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EXPERIMENTAL STUDY OF 2,4,6-TRICHLOROPHENOL AND PENTACHLOROPHENOL SOLUBILITIES IN AQUEOUS SOLUTIONS: DERIVATION OF A SPECIATION-BASED CHLOROPHENOL SOLUBILITY MODEL

Peter G. Wightman

July, 1997

A thesis submitted to the Faculty of Graduate studies
and Research in partial fulfillment of the
requirements of the degree of Master of Science

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PREFACE

The following is an excerpt from the "Guidelines Concerning thesis Preparation", as required by the Faculty of Graduate Studies and Research at McGill University:

> Candidates have the option of including, as part of the thesis, the text of one or more papers submitted to be submitted for publication, or the clearly duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.
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> If this option is chosen, **connecting texts that provide logical bridges between the different papers are mandatory**. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of papers must be integrated.
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>
> Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.
>
> In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make and explicit statement in the thesis as to who contributed to such work and to what extent**. Supervisors must attest to the accuracy of such statements at doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all authors of the co-authored papers.

Research presented in this thesis represents original research by the author in collaboration with his supervisor, Dr. Jeremy B. Fein. The thesis is divided into three chapters, the first of which being a general introduction, followed by a manuscript and conclusion. The manuscript in chapter 2 will be submitted to *Applied Geochemistry*, following final modifications. The manuscript is co-authored by Prof. Jeremy B. Fein, who proposed the research topic, advised and assisted in the establishment of the experimental methodology and interpretation of data. The majority of the experimental work and all of the analysis were completed by the author. A number of undergraduate students (Aurèle Larrivé, Rita Mansour, and Carlo Papa), co-supervised by the author and Dr. Fein, provided additional laboratory assistance throughout the duration of the project.

ABSTRACT

In this study, we report the experimentally-determined solubility of 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP), and we derive a speciation-based model for estimating the solubilities of other chlorophenols. At 25°C, the log molality of the protonated species of 2,4,6 TCP is -2.8±0.2, whereas for PCP the value is –5.1±0.4. The pK_a values that best fit the solubility data for 2,4,6 TCP and PCP are 6.0±0.3 and 4.5±0.5, respectively. At 55°C, the log molality of protonated PCP increases to -4.7±0.2 and the pK_a value decreases to 4.1 ± 0.3. Addition of a Na-chlorophenol aqueous species to the model improves the fit to each dataset and, at 25°C, we calculate log stability constants values for $NaPCP^\circ$ and $NaTCP^\circ$ of 1.1 ± 0.5 and 0.9 ± 0.4, respectively. At 55°C, the stability constant for $NaPCP^\circ$ is 0.7 ± 0.4. The results of this study enable estimations of chlorophenol solubilities under a wide range of conditions of environmental interest.

SOMMAIRE

Dans cette étude, nous déterminons la solubilité du trichlorophénol 2,4,6 (2,4,6-TCP) et du pentachlorophénol (PCP), nous derivons ensuite un modèle basé sur la spéciation afin d'estimer les solubilités des autres chlorophénols. À 25°C, le log de la molalité de l'espèce protonnée du 2,4,6 TCP est –2.8±0.2, tandis que celle du PCP est de –5.1±0.4. Les valeurs de pK_a qui correspondent le mieux aux données de solubilité pour le 2,4,6 TCP et le PCP sont 6.0±0.3 et 4.5±0.5 respectivement. À 55°C, le log de la molalité du PCP protonnée augmente à -4.7±0.2 et la valeur du pK_a diminue à 4.1±0.3. L'addition d'un complexe aqueux de Na-chlorophénol, lors de la modélisation, améliore la correspondance avec chaque base de données et, à 25°C, le log de la constante de stabilité pour $NaPCP^\circ$ et $NaTCP^\circ$ est 1.1±0.5 et 0.9±0.4, respectivement. À 55°C, la constante de stabilité pour $NaPCP^\circ$ est 0.7±0.4. Les résultats de nos expériences et notre revue nous permettent d'estimer les solubilités du chlorophénol pour une gamme élargie de conditions environnementales.

ACKNOWLEDGEMENTS

I would like to take this opportunity to offer my most heartfelt thanks to my supervisor, Dr. Jeremy B. Fein, whose constant optimism, encouragement, and invaluable guidance has made my time here at McGill both productive and enjoyable. I could not have had a better supervisor and consider myself lucky to have worked on many interesting projects with him.

I would also like to extend thanks to Lawrence Yane, Jean-François Boily, and Chris Daughney for may intriguing discussions on our group's research projects. I would also like to acknowledge Professors Williams-Jones, Mucci, and Paquette for their contributions of general geochemical knowledge.

Special thanks go out to Aurelle Larrive, Rita Mansour, and Carlos Papa for their laboratory assistance on this project. I also thank Alain, Louis, Eddy, Alex, and Gavin for their laboratory assistance on other projects, which afforded me the time to become involved in a number of projects whilst still devoting a substantial amount of time towards my teaching assistantships and this project.

My gratitude goes out to my friends; Leyla, Larry, Dave, Sandy, Jody, Erin, Kim, Jim, Annick, Sharon, Kristy, and many others who have made my life outside of work very enlightening.

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CHAPTER 1

INTRODUCTION

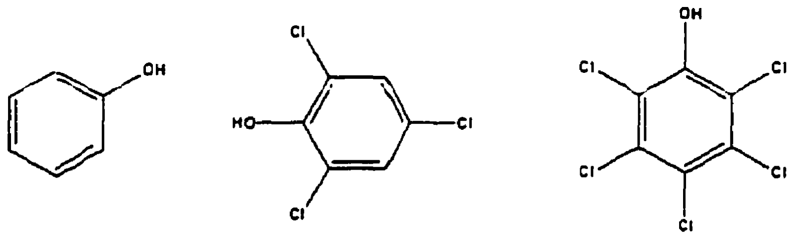
In order to remediate anthropogenic contamination of surface and ground waters, we must develop methodologies to determine the eventual fate of contaminants in the environment. One such methodology requires the knowledge of the physical and chemical properties of, and interactions between, all the components of a particular contaminated system. If these physical and chemical properties of the contaminants and various components of the soil and rock that they are in contact with are known, then the mobility and fate of the contaminant can be evaluated in a wide range of natural environments.

The migration of contaminants in the subsurface is mediated by both physical and chemical processes. The physical controls on groundwater flow are advection and hydrodynamic dispersion. These controls can be quantified through a series of equations based on Darcy's law (Freeze and Cherry, 1979). We have a reasonable understanding of these physical controls, and we can apply this understanding to model the physical transport of a contaminant in three dimensions. The chemical controls on contaminant mobility are less well-understood. The chemical parameters controlling contaminant migration are diffusion, adsorption, aqueous complexation, and organic matter partitioning. All of these chemical processes are dependent on the amount of contaminant in the system, which, in highly contaminated areas is controlled by the solubility of the chemical in question.

Phenol and chlorinated phenols are common contaminants in surface and groundwater systems. There are numerous sites of chlorinated phenol groundwater pollution due to their presence in creosote, which is or was used as a wood preservative all over the world. As a result of this extensive contamination and because of the toxic and carcinogenic effects of this class of chemicals, phenol, 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP) are listed as

EPA priority pollutants. (Keith and Telliard, 1979). In addition to the soil, soil vapour, surface and near-surface water pollution caused by their use as wood preservatives, phenol and chlorinated phenols are often constituents of the liquid waste that is disposed of by deep-well injection into aquifers at elevated temperatures (EPA, 1990). Despite the widespread occurrence of phenol and chlorinated phenols as contaminants, their solubility is not well-known in the environments of interest. This study addresses uncertainties associated with the solubility behaviour of the chlorophenols as a function of a number of environmental parameters, including: acidity of solution, ionic strength of the media, and temperature.

This study examines the solubility behavior of chlorinated phenols. The chemical structure of the phenols consists of a benzene-type ring with a phenolic (OH) group at position one. In the chlorinated phenols, one or more of the hydrogen atoms bonded to the carbon atoms is replaced by a chlorine atom. The structure of phenol, 2,4,6-trichlorophenol and pentachlorophenol are depicted in the diagrams below:



Phenol *2,4,6-Trichlorophenol* *Pentachlorophenol*

Figure 1: Chemical structure of the phenols.

The objectives of this study are to: 1) constrain the aqueous solubilities of 2,4,6-TCP and PCP with reversed experiments, 2) use this experimental data to develop a speciation-based solubility model for all of the chlorophenols, and 3) estimate the stability constants for Na-chlorophenol aqueous complexes.

CHAPTER 2

EXPERIMENTAL STUDY OF 2,4,6-TRICHLOROPHENOL AND PENTACHLOROPHENOL SOLUBILITIES IN AQUEOUS SOLUTIONS: DERIVATION OF A SPECIATION-BASED CHLOROPHENOL SOLUBILITY MODEL

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ABSTRACT

Despite the widespread occurrence of chlorophenols as groundwater contaminants, the aqueous solubilities of the chlorophenols are not well-characterized. In this study, we report the solubility of 2,4,6-Trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) based on experiments conducted as a function of pH, ionic strength and temperature, and we derive a speciation-based model for estimating the solubilities of other chlorophenols.

Narrow constraints on the aqueous solubility of both chlorophenols were made possible by conducting experiments in pure water and in 0.1 NaCl at 25°C and 55°C, from both under- and over-saturation. The solubility of the chlorophenols is pH independent under low pH conditions, and increases with increasing pH. Two properties were used to model the solubility as a function of pH: the concentration of the protonated chlorophenol species and the acidity constant (K_a) of the chlorophenol of interest. At 25°C, the log molality of the protonated species of 2,4,6 TCP is -2.8±0.2, whereas for PCP the value is -5.1±0.4. The pK_a values that best fit the solubility data for 2,4,6 TCP and PCP are 6.0±0.3 and 4.5±0.5, respectively. At 55°C, the log molality of protonated PCP increases to -4.7±0.2 and the pK_a value decreases to 4.1 ± 0.3. The differences between the pure water and 0.1M NaCl experiments cannot be fully explained by ionic strength effects, and the increased solubiltiy of the chlorophenols must be due, in part, to the presence of a Na-chlorophenol aqueous complex. Addition of this species to the model improves the fit to each dataset and allows us to determine the log stability constant for these complexes. At 25°C, the log stability constants for $NaPCP^{\circ}$ and $NaTCP^{\circ}$ are 1.1 ± 0.5 and 0.9 ± 0.4, respectively. At 55°C, the stability constant for $NaPCP^{\circ}$ is 0.7 ± 0.4.

Experimental solubility measurements are used to construct a theoretical model which defines the solubility of a chlorophenol in terms of its acidity constant and its low pH minimum solubility. A van't Hoff relationship is used to model the temperature dependence of the solubility behavior. This approach enables estimations of the aqueous solubility of other chlorophenol molecules as a function of pH, ionic strength and temperature. In order to facilitate application of this model to other chlorophenol molecules, we compile and critically review the chlorophenol solubility data that exists in the literature. In some cases, if the studies do not report them, we re-interpret the solubility data in order to yield pK_a and protonated species solubility values for most of the 20 chlorophenols. The results of our experiments and review enable estimations of chlorophenol solubilities under a wide range of conditions of environmental interest.

