

CHAPTER III

ORGANIC MATTER AND COPPER CORROSION BY- PRODUCT RELEASE: A MECHANISTIC STUDY

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Abstract- Natural organic matter in drinking water can increase copper corrosion by-product release by complexation, colloid mobilization/dispersion, and by interfering with natural aging processes which tend to decrease scale solubility as pipes age. Formation of soluble NOM complexes is most significant in low alkalinity waters containing high concentrations of NOM. In contrast, interference with solids aging occurs even where traces of NOM are present, increasing copper corrosion by-product release in all impacted waters, although the effect is most noticeable in high alkalinity waters where malachite formation is inhibited and there is a high capability to form copper carbonate complexes. Colloid mobilization only appeared to be significant at very high levels of NOM in the presence of $\text{Cu}(\text{OH})_2$ solids. The presence of organic matter can reverse copper corrosion by-product release during stagnation by 1) serving as a food source for bacteria, leading to complete removal of dissolved oxygen and subsequent re-deposition of copper onto the pipe wall in the presence of chloride or other catalysts, or 2) by sorption of soluble natural organic matter onto pipe surfaces, which decreases the complexation capacity of water in the pipe during long stagnation times.

Keywords: copper, natural organic matter, drinking water, corrosion by-products, equilibrium calculations, thermodynamic diagrams

INTRODUCTION

Although exhaustive practical experience has highlighted the practical importance of natural organic matter (NOM) in corrosion by-product release from copper pipe in drinking water,¹⁻⁷ there are few mechanistic studies in the literature which clearly identify the mechanism(s) by which NOM acts. Consequently, when considering the attractive yet costly prospect of controlling copper release to by removing NOM or manipulating water chemistry, there is little

basis for decision-making. That is, there have been some reports that NOM has little or no effect, in other cases NOM caused substantial short-term reductions in copper release,³ and in still other cases the concentration of copper release directly increases with NOM concentration in the water.^{1,7,9} Perplexing “presence or absence” effects have also been reported,^{4,5,6} in which even trace 0.1 mg/L levels of NOM produce marked (> 0.8 Cu mg/L) increases in copper release to water, while further increases in NOM concentration produce only slight additional increases to copper concentration.

Recent work has provided some insights that point to likely mechanisms of NOM action which can be readily evaluated in laboratory experiments. The experiments conducted in this work were designed based on the:

- notion that soluble copper concentrations within relatively new pipe are controlled by $\text{Cu}(\text{OH})_2$ solid equilibrium, with associated formation of soluble carbonate complexes^{8,10};
- belief that overall solubility of the $\text{Cu}(\text{OH})_2$ is reduced as the pipe ages by poorly characterized solid aging effects, with concomitant reductions in copper release^{6,10,11,12};
- discovery that predictions of copper corrosion by-product release in low alkalinity water are significantly improved by explicitly considering possible complexation of copper by NOM⁷;
- finding that copper corrosion in high alkalinity water is dramatically increased at low levels of NOM, but relatively insensitive to additional increases in NOM concentration^{4,5,6};
- hypothesis of Korshin et al. that NOM might cause mobilization of colloidal copper via particle stabilization and detachment⁵;
- report of that copper corrosion by-product release sometimes reverses during stagnation under at least some circumstances¹³.

With the exception of a few key studies,^{3,5} the important findings reported above were obtained from observations of copper corrosion in real systems with all limitations inherent to such complex situations.^{6,13,14} Thus, the first goal of this study was to attempt and reproduce the reported phenomena under laboratory controlled conditions. It was hoped that this would lead to experiments that unambiguously identified the fundamental mechanism(s) by which NOM interacts with copper.

EXPERIMENTAL

Organic Matter

Three types of organic matter were used including sodium alginate, soluble NOM and particulate NOM. The soluble NOM solution (Table 1) was concentrated from Lake Pleasant, WA by reverse osmosis, followed by filtration and ion exchange of calcium and magnesium hardness as described elsewhere.¹⁵ Particulate NOM was purchased at a local garden supply store. To prepare the sample, approximately 30 grams of peat was rinsed in 1L of deionized water, followed by filtration through a 0.45 μm filter. The particulate fraction was then scraped off of the filter and re-suspended in deionized water. After repeating the rinse 3 times, the sample was used in experiments. The sodium alginate was dosed to solutions at a concentration of 2% (W/V) two days before experiments to simulate experiments presented elsewhere.¹⁶ The resultant solutions were very viscous and certainly not representative of drinking waters found in practice, but the high concentrations were expected to highlight key effects relevant to organic matter in biofilms.

Total and Soluble Copper Measurements

In preliminary experiments, copper was analyzed by an inductively coupled plasma emission spectrophotometer (ICP-ES) according to Standard Method 3120.¹⁷ However, some of the organic matter solutions of interest, such as alginate, were too viscous to measure on the ICP without exhaustive digestion of the organic matter. Consequently, a colorimetric method described in Standard Method 3500 C¹⁷ was examined for routine analysis after sample adjustment to pH 3.0. Results between the ICP-ES and the colorimetric test were consistent in that, of 50 samples tested for total and soluble copper using both methods, the measurements for all but 4 of the samples were within 15% of each other. Moreover, “spike and recovery” tests run on alginate yielded >95% recovery if the absorbance of the solution itself was accounted for. Consequently, total copper was determined colorimetrically after adjusting the sample pH to 3.0, whereas soluble copper was determined using the same method but after sample filtration through a 0.45 μm pore size syringe filter.

