
830	28.371	25.067	29.458	22.244	12.894	60.083	54.081
835	29.007	25.061	29.493	22.405	12.932	59.813	53.792
840	28.329	25.135	29.582	21.967	13.120	60.022	53.491
845	28.490	25.286	29.532	22.160	12.924	60.106	54.341
850	28.574	25.609	29.656	22.426	12.888	59.702	53.977
855	28.461	25.369	29.625	22.652	12.915	59.798	53.531
860	28.677	25.307	29.418	22.372	12.967	60.254	54.032
865	28.771	25.277	29.378	22.237	12.976	60.031	54.107
870	28.368	25.117	29.663	22.323	13.012	59.905	54.240
875	28.757	25.825	29.681	22.017	12.935	59.877	54.411
880	28.416	25.358	29.763	22.754	12.898	60.055	53.952
885	28.625	25.238	29.593	22.172	12.870	59.809	53.927
890	28.632	25.198	29.735	22.704	13.193	59.985	54.337
895	28.486	25.555	29.467	22.338	13.178	59.924	54.064
900	28.538	25.728	29.798	22.453	13.017	59.813	54.292
905	28.652	25.583	29.367	22.547	13.268	59.972	54.300
910	28.210	25.236	29.366	22.802	12.900	60.031	54.035

Table units µmolal

RUN #	51	52	68	78	69	70	79
pH:	8	8	8	8	8	8	8
Initial conc. (µm)	30.0	30.0	30.0	30.0	60.0	60.0	60.0
solid conc. (mg/kg)	100	100	100	200	100	100	200
Temp: (C°)	25	25	25	25	25	25	25
Time (sec.)							
915	28.262	25.311	29.736	22.196	13.002	59.989	54.186
920	28.496	25.403	29.433	22.599	13.076	60.024	54.248
925	28.228	25.203	29.439	22.071	12.934	59.991	53.701
930	28.370	25.338	29.565	22.805	12.825	60.034	54.587
935	28.365	25.231	29.640	22.021	13.047	60.004	54.832
940	28.234	25.465	29.525	23.034	13.198	60.038	54.412
945	28.258	25.575	29.866	22.118	12.959	60.179	53.962
950	28.339	25.458	29.442	22.648	13.097	59.949	54.071
955	28.472	25.529	29.375	22.041	13.210	60.136	53.945
960	28.652	25.427	29.467	22.640	13.045	60.114	54.533
965	28.410	25.081	29.572	22.185	12.899	59.942	54.212
970	28.375	25.439	29.669	22.337	13.114	59.797	54.953
975	28.436	25.558	29.549	22.115	13.313	59.953	55.031
980	28.302	25.790	29.545	22.546	13.154	59.941	54.117
985	28.193	25.538	29.878	22.100	12.952	59.642	54.154
990	28.212	25.654	29.432	22.487	12.753	60.039	55.368
995	28.495	25.397	29.739	22.423	12.737	59.993	54.303
1000	28.163	25.324	29.444	22.575	12.893	59.962	54.966
1005	28.457	25.618	29.563	22.280	12.830	60.036	54.677
1010	28.302	25.407	29.498	22.096	13.107	59.895	54.506
1015	28.588	25.650	29.408	22.345	13.324	59.882	54.491
1020	28.676	25.407	29.679	22.589	12.842	59.819	55.038
1025	28.463	25.677	29.487	22.048	12.877	59.537	54.110
1030	28.355	25.656	29.469	21.720	13.137	59.965	54.983
1035	28.235	25.479	29.269	22.003	13.271	59.808	55.184
1040	28.403	25.353	29.552	22.043	13.091	59.617	54.210
1045	28.626	25.761	29.265	22.056	13.192	59.723	55.161
1050	28.341	25.444	29.462	22.296	13.136	60.128	55.202
1055	28.284	25.405	29.513	21.900	13.079	59.720	54.579
1060	28.482	25.514	29.581	22.266	13.260	59.932	55.248
1065	28.524	25.664	29.339	22.425	13.118	59.666	55.100
1070	28.420	25.511	29.389	22.200	13.329	59.675	54.880
1075	28.511	26.446	29.642	21.914	13.302	59.781	55.295
1080	28.611	26.048	29.579	22.127	13.008	59.720	54.856
1085	28.544	25.713	29.391	21.938	13.252	59.741	54.671
1090	28.598	25.953	29.330	22.251	13.127	59.748	55.371
1095	28.223	26.065	29.347	21.951	13.024	59.687	55.007
1100	28.234	25.595	29.307	22.110	12.895	59.802	55.333
1105	28.780	26.029	29.406	22.167	13.017	59.878	55.578
1110	28.341	25.926	29.513	22.352	12.910	59.660	54.900
1115	28.442	25.934	29.330	22.333	13.154	59.937	55.388
1120	28.624	26.365	29.204	21.768	13.289	59.729	55.451
1125	28.485	26.104	29.492	21.976	13.199	59.596	55.322
1130	28.722	26.019	29.516	22.323	13.349	59.668	55.248
1135	28.560	26.427	29.020	21.856	13.268	59.781	55.535
1140	28.574	26.036	29.165	22.028	13.588	59.558	55.082
1145	28.847	26.039	29.244	21.837	13.353	59.773	55.480
1150	28.834	26.245	29.291	21.974	13.249	59.496	56.218
1155	28.559	26.246	29.166	22.285	13.380	59.674	54.866
1160	28.304	25.839	29.178	21.964	13.699	59.675	55.107
1165	28.463	26.049	29.125	21.904	13.130	59.652	55.423
1170	28.519	26.007	29.148	22.201	13.511	60.177	54.717
1175	28.657	26.250	29.232	22.330	13.256	59.552	55.412
1180	28.599	25.944	29.152	22.219	13.123	59.471	55.745
1185	28.838	25.811	29.099	22.168	13.177	59.631	54.897
1190	28.693	26.228	28.988	22.162	13.460	59.696	55.786
1195	28.855	26.142	29.323	22.410	13.206	59.757	55.508