INTRODUCTION

Phenol and chlorinated phenols are common in contaminated surface and groundwater systems. Due to their presence in creosote, which is or was used as a wood preservative in at least 700 sites in the United States and Canada alone, chlorophenols are found as groundwater pollutants at numerous sites (e.g., Mueller et al, 1989; Pollard et al, 1993). As a result of this extensive contamination and the noted toxic and carcinogenic effects of this class of chemicals (Howard, 1989; 1991; Van Gestel et al., 1996), phenol, 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP) are listed as EPA priority pollutants (Keith and Telliard, 1979). In addition to the surface and near-surface water pollution caused by their use as wood preservatives, phenol and chlorinated phenols are often constituents of the liquid waste that is disposed of by deep-well injection into sedimentary aquifers at elevated temperatures (EPA, 1990). Despite the widespread occurrence of phenol and chlorinated phenols as contaminants, the physico-chemical properties which affect the mobilities of the molecules in groundwater systems are, in many cases, not well-characterised. One of the most fundamental properties that affects contaminant transport is solubility, and this study addresses uncertainties associated with the solubility behaviour of the chlorophenols.

The chemical behaviour and environmental fate of the phenols is strongly dependent on the speciation of the molecule in solution. The phenols are organic acids, and therefore, the extent of deprotonation varies with pH:

$$C_6H_5OH^{\circ}{}_{(aq)} \Leftrightarrow C_6H_5O^{-}{}_{(aq)} + H^{+}{}_{(aq)} \tag{1}$$

The mass action equation for reaction (1) is expressed as:

$$K_a = \frac{[C_6H_5O^-]\gamma_{C_6H_5O^-}[H^+]\gamma_{H^+}}{[C_6H_5OH^{\circ}]} \tag{2}$$

where K_a is the equilibrium (acidity) constant for reaction (1), γ represents the activity coefficient of the subscripted aqueous species, and the brackets represent the molality of the enclosed aqueous species.

In general, the acidity constant values for chlorinated phenols increase markedly as chlorine atoms are included on the benzene ring structure. For chlorophenols with the same number of chlorine substitutions, the values also increase with increasing proximity of the substituted chlorine atom(s) to the OH group (Kishino and Kobayashi, 1994). For instance, the negative log of the acidity constant (pK_a) for phenol is 9.9, while that of 2,4,6-TCP is 6.0, and that of PCP is 4.7 (Callahan, 1979). Therefore, under the typical near-neutral pH conditions that exist in most groundwater systems, the phenol molecule is completely protonated, while the chlorinated phenols are deprotonated to varying extents. This difference in the extent of protonation causes differences in the chemical behaviour, and hence the subsurface mobilities, of the chlorophenols. The uncharged protonated molecule is relatively hydrophobic and electrostatically inert, while the negatively charged deprotonated molecule is more influenced by electrostatic interactions. The deprotonated species, due to increased ability to be solvated by water, has a higher solubility than does protonated chlorophenol, and can form aqueous complexes with free cations in solution (Fein, 1996; Daughney and Fein, 1997). These differences also lead to different adsorption behaviours (Shimizu et al, 1992; Schellenberg et al, 1984) and organic phase partitioning behaviours (Westall et al, 1985; Jafvert et al, 1990) between the phenols. The extent to which aqueous complexation, mineral surface adsorption, or organic phase partitioning affects phenol and chlorophenol mobilities is strongly influenced by the overall solubility of the molecules in the fluid-rock systems of interest.

The solubility of the chlorophenols can be represented by the following equilibrium reactions:

$$HCP_{(s)} \Leftrightarrow HCP^{\circ}{}_{(aq)} \qquad (3)$$

$$HCP_{(aq)} \Leftrightarrow CP^{-}{}_{(aq)} + H^{+}{}_{(aq)} \qquad (4)$$

Under pH conditions where the protonated species (HCP°) dominates (at pH << pK_a), the solubility is defined by reaction (3), and should be independent of pH. At higher pH values, the solubility increases with increasing pH as more of the chlorophenol deprotonates according to reaction (4).

Previous experimental chlorophenol solubility measurements suggest that the above general description of the pH dependence of chlorophenol solubility is valid. However, there is considerable uncertainty regarding the values of the equilibrium constants for reactions (3) and (4) for each of the chlorophenols. The results of these previous solubility studies are depicted in Figures 1 and 2 for 2,4,6-TCP and PCP, respectively. The results depicted in Figures 1 and 2 are from experiments conducted at a variety of temperatures, atmospheric conditions, and in various concentrations of electrolytes. The differences in experimental conditions and analytical methods used leads to considerable scatter in the data, especially in the low pH region where, for instance, the PCP data cover a range of over one log molality unit. In addition, none of the previous experimental solubility measurements were reversed, and hence none of the studies demonstrate that thermodynamic equilibrium was attained during the experiments.

The effect of temperature on the solubility of phenol and chlorinated phenols is relatively unknown, since few reliable studies have been conducted, and those that have (Achard et al, 1996; Mulley and Metcalf, 1966; Blackman et al, 1955; Carswell and Nason, 1938; Sidgewick and Turner, 1922) have failed to give detailed information on their solution compositions and analytical methods. We can qualitatively estimate the temperature dependence of chlorophenol solubility by comparison to the temperature dependence of the solubility of quartz because aqueous silica and chlorophenol species display similar pH dependent speciation. That is, like aqueous phenols, under acidic to neutral pH conditions, aqueous silica is present as a neutral species (SiO_2°), but at high pH values, a negatively charged species ($H_3SiO_4^-$) dominates. Because of these similarities, it is likely that the temperature dependence of phenol and chlorophenol solubilities are similar to that of quartz, which exhibits a strong positive correlation between increasing temperature and solubility (e.g., Walther and Helgeson, 1977). This positive correlation between temperature and solubility is related to the effect of temperature on the polarity of the water molecule: increasing temperature decreases the polarity of water molecules, favouring solvation of neutral aqueous species.

The objective of this study is to conduct controlled, reversed solubility experiments which place rigorous constraints on the thermodynamic stabilities of the aqueous chlorophenol species, and which determine the solubility behaviour of the chlorophenols as functions of temperature, pH, and ionic strength. These results are crucial for modelling the fate and transport of chlorophenols in contaminated groundwater systems.

EXPERIMENTAL PROCEDURES

Materials Used

Pentachlorophenol (99% pure) and 2,4,6-trichlorophenol (98% pure) were obtained from Aldrich Chemical Company (Milwaukee, Wis., U.S.A.) and were used without additional purification. The trichlorophenol was ground with a mortal and pestle, and then passed through a 60 mesh sieve to increase the surface area in contact with the solution. The pentachlorophenol was used as supplied by the manufacturer, since the grain size was already sufficiently small. All experiments were conducted with distilled, de-ionized (DDI) water with an electrical resistance of greater than 18 megaohm. All other chemicals used were reagent grade.

Types of Experiments

Solubility experiments were conducted from both over- and under-saturation. In the oversaturation experiments nitric acid was added to relatively basic solutions that had previously been equilibrated to contain high concentrations of dissolved chlorophenol. Because chlorophenol solubility decreases with decreasing pH, the addition of the acid forced the precipitation of the chlorophenol, and adjusted the pH to the desired lower pH value. The procedure for the undersaturation experiments consisted of the addition of excess solid chlorophenol to chlorophenol-free aqueous solutions of different acidity. Additional adjustment of pH in the undersaturation experiments was achieved by titrating small amounts of 0.979 M sodium hydroxide or 0.981 M HNO_3 into the experimental solutions; producing experiments that spanned the pH region between 2 and 8. In addition, the over- and under-saturation experiments were conducted using two different media: 0.1M sodium chloride and pure water (without any dissolved electrolyte).

Each individual experiment was conducted in a 125 ml Teflon® bottle, stirred on a daily basis, and sampled periodically. The solution pH of each sample was measured at the temperature of the experiment, and pH calibration was conducted using buffer solutions also maintained at the temperature of the experiment. pH measurement was achieved with an Fisher Scientific Accumet 25 pH meter equipped with either gel or potassium chloride-filled combination electrodes at 25°C. At 55°C, only potassium chloride-filled electrodes were used since performance of the gel-filled electrodes deteriorated noticeably in the heated solutions.

The temperature of the experiments was controlled by a water bath at room temperature and a thermostatic bath at 55°C, which maintained the desired temperature within 1°C. Atmospheric CO_2 was not excluded from the experimental solutions. However, to avoid the photo-oxidative breakdown of trichlorophenol, these experiments were isolated from light by wrapping the reaction bottles in aluminium foil; pentachlorophenol experiments were also kept out of direct light, but not foil-wrapped. The solutions within the reaction vessels were sampled repeatedly for up to 90 days until a solubility plateau was reached. Each sample (approximately 5 ml) was passed through a 0.1 um cellulose-membrane filter before being basified with 0.1 ml of 6.0M sodium hydroxide for later analysis.

Analysis

The concentration of chlorophenol in solution was determined using high-performance liquid chromatography (HPLC). A Hewlett-Packard 1050 series HPLC system, consisting of a quaternary pump, a variable wavelength detector (set at 213 nm) and a Spectra-Physics SP8880 autosampler fitted with either 10, 20, or 100 ul sample loops, was used for chlorophenol determination. Separation was achieved using an ODS hypersil column (purchased from Hewlett Packard) at room temperature. The mobile phase consisted of a 10-75% stepwise acetonitrile gradient in water (adjusted to a pH of 2 with H_3PO_4). The flow rate was set at 2 ml/min for 7 minutes. Standard solutions spanning the entire concentration range of the experiments were prepared in the same matrix and with the same approximate pH as the samples ($pH \approx 11-12$). There were no observable breakdown products (i.e. all peaks were accounted for) detected during the analysis. The reproducibility of the peak area was better than 1% for the higher concentrations; however, for the low concentrations (near the minimum solubility of the phenol in question) the standard deviation was 5-30%.

RESULTS

Kinetics

Figure 3 depicts a typical concentration profile as a function of time for over- and under-saturation experiments conducted at two different pH values. Experiments were not continuously stirred so that solution saturation would occur over a number of weeks. This allowed us to observe a slow progression of dissolved chlorophenol towards a plateau at the solubility limit for specific pH and chlorophenol, as shown in the figure. In the undersaturation experiments, a continuously increasing aqueous concentration was observed and the concentration of chlorophenol was never observed to exceed the solubility limit. The oversaturation experiments were initially supersaturated, but as the pH of the solution was lowered beyond the equilibrium pH (by the initial addition of acid) the solution became undersaturated and then continued to approach equilibrium in the same manner as the undersaturation experiments. The oversaturation experiments generally equilibrate faster than the undersaturation experiments. This is likely due to the size and shape of the solid chlorophenols present in the experiments. In the oversaturation experiments, the precipitate is extremely fine and flaky, whereas, the solids used in the undersaturation experiments were relatively coarse and granular. In all cases, however, equilibrium was attained within 60 days. We continued the experiments until at least 3 samples were taken on the solubility plateau, and we average the solubility plateau chlorophenol concentrations to yield the equilibrium chlorophenol solubility value under each experimental condition.