Free Cu⁺²

Free cupric ion concentrations were measured during titration experiments using an Orion 94-29 Cupric Electrode, an Orion 90-02 Double Junction Reference Electrode and an appropriate ion analyzer. The instrument was calibrated using cupric ion standards at the same ionic strength and stirring rate as samples, but at pH 6.0. During measurements, the meter calibration was checked every hour to correct for drift if it was present and the entire apparatus was covered with black plastic to prevent light interference.

At pH 6.0, copper is virtually 100% cupric ion, whereas at pH 7.0 cupric ion is only about 50% of the total soluble copper even if carbonate, organic matter, and other complexing ligands are absent. This increases the inherent error of the method and warranted additional confirmation testing. To accomplish this, solutions were constituted containing malonic and dipicolinic acids, which have functional groups similar to those in the alginate and NOM but with well defined complexation constants. This allowed comparison of measurements using the electrode to those predicted by equilibrium chemistry. At very low levels of free copper (< 15 ppb), the measured [Cu²⁺] was about 25% higher than predicted; however, in samples containing above 15 ppb of free copper the predicted and measured values were in good agreement (always less than 20% difference). This confirmed the general validity of the method and established a practical quantitation limit of 15 ppb Cu⁺².

Titration and Pipe Rig Tests

Two types of experiments were conducted including titrations and pipe rig tests. Titrations were designed to illustrate fundamental aspects of copper NOM chemistry. All titrations were conducted in 1 liter glass containers at 20 +/- 0.1° C, pH 7.0, in either 1 or 2 mM NaNO₃ as specified. The general approach was to dose different levels of cupric ion to stirred solutions containing different concentrations of NOM. The pH was held constant at 7.0 +/- 0.2 throughout the experiment by dropwise addition of NaOH. After a specified time period, changes in particle and solution characteristics were monitored through measurements of free Cu⁺², soluble copper, total copper, organic matter (UV₂₅₄), and particle zeta potential.

Pipe rig tests used a modified method of Johannson (1989)¹⁸ to illustrate changes in copper corrosion by-product release in response to water quality changes and aging. The rigs were 12” long, ¾” diameter Type L tubes with a volume of approximately 100 ml. Number two rubber stoppers were used to plug the ends of each tube and the pipe after being carefully rinsed 3 times with reagent grade water. All pipes were exposed to a soft, low alkalinity, NOM free water synthesized in the laboratory (Table 2), or the same water with either 2 mg/L as TOC soluble or 2% (W/V) sodium alginate. A parallel experiment was run at pH 9.5, making 12 pipes total after duplication.

After adjusting each water to either pH 7.0 or 9.5 +/- 0.2, fresh solution was poured into the pipes each Monday, Wednesday and Friday, resulting in a regular 48, 48 and 72 hour stagnation sequence for the experiment which ran as long as one year. After each pipe was filled, they were laid horizontally with a specified mark on the pipe exterior always facing up. Solutions from within each pipe after a 72 hour stagnation time were collected weekly and monitored for soluble copper, total copper, DO and pH. Data from all duplicate pipes were statistically identical and were pooled for the comparative analysis and confidence testing. The temperature of the pipes and solutions was 20 +/- 0.1° C at all times.

Other Measurements

Sample pH was measured using a Beckman 11 pH meter and dissolved oxygen (D.O.) was measured using a Hanna Instruments HI 9141 D.O. probe. TOC was quantified in samples using a Dorhrmann DC-80 Total Organic Carbon Analyzer with a DC-80 Sludge/Sediment Sampler according to Standard Method 5310.¹⁷ In titration experiments, the concentration of NOM removed by sorption or precipitation reactions was tracked by measurements of UV absorbance at 254 nm according to Standard Method 5910 B but at solution pH 3.0. Experiments indicated that copper did not interfere with the UV measurement at this pH and that soluble UV₂₅₄ was proportional to DOC. Zeta potential was measured using electrophoresis with careful control of temperature. Measurements were conducted in triplicate and the general accuracy of the measurement was confirmed using standard particle solutions.

RESULTS AND DISCUSSION

Initial experiments illustrated fundamental interactions between copper and organic matter including complexation, NOM removal from solution by sorption and/or precipitation reactions, and particle dispersion. Thereafter, the important impact of NOM on the solubility of copper solids with aging was revealed. The final phase of experiments clearly defined, for the first time, reproducible circumstances that can actually reverse copper corrosion by-product release to water under some circumstances, and then the section concludes with a short summary.

Fundamental aspects of organic matter/copper interactions

The phenomena resulting from interactions between NOM and cupric ion may be viewed as variations of the basic complexation reaction:



where Cu^{+2} = cupric ion concentration
 L^{-Z} = organic ligand binding site with charge $-Z$
 $CuL^{(2-z)}$ = cupric organic matter complex

For a given ligand, this association is expressed through the equilibrium constant:

$$K_i = \frac{[CuL_i]}{[Cu^{+2}][L_i]} \quad \text{Equation 3-2}$$

Different classes of organic ligands are present in drinking water supplies. Of these, soluble anionic polymeric substances such as fulvic acids are dominant, although colloidal organic materials such as peat can also be significant under some circumstances.¹⁹ Ligands from biological processes such as extracellular polymeric substances (EPS) are generally not important in the bulk water phase, although they are present at extremely high concentrations on the pipe surface within omnipresent biofilms.