Table units μmolal

RUN #	80	92	105	106	81	94	82	95
pH:	4	4	4	4	4	4	4	4
Initial conc. (μm)	15.0	15.0	30.0	30.0	30.0	30.0	60.0	60.0
solid conc. (mg/kg)	200	300	100	100	200	300	200	300
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
30	10.638	6.599	23.763	23.122	19.819	15.447	39.560	32.545
35	10.228	6.507	23.449	23.098	19.292	15.939	38.647	31.789
40	9.858	5.874	23.407	22.370	18.583	14.270	37.382	30.580
45	9.102	6.128	22.914	22.586	18.877	13.531	36.249	29.853
50	9.144	5.509	22.693	22.321	17.914	14.357	34.640	28.242
55	9.349	5.164	22.394	22.152	17.894	12.881	34.133	27.100
60	8.535	5.341	21.939	21.588	16.818	12.566	33.018	26.680
65	8.163	5.631	21.331	20.946	16.205	11.685	32.462	25.292
70	7.752	4.864	21.229	21.123	15.996	11.679	31.320	24.773
75	7.972	4.684	21.061	20.991	15.815	12.044	30.518	23.227
80	7.910	3.974	21.076	20.856	15.463	11.553	30.238	23.114
85	7.438	4.362	20.737	20.535	15.121	11.140	29.729	22.352
90	7.714	4.378	20.328	20.143	14.833	10.900	29.313	21.655
95	7.306	4.369	20.262	20.088	14.661	10.232	28.555	21.655
100	6.901	3.855	20.229	19.451	14.408	10.623	28.346	21.834
105	6.972	3.122	19.931	19.646	14.110	10.219	27.696	20.985
110	6.855	3.221	19.551	19.451	14.291	10.062	27.500	19.881
115	6.570	3.692	19.185	19.455	13.112	10.396	26.893	19.995
120	6.623	3.176	19.167	19.497	13.767	9.949	26.571	19.428
125	7.062	3.008	19.154	18.832	12.889	10.264	26.494	18.812
130	7.021	3.576	18.693	18.651	13.032	9.815	25.923	18.515
135	6.893	2.997	18.579	18.674	12.840	9.646	25.849	18.075
140	6.082	3.493	18.649	18.493	12.675	9.731	25.281	18.472
145	6.203	3.999	18.378	18.249	12.419	9.165	25.727	18.178
150	6.878	3.185	18.667	17.953	11.831	8.944	25.626	17.603
155	6.408	3.138	18.099	18.106	12.143	8.838	25.005	17.521
160	6.416	2.771	18.219	18.205	11.767	8.510	24.453	16.911
165	6.020	2.214	17.834	17.920	11.688	9.144	24.788	17.301
170	6.237	2.535	17.758	17.779	11.434	9.010	24.374	17.109
175	5.967	2.936	17.531	17.855	11.723	9.120	23.954	16.959
180	6.179	2.654	17.286	17.734	11.097	8.895	24.575	16.800
185	5.649	3.093	17.529	17.436	11.250	8.659	23.924	16.119
190	5.332	2.774	17.538	17.677	11.139	8.918	23.494	16.320
195	5.443	2.913	17.489	17.274	10.911	8.631	23.515	15.994
200	5.533	2.804	16.930	16.916	10.852	8.354	24.228	15.635
205	5.828	2.610	16.993	17.128	10.794	8.510	23.258	15.975
210	5.780	2.182	17.030	16.761	11.379	8.067	23.343	16.159
215	5.360	2.234	16.871	17.030	10.838	8.282	23.196	15.834
220	5.199	2.716	16.721	16.666	10.325	8.208	23.293	15.730
225	5.489	2.556	16.716	16.675	10.583	8.304	23.642	14.503
230	5.535	2.132	16.481	17.063	10.420	8.632	22.773	15.186
235	5.702	1.689	16.448	16.787	10.695	8.119	22.758	14.777
240	5.983	2.240	16.711	16.852	10.295	8.243	23.024	15.380
245	5.620	2.381	16.307	16.555	10.284	8.656	23.035	15.119
250	5.340	2.594	15.999	16.598	10.029	8.145	22.225	15.372
255	5.675	2.028	16.168	16.941	9.999	8.043	22.141	14.728
260	5.398	2.074	16.064	16.443	9.861	7.566	21.898	15.816
265	5.390	2.313	16.239	16.494	9.969	7.945	21.993	15.577
270	5.522	2.527	16.319	16.273	10.355	7.790	22.210	14.692
275	5.380	1.926	15.840	16.205	10.120	8.188	21.595	15.030
280	5.529	1.224	15.912	16.082	9.654	8.138	22.114	14.331
285	5.895	2.210	15.642	16.123	9.964	7.537	21.950	14.848
290	5.323	1.690	15.675	16.096	9.806	8.122	21.795	14.789
295	5.889	2.022	15.386	15.805	9.405	7.641	21.564	14.810
300	5.592	1.443	15.740	15.674	9.683	7.637	21.307	14.373
305	5.392	1.675	15.566	15.986	9.373	7.925	21.436	14.239
310	5.523	1.809	15.687	15.523	9.745	7.928	21.674	14.277
315	5.499	1.439	15.512	15.898	9.334	7.547	21.601	14.343
320	5.165	1.685	15.608	15.786	9.465	7.608	21.519	14.268

Table units µmolal

RUN #	80	92	105	106	81	94	82	95
pH:	4	4	4	4	4	4	4	4
Initial conc. (µm)	15.0	15.0	30.0	30.0	30.0	30.0	60.0	60.0
solid conc. (mg/kg)	200	300	100	100	200	300	200	300
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
325	5.920	1.741	15.770	16.910	9.218	7.942	21.282	13.854
330	6.124	1.660	15.506	15.569	8.951	8.306	21.081	13.534
335	5.509	1.372	15.654	15.522	9.253	7.683	21.204	13.937
340	5.782	1.881	15.303	15.881	9.016	7.881	21.445	14.554
345	5.783	1.335	15.196	15.314	9.528	7.918	21.258	14.294
350	5.798	1.078	15.118	15.584	9.265	8.115	21.091	14.114
355	5.628	1.077	15.196	15.498	8.896	7.573	21.283	13.676
360	5.314	1.728	15.543	15.519	9.053	7.481	21.512	13.883
365	5.547	1.804	15.244	15.484	9.526	7.758	21.598	14.084
370	5.484	1.059	15.113	15.120	9.007	8.050	21.426	13.845
375	5.582	1.608	15.309	15.394	8.656	7.495	21.280	13.783
380	5.505	1.393	15.386	14.990	9.293	7.610	21.094	13.984
385	5.195	1.565	15.319	15.259	8.791	7.794	21.341	13.872
390	5.071	1.063	14.978	15.453	8.854	6.751	21.070	14.133
395	5.295	1.002	14.880	15.017	8.543	7.127	21.492	14.274
400	5.446	0.700	14.918	15.292	9.285	7.665	21.394	13.989
405	6.089	1.596	14.911	15.267	8.920	8.408	21.754	14.193
410	5.763	1.282	14.600	15.410	9.016	7.488	20.536	14.167
415	5.441	0.510	14.880	14.983	8.790	7.832	20.979	13.778
420	5.810	1.519	14.705	15.093	8.833	8.007	21.400	13.384
425	5.531	1.678	14.581	15.204	8.920	7.924	20.882	14.045
430	5.889	1.684	14.814	14.835	8.827	8.273	21.287	13.865
435	5.811	1.723	14.799	15.033	9.874	8.031	21.038	13.855
440	6.042	1.140	14.511	15.079	8.810	7.648	20.926	13.276
445	6.042	1.609	15.027	14.680	9.517	7.727	20.385	13.074
450	5.894	0.764	14.603	15.076	9.209	8.044	21.025	14.326
455	6.153	1.576	14.282	15.007	10.126	7.636	20.974	13.766
460	5.754	1.215	14.460	15.128	9.117	7.849	21.035	14.540
465	6.048	1.123	14.352	14.782	9.185	7.038	21.073	13.595
470	6.058	1.358	14.352	14.860	9.335	7.555	20.565	13.906
475	5.643	1.536	14.193	14.889	8.984	7.327	20.601	13.517
480	5.718	1.129	14.298	14.902	9.669	8.679	20.677	13.711
485	6.171	1.443	14.325	14.928	8.887	7.777	20.946	13.596
490	6.289	1.540	14.224	14.632	9.555	7.293	20.515	13.446
495	5.699	2.146	14.255	14.899	8.924	7.578	20.124	14.147
500	6.246	1.350	14.252	14.687	9.555	7.994	20.172	13.926
505	5.960	1.569	14.438	14.451	9.152	8.084	20.267	14.208
510	6.065	1.077	14.442	14.626	9.690	6.766	20.242	13.741
515	6.431	1.012	14.258	14.566	9.582	8.039	20.010	13.142
520	5.687	1.718	14.265	14.661	9.955	7.565	20.286	14.690
525	5.296	1.572	14.120	14.873	9.923	7.600	20.549	13.536
530	6.050	1.239	13.882	14.505	9.343	7.526	19.894	13.665
535	6.644	1.956	14.220	14.340	10.549	7.342	20.275	13.521
540	5.060	1.784	14.141	14.367	9.877	7.657	20.245	13.198
545	5.440	1.768	13.725	14.311	10.521	7.684	20.108	13.844
550	5.333	2.098	14.116	14.395	10.135	7.981	20.502	13.094
555	5.169	1.792	14.123	14.160	10.217	7.468	20.293	13.440
560	5.887	2.167	14.168	14.455	10.394	8.220	20.167	13.218
565	5.169	1.510	13.931	14.223	9.935	7.639	20.376	13.144
570	5.392	0.982	13.901	14.780	10.611	8.115	20.374	13.210
575	5.347	2.053	13.769	14.166	9.971	7.844	20.225	13.379
580	5.635	2.236	13.528	14.368	10.467	7.866	19.983	13.092
585	5.594	2.448	13.924	14.285	10.357	8.040	20.000	13.305
590	5.511	2.235	13.739	14.030	10.810	8.139	19.967	13.401
595	5.580	2.630	14.110	14.023	10.126	7.997	19.939	13.547

