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A Model for Estimating the Impact of Orthophosphate on Copper in Water

DARREN A. LYTLE¹, MICHAEL R. SCHOCK¹, JORDAN LEO², BENJAMIN BARNES³

¹US Environmental Protection Agency, ORD, NRMRL, WSWRD, TTEB, Cincinnati, Ohio

²College of Engineering and Applied Sciences, Chemical Engineering, University of Cincinnati, Cincinnati, Ohio

³Department of Natural Resources, Chemistry, University of Maryland Eastern Shore, Princess Anne, Md

Abstract

The nature of copper phosphate minerals in drinking water distribution systems has remained largely unsolved despite being an important link to reducing cuprosolvency. Chemical equilibrium modeling has also largely failed to accurately predict soluble copper in the presence of orthophosphate. The objective of this work was to develop and validate an empirical copper solubility model that considered pH, dissolved inorganic carbon (DIC), and orthophosphate from a series of bench-scale copper precipitation experiments. An empirical model was constructed that allows for the determination of copper levels in a system given pH, DIC, and orthophosphate data. The predictive reliability of this model was assessed by evaluating a collection of cuprosolvency data from two decades of research and field observations and water treatment reports. The tests yielded a firm correlation between predicted and observed copper levels attested by a regression coefficient of 0.86 for a total of 851 observations.

Keywords

copper; corrosion; cuprosolvency; orthophosphate; solubility; water treatment

INTRODUCTION

Copper contamination of drinking water is a concern for water providers in the United States. In 1991, the US Environmental Protection Agency (USEPA) promulgated the Lead and Copper Rule (USEPA 2008), which established the maximum contaminant level goal and copper concentration action level (AL) as 1.3 mg/L in drinking water (*Federal Register* 1992, 1991a, 1991b). Consumption of water containing elevated levels of copper can result in a wide range of health effects, particularly in infants and young children (NRC 2000). The preeminence of copper pipes and fixtures in the United States and much of the rest of the developed world has made meeting the AL an important and necessary requirement. The extent to which copper leaches from pipes and fixtures into drinking water depends upon several physical and chemical conditions, including temperature, total organic carbon, dissolved inorganic carbon (DIC), and chloride (Boulay & Edwards 2001); sulfate, polyphosphate, and orthophosphate (Schock et al. 1995); the age of the copper pipes in the

system (Edwards et al. 2001, Lagos et al. 2001); microbial activity (Reyes et al. 2008); disinfectant type (Boyd et al. 2008); water stagnation time (Merkel et al. 2002); and other factors. The mechanism by which these parameters impact copper varies, but in many cases, a mineralogical change that affects copper solubility or equilibrium conditions occurs.

Cuprosolvency in drinking water is largely controlled by the solubility of corrosion byproducts that form on the surface of copper-containing materials. Several copper minerals, including cuprous compounds cuprite (Cu_2O) and copper (I) hydroxide (CuOH) and the cupric compounds tenorite (CuO), copper (II) hydroxide ($\text{Cu}(\text{OH})_2$), and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) (Schock et al. 1995), have been identified as important solid mineral phases in drinking water systems. In the presence of pure water alone, copper does not corrode appreciably (Schock et al. 1995). In the presence of oxidizing agents, such as dissolved oxygen, free chlorine, monochloramine, and others, however, copper metal is oxidized, and the formation of Cu_2O and CuOH is predicted on copper surfaces (Schock et al., 1995). With a sufficient oxidation potential, copper (I) compounds are subsequently oxidized to copper (II) species over time (Schock et al. 1995).

Copper (II) mineral phases and subsequent copper solubility in water have been observed to evolve over time, or “age.” This important transition has been conceptually captured in the cupric hydroxide model described by Schock et al. (1995). The cupric hydroxide model was derived from field and experimental observations as well as theoretical geochemical considerations. The model describes the transition of copper (II) from relatively soluble, amorphous cupric hydroxide ($\text{Cu}(\text{OH})_2$) to thermodynamically favored and relatively insoluble malachite or tenorite, depending on water chemistry, with time. The transition can take from years to decades depending on water quality, water usage, and other factors. Although the cupric hydroxide model has been supported by benchtop and field conditions (Schock & Fox 2001, Schock et al. 1995), the model is unreliable when orthophosphate (PO_4^{3-}) is present because it stops or slows the aging process. Hypothetically, copper phosphate minerals that resemble minerals such as $\text{Cu}_3(\text{PO}_4)_2$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ may form on the basis of solubility chemistry and may develop in place of cupric hydroxide (Schock et al. 1995) and other species, although they have not been observed in actual drinking water distribution systems.