Even within a given class of ligand, a wide range of copper binding sites may be present, each with a distinct complexation constant “K” and concentration that varies with pH and ionic strength. Considering this, several approaches can be used to model copper binding including: distributed binding strength (infinite variation in ligand binding strength), multiple ligand binding strength (a finite number of discrete sites with varying concentration) and single ligand binding.²⁰ As a net result of these interactions, cupric ion in natural waters is present as free copper (Cu^{2+}), soluble inorganic complexes (Cu-Ing) such as $\text{Cu}(\text{OH})_x^{2-x}$ or CuHCO_3^+ , soluble organic complexes (Cu-DOM), particulate organic complexes (Cu-POM), and inorganic precipitates (cupric solids).

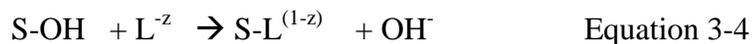
$$[\text{Cu}]_{\text{total}} = \text{Cu}^{2+} + \text{Cu-Ing} + \text{Cu-DOM} + \text{Cu-POM} + \text{Cupric solids} \quad (\text{Equation. 3-3})$$

As corrosion and dissolution of scale proceed within an aerobic copper pipe, the drinking water is equilibrated with the pipe during stagnant flow periods and vice versa, essentially titrating the solution with cupric ions. Consequently, a range of phenomena relevant to corrosion by-product release can be examined by simply titrating of solutions containing various organic matter sources while tracking changes in free copper and soluble copper. Of course, if total copper concentrations are below the solubility product of inorganic copper solids [i.e., about 6 mg/L at pH 7.0 and 23° C for fresh $\text{Cu}(\text{OH})_2$],¹¹ formation of copper organic complexes can only decrease free copper concentrations compared to solutions in which organic matter is absent (Figure 3-1). Approximate linearity in plots of free copper versus total copper for solutions containing 2 mg/L particulate organic matter and 2 mg/L soluble organic matter demonstrate that, over the free copper concentration range of interest in drinking water (\cong 0.015-1.5 mg/L free copper), multiple ligand models did not fit the experimental data significantly better than models using a single binding site. Thus, a single ligand model with complexation constants valid over this range (Table 1) was used throughout this investigation. This approximation is not likely to be valid at much lower levels of free copper.^{7,18}

The nature of the organic matter ligand determines whether complexation produces particulate, soluble, or some combination of particulate and soluble copper reaction products. In the case of soluble NOM, the resulting complex is completely soluble, whereas the complex is completely

insoluble in the case of particulate NOM (Figure 3-1). Interestingly, although the alginate solution contained virtually 100% soluble organic matter, addition of cupric ion and subsequent binding to alginate produced an insoluble precipitate that was visible during the titration and could be at least partly removed by filtration. Thus, copper addition to solutions containing alginate produced a mixture of soluble and particulate copper. In the context of equation 1, formation of particulate copper alginate solids may be appropriately viewed as a precipitation reaction, in which a copper-alginate solubility product is exceeded.

Another important reaction involves colloid mobilization or dispersion of pre-existing solids. That is, in some circumstances in natural waters, anionic organic matter can sorb to pre-existing copper solid surfaces and disperse particles similar to action of anti-scaling agents or anti-coagulants.²¹ The basic reaction begins with sorption of organic matter to pre-existing copper surfaces by surface complexation reactions of the type:



where S-OH = surface complexation site on a copper solid or particle

To illustrate this reaction, soluble NOM was titrated to solutions containing freshly precipitated Cu(OH)_2 solids prepared according to methods published elsewhere (titration of 0.5 mM $\text{Cu(NO}_3)_2$ solutions to pH 7.0).¹¹ After allowing 12 hours of aging, the resulting particle zeta potential was determined. The amount of NOM sorbed onto the pre-existing particles was also determined by filtration through a 0.02 μm pore size filter. At pH 7.0 and in the complete absence of organic matter, Cu(OH)_2 solids have a highly positive surface charge in 1 mM NaNO_3 solutions (Figure 3-2). However, as the concentration of soluble NOM in the water at equilibrium increases, the concentration of organic matter on the particle surface increases and particle zeta potential (surface charge) decreases. In fact, the particle zeta potential decreases to below about -20 to -30 mV, values below which particle dispersion begins to become visually significant, when soluble NOM in the water is only about 1-2 mg/L. Above soluble NOM levels of about 2 mg/L, only slight effects on particle zeta potential and sorption density are observed.

Dispersion of pre-existing colloids by sorbed NOM can be dramatic. To illustrate, fresh $\text{Cu}(\text{OH})_2$ solids were prepared and, after about 2 hours of aging, soluble copper in the water was stable at 6.2 mg/L consistent with $\text{Cu}(\text{OH})_2$ equilibrium (Figure 3-2). Aliquots of this solution were then spiked with either 2 or 20 mg/L NOM. Three minutes after spiking 20 mg/L NOM to the water, the zeta potential decreased to below -35 mV and more than 97% of the copper passed through a 0.45 μm pore size filter. Interestingly, however, only 12 mg/L of this copper passed through a 0.02 μm pore size filter, supporting the notion that the copper was mostly in the form of a stable copper colloid with some soluble complex formation. No change in copper solubility occurred with the 2 mg/L NOM spike, mostly likely because the particle zeta potential only decreased from + 35 mV down to +10 mV.