Table units µmolal

RUN #	84	123	124	125	89	85	90	86
pH:	8	8	8	8	8	8	8	8
Initial conc. (µm)	15.0	15.0	15.0	15.0	15.0	30.0	30.0	60.0
solid conc. (mg/kg)	200	200	200	200	300	200	300	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
30	10.954	10.975	10.655	11.053	10.697	25.374	23.023	56.011
35	11.216	10.673	10.299	10.545	9.742	24.879	22.384	55.230
40	10.942	10.555	10.853	10.346	9.512	24.914	21.842	55.865
45	10.188	9.724	9.826	9.970	9.270	24.394	21.482	54.989
50	10.127	9.587	9.378	9.826	8.181	24.316	20.506	55.789
55	9.831	9.678	9.629	9.278	9.007	24.042	20.739	54.782
60	9.699	8.565	9.572	9.453	8.425	24.144	20.614	55.003
65	9.394	8.800	9.357	8.965	8.461	23.211	20.479	55.265
70	9.212	9.057	8.855	8.827	7.997	23.594	19.624	54.993
75	8.906	8.459	7.936	8.580	7.855	23.150	19.696	54.464
80	9.576	8.656	8.174	8.226	7.650	23.391	19.466	54.200
85	9.000	8.360	8.459	8.272	7.237	23.154	19.347	53.994
90	8.742	8.807	7.825	8.273	7.210	23.306	19.464	54.036
95	8.660	7.981	7.506	8.252	6.879	22.695	18.957	53.998
100	9.043	8.069	7.572	8.068	7.034	22.082	19.244	53.782
105	8.552	8.028	7.265	7.672	6.948	22.299	19.344	53.461
110	8.476	7.982	7.911	7.982	6.936	22.601	19.086	53.873
115	8.553	7.616	7.170	7.425	6.384	22.117	19.622	53.734
120	8.944	7.931	6.956	7.337	6.601	22.185	19.056	53.087
125	8.773	8.023	7.293	7.541	6.756	21.848	18.793	53.658
130	8.218	7.354	6.990	7.220	6.073	21.467	19.021	53.203
135	8.065	7.906	6.673	7.273	6.657	21.742	18.626	53.351
140	8.197	7.527	6.669	6.966	6.152	21.832	18.767	53.285
145	9.061	7.594	7.128	6.858	6.530	21.753	18.780	53.181
150	7.945	7.302	7.081	6.989	6.574	21.875	18.415	53.186
155	8.253	7.288	6.357	6.801	6.403	21.575	19.242	53.184
160	8.721	7.548	6.176	6.948	6.396	21.600	18.449	53.409
165	8.549	6.888	6.400	6.984	5.908	21.426	18.305	53.185
170	8.332	7.072	6.348	6.695	6.069	21.089	18.614	52.876
175	8.407	7.280	6.333	6.615	5.725	20.918	18.398	52.585
180	8.344	6.937	6.256	7.170	5.792	20.982	18.160	52.676
185	8.308	7.153	5.976	6.215	5.959	20.925	17.871	52.644
190	8.132	6.952	6.589	6.211	5.849	21.144	18.091	52.093
195	7.793	7.202	6.204	7.036	6.004	20.999	18.147	52.676
200	8.212	6.757	5.796	6.483	5.709	20.670	18.024	52.682
205	8.492	7.183	5.815	6.420	5.826	20.789	18.297	52.398
210	8.230	6.829	5.974	6.218	6.293	20.860	18.160	51.992
215	8.043	6.974	6.031	6.550	5.565	20.673	18.588	52.106
220	7.697	6.567	5.648	6.407	5.748	20.650	18.617	52.707
225	8.302	7.084	5.709	6.045	5.697	20.923	18.495	52.258
230	9.000	6.821	5.900	5.972	5.825	20.554	17.787	52.400
235	8.244	6.601	5.608	6.235	5.570	20.519	18.861	52.300
240	7.968	6.891	5.491	6.758	5.974	20.828	18.815	51.870
245	8.415	6.900	5.985	6.780	5.206	20.895	18.522	51.839
250	7.972	6.446	5.926	6.194	5.640	20.755	18.400	52.341
255	8.334	6.725	5.589	6.236	5.507	21.148	18.190	51.846
260	7.846	6.677	5.401	6.258	6.113	20.499	19.053	51.455
265	8.451	6.421	5.254	5.893	5.641	20.365	18.095	51.817
270	8.120	6.235	5.360	6.309	5.404	20.358	18.510	51.547
275	8.245	6.216	5.570	6.503	5.631	20.223	18.710	51.534
280	8.002	6.355	5.539	6.165	5.307	20.626	18.214	51.314
285	7.743	6.199	5.401	6.051	5.877	20.117	18.050	51.399
290	8.415	6.756	5.773	6.206	5.698	20.886	18.115	50.860
295	8.403	6.264	5.449	5.987	4.829	20.579	18.464	51.583
300	8.126	6.568	5.346	5.725	5.079	20.655	18.503	51.396
305	7.594	6.130	5.699	5.898	5.898	20.322	18.461	51.214
310	7.646	6.240	5.614	5.783	5.207	20.536	18.328	51.529
315	8.017	6.352	6.151	5.756	5.661	20.325	18.249	51.579
320	7.804	6.019	5.315	5.692	5.181	20.983	17.984	52.093