It is important to understand the effect of orthophosphate on copper corrosion in drinking water distribution systems, as it is a widely used corrosion inhibitor for both lead and copper control (Grace et al. 2012, Schock & Fox 2001, Benjamin et al. 1990). Although the mechanism by which inhibition occurs is not well understood, Schock et al. (1995) proposed that copper phosphate precipitates interfere with the usual cupric hydroxide-to-malachite/tenorite aging process described previously by stopping or slowing the beneficial aging process. Further support for this theory resulted from work by Edwards et al. (2001), who found that the addition of various anionic solutions, including an orthophosphate solution, to a copper surface and to preformed cupric hydroxide films led to significant short-term decreases in copper solubility but long-term deviations from predicted solubility trends. These observations were again attributed to interference of the copper phosphate minerals with the formation of malachite and tenorite (Edwards et al. 2001). A third study by Dartmann et al. (2004) reported similar observations.

According to the copper aging model and known relationships between copper solubility and water chemistry, newer copper plumbing systems in regions of the United States with high DIC (greater than ~30 mg C/L) waters will be the most challenging with regard to reducing copper solubility. In addition, high concentrations of DIC are often accompanied by significant calcium levels, particularly in groundwater in the midwestern United States. The highly buffered water and potential for scaling may rule out pH adjustment to reduce copper levels, which is a reasonable approach in many other waters, leaving orthophosphate as the most reasonable option. The effectiveness of orthophosphate to reduce copper in such conditions has been illustrated in full-scale applications (Grace et al. 2012, Schock & Sandvig 2009, Schock & Fox 2001).

Subsequently, some observational work performed on copper in water systems in the presence of orthophosphates and/or polyphosphates led to the development of several cuprosolvency models, all with various deficiencies. Edwards et al. (2002) formulated a simple quantitative model based on the effects of orthophosphates and polyphosphates on cuprosolvency over time. The model reportedly had a regression coefficient (R^2) of 0.81. Souissi and Triki (2008) investigated the effect of chloride and sulfate on the formation of copper phosphate minerals using copper coupon corrosion studies. An empirical model for cuprosolvency in variable chloride, sulfate, and orthophosphate environments was created on the basis of these results using Doehlert experimental design methods. However, the model only applied to water treatment conditions with chloride and sulfate and has not been as useful for other systems. Another model for predicting soluble copper was constructed by Gho et al. (2008) using a Box–Behnken design. This model was applied to treatment strategies that relied on the use of polyphosphates but did not focus on those using orthophosphate. Generally, the tendency of copper to form metastable and often amorphous phases makes quantitative predictive modeling based on copper solubility difficult and highly uncertain.

The uncertainty regarding solubility modeling is matched only by that of conclusively identifying copper phosphate minerals formed in water. Edwards et al. (2001) attempted to identify the structure of copper phosphate solids precipitated from synthetic waters using X-ray diffraction (XRD) and elemental analysis. They found that copper phosphate solids were amorphous (Edwards et al. 2001) and had a Cu:PO₄ (copper-to-phosphate) molar ratio of 1.5 ± 0.06 . Lytle et al. (2013) reported Cu:PO₄ molar ratios between 3 and 6 depending on the DIC of the water based on copper precipitation tests in the presence of orthophosphate. Known copper phosphate minerals include Cu₃(PO₄)(OH)₃ (corneite), Cu₅(PO₄)₂(OH)₄ (pseudo-malachite), Cu₂(PO₄)(OH) (libethenite), and Cu₃(PO₄)₂·H₂O, which have Cu:PO₄ molar ratios of 3, 2.5, 2, and 1.5, respectively (Table 1).

Given the limitations of our understanding on how orthophosphate interacts with copper, there is a clear need to improve the ability to predict the amount of copper leached from plumbing materials and copper solubility in drinking water. The objective of this research was to develop an empirical model to predict soluble copper as a function of pH, DIC, and orthophosphate concentrations based on an extensive series of batch-scale solubility experiments. The model was then validated using 851 data sets from a large collection of

bench-scale batch tests, field observations, and water treatment facility reports spanning 20 years of work.

MATERIALS AND METHODS

Previous work demonstrated that a simple jar test solubility study could reliably predict the impact of orthophosphate on copper levels in a building's copper plumbing system (Grace et al. 2012). On the basis of this approach, copper (II) solubility and particle formation experiments were conducted in a 1.2 L glass reaction cell. The top of the cell contained ports for injecting acid and base; collecting water samples; and inserting a pH electrode, a dissolved oxygen/temperature probe, a mechanical stirrer, and a gas feed tube. A computer software-controlled dual titrator system¹ was used to maintain a constant pH by rapidly adding small increments of acid or base to compensate for pH changes caused by the addition of copper and by subsequent chemical reactions. The computer software² recorded pH values and titrant volumes, which were maintained in a data file.