Complexation, colloid stability, and NOM sorption to precipitated solids must all be considered in order to interpret results of titrations over a wide range of copper doses at pH 7.0 when soluble NOM is present. In the absence of NOM, soluble copper increases steadily until the solubility product is exceeded at about 6 mg/L copper, after which time most additional copper added to the solution precipitated. In the presence of NOM, however, and at relatively low levels of copper addition well below the solubility product of $\text{Cu}(\text{OH})_2$ solids, formation of soluble NOM complexes increases solubility of copper. In fact, measurements of NOM-bound copper (NOM bound copper = total copper - free Cu^{+2} - calculated copper hydroxide complexes) were in very good agreement with that predicted by the single ligand binding model (Figure 3-3). At very high levels of copper addition (above 10 mg/L), as much as 80% of the soluble NOM is removed from solution by sorption reactions. In this range, soluble copper concentrations in solutions containing NOM can decrease markedly, since there is less NOM in solution to form soluble copper complexes. In the intermediate copper dose range, combined effects of soluble complexes and stabilized colloids tend to increase solubility compared to solutions without NOM.

Role of NOM in $\text{Cu}(\text{OH})_2$ Aging

Complexation and colloid mobilization are two important mechanisms leading to increased copper corrosion by-product release in the presence of natural organic matter. Given the importance of scale identity in controlling overall by-product release,^{11,12,13} another key

mechanism of interaction might involve altering the identity of the scale layer itself. To investigate this possibility, the experiment depicted in Figure 3-3 was allowed to continue while stirring at 20°C for several weeks. Consistent with the gradual transition of fresh $\text{Cu}(\text{OH})_2$ to tenorite with aging in such circumstances, soluble and free copper decreased markedly in the absence of NOM. At first glance, the increased copper solubility in the presence of NOM might be suspected to result from complexation; however, this is completely inconsistent with the *higher* free copper concentrations observed when NOM is present (Figure 3-4). This can only be explained by the presence of a higher solubility solid phase compared to the system without NOM.

For example, after 7 days aging in the absence of NOM, free copper was 0.55 mg/L while soluble copper was 1.17 mg/L (Figure 3-4). Making the reasonable assumption that the difference of 0.62 mg/L is attributable to soluble hydroxide complexes such as $\text{Cu}(\text{OH})_2^\circ$, the fixed ratio of copper hydroxide complexes to free copper is calculated as 1.12 to 1 in this system. In comparison, after 7 days in the solution that initially contained 8 mg/L NOM, the free copper concentration was 1.40 mg/L and the hydroxide complexes are calculated to be 1.57 mg/L. The remaining soluble copper ($3.94 - 1.40 - 1.57 = 0.97$ mg/L) may be attributed to soluble organic complexes with the small amount (≈ 1.5 mg/L TOC) organic matter left in solution after solids precipitation (Figure 3-3). In summary, of the 336% increase in copper solubility due to NOM in this case, only about 1/3 is directly attributed to organic matter complexation, the remainder is due to the higher free copper associated with a higher solubility solid phase. Even this underestimates the importance of the higher solubility solid, since according to equation 3-1 the concentration of soluble copper organic matter complexes will also increase as the result of higher free copper concentrations. Similar effects were observed when 2 mg/L NOM was initially present (Figure 3-4).

Is there any evidence that NOM interferes with scale aging under practically relevant conditions? To answer this question, two experiments were conducted. The first experiment used the pipe rigs from which data at various experimental times were compiled (Figure 3-5). At pH 7.0 and in the absence of NOM, copper corrosion by-product release after 48 hours of stagnation averaged 0.79 in the first month, eventually decreasing to 0.63 mg/L after 8-10 months of

experimental time. In contrast, for the same condition but with 2 mg/L NOM present, copper release *increased* from 1.6 to 2.2 mg/L NOM over the same time period. This increase with aging was significant at 95% confidence, as was the higher copper release in the presence of NOM compared to the system without NOM at pH 7.0.

At pH 7.0, the vast majority of the copper corrosion by-products were soluble. Based on the soluble copper concentrations and the hydroxide formation constants described earlier, it is estimated that 0.37 and 0.29 mg/L Cu^{+2} were present in the pipes without NOM at the new and old condition, respectively. Using the single ligand model and the assumption of equilibration with 2 mg/L soluble NOM, these free copper concentrations would be predicted to form 0.75 and 0.65 mg/L soluble organic matter complexes, respectively. In relatively new pipes, this predicted increase in copper is very consistent with that observed in the presence of 2 mg/L NOM, suggesting that the scale in such pipes was equilibrated with the same concentration of free copper with or without NOM present. However, in the older pipes, the increase in solubility was 0.87 mg/L higher than is predicted based on NOM complexation, and the assumption of identical free copper concentrations is not valid—the implication is that a scale formed in the presence of NOM that maintained a higher concentration of free copper.