The total concentrations of nitrate, chlorine and sodium added to the experiments are listed in Table 1. The solubilities of the two chlorophenols are shown in Figures 4, 5, and 6 as functions of pH. The solubility is independent of ionic strength and pH at extremely low pH. At 25°C, the molality of dissolved chlorophenol increases from this minimum solubility at low pH ($10^{-5.1\pm0.2}$ for PCP and $10^{-2.8\pm0.1}$ for 2,4,6-TCP) to steadily increasing values at higher pH, with an approximately linear relationship between log molality and pH above the pK_a of each chlorophenol. Under high pH, high total Na conditions, however, the log molality versus pH slope increases and becomes non-linear. It is possible that this non-linear increase in solubility with increasing pH is a result of the presence of a sodium chlorophenol aqueous complex which increases the total chlorophenol solubility as the concentration of the chlorophenolate and total sodium increases.

The PCP solubility experiments conducted in a 0.1M electrolyte are in good agreement over the entire pH range with the measurements conducted by Arcand et al. (1996), who used an experimental procedure similar to that of our over-saturation experiments. Other previous PCP studies overestimated the aqueous solubilities by as much as an order of magnitude under low pH conditions. The 2,4,6-TCP study conducted by Yoshida et al (1987) is consistent with our data under low pH conditions, despite the slight temperature difference in experimental conditions (20°C as opposed to 25°C). The data sets are consistent at higher pH values as well, but the solubility is not well-constrained by the data of Yoshida et al. (1987) since their study only conducted experiments in pure water from oversaturation. Because our study is the first to demonstrate the attainment of equilibrium through experimental solubility reversals and time-dependent sampling, it is likely that our data most accurately reflect the pH and ionic strength dependence of the studied chlorophenols.

At 55°C, the PCP solubility behaviour as a function of pH is similar to those observed at 25°C for 2,4,6-TCP and PCP. The minimum solubility of PCP at 55°C is a factor of 2.4 higher than the 25°C value, with a molality of $10^{-4.7\pm0.2}$. In addition, the departure from pH-independent solubility behaviour occurs at a noticeably lower pH than at 25°C, suggesting that the pK_a value and/or the stability of the possible Na-complex for PCP changes with increasing temperature. Comparison of our 55°C data to those of previous studies is difficult because other studies of chlorophenol solubilities at elevated temperatures do not cite the pH and ionic strength conditions of their experimental solutions.

THERMODYNAMIC MODELLING

The thermodynamic treatment of our data employs a standard state for all aqueous species of a hypothetical one molal solution with unit activity at the temperature and pressure of interest. The standard states for solid chlorophenol and for water are the pure phases at the temperature and pressure of interest. All aqueous concentrations are listed in terms of molality, and molal activity coefficients are used to quantify the changes in activity with respect to the standard state. Activity coefficients for all neutral species are assumed to equal unity. Activity coefficients of charged species are calculated using an extended Debye-Hückel equation:

$$\log(\gamma_i) = \frac{-Az_i^2\sqrt{I}}{1+Ba\sqrt{I}} + bI \qquad \textbf{(5)}$$

where I represents the ionic strength of the solution, z is the charge of the ionic species of interest, and where values for Debye-Hückel parameters A, B and b at the temperature of interest, and the value for a, the electrolyte size parameter, are given in Helgeson et al. (1981).

The equilibria which constrain the aqueous chemistry in the experimental systems are the following:

$$HCP_{(s)} \Leftrightarrow HCP^{\circ}_{(aq)} \qquad (6)$$

$$HCP^{\circ}_{(aq)} \Leftrightarrow CP^{-}_{(aq)} + H^{+}_{(aq)} \tag{7}$$

$$CO_{2\,(g)} + H_2O \Leftrightarrow H_2CO_3{}^{*}{}_{(aq)} \tag{8}$$

$$H_2CO_3{}^{*}{}_{(aq)} \Leftrightarrow HCO_3{}^{-}{}_{(aq)} + H^{+}_{(aq)} \tag{9}$$

$$HCO_3{}^{-}{}_{(aq)}) \Leftrightarrow CO_3{}^{2-}{}_{(aq)} + H^{+}_{(aq)} \tag{10}$$

$$NaCl^{\circ}_{(aq)} \Leftrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} \tag{11}$$

$$HCl^{\circ}_{(aq)} \Leftrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} \tag{12}$$

$$NaOH^{\circ}_{(aq)} \Leftrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)} \tag{13}$$

$$HNO_3{}^{\circ}{}_{(aq)} \Leftrightarrow H^{+}_{(aq)} + NO_3{}^{-}{}_{(aq)} \tag{14}$$

$$NaNO_3{}^{\circ}{}_{(aq)} \Leftrightarrow Na^{+}_{(aq)} + NO_3{}^{-}{}_{(aq)} \tag{15}$$

$$H_2O \Leftrightarrow H^{+}_{(aq)} + OH^{-}_{(aq)} \tag{16}$$

The mass action equations for these equilibria are as follows:

$$K_{(6)} = [HCP^{\circ}] \tag{17}$$

$$K_{(7)} = \frac{[CP^{-}]\gamma_{CP^{-}}[H^{+}]\gamma_{H^{+}}}{[HCP^{\circ}]} \tag{18}$$

$$K_{(8)} = \frac{[H_2CO_3^{*}]}{f_{CO_2}} \tag{19}$$

$$K_{(9)} = \frac{[HCO_3^{-}]\gamma_{HCO_3^{-}}[H^{+}]\gamma_{H^{+}}}{[H_2CO_3^{*}]} \tag{20}$$

$$K_{(10)} = \frac{[CO_3^{2-}]\gamma_{CO_3^{2-}}[H^{+}]\gamma_{H^{+}}}{[HCO_3^{-}]\gamma_{HCO_3^{-}})} \tag{21}$$

$$K_{(11)} = \frac{[Na^{+}]\gamma_{Na^{+}}[Cl^{-}]\gamma_{Cl^{-}}}{[NaCl^{\circ}]} \tag{22}$$

$$K_{(12)} = \frac{[H^+]\gamma_{Na^+}[Cl^-]\gamma_{Cl^-}}{[HCl^\circ]} \tag{23}$$

$$K_{(13)} = \frac{[Na^+]\gamma_{Na^+}[OH^-]\gamma_{OH^-}}{[NaOH^\circ]} \tag{24}$$

$$K_{(14)} = \frac{[H^+]\gamma_{H^+}[NO_3^-]\gamma_{NO_3^-}}{[HNO_3^\circ]} \tag{25}$$

$$K_{(15)} = \frac{[Na^+]\gamma_{H^+}[NO_3^-]\gamma_{NO_3^-}}{[NaNO_3^\circ]} \tag{26}$$

$$K_{(16)} = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} \tag{27}$$

where $K_{(i)}$, [i], f_i, and γ_i are the equilibrium constant, molality, fugacity, and activity coefficient, respectively, of the subscripted species. Values for $K_8 - K_{16}$ are well-established, and we use the values given by Martell and Smith (1976) for K_{15} and those by Wolery (1982) for the remainder. Because each species activity, except that of H^+ and $CO_{2(g)}$, is an unknown parameter, and because we consider values for K_6 and K_7 to be unknown as well, $K_{(6)} - K_{(16)}$ are 11 equations, written in terms of 16 unknown parameters. The chemical system is further constrained by the following mass balance constraints:

$$[CP]_{TOTAL} = [HCP^\circ] + [CP^-] \tag{27}$$

$$[Cl]_{TOTAL} = [Cl^-] + [NaCl^\circ] + [HCl^\circ] \tag{28}$$

$$[NO_3]_{TOTAL} = [NO_3^-] + [HNO_3^\circ] + [NaNO_3^\circ] \tag{29}$$

$$[Na]_{TOTAL} = [Na^+] + [NaOH^\circ] + [NaNO_3^\circ] + [NaCl^\circ] \tag{30}$$

Because we know or measure the total concentrations shown in equations 27 through 30, the system is now defined by 15 equations written in terms of 16 unknowns. Note that because we have a system with more unknowns than equations, a single solubility measurement is not sufficient to determine values for K_6 and K_7. We first consider only the low pH experiments for which we can neglect reaction 7. Each low pH experiment (more than 1.5 log units below the pK_a for the particular chlorophenol) yields a distinct value for K_6, and we use the resulting average value in subsequent calculations.

With a value for K_6, a single higher pH solubility measurement can be applied to the set of equations to define a value for K_7. We use a Newton-Raphson iteration technique to solve the non-linear set of equations for each solubility measurement. If the speciation model described above is correct, then the resulting calculated values for K_7 would be independent of pH and Na concentration. In fact, the pK_a (or K_7) values calculated in this manner are relatively constant for experiments with low total Na content, but vary significantly for experiments with high total Na. Experiments with higher total sodium content consistently produce lower pK_a values, and there is a trend of decreasing pK_a values as the pH and sodium content of the solution increase.

There are three major changes occurring as the pH of the experiments increases: 1) there is a higher proportion of deprotonated chlorophenol in solution, as defined by reaction 7, 2) the concentration of Na^+ increases as more NaOH titrant was required to increase the pH to the experimental value, and 3) the ionic strength of the solution increases as a result of both 1) and 2). Increasing the ionic strength from 0.01 to 0.1 decreases the activity coefficient (for a monovalent ion) from 0.90 to 0.78; this increases the modelled solubility by approximately 15% or 0.06 log units. The observed solubility increase, however, is at least 0.3 log units at a given pH at the highest pH values studied. Therefore, we conclude that the observed enhanced solubility cannot be accounted for by the increased ionic strength of the solutions, and must be attributable to the increased chlorophenolate and/or Na^+ activities. These observations are best explained by the presence of a Na-chlorophenolate complex that becomes important at pH values above the pK$_a$, where the majority of the chlorophenol is deprotonated and where sodium concentrations are high as a result of the presence of an electrolyte or increased amounts of titrant.

In order to incorporate the effect of sodium complexation in our model, a 1:1 Na-chlorophenolate complex equilibrium was added to our model:

$$NaCP^{\circ}_{(aq)} \Leftrightarrow Na^{+}_{(aq)} + CP\text{-}_{(aq)} \tag{31}$$

with the associated mass action equation:

$$K_{(31)} = \frac{[Na^{+}]\gamma_{H}.CP^{-}]\gamma_{CP}}{[NaCP^{\circ}]} \tag{32}$$

and the NaCP° species was included in the mass balance equations for total sodium and chlorophenol.

The equilibrium constant for the Na-chlorophenolate complex (K_{31}) is determined using high pH, high [Na] solubility measurements and the already-determined averaged values for [HCP°] and pK$_a$ (the latter obtained from the low Na experiments only). The resulting averaged values of [HCP°], pK$_a$, and the log stability constant for the NaCP° complex, and their 1s deviations, are compiled in Table 3 for both modelling procedures.