Experiments were initiated by adding 1 L of double deionized (DDI) water to the reaction cell. DDI water was prepared by passing distilled water through a deionizing water system³ and had a resistivity of 18.2 MΩ cm. An appropriate amount of sodium bicarbonate and orthophosphate was then added to the water, at which time the acid/base titration system was programmed to the desired pH and started. After the pH stabilized, cupric perchlorate [Cu(ClO₄)₂·H₂O] was added to give an initial copper concentration of approximately 4, 8, or 16 mg/L, depending on the anticipated copper solubility. Samples were drawn out of the cell with a syringe approximately 10 min after the cupric perchlorate, and other chemicals had time to mix and react at the desired pH. Three experimental approaches were considered: incremental precipitation, incremental dissolution, and single pH testing. Incremental precipitation experiments were conducted by initially programming the titrator to a relatively low pH (~6.5). The pH was incrementally increased by 0.3–0.6 units to a final value of approximately 8.5. Soluble copper measurements were taken at each pH increment at approximately 10 min after the pH stabilized. The 10 min mixing time was experimentally found to be sufficient to mix chemicals and allow soluble copper levels to reach steady levels without being long enough to experience signs of mineralogical aging. Particulate copper was separated from soluble copper using 0.20 μm polypropylene disk syringe filters.⁴ The research team has found that filtration through a filter with a pore size smaller than 0.45 μm (commonly used size) is more effective at capturing particles. Incremental dissolution experiments were initiated by adding copper to the reaction vessel at a pH of approximately 8.5. The titrator was programmed to incrementally decrease the pH by 0.3–0.6 units to a final pH of 6.5. Soluble copper measurements were taken at each pH increment at approximately 10 min following pH stabilization. Single pH experiments were conducted with the titrator programmed at a constant pH value. Copper was measured at the programmed pH, after which the water was disposed of, and a fresh reaction solution was prepared to repeat the test at the next desired pH level.

Unless otherwise specified, all chemicals used in this study were of analytical reagent grade. Dilute 0.6 M HCl⁵ and 0.5 N NaOH⁶ were used to adjust the pH. Sodium bicarbonate⁷ was added to the cell to achieve the desired DIC concentration. Copper was added as cupric

perchlorate ($\text{Cu}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$),⁸ calcium was added as calcium hydroxide ($\text{Ca}(\text{OH})_2$),⁹ orthophosphate was added as sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$),¹⁰ and polyphosphate was added as sodium hexametaphosphate.¹¹

The pH was measured with a benchtop pH/ISE (ion selective electrode) meter¹² and a combination pH electrode with temperature corrections.¹³ The instrument was standardized daily using a two-point calibration with pH 7 and 10 standard solutions.¹⁴ Dissolved oxygen was measured with a dissolved oxygen meter¹⁵ and a dissolved oxygen probe.¹⁶ Copper and orthophosphate were measured with a spectrometer¹⁷ and by inductively coupled plasma (ICP) spectroscopy (USEPA 1990). DIC was analyzed directly using a standard coulometric method (Schock & George 1991).

A subsection of tests was conducted in the single pH mode to perform extensive and detailed particle analysis and identification. Aqueous copper suspensions were filtered through 0.20 μm filter paper using vacuum filtration. The filter was placed in a petri dish to dry under atmospheric conditions. Once dried, the copper solids were submitted for XRD analysis.

Over time, two theta–theta diffractometers¹⁸ with a copper X-ray tube were used to identify crystalline phases of the copper precipitates. Filters were mounted on plastic back plates using spray adhesive in such a way that the focus plane was at the filter surface. The XRD tube was operated at 35 keV and 40 mA for the analyses. Scans were performed over a 2-theta range between 5° and 90°, with a step of 0.02° and a 1 s count time at each step. Pattern analysis was performed generally following ASTM procedures (ASTM 1996) using computer software,¹⁹ with reference to the 2002 ICDD PDF-2 or ICDD PDF-4 data files.²⁰ XRD *d*-spacing results were compensated for sample displacement caused by filter thickness by the way the filter media were mounted and inserted into the sample holder. XRD *d*-spacing results were not corrected for displacement caused by deposit thickness on top of the filter surface.

Glassware used for the preparation of standards and solutions was cleaned using a 5% solution of soak cleaner,²¹ followed by thorough rinsing with deionized water. Reused glassware was immediately cleaned by soaking in 10% volume per volume (v/v) concentrated nitric acid (HNO_3) and rinsing with DDI water. Air displacement micropipettes with disposable tips were used for handling and transferring solutions.