A second experiment provided another perspective on this issue. After the above experiment was completed, 3 new pipes were started at the pH 7.0 condition and exposed for 2 months. Thereafter, solutions with 0 and 2 NOM were added to these new pipes and the old pipes in sequence. Before adding the sample with 2 mg/L, the pipe was filled 3 times over 15 minute intervals to equilibrate the NOM with scale on the pipe wall. In the pipes never exposed to NOM, copper release was slightly lower in the old pipes than in the newer pipes (Figure 3-5). Based on the estimated free copper concentration in each case and the assumption that free copper would stay constant, the single ligand model was used to predict soluble copper concentrations expected in the presence of 2 mg/L NOM (Figure 3-5). That prediction agreed very well with the experimental observation, supporting the idea that the identity of the higher solubility scale solid did not develop immediately upon NOM addition in pipes aged 2-12 months, but that this interference required some time to develop.

The key implications of these findings are synthesized in Figure 3-6. The concentration of soluble copper equilibrated with $\text{Cu}(\text{OH})_2$ solids and, by implication, copper pipe is:

$$\text{Soluble Cu} = \text{Cu}^{+2} + \text{Cu}^{+2}\text{-hydroxide} + \text{Cu}^{+2}\text{-carbonate} + \text{Cu}^{+2}\text{-NOM} \quad \text{Equation 3-4}$$

The log K of $\text{Cu}(\text{OH})_2$ solids decreases from 9.36 down to 7.4 as solids age.¹¹ At a given time of aging, the actual log K will tend to be higher in systems held at lower pH, lower temperature, or in the presence of NOM as illustrated in this work (Figure 3-4). This leads to higher concentrations of free copper and cupric hydroxide complexes after equilibration in pipes. In this simplistic model, the upper line in Figure 3-6 denotes the minimum copper corrosion by-product release in the presence of $\text{Cu}(\text{OH})_2$ solids of the indicated solubility.

Depending on the NOM and bicarbonate present, this minimum will be increased due to formation of complexes (Figure 3-6). For $\text{Cu}(\text{OH})_2$ with a log K of 8.56, which seems close to that estimated for relatively new pipes in water distribution systems,⁶ each mg/L of CaCO_3 alkalinity at pH 7.0 will add 0.75 mg/L soluble copper in carbonate complexes. Assuming the NOM described in this work is a suitable model for those present in other waters, each mg/L of NOM TOC will add another 0.38 mg/L copper organic matter complexes. In contrast, in the presence of tenorite solids which are more likely to form at higher temperatures, pHs, and in the absence of NOM, every 50 mg/L alkalinity adds only 0.08 mg/L copper and every mg/L NOM adds only 0.06 mg/L copper. Under such circumstances, corrosion by-product release is likely to be very low and not strongly impacted by NOM or alkalinity.

As a final point, the other key solid phase thought to be an important scale in copper pipes is malachite. At pH 7.0 and above about 80 mg/L alkalinity, free copper in the presence of malachite is about equal or less than that for tenorite in Figure 3-6. Thus, if malachite controls solubility, the maximum concentration of soluble copper is expected to be very low (< 0.2 mg/L) and is only a weak function of NOM concentration and alkalinity. This is consistent with the data presented in Korshin et al. (1996) in the absence of NOM.⁵ However, if traces of NOM were to prevent malachite formation, resulting in a cupric hydroxide solid phase instead, copper solubility could increase dramatically even at low levels of NOM. This idea has precedence in

the “trace organic” effect noted by Campbell,²² in that very low levels of organic matter completely change the type of calcite solids precipitated on pipes. It is also consistent with the “presence or absence” adverse effect noted in laboratory work with copper⁵ and in utility monitoring data.⁶ Additional work is necessary to determine whether this “NOM inhibition of solids aging” theory, the Korshin et al (1996) “colloid mobilization mechanism,” or some combination of the two theories is key to NOM impacts on copper corrosion by-product release in high alkalinity waters.

Mechanisms Leading to Reversal of Corrosion By-Product Release

During the pipe rig tests, intensive sampling was conducted after holding water in the pipe at various stagnation times to obtain by-product release profiles. In general, the concentration of soluble copper released to the water increased and gradually leveled off at a maximum value, similar to expectations for a surface activated or diffusion controlled dissolution processes. However, in two situations, by-product release would rise, reach a peak, and then decrease rapidly (Figure 3-7).

The first of these situations occurred in pipe rig tests with soluble NOM. To illustrate the mechanisms involved, 1 liter of the synthesized drinking water solution was recirculated (@ 1 gpm) in a closed loop while holding pH constant at 7.2. 5 mg/L DOC was spiked to the solution at $t = 0$ minutes and DO was saturated throughout the experiment. With time and as the pipe corroded, DOC in the water decreased (Figure 3-7), presumably due to sorption onto freshly formed $\text{Cu}(\text{OH})_2$ solids on the pipe wall. This resulted in a steadily decreasing solution complexation capacity, since organic ligands were being removed from solution. The net result is that soluble copper rapidly rose to that predicted by the solubility model, and then decreased rapidly as ligands were removed (Figure 3-7). This is analogous to the experiment illustrated in Figure 3-3, except that particulate copper is removed onto the pipe wall instead of requiring filtration.

The second phenomena occurred only in pipes that had biodegradable organic matter present and in which the dissolved oxygen concentration rapidly decreased to 0 (Figure 3-8). In such circumstances, very sharp peaks in copper by-product release occurred at the point where DO

dropped to nearly 0 mg/L, after which time copper steadily decreased. This phenomena was most recently reported by Werner et al. (1994),¹³ who hypothesized that when dissolved oxygen disappeared, previously released cupric ion could be reduced to form less soluble cuprite [Cu(OH)] which subsequently precipitated onto the pipe wall.