The fit of the model to the experimental data is depicted in Figures 4, 5, and 6. The pK$_a$ value for PCP that we calculate from the experimental results is 4.5, a value slightly lower than the accepted value of 4.7. However, there is considerable uncertainty in the literature value, with pK$_a$ values ranging from 4.2 to 4.9 (Arcand et al., 1995). A good fit to the experiments conducted in water is obtained without the need for Na-complexation because of the low Na content of the experimental solutions. However, when the resulting pK$_a$ value is used to model the 0.1M NaCl data (i.e. with additional ionic strength considerations, but without considering

Na-chlorophenolate complexation), the model underestimates the observed solubility. Addition of a $NaPCP^{\circ}$ aqueous complex to the model greatly improves the fit to the 0.1M NaCl data, and does not affect the value of the predicted pK_a obtained from the experiments conducted in pure water. In fact, the agreement between the data and the model which includes $NaPCP^{\circ}$ is better than that depicted in the figures. The data shown in the figures correspond to experiments conducted at a range of Na concentrations due to differences in titrant volumes in each experiment. However, the model is calculated using an intermediate Na concentration of 0.1 molal, which is considerably less than the Na concentration of the highest pH experiments. Therefore, some of the visual discrepancies between the model fits and the data arise from comparing different Na concentrations.

The pK_a value calculated for 2,4,6-TCP from our data is 6.0, a value identical to the accepted literature value. As was done with PCP, the data obtained from the pure water experiments is used to determine the pK_a. This calculated pK_a value was used along with the [$HTCP^{\circ}$], and the high pH 0.1 molal NaCl experimental data, to determine the log stability constant for the $NaTCP^{\circ}$ complex. Because the concentration of Na used in the pure water experiments was quite high (due to the relatively high solubility of 2,4,6-TCP relative to PCP), the pK_a obtained from these experiments was re-evaluated using the stability constant determined for the $NaTCP^{\circ}$ complex. The pK_a value does not change significantly following this re-interpretation, so we can conclude that Na-complexation does not significantly affect the pure water solubility measurements.

The log stability constant values obtained for the Na-chlorophenolate 1:1 aqueous complexes are consistent with log stability constants determined by Daughney and Fein (1997) for other metal-chlorophenolate complexes. The inclusion of our stability constant values on a plot of the log stability constants for 2,4,6 TCP vs. the log stability constants for PCP (Figure 7) leads to a correlation coefficient of 0.983. Our Na-chlorophenolate stability constant values provide a low end constraint on this comparative diagram, allowing for better determination of other relevant metal-chlorophenolate complexes with intermediate thermodynamic stabilities, such as Ca- and Mg-chlorophenolate complexes.

Our value for the pK_a for PCP at 55°C is the only one determined for any chlorophenol at elevated temperature. Few experiments were conducted at high pH with low concentrations of Na because large amounts of NaOH were necessary to fully dissolve the PCP. To account for this, the same re-evaluation procedure was followed as was done with the 25°C TCP experiments. During the multiple re-evaluations, the pK_a value increased from 4.0 (calculated without considering Na-PCP complexation) to a final value of 4.1 (calculated by considering Na-PCP complexation). The log stability constant for $NaPCP^{\circ}$ is constrained only by the two highest pH data points. Therefore, we conclude that aqueous $NaPCP^{\circ}$ complexation is only important at extremely high pH values and high total Na molalities at 55°C, and that the value that we report for the stability constant is poorly constrained. This is further demonstrated in Figure 6, where both the model that uses pK_a values determined without consideration of $NaPCP^{\circ}$ complexation, and the model that is produced by including a $NaPCP^{\circ}$ complex, appear to fit the data equally well. However, since the standard deviation of the pK_a value is decreased by the inclusion of a $NaPCP^{\circ}$ complex, we have reported the $NaPCP^{\circ}$ stability constant value, despite the relatively high uncertainty associated with it.

DISCUSSION

The excellent fit of the models to our experimental data illustrates that we can accurately model the solubility of 2,4,6 trichlorophenol and pentachlorophenol based on five parameters:

pK_a, $[HCP^{\circ}]$, pH, ionic strength, and the extent of metal-chlorphenolate complexation. This success suggests that if the pK_a value and $[HCP^{\circ}]$ are known for any other chlorophenol, its solubility can be estimated with the same approach. We have compiled data for these two parameters for most of the 20 chlorophenols, based on previously reported experiments, in Table 4. Because $[HCP^{\circ}]$ is independent of pH and ionic strength, it can be directly determined from solubility measurements that are conducted at pH values much less than the pK_a of the chlorophenol of interest. However, some previous studies were conducted under higher pH conditions, and the results are reported as a total chlorophenol concentration, rather than specific concentrations of each chlorophenol species. In these cases, manipulation of available data into $[HCP^{\circ}]$ and pK_a is possible if: 1) the pH values of the equilibrated solutions are known, 2) environmental conditions (temperature, system open or closed to atmospheric CO_2) are defined, and 3) the type and concentration of electrolyte used is described. The latter is imperative in order to reference pK_a values to zero ionic strength if they are only reported for finite ionic strength conditions. In this way, we have re-evaluated both the solubility and the pK_a data from a comprehensive chlorophenol solubility study conducted by Ma et al (1993), and the results are shown in Table 4. The effect of possible sodium complexation was not considered in the reinterpretation because Ma et al. do not cite the Na content of their experiments.

With these parameters now available, we can construct a simplified solubility model that can be used to estimate the solubility of any chlorophenol under a wide range of environmental conditions. We start with the assumption that the total aqueous solubility of a chlorophenol is equal to the sum of the molalites of the protonated and deprotonated species, or:

$$[CP]_{TOTAL} = [HCP^{\circ}] + [CP^{-}] \tag{33}$$

Na-chlorophenolate complexation can also be included in the model if it is determined to be significant under the experimental conditions, but is left out here both for simplicity and because it would only be significant for some of the chlorophenols. By rearranging the mass action equation for the deprotonation of chlorophenol (i.e., equation 18) we obtain:

$$[CP^-] = \frac{K_a[HCP^\circ]}{\gamma_{H^+}[H+]\gamma_{CP^-}} \tag{34}$$

and since $\gamma_{H^+}[H^+] = 10^{-pH}$ and $K_a = 10^{-pKa}$, equation 33 can be rewritten as:

$$[CP]_{TOTAL} = [HCP^\circ] + [HCP^\circ] \bullet \left(\frac{10^{(pH-pKa)}}{\gamma_{CP-}} \right) \tag{35}$$

or

$$[CP]_{TOTAL} = [HCP^\circ] \bullet \frac{(1+10^{pH-pKa})}{\gamma_{TCP^-}} \tag{36}$$

Equation 36 enables estimations of chlorophenol solubilities at specified equilibrium pH and ionic strength values, if values for [HCP^o] and pK$_a$ are known.

Temperature Extrapolation

Our study of pentachlorophenol solubility at elevated temperature allows us to evaluate the temperature dependence of the solubility behaviour, using the van't Hoff equation:

$$\ln\left(\frac{K_{T1}}{K_{T2}}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{37}$$

where K_{T1} and K_{T2} represent equilibrium constants at absolute temperatures T_1 and T_2, and ΔH is the standard enthalpy of the reaction, which is assumed to be constant over the temperature range of interest. This may not be the case. Our study only evaluates the solubility at two temperatures, which does not constrain the applicability of the van't Hoff equation in accounting for the temperature dependence. However, in the absence of additional data, the van't Hoff equation should provide reasonable estimates of the temperature dependence in relatively low temperature environments. Substituting the acidity constants determined for PCP at 25 and 55°C, the equation can be solved for ΔH°, yielding a value of 25.0 KJ/mole.

Error Analysis

Measurement of extremely small quantities of organic acids by liquid chromatography leads to significant, but acceptably low, analytical uncertainties. As mentioned previously, the analytical uncertainty was highest (5-30%) when measuring the concentrations of chlorophenol near the minimum solubility limit ($10^{-5.2}$ for PCP and $10^{-3.0}$ for TCP), implying that at these concentrations we are likely approaching the detection limit of the HPLC set-up, and that the non-linear calibration encountered at these concentrations gives rise to relatively high uncertainties associated with analytical results. For experiments where the amount of dissolved chlorophenol exceeds these minimum solubility values by approximately 0.5 log units or more, the analytical uncertainty is considerably less, on the order of 1-2%. The analytical uncertainty in the total chlorophenol measurements is shown in Figures 4,5 and 6 by the size of the data points. The approximate uncertainty in [HCP°], pK_a, and log stability constant for the Na-CP complexes are listed as 1s errors in Table 3. Uncertainty in the concentration of the protonated form includes the analytical uncertainty as well as the error induced by averaging a number of low solubility values. Uncertainty in the modelled pK_a value was calculated by carrying over the error in the minimum solubility value and combining it with the standard deviation of results obtained from the modelling. The errors in the log stability constants of the Na-chlorophenolate aqueous complexes were similarly obtained by inclusion of the error in the pK_a determination.

CONCLUSIONS

Reversed solubility experiments were conducted for 2,4,6-trichlorophenol and pentachlorophenol, placing narrow constraints on the maximum aqueous concentration of these organic acids as functions of pH, ionic strength, aqueous Na concentration, and temperature. Analysis of the experimental data reveals the existence of three distinct forms of chlorophenol in solution, each having different pH dependencies. These three aqueous chlorophenol species exhibit different hydrophobic and electrostatic properties, causing chlorophenol solubility to vary as a function of pH. The solubility of the chlorophenols can be quantified using a speciation-based theoretical model that relates the pK_a of the chlorophenol, log stability constant of the Na-chlorophenolate complex, and the concentration of the neutral chlorophenol species to the chlorophenol solubility in a solution of a particular pH and ionic strength. Fitting the experimental data to this model allows us to determine the pK_a values, [HCP°] concentrations, and the stability constants for the Na-chlorophenolate complexes for TCP and PCP. At room temperature, the concentration of the protonated chlorophenol species is $10^{-2.8\pm0.2}$ and $10^{-5.1\pm0.4}$ molal for 2,4,6 TCP and PCP, respectively. The calculated pK_a values are 6.0±0.3 for 2,4,6 TCP and 4.5±0.5 for PCP. At 55°C, the molality of protonated PCP increases to $10^{-4.7\pm0.2}$ and the pK_a decreases to 4.0 ± 0.3. Log stability constants for a 1:1 Na-chlorophenolate aqueous complex are 0.7 ± 0.4, and 1.1 ± 0.5 for 2,4,6 TCP and PCP, at 25°C, and 0.9 ± 0.4 for PCP at 55°C.

Using the speciation-based solubility model, along with re-evaluated values for low pH chlorophenol solubility and pK_a of other chlorophenols, enables the prediction of the solubility of each type of chlorophenol over a wide range of pH, ionic strength, and temperature conditions. Additional data on Na- and other metal-chlorophenolate aqueous complexes are necessary to account for the effect of these complexes on the solubility of chlorophenols other than those studied here. However, the experimental solubilities reported in this study, and the estimated solubilities based on the speciation-based solubility model, provide quantitative constraints on the solubility, and hence the fate and mobility of chlorophenols in contaminated surface and groundwater systems.

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Table 1: Compositions of Experimental Solutions.