RESULTS AND DISCUSSION

Effect of pH and DIC on cuprosolvency.

“Control” copper precipitation runs were performed as previously described but in the absence of orthophosphate to evaluate the impact of pH and DIC on copper solubility (Figure 1). The results clearly illustrate the strong dependence of copper levels on pH and DIC. Soluble copper concentrations increased with decreasing pH and increasing DIC. While copper control in low DIC waters by pH adjustment can be relatively straightforward, reducing copper levels by pH adjustment in high DIC waters can be extremely challenging and may not be practical. The large amounts of caustic needed to overcome the buffering of the water or the tendency to precipitate excess calcium that often accompanies many high

DIC waters, such as in the midwestern United States, may lead to aesthetic issues. Precipitated solids were amorphous on the basis of XRD analysis.

Effect of pH, DIC, and orthophosphate on cuprosolvency.

The effect of orthophosphate on copper solubility was initially examined by measuring filtered copper (II) levels in water containing targeted orthophosphate dose levels of 1, 2, 3, and 5 mg PO₄/L and 10, 50, and 100 mg C/L DIC over a pH range of approximately 6.5–8.5 (Figures 2 and 3). Although the targeted initial orthophosphate doses were achieved, orthophosphate was rapidly incorporated into the copper phosphate solid following copper additions. Therefore, the “actual” orthophosphate doses reported in this work are the soluble orthophosphate concentrations in equilibrium with the solid phase, as would be the case in a drinking water distribution system. Specifically, the actual orthophosphate doses were reported as the average soluble orthophosphate concentration over the respective pH range for a given run (Figures 2, part B; 3, part B; 4, part B).

Orthophosphate reduced copper solubility at all pH values but was particularly effective below pH 8, where higher copper levels were present in the absence of orthophosphate and at all DICs evaluated (Figures 2, part A, and 3, part A). The degree of soluble copper reduction increased with increasing orthophosphate concentration. For example, at pH 7.0 and DIC 10 mg C/L, orthophosphate reduced copper levels from approximately 2.25 to 1.3, 0.7, 0.6, and 0.4 mg/L at doses of 0.1, 0.6, 1.5, and 3.1 mg PO₄/L, respectively. XRD analysis of precipitated solids did not identify any crystalline copper phases. Prefiltered and post-filtered copper and orthophosphate aqueous concentrations were used to estimate the molar ratio of Cu:PO₄ in the precipitated solids (Figures 2, part C; 3, part C; 4, part C). In the case of DIC 10 mg C/L, Cu:PO₄ ratios ranged from approximately 2.7 to 4 (Figure 2, part C) and remained fairly constant across the entire pH range, with the exception of the 0.1 mg PO₄/L condition, where the ratio increased from approximately 3.6 to 6 with increasing pH. However, given the very low orthophosphate level of 0.1 mg PO₄/L, the observation may be attributed to insufficient orthophosphate present to meet the stoichiometric requirement. XRD analysis indicated that the solids were amorphous in nature at all conditions evaluated.

The Cu:PO₄ molar ratios in precipitated solids were also analyzed as a function of increasing DIC concentration (Table 2). At DIC 10 mg C/L, the Cu:PO₄ ratio remained largely constant for the three pH values tested, and the Cu:PO₄ ratio decreased with increasing orthophosphate concentration in all three cases. At DIC 50 mg C/L, there was greater variability between pH values and within each plot: at pH 6.77, the Cu:PO₄ ratio increased dramatically with increasing orthophosphate concentration; at pH 7.54, there was less of an increase; and at pH 8.32, a decrease in the Cu:PO₄ ratio was observed with increasing orthophosphate concentration. There was great variability between Cu:PO₄ ratios at different pH values in the DIC 100 mg C/L tests. In all cases, however, the Cu:PO₄ ratio decreased with increasing orthophosphate concentration.

Orthophosphate reduced copper solubility at all pH values in water containing 50 mg C/L DIC but was particularly effective below pH 8, and the degree of reduction increased with increasing effective orthophosphate concentration (Figure 3, parts A and B). For example, at

pH 7.0, orthophosphate reduced copper levels from approximately 5.1 to 2.7, 2.2, 1.4, and 1.2 mg/L at doses of 0.36, 1.0, 1.9, and 4.2 mg PO₄/L, respectively. XRD analysis of precipitated solids did not identify any crystalline copper phases. Cu:PO₄ ratios in the precipitated solids converged to approximately 4 above pH 7.3, with the exception of the lowest orthophosphate concentration of 0.36 mg PO₄/L (Figure 3, part C). At the lowest orthophosphate dose, the ratio gradually increased from 4 to 6 with increasing pH, which may have been related to the decrease in soluble orthophosphate levels to very low levels with increasing pH.