We attempted to reproduce this phenomena in well controlled beaker experiments. The general protocol involved addition of 1 mg/L as Cu²⁺ to 1 mM NaNO₃ solutions which also contained 30 gram of copper metal (Cu⁰). The oxygen was then removed by purging the sample with a 95% N₂/5% H₂ mixture. Multiple experiments using this arrangement illustrated no detectable decrease in Cu²⁺ concentration. After trying many different approaches, it was discovered that when 10⁻³ M NaCl was also present as a catalyst, soluble and free copper decreased rapidly when dissolved oxygen was removed from solution. In sum, if copper metal, no dissolved oxygen and a Cl⁻ catalyst are present, copper corrosion by-product release can be readily reversed apparently in accordance with the Werner et al. (1994) hypothesis. The role of organic matter is to promote microbial growth which, in turn, leads to reduced DO necessary to drive the reaction.

Overall Summary of Organic Matter Effects

The overall effects of organic matter on copper corrosion by-product release can be conceptualized quite simply (Figure 3-9). In the presence of oxygen, copper metal corrodes forming a solid scale layer of Cu(OH)₂ or malachite. This scale layer equilibrates with the water, controlling the free copper concentration. Free copper can react with organic matter in solution, forming either soluble complexes, particulate complexes, or precipitates depending on the nature of the organic ligand. All of these reactions tend to increase copper corrosion by-product release. The interaction of organic matter with scale, and interruption of solids aging, tends to maintain higher free copper concentrations in solution than in cases where NOM is completely absent. This increases the concentration of both organic and inorganic copper complexes.

Under some circumstances, the presence of organic matter can lead to reversal of copper corrosion by-product release. If bacteria can utilize the organic matter and remove all of the DO (or DO is otherwise consumed), soluble copper concentrations will decrease if chloride or other suitable catalysts are present. Similarly, sorption of soluble NOM onto freshly formed copper

surfaces can decrease the solution complexation capacity, causing re-deposition of previously released cupric ion onto the pipe wall. Under at least some circumstances, NOM can sorb onto scale surfaces and cause detachment of particulate copper due to development of unfavorable surface charge or other dispersive effects, but it is unclear whether this effect is significant at typical NOM concentrations in drinking water systems.⁵

CONCLUSIONS

- Natural organic matter in drinking water can increase copper corrosion by-product release by complexation and/or colloid mobilization/dispersion.
- Formation of soluble NOM complexes is most significant in low alkalinity waters containing high concentrations of NOM.
- Even at low soluble NOM concentrations, incorporation of natural organic matter into a pipe scale layer will interfere with natural aging processes, maintaining higher than anticipated free copper concentrations than in the absence of NOM. This effect will tend to increase the soluble concentration of copper hydroxide, copper carbonate and copper NOM complexes in a wide range of waters.
- Colloid mobilization is certainly possible, but seems to be most important only at very high levels of NOM and in the presence of $\text{Cu}(\text{OH})_2$ solids.
- The presence of organic matter can reverse copper corrosion by-product release during stagnation by:
 - 1) serving as a food source for bacteria, leading to complete removal of DO and subsequent re-deposition of copper onto the pipe wall in the presence of chloride or other catalysts;
 - 2) gradual sorption of soluble natural organic matter onto scale on copper pipe surfaces, decreasing the soluble copper complexation capacity of water and leading to reduced copper concentrations after long stagnation times.

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Table 1. Key characteristics of concentrated soluble NOM stock solution.

Parameter	Value
DOC	1150 mg/L
Humic DOC*	219 mg/L
Sum Hardness (Ca, Mg, Al)	< 4 mg/L
pH	6.2
Net anionic charge at: pH 6.2 pH 7.0 pH 11.0	9.7 meq/g DOC 10.1 “ 11.2 “
K _{Cu} (@ pH 7.0)	1.44 x 10 ⁻⁵
L _t	13 mM sites/g DOC [#]
Cu	2 mg/L

*Fraction precipitating at pH 1.0

[#]Valid at 7.0 over the concentration range of 0.015-1.5 mg/L free copper.

Table 2. Low alkalinity-soft water synthesized* for use in pipe rig experiments. pH was adjusted to 7.0 or 9.5 with addition of reagent grade NaOH and HNO₃.

Ion	Concentration (mg/L)
Magnesium	3
Chloride	9
Calcium	5
Nitrate	16
Sulfate	16
Sodium	17
Silica	20
Alkalinity (as CaCO ₃)	5