I.D.	Type	Final pH	[PCP]	[Na]	[NO3]	[Cl]
PCP Experiments at 25°C						
1-1	U-H_2O	2.11	-4.951		-1.785	
1-2	U-H_2O	3.07	-4.963		-2.780	
1-3	U-H_2O	4.15	-4.983		-3.800	
1-4	U-H_2O	5.80	-3.783	-3.546		
1-5	U-H_2O	6.57	-3.009	-2.778		
1-6	U-H_2O	7.21	-2.317	-2.003		
2-1	U-NaCl	2.08	-5.211	-1.008	-1.789	-1.008
2-2	U-NaCl	3.12	-5.360	-1.001	-2.777	-1.001
2-3	U-NaCl	4.05	-5.008	-1.001	-3.776	-1.001
2-4	U-NaCl	5.60	-3.673	-0.999		-1.001
2-5	U-NaCl	6.26	-2.989	-0.994		-1.001
2-6	U-NaCl	7.15	-1.977	-0.963		-1.005
3-1	O-NaCl	1.91	-4.944	-0.897	-1.540	-1.017
3-2	O-NaCl	3.13	-5.147	-0.886	-1.716	-1.014
3-3	O-NaCl	4.60	-4.619	-0.881	-1.695	-1.015
3-4	O-NaCl	5.07	-4.203	-0.891	-1.791	-1.011
3-5	O-NaCl	6.38	-2.859	-0.880	-1.789	-1.012
3-6	O-NaCl	7.26	-1.891	-0.874	-2.286	-1.007
TCP Experiments at 25°C						
4-1	U-H_2O	2.83	-2.917		-2.797	
4-2	U-H_2O	2.83	-2.900		-2.796	
4-3	U-H_2O	6.86	-1.757	-1.801		
4-4	U-H_2O	7.88	-0.957	-1.039		
5-1	O-H_2O	3.08	-2.871	-1.040	-1.062	
5-2	O-H_2O	6.06	-2.581	-1.006	-1.043	
6-1	U-NaCl	2.65	-2.707	-1.007	-1.702	-1.007
6-2	U-NaCl	2.63	-2.739	-0.999	-2.696	-0.999
6-3	U-NaCl	6.34	-2.134	-0.998	-3.693	-0.998
6-4	U-NaCl	6.79	-1.740	-0.991		-0.999
6-5	U-NaCl	7.60	-1.007	-0.637		-1.068
7-1	O-NaCl	2.84	-2.879	-0.776	-0.801	-1.077
7-2	O-NaCl	5.23	-2.839	-0.776	-0.802	-1.077
7-3	O-NaCl	7.39	-1.092	-0.742	-0.995	-1.048
7-4	O-NaCl	7.49	-1.030	-0.773	-0.789	-1.079
PCP Experiments at 55°C						
8-1	U-H_2O	1.93	-4.798		-1.703	
8-2	U-H_2O	2.81	-4.701		-2.692	
8-3	U-H_2O	4.16	-4.330		-4.588	
8-4	U-H_2O	5.14	-3.632	-3.658		
8-5	U-H_2O	6.19	-2.581	-2.545		
8-6	U-H_2O	7.10	-1.503	-1.510		
9-1	O-H_2O	2.10	-4.636	-0.842	-0.383	
9-2	O-H_2O	3.70	-4.461	-0.923	-0.948	
9-3	O-H_2O	5.88	-2.899	-0.883	-0.924	
9-4	O-H_2O	6.54	-2.123	-0.891	-0.910	
9-5	O-H_2O	7.33	-0.945	-0.361	-0.426	
9-6	O-H_2O	7.34	-0.925	-0.362	-0.407	

Note: all concentrations are total concentrations, reported in terms of log molality.
'U' implies that equilibrium was approached from undersaturation.
'O' implies that equilibrium was approached from oversaturation.

Table 2: Dissociation Constants used in the Modelling.

Equation #	Value at 25°C	Value at 55°C
8	-1.469[a]	-1.751[a]
9	-6.345	-6.266
10	-10.325	-10.147
11	0.777	N/A
12	0.670	N/A
13	-0.709	-0.715
14	1.303	0.999
15	-0.600[b]	-0.610[c]
16	-13.995	-13.145

[a] $[H_2CO_3]_{are}$ set by $f_{CO2}=10^{-3.5}$ and values for Henry's law constant given by Wolery (1992).

[b] The dissociation constant for $NaNO_3$ is from Martell and Smith (1976).

[c] Value extrapolated from 25°C using van't Hoff equation.

All other dissociation canstants are from Wolery (1992).

N/A implies that the value is not applicable.

Table 3: Thermodynamic Modeling Results

	Temperature	PCP (25°C)	PCP (55°C)	TCP (25°C)
Modelled without Na-complex	log [HCP]	-5.1	-4.7	-2.8
	1s	0.4	0.2	0.2
	pK_a	4.4	4.0	5.9
	1s	0.5	0.4	0.4
Modelled with Na-complex	log K (NaCP°)	1.1	0.9	0.7
	1s	0.5	0.4	0.4
	pK_a	4.5	4.1	6.0
	1s	0.4	0.3	0.3

Table 4: Re-evaluation of solubility data from Ma et al (1993) into [HCP°] using selected pK_a values.

Chlorophenol	pK_a reported in Ma et al (1993)	pK_a reported elsewhere	Average pK_a used for the recalculation	Cited pH	log Total Molality	Re-evaluated log [HCP°]
Phenol	9.92	9.9[a]	9.91	4.6	-0.027	-0.03
2	8.52	8.3[a]	8.41	4.8	-0.743	-0.74
3	8.79	8.9[a]	8.85	4.6	-0.763	-0.76
4	9.37	9.2[a]	9.29	4.6	-0.688	-0.69
2,3	7.71	7.6[a]	7.66	4.9	-1.298	-1.30
2,4	7.90	7.8[a]	7.85	5.1	-1.468	-1.47
2,5	-	7.3[a]	7.30	-	-	-
2,6	6.78	6.6[a]	6.69	4.5	-1.79	-1.80
3,4	8.62	-	8.62	5.1	-1.246	-1.25
3,5	8.25	-	8.25	4.7	-1.343	-1.34
2,3,4	6.97	-	6.97	5.1	-2.334	-2.34
2,3,5	-	7.4[b]	7.40	-	-	-
2,3,6	-	6.6[b]	6.60	4.5	-2.524	-2.53
2,4,5	6.72	6.9[a]	6.81	4.9	-2.48	-2.49
2,4,6	5.99	6.0[a]	6.00	4.7	-2.445	-2.47
3,4,5	-	7.84[c]	7.80	-	-	-
2,3,4,5	5.64	-	5.64	4.9	-3.145	-3.22
2,3,4,6	5.22	5.2[a]	5.21	5.1	-3.103	-3.35
2,3,5,6	5.03	-	5.03	5.0	-3.37	-3.65
PCP	4.74	4.69[d]	4.72	4.8	-4.161	-4.49

No experiments were conducted with 2,5-MCP, 2,3,5-TCP, or 3,4,5-TCP.

[a] Kishino and Kobayashi (1994)

[b] mid-range of values given by Arcand et al (1995)

[c] Dean (1992)

[b] Chamberlain et al (1996)

FIGURE CAPTIONS

Figure 1: Summary of previous solubility studies for PCP at room temperature.

Figure 2: Summary of previous solubility studies for 2,4,6-TCP at room temperature. Dashed curve represents the model fit proposed by Yoshida et al (1987) based on a pK_a of 6.06.

Figure 3: The typical time dependence of PCP concentration for selected under- and over-saturation solubility experiments at 25°C, 0.1 molal NaCl electrolyte.

Figure 4: PCP solubility data at 25°C. Size of symbols depicts the uncertainty in the total PCP concentration. Model fits to the data are shown: dashed curve is model with pKa of 4.5 and $[Na]_{TOTAL}$ equal to zero; dot-dashed curve is model with pKa of 4.5 and $[Na]_{TOTAL}$ and $[Cl]_{TOTAL}$ equal to 0.1 molal; and solid curve is same as previous with the addition of a $NaPCP^{\circ}$ complex with a log stability constant of 1.1.

Figure 5: 2,4,6-TCP solubility data at 25°C. Size of symbols depicts the uncertainty in the total TCP concentration. Model fits to the data are shown: dashed curve is model with pKa of 6.0 and $[Na]_{TOTAL}$ equal to 0.1 molal; solid curve is model with pKa of 6.0 and $[Na]_{TOTAL}$ and $[Cl]_{TOTAL}$ equal to 0.1 molal; and dot-dashed curve is same as previous with the addition of a $NaTCP^{\circ}$ complex with a log stability constant of 0.7.

Figure 6: PCP solubility data at 55°C. Size of symbols depicts the uncertainty in the total PCP concentration. Model fits to the data are shown: solid curve is model with pKa of 4.0 and $[Na]_{TOTAL}$ equal to 0.1 molal; dotted curve is model with pKa of 4.1 and $[Na]_{TOTAL}$ equal to 0.1 molal; and dashed curve is same as previous with the addition of a $NaPCP^{\circ}$ complex with a log stability constant of 0.9. Note: all models appear to fit the data equally well.

Figure 7: Correlation between experimentally-determined metal-PCP and metal-TCP log stability constant values.