Table units µmolal

RUN #	84	123	124	125	89	85	90	86
pH:	8	8	8	8	8	8	8	8
Initial conc. (µm)	15.0	15.0	15.0	15.0	15.0	30.0	30.0	60.0
solid conc. (mg/kg)	200	200	200	200	300	200	300	200
Temp: (C°)	25	25	25	25	25	25	25	25
Time (sec.)								
325	7.599	6.055	5.487	5.777	4.547	20.134	18.520	51.691
330	8.367	6.027	6.074	6.014	5.078	20.134	19.063	51.558
335	8.472	6.432	5.448	5.447	5.150	20.165	18.222	51.674
340	7.853	5.791	5.713	5.649	4.788	19.789	18.837	51.073
345	7.711	6.119	5.798	5.796	5.533	20.502	18.781	51.625
350	8.174	5.904	5.759	5.759	5.097	20.007	18.404	51.386
355	8.596	6.027	6.055	5.935	5.585	20.011	18.239	51.440
360	7.979	6.326	5.790	6.134	5.039	20.324	19.082	50.990
365	7.958	5.935	6.169	5.742	5.829	19.987	18.639	50.839
370	7.449	6.013	5.938	5.522	5.266	20.235	18.338	50.854
375	8.233	6.071	5.976	5.325	5.063	20.293	18.406	50.949
380	7.634	6.070	5.980	5.835	5.199	19.866	18.769	51.320
385	7.596	5.958	6.072	5.497	5.237	19.983	18.840	51.386
390	7.864	6.144	6.457	5.540	5.433	19.992	18.270	50.864
395	8.056	6.578	5.883	5.714	5.296	20.003	18.528	51.324
400	8.032	6.216	5.987	5.443	5.148	19.784	18.380	51.494
405	7.352	6.322	5.948	5.204	5.087	20.142	18.622	51.179
410	7.817	5.926	6.222	5.924	4.905	20.365	18.148	51.374
415	7.855	6.006	6.261	5.370	4.770	19.662	19.479	51.468
420	8.148	6.172	5.972	5.102	4.861	20.154	18.637	51.757
425	7.798	6.275	6.020	5.126	4.547	20.094	18.575	51.369
430	7.282	5.951	6.457	5.715	6.139	19.844	18.271	51.536
435	7.951	6.319	6.121	5.564	5.211	19.818	18.036	51.355
440	8.440	6.058	5.783	5.625	4.896	19.696	18.525	51.895
445	8.291	5.931	5.873	5.653	5.098	20.084	17.669	51.287
450	7.625	5.853	5.797	5.866	5.491	19.884	18.895	51.324
455	7.642	6.024	6.086	5.996	5.787	19.689	18.789	50.895
460	7.903	6.118	5.858	6.249	5.158	19.726	18.503	51.662
465	7.613	5.871	6.400	5.800	5.663	19.421	18.433	50.698
470	7.828	5.959	6.594	6.358	5.278	19.569	18.412	50.968
475	7.298	5.983	5.639	6.022	4.778	19.709	18.271	51.597
480	10.110	5.750	5.475	6.131	4.912	19.639	18.054	51.604
485	7.798	6.146	5.841	6.207	4.875	19.478	17.977	52.142
490	7.577	5.777	6.381	6.184	5.561	20.028	18.068	51.271
495	7.572	6.181	5.841	6.058	5.731	20.164	18.293	51.953
500	7.490	6.025	5.900	6.039	5.062	19.773	17.875	51.761
505	7.812	5.627	5.667	5.935	4.698	19.760	18.041	51.540
510	7.673	6.032	5.818	5.859	4.938	20.435	17.813	51.692
515	7.590	5.692	5.878	5.837	4.985	19.246	18.157	51.646
520	7.716	6.374	5.546	5.793	5.367	19.444	17.671	51.611
525	7.784	5.962	6.205	5.594	5.015	19.419	17.795	51.562
530	7.359	5.762	6.282	5.931	4.759	19.250	17.695	51.185
535	7.315	5.921	5.689	6.162	5.016	20.004	17.965	51.014
540	7.259	5.767	5.409	5.655	5.709	19.387	17.936	51.204
545	7.876	6.092	6.035	5.928	5.384	20.023	18.062	51.073
550	8.156	6.050	5.559	5.680	5.213	19.717	17.826	50.991
555	7.646	5.983	6.254	5.706	5.196	19.518	17.313	51.129
560	8.035	6.099	5.909	5.831	5.494	19.864	17.325	50.959
565	7.621	5.960	6.076	5.334	4.859	19.904	17.900	51.450
570	8.154	5.749	5.651	5.380	5.590	19.762	17.527	51.406
575	7.460	6.263	6.388	5.648	5.733	20.161	17.850	51.569
580	7.920	5.813	5.754	5.824	5.927	19.525	17.432	51.615
585	8.043	5.791	6.222	5.499	5.860	19.804	17.122	51.799
590	7.932	5.978	6.608	5.304	5.167	19.647	17.146	52.049
595	7.484	5.999	6.233	5.531	5.522	19.990	17.438	52.107

Table units µmolal

RUN #	91	133	134	135	139	140	141
pH:	8	8	8	8	8	8	8
Initial conc. (µm)	60.0	15.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	300	200	200	200	200	200	200
Temp: (C°)	25	10	10	10	50	50	50
Time (sec.)							
30	51.344	12.036	11.157	10.079	6.674	7.289	6.979
35	51.467	11.641	10.038	9.760	6.384	7.084	7.237
40	51.584	11.689	10.538	9.087	6.107	6.668	6.466
45	49.864	11.346	10.116	9.034	5.975	6.958	6.153
50	49.409	11.193	9.636	8.691	6.161	6.567	5.746
55	50.423	10.862	9.920	8.268	5.389	5.975	5.857
60	48.984	10.684	9.049	8.460	5.629	5.781	5.727
65	48.509	10.432	9.473	7.822	5.024	5.815	5.192
70	49.968	10.762	8.742	7.701	5.030	5.941	5.350
75	48.066	9.962	9.041	7.325	4.717	5.688	5.166
80	48.394	10.240	8.827	7.285	4.763	5.614	5.354
85	49.188	10.230	7.720	7.004	4.735	5.672	4.787
90	48.509	9.693	8.467	6.742	4.921	5.121	5.113
95	48.070	9.985	7.848	6.719	4.526	5.406	5.269
100	48.423	9.469	7.793	6.763	4.883	4.997	4.905
105	47.499	9.762	7.621	6.275	4.867	5.065	4.533
110	47.200	9.121	7.557	6.330	4.289	4.807	4.252
115	48.282	9.046	7.903	6.649	4.295	4.565	4.391
120	47.848	9.030	7.291	6.072	3.799	5.271	4.299
125	46.590	8.887	7.660	6.243	4.772	4.726	4.711
130	47.123	9.247	7.116	5.743	3.973	4.330	4.351
135	46.737	8.456	7.206	5.801	4.302	4.451	4.426
140	46.497	8.474	7.608	5.512	4.390	4.302	4.416
145	46.685	8.645	6.688	5.618	3.931	4.259	3.725
150	46.861	8.636	6.929	5.560	4.171	4.384	4.005
155	46.136	8.195	7.032	5.701	4.175	4.321	3.846
160	46.002	8.316	6.893	5.316	4.177	4.101	3.904
165	46.917	8.248	7.198	5.858	4.112	3.994	3.416
170	45.779	8.366	6.276	5.405	3.983	4.048	3.852
175	45.407	8.169	6.973	4.954	3.580	3.986	4.043
180	45.938	8.421	6.505	5.346	3.783	4.118	3.489
185	45.955	8.219	6.281	5.426	3.524	4.126	3.512
190	45.491	7.804	6.219	5.014	3.674	4.094	3.306
195	46.019	8.253	5.650	5.471	3.821	3.786	3.529
200	45.984	7.253	6.481	4.803	3.575	3.907	3.509
205	45.120	7.953	5.644	4.815	3.780	4.253	3.591
210	45.428	7.896	6.281	4.797	3.455	3.863	3.581
215	45.783	8.152	6.321	4.768	3.564	3.813	3.608
220	45.148	7.820	5.656	4.889	3.327	4.149	3.354
225	45.920	7.283	5.831	4.801	3.564	3.999	3.268
230	45.722	8.009	5.285	4.611	3.169	4.206	3.499
235	45.413	7.267	5.968	5.079	3.757	3.998	2.945
240	45.030	7.281	5.490	4.696	2.849	4.169	3.119
245	46.340	7.062	5.816	4.295	2.987	4.268	3.407
250	45.831	7.111	5.680	4.611	3.730	3.901	3.200
255	45.106	8.433	5.689	4.545	3.246	3.995	3.234
260	45.788	7.683	5.834	4.344	3.367	3.962	3.253
265	45.282	7.334	5.767	4.594	3.205	4.021	3.313
270	45.134	7.302	5.684	4.641	3.064	3.599	3.444
275	45.711	7.007	5.849	4.979	3.238	4.011	3.356
280	45.696	7.395	5.206	4.612	3.179	4.090	3.155
285	45.405	7.326	5.185	3.977	3.222	4.056	3.409
290	45.451	7.215	5.217	4.796	3.249	3.711	3.317
295	46.204	7.763	5.667	4.223	3.272	3.875	3.302
300	45.479	6.984	5.172	4.256	3.065	3.889	3.739
305	45.931	7.283	5.276	4.811	3.307	3.895	3.272
310	45.758	7.232	4.860	4.218	3.172	4.176	3.562
315	45.465	6.773	4.707	4.585	2.684	4.468	3.083
320	44.986	7.589	4.812	4.360	2.958	4.174	3.239