Orthophosphate reduced copper solubility at all pH values in water containing 100 mg C/L DIC but was also particularly effective below pH 8 where higher copper levels were present in the absence of orthophosphate (Figure 4, parts A and B). Although copper levels decreased with increasing effective orthophosphate concentration, the degree of benefit was far less evident than at other DICs (Figure 4, part A). For example, at pH 7.0, orthophosphate reduced copper levels from approximately 11 to 2.8, 2.9, 2.5, and 2.2 mg/L at doses of 0.76, 1.5, 2.3, and 4.1 mg PO₄/L, respectively. XRD analysis of precipitated solids did not identify any crystalline copper phases. Cu:PO₄ ratios in the precipitated solids were quite variable and ranged from approximately 2 to 7.5 (ignoring one apparent outlier).

There were no differences in copper (II) solubility between experimental particle formation approaches in all DIC waters performed in the presence of orthophosphate (Figure 5). As previously described, precipitation and dissolution were run at DIC 10 mg C/L and a target orthophosphate dose of 3 mg PO₄/L. An additional dissolution was run with 100 mg Ca/L (data not shown). In all cases, the orthophosphate reduced copper levels with increasing pH, particularly below 8. Calcium did not affect copper concentrations.

The data clearly illustrated the effectiveness of orthophosphate to reduce copper levels associated with freshly precipitated copper, representing relatively new copper piping. This is particularly obvious and important in high DIC waters that support high copper solubility.

Effect of polyphosphate on cuprosolvency.

The effect of polyphosphate on copper (II) solubility was tested by adding 3 mg/L total PO₄ (0.03 mM) of polyphosphate in the form of sodium hexametaphosphate to the test cell water (having an initial copper concentration of 4 mg/L) over the pH interval of 6.5–7.8. “Hexametaphosphate” is a mixture of long-chained polyphosphates having 5–21 PO₃ linkages, and it is used in drinking water treatment to prevent calcium and iron precipitation. Polyphosphates have also been linked to the increase of lead in distribution systems through chemical complexation and particle stabilization mechanisms (Cantor et al. 2000, Holm & Schock 1991, Holm & Smothers 1990). All of the copper initially added to the test cell appeared to remain soluble over the entire pH range tested on the basis of visual examination of suspensions and 0.2 µm filtrations (Figure 6). The results initially suggested that hexametaphosphate greatly increased copper (II) solubility (analysis limited to cases in which soluble copper was less than the 4 mg/L added). Previous related work with iron, however, showed that polyphosphates prevent iron precipitation through a colloidal dispersion mechanism by imparting a negative charge on very small iron colloids essentially invisible to the eye, thereby dispersing them through a charged repulsion mechanism (Lytle

& Snoeyink 2002). Thus, the potential for this mechanism to affect copper in a similar manner could be consistent with these observations. To test the validity of this mechanistic hypothesis, test runs were repeated using 100 mg Ca/L (2.5 mM), following the ferric iron experiments of Lytle and Snoeyink (2002). The results (Figure 6) show that soluble copper levels over the tested pH range were similar to the control (without hexametaphosphate or orthophosphate). Unlike orthophosphate, hexametaphosphate did not reduce copper solubility above pH 7.2, while a relatively small reduction may have been observed between pH 6.5 and 7.2. Calcium largely negated the inhibitive effect of the hexametaphosphate for cupric oxyhydroxide or hydroxycarbonate formation, but the hexametaphosphate did not impart any advantage in reducing the solubility of copper (II) as orthophosphate did. This observation is consistent with field observations of the relatively poor effectiveness of polyphosphates and blended phosphates relative to orthophosphate for reducing cuprosolvency in hard, high-alkalinity groundwaters. The potential for adverse effects on total copper levels in the water is suggested to be higher in softer waters at a given DIC level. The mechanism of the calcium effect could not be identified in these experiments, but two reasonable hypotheses are proposed. The polyphosphate was preferentially tied up with the calcium as an aqueous complex and was unavailable to interact with copper. Virtually no reliable formation constants are reported in the literature for copper polyphosphate complexes, although they are known to bind strongly with calcium and other divalent and trivalent metals. Alternatively, hexametaphosphate could have interacted with the cupric colloid surface shortly after nucleation through adsorption and then dispersed the colloids through a charged mechanism, as described for iron by Lytle and Snoeyink (2002).