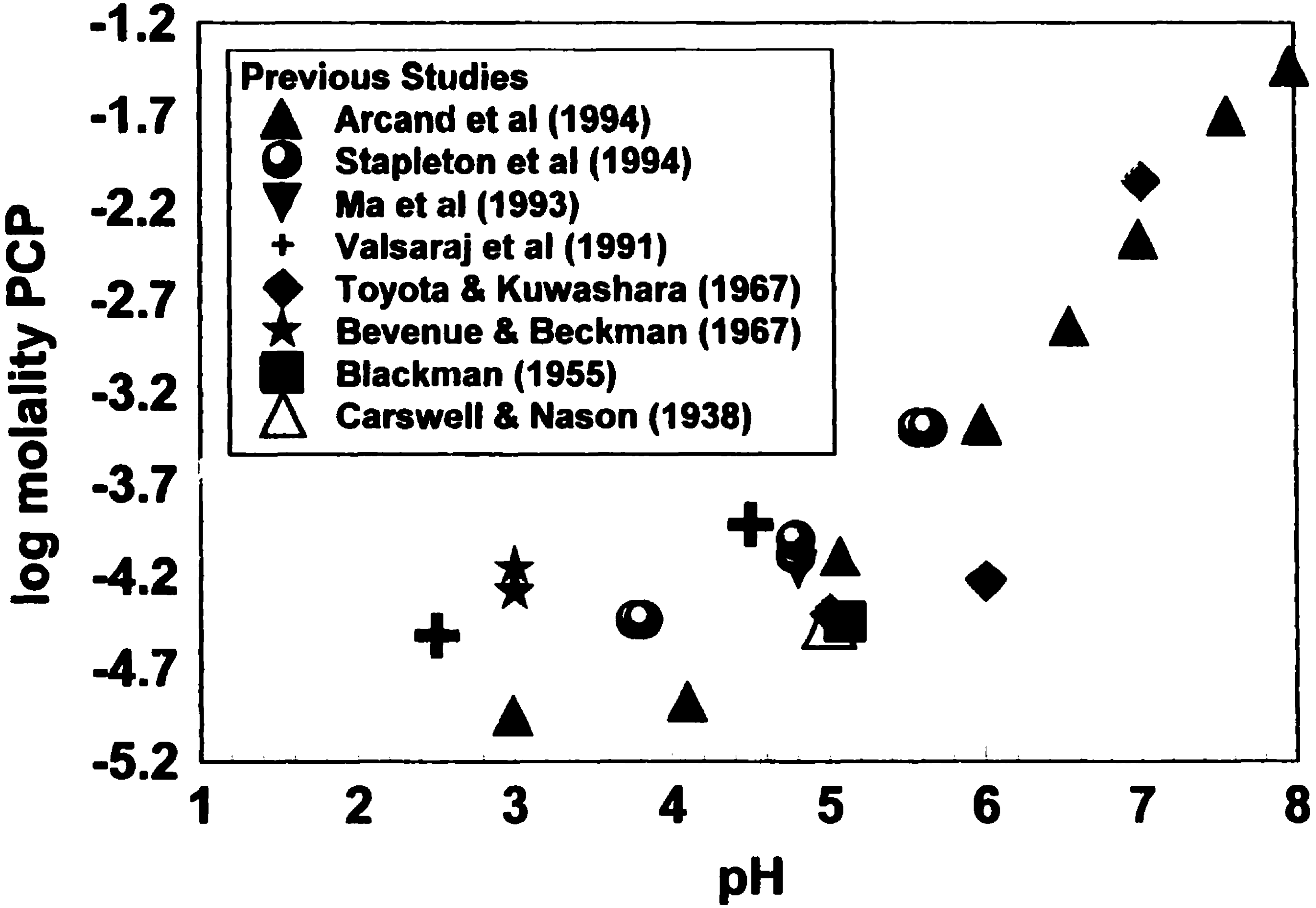

Previous Studies
▲ Arcand et al (1994)
Stapleton et al (1994)
▼ Ma et al (1993)
+ Valsaraj et al (1991)
◆ Toyota & Kuwashara (1967)
★ Bevenue & Beckman (1967)
■ Blackman (1955)
△ Carswell & Nason (1938)
log molality PCP
-1.2
-1.7
-2.2
-2.7
-3.2
-3.7
-4.2
-4.7
-5.2
1
2
3
4
5
6
7
8
pH

Figure 1

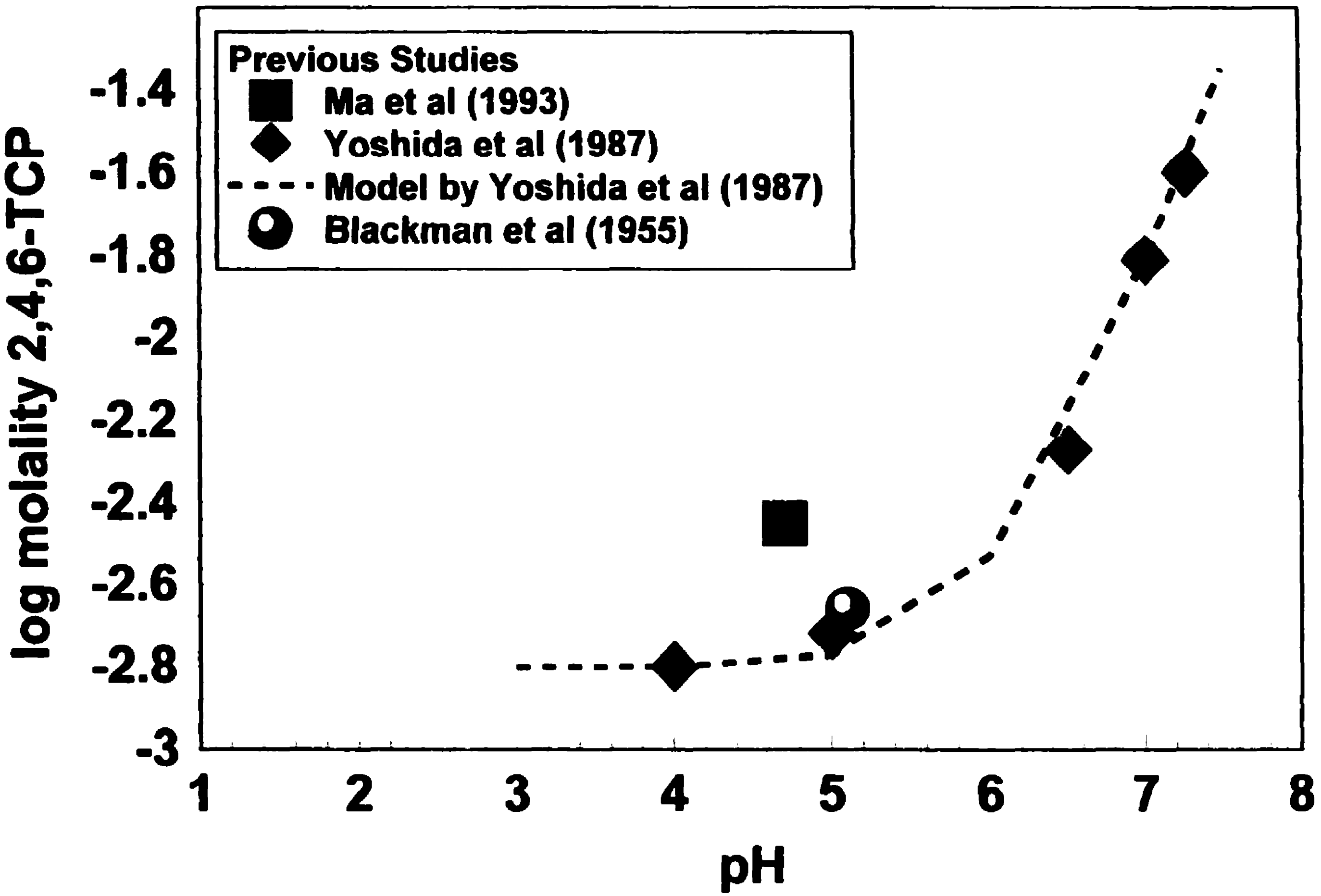

Previous Studies
■ Ma et al (1993)
◆ Yoshida et al (1987)
- - - - Model by Yoshida et al (1987)
● Blackman et al (1955)
log molality 2,4,6-TCP
-1.4
-1.6
-1.8
-2
-2.2
-2.4
-2.6
-2.8
-3
1
2
3
4
5
6
7
8
pH

Figure 2

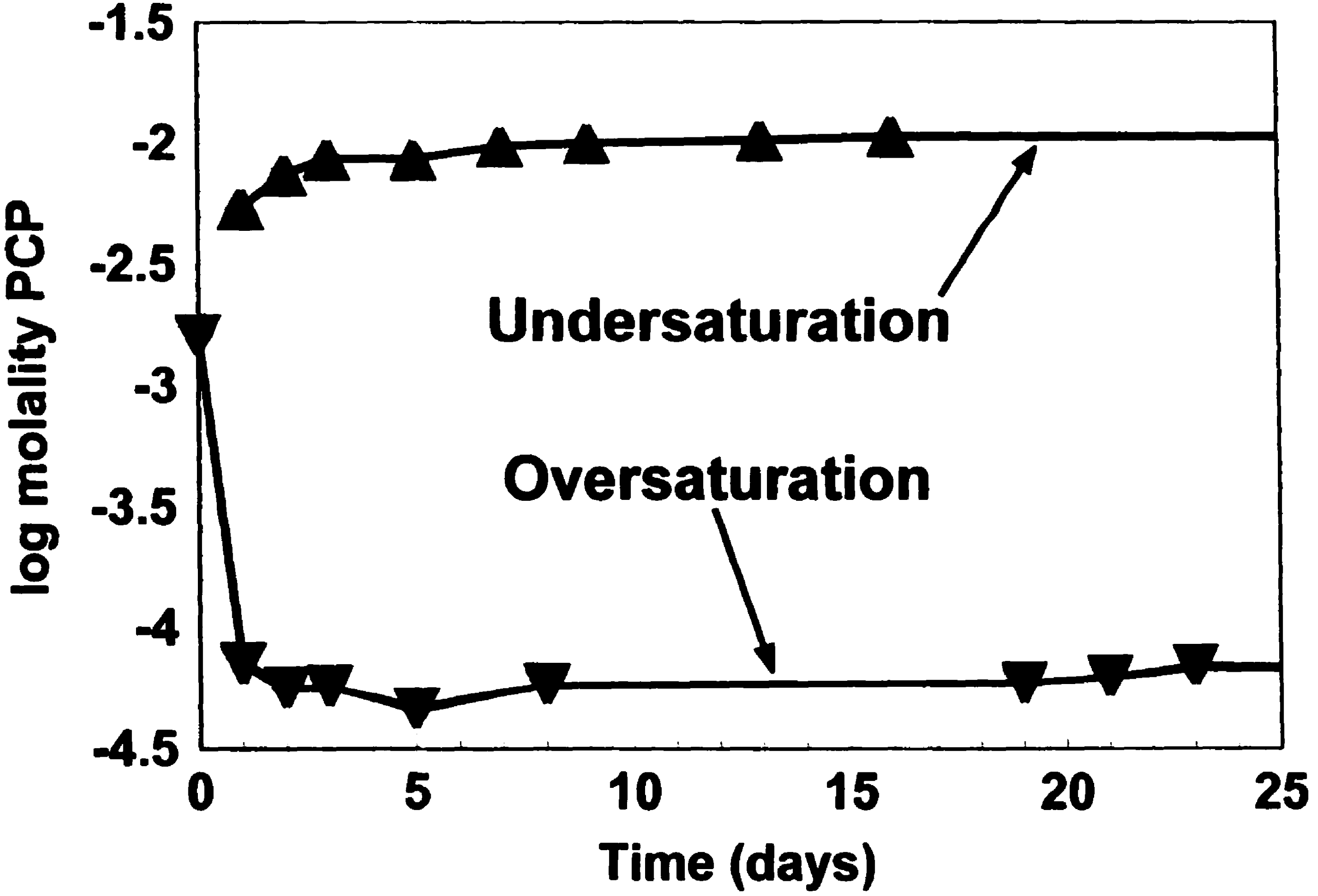

-1.5
-2
-2.5
-3
-3.5
-4
-4.5
log molality PCP
0
5
10
15
20
25
Time (days)
Undersaturation
Oversaturation