Table units µmolal

RUN #	91	133	134	135	139	140	141
pH:	8	8	8	8	8	8	8
Initial conc. (µm)	60.0	15.0	15.0	15.0	15.0	15.0	15.0
solid conc. (mg/kg)	300	200	200	200	200	200	200
Temp: (C°)	25	10	10	10	50	50	50
Time (sec.)							
325	46.096	6.649	4.615	3.883	3.055	4.196	3.480
330	45.923	7.166	5.686	4.313	3.022	4.413	3.618
335	45.313	7.323	4.626	4.105	3.445	4.268	3.780
340	46.232	6.908	4.715	3.525	2.958	4.107	3.412
345	46.123	6.721	5.234	4.269	3.143	4.459	3.612
350	44.657	6.382	4.356	4.171	2.826	4.196	3.496
355	45.913	6.906	4.827	4.012	2.763	4.133	3.620
360	45.875	6.457	4.348	3.870	3.330	4.256	3.610
365	45.437	6.483	4.702	3.853	2.746	3.997	3.291
370	44.818	6.937	4.085	3.952	2.959	4.144	3.629
375	46.735	6.726	4.478	3.863	2.851	4.196	3.208
380	45.653	6.816	4.382	3.421	2.735	3.846	3.647
385	45.765	6.616	3.956	4.026	2.918	4.233	3.485
390	45.428	6.577	4.430	3.751	2.958	3.766	3.748
395	45.032	6.982	4.105	3.519	2.502	4.392	3.274
400	45.006	6.322	3.808	4.260	2.868	4.337	3.162
405	45.881	6.639	4.170	3.688	3.095	3.939	3.127
410	45.233	6.518	3.698	3.563	2.527	4.070	3.457
415	45.412	6.655	4.381	3.663	3.052	4.225	3.143
420	45.454	6.948	3.729	3.212	2.771	4.079	3.057
425	45.037	6.312	3.969	3.597	2.505	4.071	3.372
430	44.766	6.710	3.997	3.487	2.824	4.184	3.097
435	45.171	6.435	3.494	3.361	2.734	4.179	3.429
440	45.041	6.451	4.007	3.460	2.822	4.347	2.954
445	45.516	6.567	3.324	3.415	2.916	4.382	3.135
450	44.732	6.324	4.061	3.331	2.696	4.398	3.196
455	45.332	7.057	3.332	3.486	2.920	4.280	3.012
460	45.174	6.118	3.248	2.990	3.021	4.021	3.170
465	44.534	6.612	3.696	3.396	2.696	4.533	3.020
470	45.920	6.485	3.324	2.897	3.059	4.213	3.235
475	45.564	6.153	3.622	2.804	2.624	5.092	2.808
480	45.462	6.916	3.364	2.973	2.750	4.122	2.797
485	45.730	6.639	3.203	3.129	2.462	4.169	2.924
490	45.766	6.505	3.650	2.849	3.375	4.447	3.065
495	45.236	6.244	3.373	2.808	2.696	4.291	3.743
500	45.450	6.381	3.489	2.418	2.742	3.883	3.079
505	45.484	6.324	2.937	2.488	2.478	4.537	3.545
510	44.995	6.108	3.426	2.967	2.378	4.766	2.835
515	45.101	6.068	2.842	2.548	3.350	4.268	3.510
520	45.693	6.461	3.063	2.681	2.588	4.502	3.344
525	45.099	6.068	3.014	2.907	2.700	4.499	3.398
530	44.172	6.668	3.010	2.884	2.963	4.200	3.691
535	44.975	5.837	2.798	3.258	3.157	4.403	3.708
540	44.965	6.237	3.167	2.924	2.947	4.638	3.689
545	45.102	6.742	2.798	2.911	3.006	4.508	3.755
550	44.773	6.023	2.976	2.794	3.136	4.492	4.098
555	45.242	6.416	2.799	2.386	3.365	4.573	3.844
560	44.505	6.213	3.124	3.281	2.965	4.507	4.033
565	44.495	6.680	3.038	3.018	3.083	4.399	3.925
570	45.146	6.401	3.238	2.838	3.085	4.821	3.731
575	45.408	6.117	3.722	3.199	3.317	5.227	5.107
580	44.674	6.439	3.567	2.800	3.478	5.154	3.828
585	44.921	6.251	3.612	3.130	3.110	4.924	4.052
590	44.818	6.480	3.801	3.007	3.703	4.646	4.281
595	44.754	6.700	3.724	2.726	3.355	4.281	3.731