Regardless of the mechanism, the experimental data established that hexametaphosphate (and potentially other polyphosphates) could be detrimental relative to orthophosphate alone for the control of copper levels at the consumer's tap. In practical applications, the magnitude of the detrimental effect would be strongly influenced by common water constituents such as hardness, ions, other divalent metals such as ferrous iron or manganous manganese, and the ionic strength.

Solubility modeling.

The FORTRAN computer model for predicting copper solubility (Schock et al. 1995), CU2SOL, was updated to Java computer programming language and tested against the data observed in the previously described experiments. The first test was under the assumption that $\text{Cu}(\text{OH})_2$ was the stable copper mineral; the second test allowed for the possibility of $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{OH})_2$ precipitation. As anticipated, these fundamental equilibrium solubility models based on the cupric hydroxide model failed to reasonably predict the soluble copper concentrations in the presence of orthophosphate. Although our current understanding of specifically how copper (II) interacts with orthophosphate remains inadequate, the relationship between copper and orthophosphate concentration, and pH and DIC, has been observed to be consistent, reproducible, and predictable on the basis of this work and the authors' experience. As a result, an empirical model based on the controlled experimental data provided previously was developed. This model can be used to predict copper levels as a function of pH, DIC, and orthophosphate concentration inputs. Specifically, laboratory data (presented in Figures 2–5, and additional runs) covering a pH

range of 6.48–8.52; soluble orthophosphate concentrations ranging from 0.2 to 3.1 mg PO₄/L; and DIC levels of 10, 50, and 100 mg C/L DIC were used to develop the model. A total of 84 experimental observations were used to establish the model using Microsoft Excel's data analysis tools. The resulting best fit empirical model was calculated as follows:

$$\text{Cu} = (56.68) \exp[(-0.77)(\text{pH})] \exp[(-0.20)(\text{PO}_4)](\text{DIC})^{0.59} \quad (1)$$

where Cu is the predicted copper concentration (mg/L), PO₄ is orthophosphate concentration (mg PO₄/L), pH is the measured pH, and DIC is the DIC concentration (mg C/L). The final model fit resulted in a good R^2 value of 0.92.

The predictability of the model was evaluated using bench- and pilot-scale laboratory data and full-scale field data collected from several studies performed under a range of conditions reported over the past 20 years (Table 3). Copper levels generated during full- and pilot-scale studies were associated with corroding copper pipes rather than being generated from precipitation experiments and were below 2.5 mg/L. The measured pH, DIC, and orthophosphate concentrations for 851 observations were entered as the model parameters, and the resulting predicted copper concentrations were compared with the measured copper values (Figure 7, part A). The empirical model predicted actual measured copper levels reasonably well with an R^2 value of 0.86. In general, the model was conservative in that it tended to overestimate copper levels, particularly at lower actual copper concentrations. An analysis of residuals (difference between actual and predicted copper concentrations) broken down by data set type was also examined (Figure 7, part B). Pilot data residuals were relatively small across the entire range of actual copper concentrations. The model tended to slightly overpredict copper at low actual copper levels (less than ~0.75 mg/L) and slightly underpredict copper at higher actual copper levels (greater than ~1.5 mg/L). Residuals associated with field data were also relatively small, with the exception of several outliers at the low and high ends of the actual copper range. The model slightly overpredicted copper levels associated with field data. Finally, two distinct groups of laboratory data were evident (Figure 7, part B). One group at actual copper levels less than 0.5 mg/L were predicted relatively well, although they were slightly overestimated by the model, and the slope of the associated regression line (not shown) was similar to the slope of the field data regression line. The other group of data fell between actual copper levels of approximately 0.3 and 1 mg/L. The model overpredicted copper levels to the greatest extent of all data, and the slope of the associated regression line (not shown) was also similar to the slope of the field data regression line. In general, the model reasonably predicted copper levels with a greater tendency to be conservative (i.e., overestimate copper). The practical implication is that the orthophosphate dose estimated by the model to achieve the desired copper solubility would tend to be conservatively high. Differences between actual and predicted copper levels could be associated with experimental artifacts, measurement errors, initial copper mineral age, or the equilibrium state of actual copper levels in the field systems.

The empirical model output was used to illustrate the predicted copper solubility as a function of orthophosphate concentration, pH (6.5, 7, 7.5, and 8) and DIC (10, 25, 50, 75, and 100 mg C/L). Figure 8 provides reasonable estimates of the orthophosphate dosage needed to reduce the copper to desired levels at a given pH value and DIC concentration. For

example, approximately 2 mg/L of orthophosphate at pH 7 and DIC 25 mg C/L is predicted to reduce the copper level from 1.73 to approximately 1.16 mg/L. At pH 7.5 and DIC 75 mg C/L, 3 mg/L of orthophosphate is predicted to reduce the copper level from 2.26 to approximately 1.24 mg/L.