* added as reagent grade MgCl₂, Ca(NO₃)₂*4H₂O, Na₂SO₄, Na₂SiO₃, and Na₂CO₃

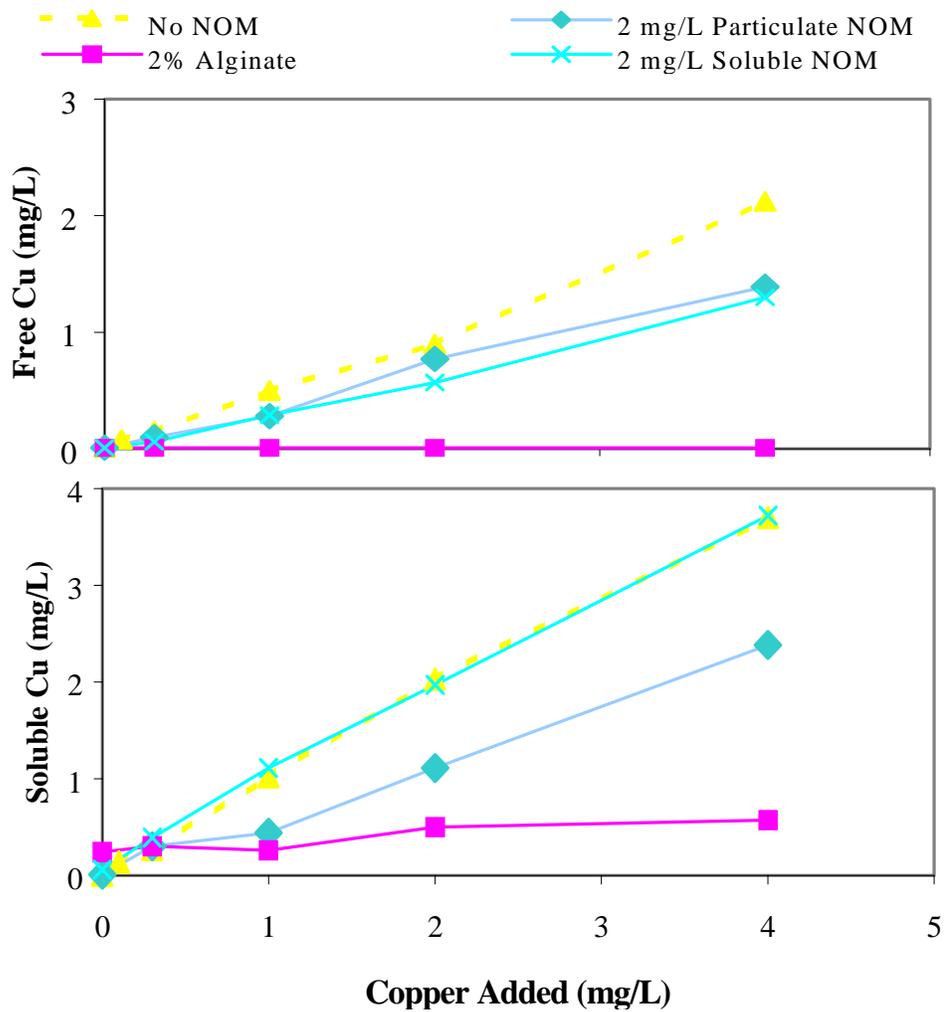


Figure 3-1: Free copper (above) and soluble copper (below) after titrating solutions containing different types of organic matter.