Table units µmolal

RUN #	115	116	117	102	103	104
pH:	8	8	8	4	4	4
Initial conc. (µm)	15.0	15.0	15.0	30.0	30.0	30.0
solid conc. (mg/kg)	200	200	200	100	100	100
Temp: (C°)	70	70	70	10	10	10
Time (sec.)						
30	4.056	4.905	5.429	20.412	19.504	19.498
35	5.452	4.677	5.777	20.141	19.831	19.123
40	5.424	5.156	4.850	19.791	19.106	18.872
45	4.734	4.360	5.411	19.655	18.634	18.648
50	5.480	4.514	5.636	19.054	18.646	18.932
55	5.599	4.385	4.547	19.086	18.298	18.636
60	5.048	3.853	4.748	19.188	18.255	17.815
65	5.464	3.621	4.949	19.026	17.941	17.618
70	4.685	3.775	4.308	18.748	17.996	17.597
75	5.159	3.907	4.352	18.192	17.281	17.756
80	5.138	3.981	4.522	18.496	17.116	17.272
85	4.739	3.885	4.213	17.845	17.099	17.608
90	4.980	3.541	4.056	17.985	17.097	17.223
95	4.533	3.213	3.951	17.813	16.567	17.127
100	4.846	3.313	4.145	17.623	16.514	16.871
105	4.871	3.411	4.001	17.566	16.419	16.873
110	4.790	3.483	3.921	17.288	16.268	16.714
115	4.779	3.042	3.894	16.773	16.223	16.518
120	4.496	3.087	3.832	16.779	16.056	16.185
125	4.788	2.988	3.790	16.834	15.613	16.285
130	4.688	2.997	3.565	16.587	15.371	15.865
135	4.777	2.931	3.654	16.148	15.786	15.644
140	4.828	3.014	3.536	16.481	15.477	15.155
145	4.484	2.770	3.111	16.125	14.839	15.135
150	4.779	2.653	3.400	15.962	14.897	15.239
155	4.718	2.808	3.516	15.678	14.846	14.888
160	4.791	2.770	3.230	15.599	14.761	14.510
165	4.942	2.760	3.358	15.378	14.242	14.454
170	4.596	2.489	3.776	15.810	14.192	14.166
175	4.779	2.598	3.257	15.479	14.540	14.412
180	4.676	2.670	3.112	15.967	14.107	14.172
185	5.033	2.719	3.564	15.265	13.734	14.134
190	5.197	2.758	3.062	14.748	13.851	14.085
195	5.140	2.490	2.958	14.587	14.014	14.034
200	5.298	2.345	3.008	14.624	13.426	13.582
205	5.247	2.501	3.091	14.491	13.657	13.409
210	5.578	2.618	3.084	14.907	13.658	13.781
215	5.309	2.829	2.906	14.707	13.330	13.715
220	5.828	2.379	2.825	14.452	13.474	13.477
225	5.912	2.248	2.945	14.245	13.178	13.654
230	5.653	2.410	3.271	14.014	12.973	13.221
235	6.233	2.433	2.743	13.723	13.501	13.268
240	5.668	2.535	3.021	13.404	13.541	12.794
245	6.313	2.341	3.282	13.961	13.523	12.957
250	5.644	2.310	2.817	14.324	13.749	12.306
255	5.564	2.283	2.906	13.919	13.289	12.790
260	5.715	2.369	3.006	14.166	13.164	12.632
265	5.250	2.574	2.705	13.650	13.570	12.565
270	5.502	2.249	2.869	13.650	13.924	12.267
275	5.277	2.210	2.853	13.916	13.354	12.426
280	5.199	2.383	2.685	13.614	13.618	12.726
285	5.242	2.594	2.792	13.378	13.327	12.291
290	4.996	2.915	2.959	12.893	13.109	12.208
295	5.108	2.454	2.691	13.528	13.444	12.196
300	5.003	2.182	2.687	13.919	13.553	12.238
305	4.936	2.283	3.069	14.048	13.501	12.320
310	5.020	2.457	2.938	12.858	13.182	11.983
315	4.682	2.644	3.332	12.975	13.669	12.027
320	4.998	2.248	3.019	12.837	13.653	11.498

Table units µmolal

RUN #	115	116	117	102	103	104
pH:	8	8	8	4	4	4
Initial conc. (µm)	15.0	15.0	15.0	30.0	30.0	30.0
solid conc. (mg/kg)	200	200	200	100	100	100
Temp: (C°)	70	70	70	10	10	10
Time (sec.)						
325	4.584	2.225	2.743	13.133	13.550	11.506
330	5.048	2.165	2.934	13.490	13.944	11.039
335	4.721	2.484	2.975	13.227	14.134	11.155
340	4.398	2.598	2.607	12.996	13.931	11.207
345	4.386	2.503	2.671	12.858	14.032	11.045
350	4.214	2.388	2.713	12.681	13.907	11.250
355	4.292	2.384	2.763	13.050	14.425	11.158
360	4.248	2.493	3.053	13.160	14.132	10.961
365	4.370	2.617	3.025	13.145	14.220	10.963
370	4.134	2.396	2.657	13.055	13.970	11.252
375	4.183	2.304	2.818	13.020	13.883	10.538
380	4.186	2.330	2.939	13.106	13.965	10.818
385	3.881	2.496	2.633	13.011	13.543	10.768
390	4.086	2.767	3.032	13.124	13.131	10.656
395	3.710	2.918	2.808	13.400	13.303	10.710
400	3.990	2.637	2.572	13.118	13.618	10.788
405	3.921	2.673	2.853	13.444	13.336	10.705
410	3.842	2.630	2.873	13.438	13.182	10.359
415	4.241	2.970	2.524	13.231	12.742	10.883
420	3.651	2.952	2.687	12.645	12.804	10.649
425	3.854	2.728	2.865	12.621	12.399	10.482
430	3.977	2.965	2.742	12.207	12.550	10.530
435	3.609	3.149	3.063	12.288	12.517	10.215
440	3.732	3.107	2.670	12.726	13.169	10.631
445	3.435	3.086	2.504	12.543	13.172	10.811
450	3.874	3.112	2.944	12.605	12.806	10.869
455	3.532	3.035	2.853	13.007	12.837	11.307
460	4.047	3.105	2.506	13.536	12.705	11.403
465	3.707	3.512	2.868	13.200	12.141	11.410
470	3.913	3.142	2.753	13.138	12.293	11.766
475	3.761	3.784	2.726	12.920	12.808	10.601
480	3.545	3.139	2.781	13.345	12.629	10.247
485	3.572	3.433	2.643	13.524	12.406	9.846
490	3.559	4.468	2.749	13.145	12.451	10.115
495	3.446	3.372	2.661	13.362	12.800	10.101
500	3.767	3.090	2.418	13.899	12.526	9.712
505	3.373	3.227	2.655	13.107	11.871	9.653
510	3.829	3.311	2.825	12.954	12.457	9.621
515	3.347	3.424	2.390	12.772	12.244	9.428
520	3.528	3.708	2.507	13.490	12.365	9.695
525	3.352	3.086	2.287	13.617	12.557	9.549
530	3.303	3.252	1.962	14.002	12.355	9.544
535	3.207	3.198	1.944	14.471	12.509	9.583
540	3.176	3.589	1.930	14.370	12.265	9.711
545	3.227	3.453	1.708	13.191	12.189	9.762
550	3.369	3.436	1.530	13.329	12.307	9.582
555	3.289	3.928	1.776	13.053	12.677	9.764
560	3.525	3.416	1.477	12.976	12.797	9.873
565	3.049	3.642	1.530	13.223	12.816	9.630
570	3.230	3.526	1.459	12.988	12.259	9.494
575	3.448	4.143	1.269	12.729	12.066	9.690
580	3.183	3.655	1.338	13.109	12.358	9.460
585	3.418	4.060	1.337	13.493	12.389	9.396
590	3.808	4.130	1.265	12.399	12.107	9.498
595	4.346	4.253	1.299	12.178	12.073	9.288