Figure 3

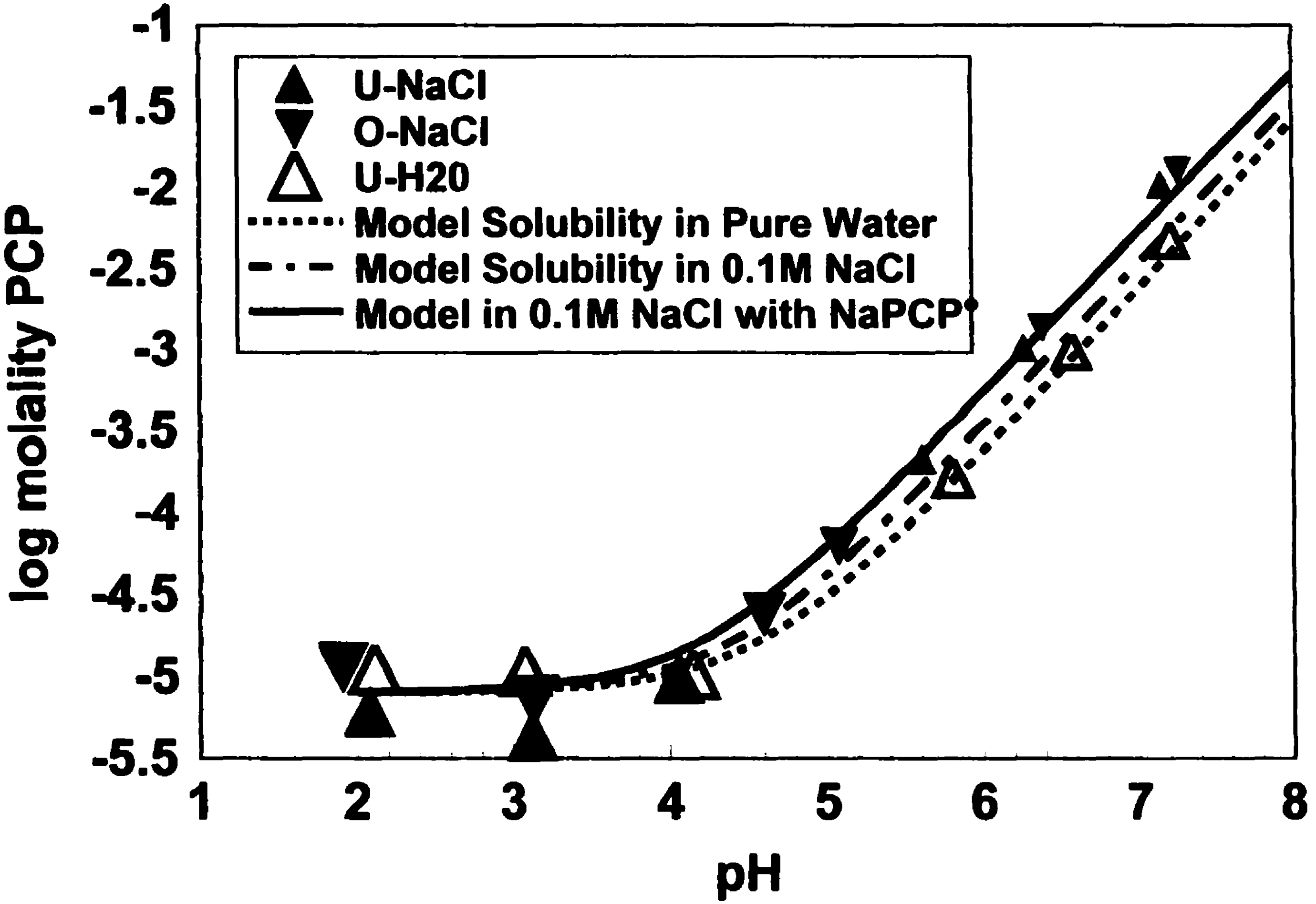

-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
log molality PCP
1
2
3
4
5
6
7
8
pH
▲ U-NaCl
▼ O-NaCl
△ U-H20
Model Solubility in Pure Water
Model Solubility in 0.1M NaCl
Model in 0.1M NaCl with NaPCP*

Figure 4

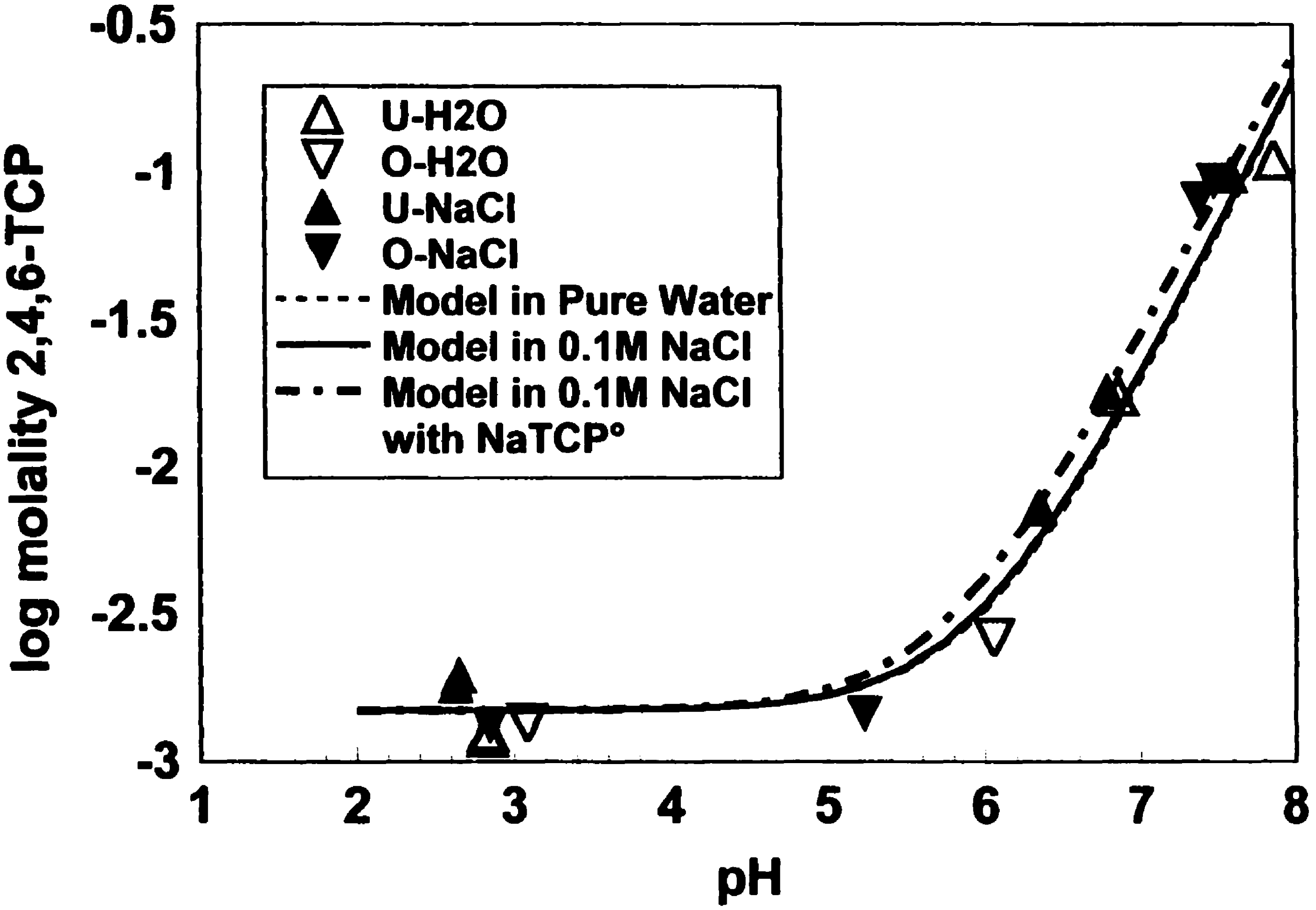

-0.5
-1
-1.5
-2
-2.5
-3
log molality 2,4,6-TCP
1
2
3
4
5
6
7
8
pH
△ U-H2O
▽ O-H2O
▲ U-NaCl
▼ O-NaCl
Model in Pure Water
Model in 0.1M NaCl
Model in 0.1M NaCl with NaTCP°