The effect of orthophosphate dose on copper (II) solubility as a function of pH and DIC was more closely examined to provide water systems with an orthophosphate dose starting point to reduce copper levels. Figure 9 provides different minimum orthophosphate dosages, predicted by the empirical model, to reduce the copper to just below the 1.3 mg/L AL. Water systems can easily find the minimum approximate orthophosphate dose needed given the pH and DIC of the water while considering the model to be conservative (i.e., overestimated copper), particularly at lower copper levels. For example, at pH 7.3 and DIC 62, an orthophosphate dose slightly above 3.0 mg/L is predicted to be necessary to reduce the amount of copper to just below the 1.3 mg/L AL. The effectiveness of this prediction was evaluated by comparing actual pilot data. In the Indian Hill pilot study (Schock & Fox 2001), an orthophosphate dose of 3.17 mg/L added to pH 7.30, DIC 62 mg C/L water resulted in 1.24 mg/L of copper. Thus, the figure should provide easy, reasonably accurate, and conservative estimates of an orthophosphate dose (i.e., the model tends to overpredict doses, particularly at lower copper levels) needed to reduce copper levels below the 1.3 mg/L AL.

CONCLUSIONS

A series of bench-scale solubility tests for copper in the presence of varying DIC and orthophosphate concentration, as well as varying pH levels, confirmed several previous predictions and observations. These data were tested against the predictions of the traditional cupric hydroxide model and yielded poor results, further illustrating the deficiencies of the model in the presence of orthophosphate water treatment. The data collected, however, enabled the development of a new model of cuprosolvency for predicting copper levels in orthophosphate-treated water. The new model was tested against data obtained from a wide range of testing performed over the course of two decades through bench-scale tests, field observations, and water treatment reports and yielded reasonably accurate results in most cases, particularly given the range of data sources and controls and conditions under which previous data sets were generated. It was demonstrated that the new model will enable water treatment facilities to apply a more precisely calculated amount of orthophosphate to meet regional DIC and pH conditions to maintain copper levels below the USEPA-specified AL at worst-case new copper construction sites. This work was not intended to imply that orthophosphate is the solution to reducing elevated copper levels in all cases. Adjustment of pH is a reasonable alternative in many conditions; however, pH adjustment would be challenging in some water chemistries. For example, in waters with elevated DIC concentrations (greater than ~30–35 mg C/L), strong buffering and increased scaling tendencies may restrict the ability to increase pH to levels necessary to reduce copper solubility to a desired level. Orthophosphate may be a more effective solution in such cases. Finally, particulate copper release and other copper release control mechanisms and complicating factors, such as diffusion barrier films and incorporation of mixed metals into

mineral phase structure, are not considered in this work, as is the case in all solubility models.

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FIGURE 1:

The effect of dissolved inorganic carbon and pH on soluble copper (based on 0.2 μm filtration) (23°C, $I = 0.01\text{ M}$). Regression plots are based on predictions made by CU2SOL using selected thermodynamic constants. CU2SOL is a FORTRAN computer model for predicting copper solubility.

FIGURE 2:

The effect of pH at dissolved inorganic carbon 10 mg C/L on soluble copper (based on 0.2 μ m filtration) (A), soluble PO₄ (B), and Cu:PO₄ molar ratio of precipitated solids (C). AL—action level, Cu—copper, PO₄—phosphate

FIGURE 3:

The effect of pH at dissolved inorganic carbon 50 mg C/L on soluble copper (based on 0.2 μ m filtration) (A), soluble PO₄ (B), and Cu:PO₄ molar ratio of precipitated solids (C). AL—action level, Cu—copper, PO₄—phosphate.

FIGURE 4:

The effect of pH at dissolved inorganic carbon 100 mg C/L on soluble copper (based on 0.2 μm filtration) (A), soluble PO_4 (B), and Cu: PO_4 molar ratio of precipitated solids (C). AL—action level, Cu—copper, PO_4 —phosphate.

FIGURE 5:

The effect of pH at dissolved inorganic carbon 10 mg C/L on soluble copper (based on 0.2 μ m filtration) (A), soluble PO₄ (B), and Cu:PO₄ molar ratio (C). AL—action level, Cu—copper, PO₄—phosphate.

FIGURE 6:
The effect of hexametaphosphate on filtered 0.2 μm) copper (4 mg/L copper dose, 10 mg C/L, 23°C).