Table units µmolal

RUN #	136	137	138	108	109	110	111
pH:	4	4	4	4	4	4	4
Initial conc. (µm)	30.0	30.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	100	100	100	100	100	100
Temp: (C°)	50	50	50	70	70	70	70
Time (sec.)							
30	21.301	20.666	22.288	28.379	23.414	23.310	45.818
35	20.801	20.797	22.463	28.248	24.412	23.891	44.945
40	20.950	19.993	22.142	28.241	22.772	23.504	45.563
45	20.480	20.285	21.885	28.173	23.677	23.246	45.588
50	20.370	20.539	21.812	28.093	23.852	23.462	45.535
55	20.183	20.322	21.636	28.014	22.991	23.765	45.069
60	20.066	19.990	21.528	28.024	23.634	23.758	45.087
65	19.742	19.700	21.492	28.073	23.805	23.628	44.960
70	19.836	19.755	21.333	28.129	23.213	23.146	44.925
75	19.800	19.946	21.098	28.067	23.337	23.505	44.822
80	19.535	19.835	21.094	28.119	23.515	23.502	44.862
85	19.329	19.541	20.860	28.018	22.825	23.500	44.788
90	19.332	19.353	21.036	28.045	22.950	23.220	44.259
95	19.177	19.437	21.036	27.950	23.031	22.963	44.237
100	19.110	19.398	20.583	27.877	23.347	23.409	43.895
105	18.910	19.323	20.590	27.887	22.996	23.496	43.516
110	18.690	19.229	20.356	27.822	22.723	23.175	43.520
115	18.668	18.697	20.490	27.853	22.506	22.748	43.360
120	18.696	18.799	20.470	27.880	22.356	23.112	43.467
125	18.771	18.742	20.299	27.860	22.527	22.960	42.908
130	18.543	18.827	20.144	27.863	22.198	23.012	43.135
135	18.480	18.593	20.021	27.828	22.147	22.988	42.998
140	18.477	18.827	20.085	27.750	22.627	22.665	42.883
145	18.425	18.598	19.940	27.677	22.294	22.829	42.592
150	18.054	18.376	20.009	27.638	22.108	22.927	42.852
155	18.106	18.319	19.866	27.640	22.304	22.823	42.503
160	18.319	18.349	19.621	27.647	22.157	22.494	42.385
165	17.962	18.164	19.785	27.667	22.090	22.614	42.503
170	17.854	18.138	19.625	27.640	21.971	22.676	42.419
175	17.770	17.964	19.697	27.633	21.878	22.638	42.304
180	17.697	17.978	19.466	27.551	21.690	22.378	42.084
185	17.560	18.106	19.431	27.588	21.708	22.475	42.024
190	17.921	17.958	19.298	27.579	21.728	22.463	41.866
195	17.563	17.942	19.254	27.449	21.554	22.347	41.861
200	17.459	17.808	19.367	27.375	21.842	22.366	41.654
205	17.436	17.873	19.207	27.387	21.654	22.436	41.754
210	17.725	17.746	19.189	27.399	21.289	22.529	41.676
215	17.309	17.999	19.051	27.410	21.606	22.231	41.888
220	17.099	17.996	19.165	27.427	21.316	22.232	41.598
225	17.171	17.721	18.985	27.441	21.215	22.284	41.379
230	17.450	17.726	18.788	27.463	21.698	22.207	41.846
235	17.190	17.808	19.142	27.444	21.607	21.974	41.506
240	17.326	17.563	18.762	27.351	21.215	22.410	41.397
245	17.039	17.895	18.721	27.262	21.448	22.193	41.266
250	17.087	17.535	18.767	27.212	21.211	21.925	41.486
255	17.297	17.485	18.677	27.206	21.267	22.067	40.933
260	16.872	17.341	18.608	27.399	21.140	22.133	41.023
265	17.063	17.458	18.467	27.506	21.240	22.115	41.077
270	16.708	17.381	18.522	27.571	20.887	21.890	41.219
275	16.809	17.528	18.391	27.571	21.106	21.834	40.714
280	16.694	17.193	18.425	27.491	21.195	21.866	40.865
285	16.857	17.192	18.430	27.523	21.033	21.842	40.823
290	16.810	17.374	18.150	27.454	20.888	21.902	40.390
295	16.682	17.084	18.459	27.396	20.896	21.694	40.601
300	16.540	17.210	18.389	27.330	20.779	21.737	40.510
305	16.769	16.997	17.977	27.332	20.828	21.698	40.462
310	16.571	17.058	18.254	27.303	21.119	21.917	40.391
315	16.530	17.222	18.088	27.389	20.699	21.696	40.510
320	16.431	16.986	18.182	27.372	20.727	21.702	40.169

Table units µmolal

RUN #	136	137	138	108	109	110	111
pH:	4	4	4	4	4	4	4
Initial conc. (µm)	30.0	30.0	30.0	30.0	30.0	30.0	60.0
solid conc. (mg/kg)	100	100	100	100	100	100	100
Temp: (C°)	50	50	50	70	70	70	70
Time (sec.)							
325	16.588	17.177	18.085	27.330	20.728	21.743	40.154
330	16.533	17.133	18.015	27.355	20.466	21.863	40.420
335	16.408	16.959	17.960	27.278	20.641	21.720	40.143
340	16.257	16.836	17.941	27.156	20.769	21.712	40.248
345	16.137	16.794	17.729	27.151	20.385	21.778	40.284
350	16.418	17.079	17.893	27.067	20.539	21.607	40.290
355	16.213	16.941	17.917	26.977	20.674	21.518	40.221
360	16.348	16.691	17.849	27.087	20.409	21.599	40.009
365	16.063	16.957	17.707	27.025	20.326	21.600	40.184
370	16.113	16.997	17.553	27.064	20.877	21.660	40.052
375	16.443	16.733	17.672	27.022	20.395	21.390	40.018
380	16.266	16.835	17.557	27.004	20.217	21.376	40.053
385	16.236	16.682	17.649	26.971	20.427	21.250	39.842
390	16.117	16.758	17.475	26.894	20.232	21.645	39.394
395	16.602	16.738	17.267	26.793	20.331	21.497	39.703
400	16.172	17.779	17.168	26.740	20.351	21.342	39.844
405	16.286	16.742	17.267	26.788	20.431	21.430	39.546
410	16.224	16.647	17.067	26.818	20.212	21.275	39.659
415	16.082	16.545	17.303	26.754	20.288	21.142	39.383
420	16.144	16.610	17.102	26.612	20.158	21.349	39.226
425	16.256	16.598	17.020	26.583	19.993	21.260	39.547
430	16.240	16.535	17.125	26.569	20.124	21.014	39.584
435	16.230	16.547	17.200	26.520	20.119	21.216	39.342
440	16.222	16.549	17.094	26.456	19.927	21.218	39.365
445	16.286	16.525	16.900	26.450	20.103	21.332	39.268
450	16.169	16.590	17.155	26.520	20.102	21.086	39.357
455	16.243	16.652	16.725	26.559	20.071	21.072	39.195
460	16.375	16.598	16.900	26.562	20.024	21.019	39.240
465	16.030	16.810	16.783	26.569	20.159	21.118	38.975
470	16.360	16.608	16.848	26.501	19.919	20.824	38.996
475	16.116	16.453	17.054	26.468	19.947	20.788	38.906
480	15.893	16.413	16.821	26.386	20.075	20.577	38.989
485	16.136	16.386	16.897	26.331	20.003	20.635	38.631
490	16.138	16.564	16.628	26.302	19.927	20.480	38.838
495	16.008	16.354	16.686	26.235	20.017	20.502	38.794
500	15.981	16.405	16.534	26.220	19.626	20.634	38.554
505	16.185	16.394	16.611	26.180	19.796	20.648	38.418
510	15.831	16.504	16.603	26.213	20.013	20.400	38.454
515	15.787	16.209	16.385	26.111	19.745	20.188	38.394
520	15.983	16.633	16.627	26.077	19.695	20.413	38.222
525	16.170	16.532	16.530	25.960	19.783	20.334	38.166
530	15.768	16.396	16.392	25.882	19.605	20.206	38.083
535	15.776	16.641	16.415	25.914	19.560	20.233	37.876
540	15.642	16.539	16.656	25.798	19.915	20.135	37.822
545	15.827	16.450	16.508	25.778	19.818	20.903	37.953
550	15.681	16.573	16.425	25.739	19.850	20.138	38.151
555	15.777	16.304	16.322	25.648	19.624	20.487	37.700
560	15.732	16.383	16.302	25.642	19.558	19.949	37.687
565	15.709	16.429	16.285	25.778	19.590	20.194	37.614
570	15.886	16.319	16.036	25.705	19.628	20.109	37.483
575	15.691	16.215	16.382	25.613	20.045	20.129	37.406
580	15.780	16.639	16.291	25.538	19.723	19.804	37.600
585	15.763	16.445	16.176	25.582	19.534	19.738	37.452
590	15.828	16.266	16.240	25.522	19.463	19.813	37.577
595	15.425	16.542	16.089	25.444	19.353	19.868	37.669