Figure 5

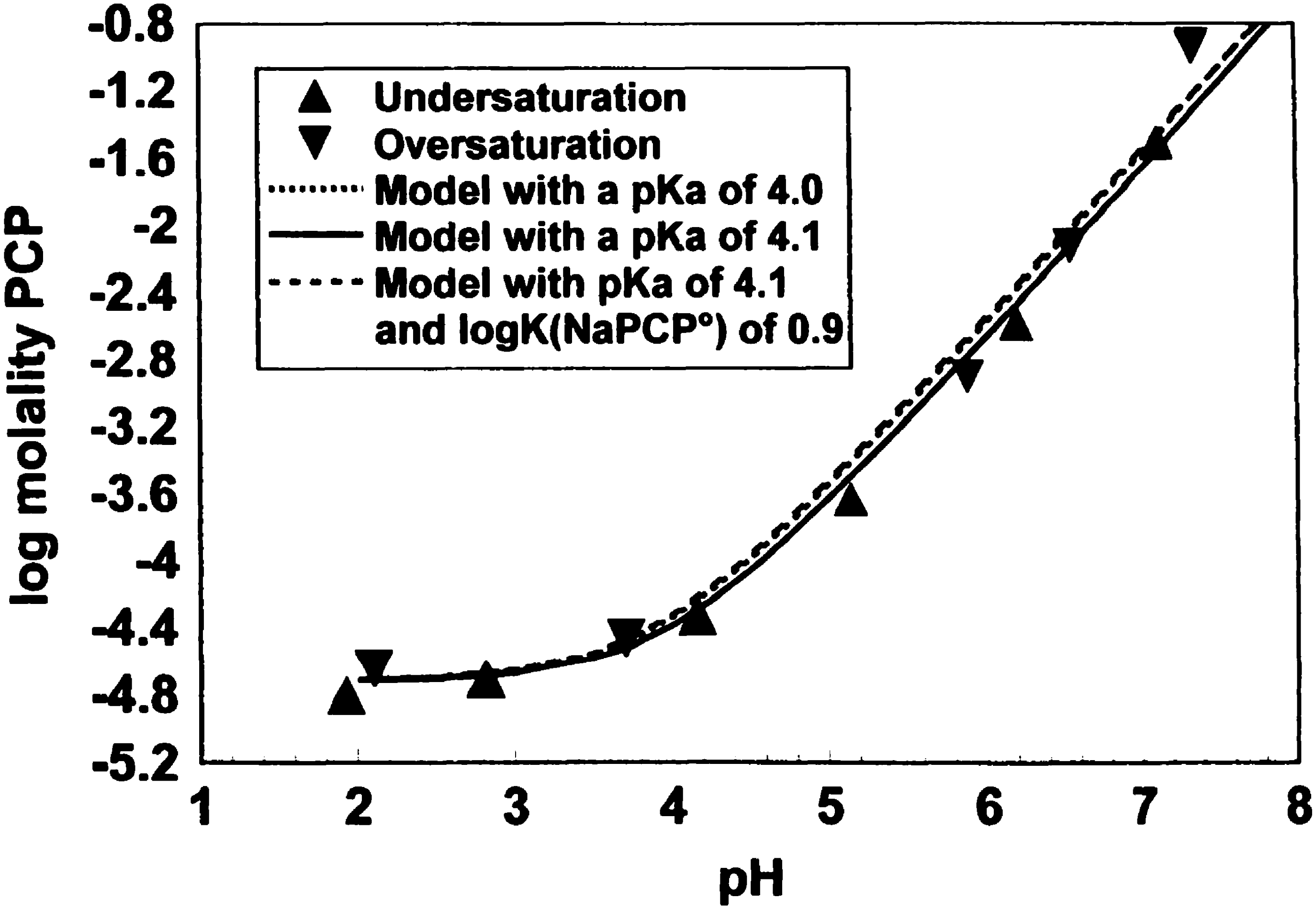
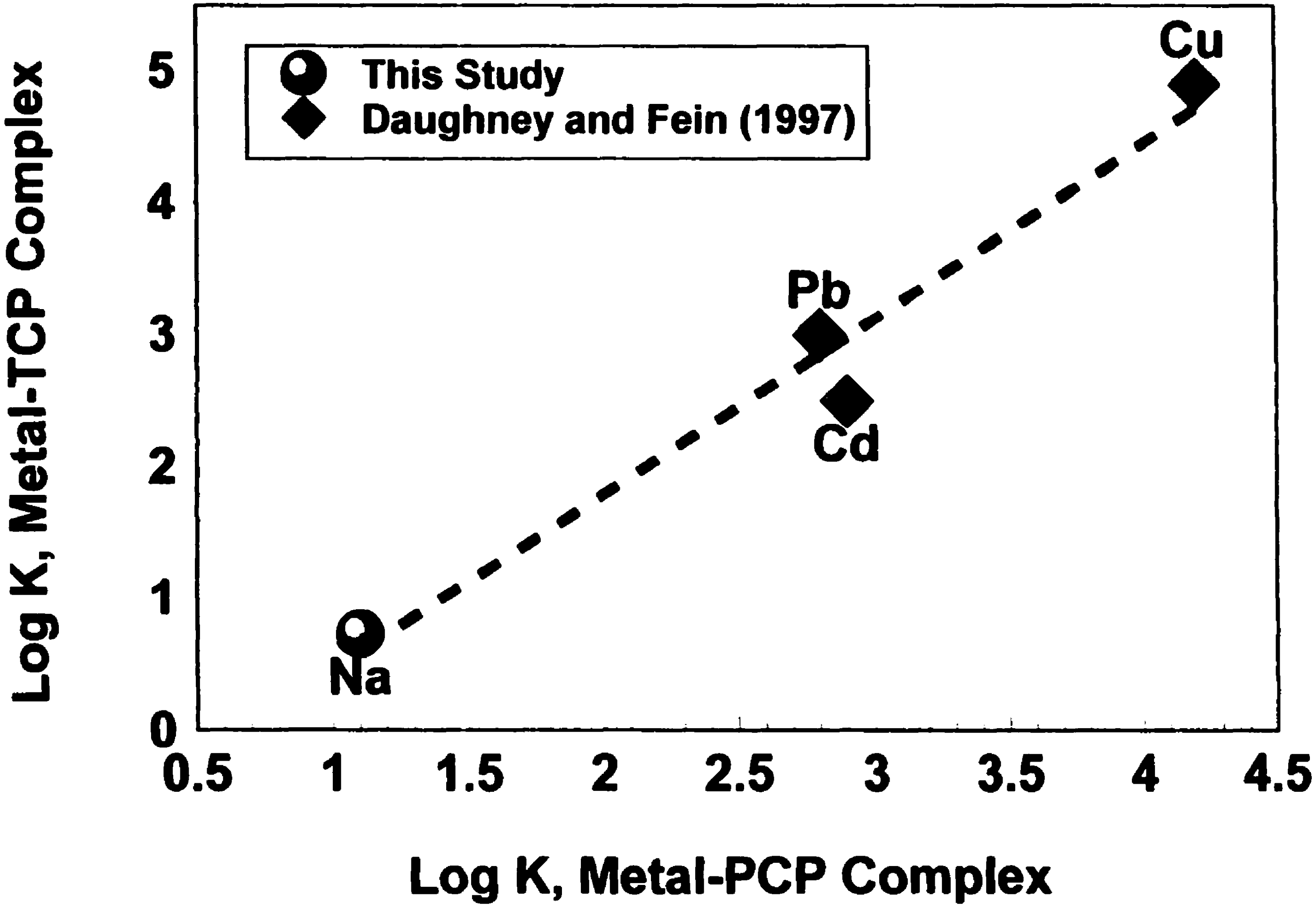

-0.8
-1.2
-1.6
-2
-2.4
-2.8
-3.2
-3.6
-4
-4.4
-4.8
-5.2
log molality PCP
1
2
3
4
5
6
7
8
pH
▲ Undersaturation
▼ Oversaturation
Model with a pKa of 4.0
Model with a pKa of 4.1
Model with pKa of 4.1 and logK(NaPCP°) of 0.9

Figure 6



This Study
Daughney and Fein (1997)
Cu
Pb
Cd
Na
0
1
2
3
4
5
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Log K, Metal-TCP Complex
Log K, Metal-PCP Complex

Figure 7

CHAPTER 3

CONCLUSION

Reversed solubility experiments were conducted for 2,4,6-trichlorophenol and pentachlorophenol, placing narrow constraints on the maximum aqueous concentration of these organic acids as functions of pH, ionic strength, aqueous Na concentration, and temperature. Analysis of the experimental data reveals the existence of three distinct forms of chlorophenol in solution, each having different pH dependencies. These three aqueous chlorophenol species exhibit different hydrophobic and electrostatic properties, causing chlorophenol solubility to vary as a function of pH. The solubility of the chlorophenols can be quantified using a speciation-based theoretical model that relates the pK_a of the chlorophenol, log stability constant of the Na-chlorophenolate complex, and the concentration of the neutral chlorophenol species to the chlorophenol solubility in a solution of a particular pH and ionic strength. Fitting the experimental data to this model allows us to determine the pK_a values, [HCP°] concentrations, and the stability constants for the Na-chlorophenolate complexes for TCP and PCP. At room temperature, the concentration of the protonated chlorophenol species is $10^{-2.8\pm0.2}$ and $10^{-5.1\pm0.4}$ molal for 2,4,6 TCP and PCP, respectively. The calculated pK_a values are 6.0±0.3 for 2,4,6 TCP and 4.5±0.5 for PCP. At 55°C, the molality of protonated PCP increases to $10^{-4.7\pm0.2}$ and the pK_a decreases to 4.0 ± 0.3. Log stability constants for a 1:1 Na-chlorophenolate aqueous complex are 0.7 ± 0.4, and 1.1 ± 0.5 for 2,4,6 TCP and PCP, at 25°C, and 0.9 ± 0.4 for PCP at 55°C.

Using the speciation-based solubility model, along with re-evaluated values for low pH chlorophenol solubility and pK_a of other chlorophenols, enables the prediction of the solubility of each type of chlorophenol over a wide range of pH, ionic strength, and temperature conditions. Additional data on Na- and other metal-chlorophenolate aqueous complexes are necessary to account for the effect of these complexes on the solubility of chlorophenols other than those studied here. However, the experimental solubilities reported in this study, and the estimated solubilities based on the speciation-based solubility model, provide quantitative constraints on the solubility, and hence the fate and mobility of chlorophenols in contaminated surface and groundwater systems.

IMAGE EVALUATION
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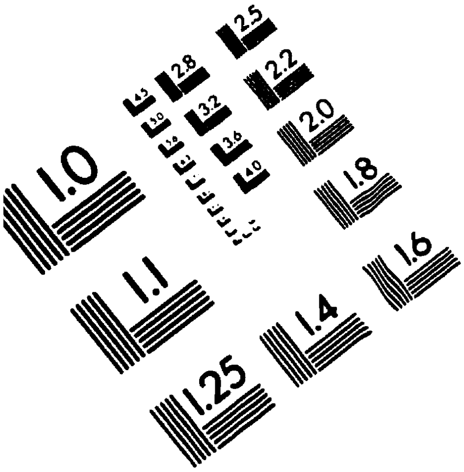

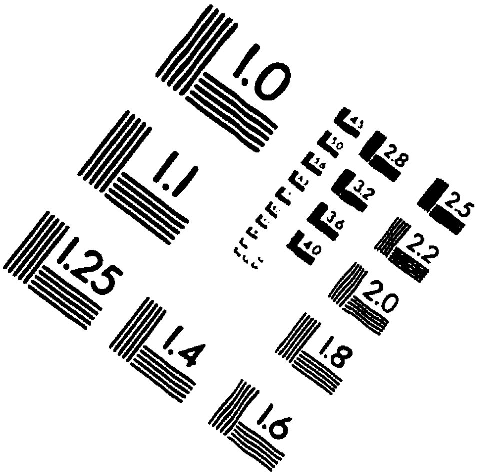

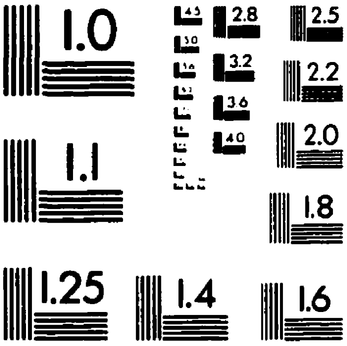

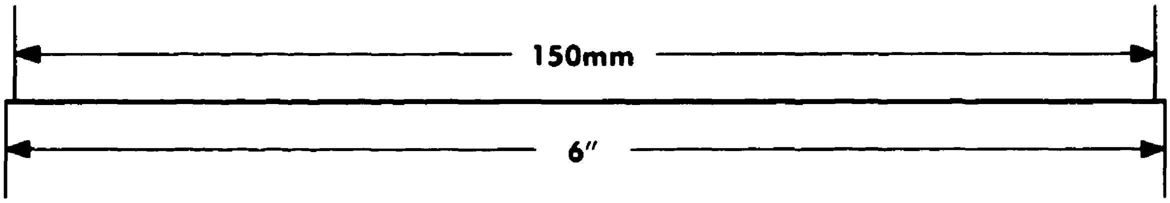

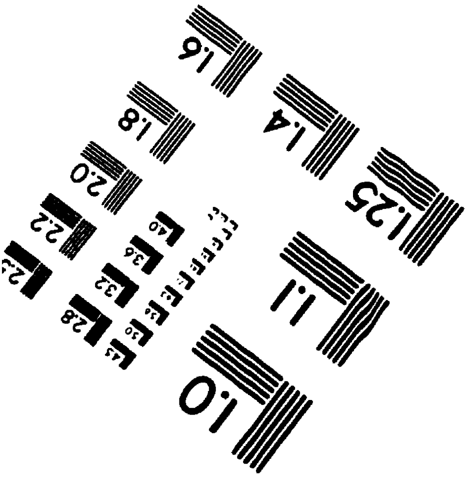

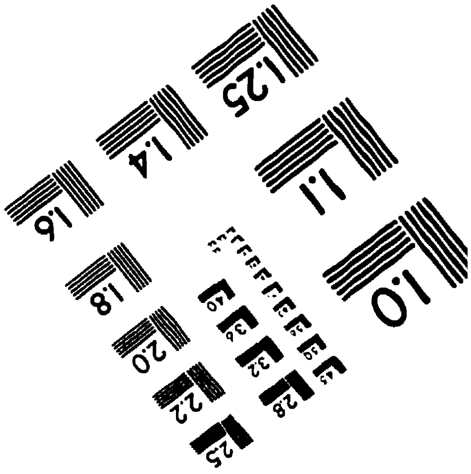

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