FIGURE 7:

A comparison of actual copper values of field, laboratory, and pilot data versus the copper values predicted by the empirical model based on pH, dissolved inorganic carbon, and orthophosphate dose (A) and residual copper levels (i.e., difference between actual and predicted copper concentrations) (B).

FIGURE 8:

The effect of orthophosphate and dissolved inorganic carbon on model-predicted soluble copper at pH values of 6.5 (A), 7 (B), 7.5 (C), and 8 (D). PO_4 —phosphate.

FIGURE 9:

The minimum orthophosphate dose (mg PO₄/L) needed to reduce the soluble copper below the 1.3 mg/L AL at various pH and DIC levels. AL - action level, DIC - organic carbon, PO₄ - phosphate

TABLE 1:

Some copper phosphate mineral species.

Name	Formula
Cornetite	$\text{Cu}_3(\text{PO}_4)(\text{OH})_3$
Libethenite	$\text{Cu}_2(\text{PO}_4)\text{OH}$
Ludjibaite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
Reichenbachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
Pseudomalachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$
Copper (II) phosphate	$\text{Cu}_3(\text{PO}_4)_2$
Copper (I) phosphate	Cu_3PO_4
Copper (II) hydrogen phosphate	CuHPO_4
Copper (II) metaphosphate	$\text{Cu}_2\text{P}_4\text{O}_{12}$
Copper (II) ultraphosphate	$\text{Cu}_2\text{P}_8\text{O}_{22}$
Amorphous copper phosphates	Various

TABLE 2:

Copper-to-phosphate molar ratio ranges for each DIC and pH.

Approximate PO ₄ Range—mg/L	Cu:PO ₄ Molar Ratio	pH
DIC 10 mg C/L		
0.5–3	3.18±0.54	6.77
0.5–3	3.32±0.52	7.60
0.5–3	3.37±0.50	8.36
DIC 50 mg C/L		
1–5	4.34±1.80	6.77
1–4	3.83±0.31	7.54
0.5–4	3.70±0.54	8.32
DIC 100 mg C/L		
1–5	4.15±2.37	6.74
1–4	4.70±1.11	7.59
1–4	4.72±0.82	8.34

Cu—copper, DIC—dissolved inorganic carbon, PO₄—phosphate

TABLE 3:

Previous studies used for the verification of the new model.

Study Type	Room/Study	No. of Observations	Average pH	Average Phosphate—mg PO ₄ /L	DIC—mg C/L	Date
Full-scale	AP ^a	12	7.35	3.19	73	October 2006–July 2007
Full-scale	AG ^a	12	7.35	3.27	73	October 2006–July 2007
Full-scale	B14 ^a	11	7.35	3.29	73	October 2006–July 2008
Laboratory	NA ^b	111	9.17	2.48	10	March 2010–August 2011
Laboratory	NA ^b	75	7.15	3.08	10	November 2010–June 2011
Laboratory	NA ^b	165	7.14	3.11	50	June 2011–March 2012
Pilot	201 ^b	15	6.59	2.56	5	June 1994–August 1994
Pilot	202 ^b	16	7.07	2.8	5	June 1994–August 1994
Pilot	203 ^b	16	7.99	2.81	5	June 1994–August 1994
Pilot	204 ^b	16	8.98	2.89	5	June 1994–August 1994
Pilot	405 ^b	18	6.52	2.75	10	February 1995–June 1995
Pilot	406 ^b	18	7.07	2.85	10	February 1995–June 1995
Pilot	407 ^b	18	8	2.91	10	February 1995–June 1995
Pilot	408 ^b	18	8.96	2.94	10	February 1995–June 1995
Pilot	609 ^b	35	6.57	2.69	25	October 1996–June 1997
Pilot	610 ^b	45	7.06	2.94	25	October 1996–June 1997
Pilot	611 ^b	45	8.08	3.02	25	October 1996–June 1997
Pilot	612 ^b	45	8.95	2.97	25	October 1996–June 1997
Pilot	705 ^b	36	6.52	2.49	50	February 1997–August 1997
Pilot	706 ^b	37	7.04	2.84	50	February 1997–August 1997
Pilot	707 ^b	36	8.02	3	50	February 1997–August 1997
Pilot	708 ^b	36	8.97	3	50	February 1997–August 1997

Study Type	Room/Study	No. of Observations	Average pH	Average Phosphate—mg PO ₄ /L	DIC—mg C/L	Date
Pilot	Ohio Water System ^c	15	7.3	3.3	63	March 1998–June 1998

^aGrace et al. (2012)

^bSchock et al. (1995)

^cSchock & Fox (2001)