Regression data from the kinetic experiments.

Sample #	pH	Initial PCP conc. (µm)	HDTMA-clay conc (mg/kg)	Temp. (K)	slope (mg/kg/µm)	y-intercept (mg/kg)	r^2
LN#6-P128	4	20	100	10	9.75E-03	4.61E-01	0.9843
LN#6-P122	4	20	100	10	9.91E-03	3.75E-01	0.9821
102	4	30	100	10	6.53E-03	5.90E-01	0.9690
103	4	30	100	10	8.10E-03	5.65E-01	0.9765
104	4	30	100	10	4.95E-03	5.46E-01	0.9713
133	8	15	200	10	6.66E-03	2.23E-01	0.9584
134	8	15	200	10	4.94E-03	3.31E-01	0.9117
135	8	15	200	10	6.50E-03	3.96E-01	0.9507
LN#6-P146	8	20	100	10	1.13E-02	2.90E-01	0.9058
LN#6-P124	8	20	100	10	9.84E-03	6.51E-01	0.8772
43	4	15	100	25	6.92E-03	1.68E-01	0.9701
80	4	15	200	25	1.10E-02	3.87E-01	0.9118
72	4	15	200	25	8.53E-03	5.29E-01	0.9297
47	4	15	200	25	9.49E-03	3.69E-01	0.9764
92	4	15	300	25	8.28E-03	7.13E-01	0.8664
LN#6-P101	4	20	100	25	8.67E-03	7.98E-01	0.7246
LN#6-114-A	4	20	100	25	9.49E-03	5.83E-01	0.9651
66	4	30	100	25	6.95E-03	3.19E-02	0.9949
44	4	30	100	25	7.84E-03	9.01E-02	0.9941
45	4	30	100	25	6.15E-03	1.34E-01	0.9888
106	4	30	100	25	6.38E-03	3.67E-01	0.9847
105	4	30	100	25	6.41E-03	2.85E-01	0.9907
81	4	30	200	25	1.02E-02	3.45E-01	0.9867
75	4	30	200	25	9.39E-03	3.23E-01	0.9781
94	4	30	300	25	9.76E-03	7.84E-01	0.9411
62	4	60	100	25	6.70E-03	9.25E-02	0.9966
63	4	60	100	25	7.43E-03	1.84E-01	0.9972
64	4	60	100	25	6.26E-03	2.86E-01	0.9953
82	4	60	200	25	1.02E-02	5.00E-01	0.9805
76	4	60	200	25	9.15E-03	3.45E-01	0.9912
95	4	60	300	25	1.15E-02	5.85E-01	0.9857
67	8	15	100	25	7.52E-03	-5.84E-01	0.9297
49	8	15	100	25	5.93E-03	3.06E-01	0.8754
53	8	15	100	25	7.65E-03	1.63E-01	0.9264
50	8	15	100	25	7.16E-03	3.27E-01	0.9441

Regression data from the kinetic experiments.

Sample #	pH	Initial PCP conc. (µm)	HDTMA-clay conc (mg/kg)	Temp. (K)	slope (mg/kg/µm)	y-intercept (mg/kg)	r^2
84	8	15	200	25	8.53E-03	6.65E-01	0.7233
84	8	15	200	25	8.53E-03	6.65E-01	0.7233
77	8	15	200	25	9.89E-03	2.68E-01	0.9031
77	8	15	200	25	9.89E-03	2.68E-01	0.9031
123	8	15	200	25	8.28E-03	4.50E-01	0.9193
123	8	15	200	25	8.28E-03	4.50E-01	0.9193
124	8	15	200	25	1.26E-02	1.83E-01	0.9428
124	8	15	200	25	1.26E-02	1.83E-01	0.9428
125	8	15	200	25	9.23E-03	3.50E-01	0.9492
125	8	15	200	25	9.23E-03	3.50E-01	0.9492
89	8	15	300	25	9.99E-03	4.27E-01	0.9237
51	8	30	100	25	1.10E-02	-4.26E-01	0.8376
68	8	30	100	25	9.28E-03	-6.20E-01	0.9538
52	8	30	100	25	6.55E-03	2.77E-01	0.8847
78	8	30	200	25	1.01E-02	4.06E-01	0.8930
85	8	30	200	25	7.90E-03	3.68E-01	0.9549
90	8	30	300	25	9.28E-03	7.77E-01	0.8800
69	8	60	100	25	6.87E-03	-2.31E+00	0.8830
70	8	60	100	25	9.28E-03	-1.73E+00	0.9367
79	8	60	200	25	7.88E-03	-1.36E-01	0.9727
86	8	60	200	25	6.64E-03	4.37E-01	0.9171
91	8	60	300	25	9.81E-03	4.77E-01	0.8954
LN#6-P130	4	20	100	40	1.15E-02	6.53E-01	0.8950
LN#6-P132	4	20	100	40	1.13E-02	5.87E-01	0.9557
LN#6-P134	8	20	100	40	1.78E-02	1.25E+00	0.8700
LN#6-P136	8	20	100	40	6.99E-03	1.14E+00	0.7655
137	4	30	100	50	6.13E-03	9.09E-01	0.9625
138	4	30	100	50	3.97E-03	6.88E-01	0.9821
136	4	30	100	50	6.20E-03	7.99E-01	0.9821
140	8	15	200	50	1.35E-02	8.50E-01	0.7441
141	8	15	200	50	9.22E-03	9.25E-01	0.7527
139	8	15	200	50	6.74E-03	1.01E+00	0.8472
108	4	30	100	70	1.92E-03	4.30E-01	0.9363
110	4	30	100	70	2.31E-03	8.69E-01	0.7597
109	4	30	100	70	4.01E-03	7.43E-01	0.8171
111	4	60	100	70	3.99E-03	8.49E-01	0.9638
116	8	15	200	70	1.90E-02	1.31E+00	0.6494
115	8	15	200	70	1.39E-03	1.75E+00	0.1121
117	8	15	200	70	5.27E-03	1.05E+00	0.8922