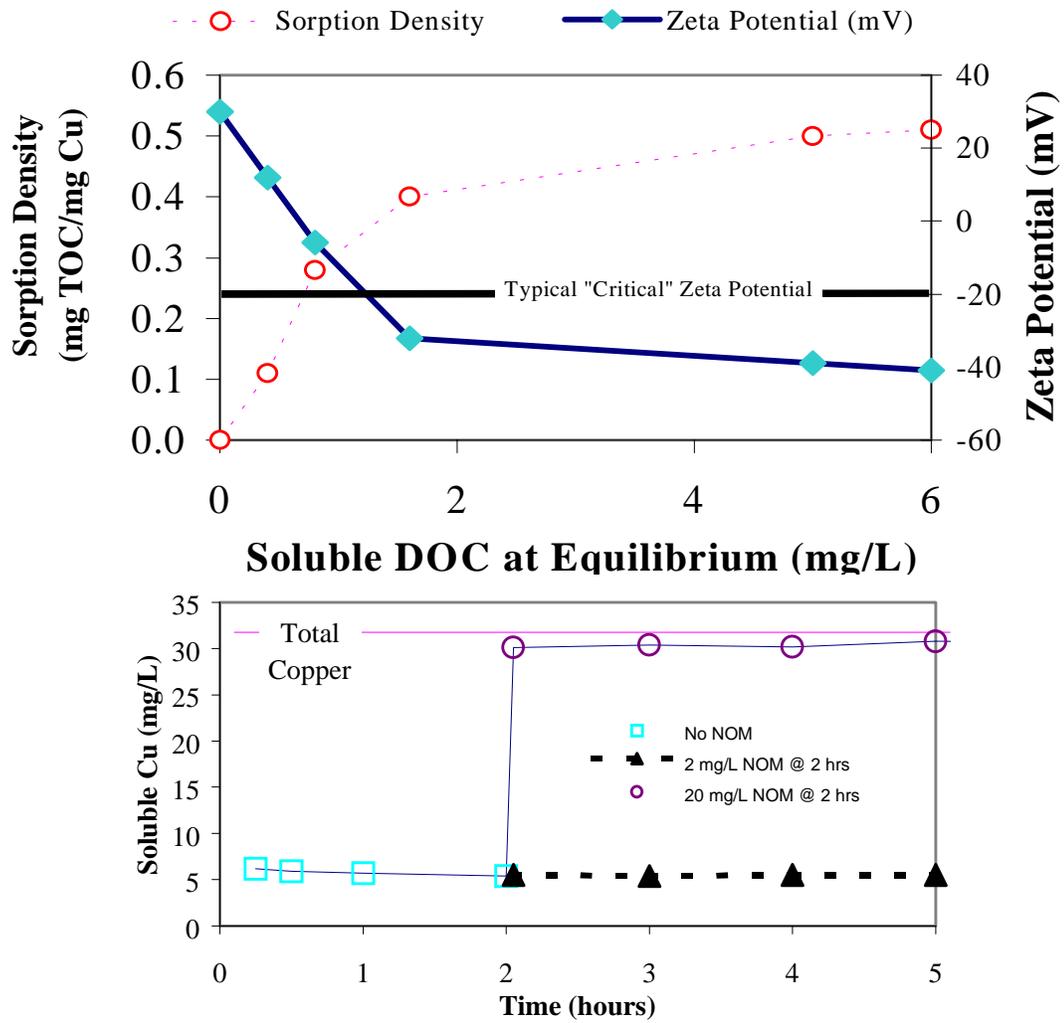


Figure 3-2: Effect of NOM on particle zeta potential (above). Added NOM can have either drastic or no effect on soluble copper, depending on the concentration added due to a dispersion effect (below). Conditions: pH 7.0, I = 2 mM NaNO₃, 20° C.

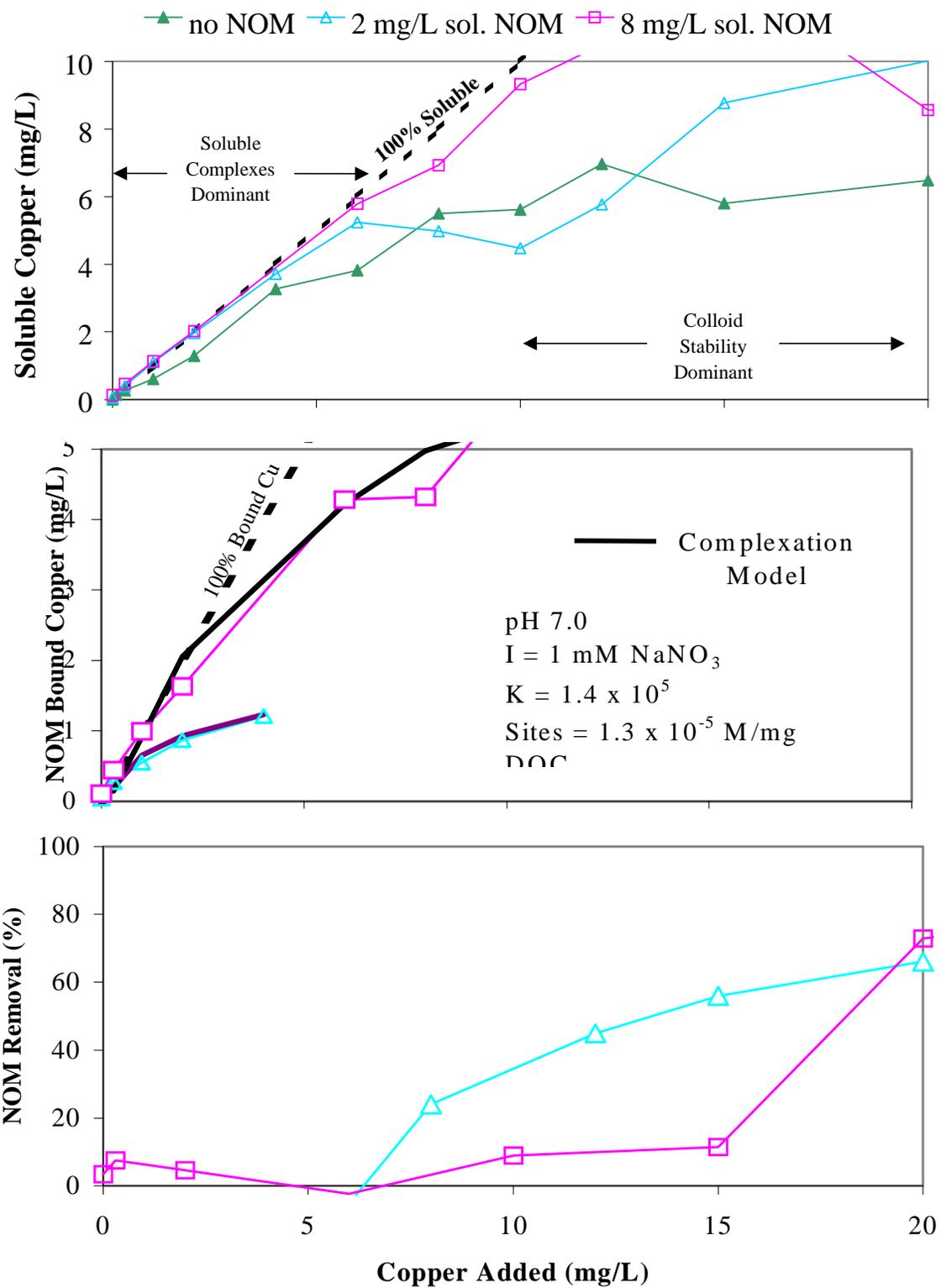


Figure 3-3: Soluble copper concentrations are a complex function of total copper added and NOM concentration (above). At low levels of total copper, increased solubility is consistent with complexation models (middle). At high levels of copper, NOM is removed from solution by sorption onto precipitating cupric solids (below).

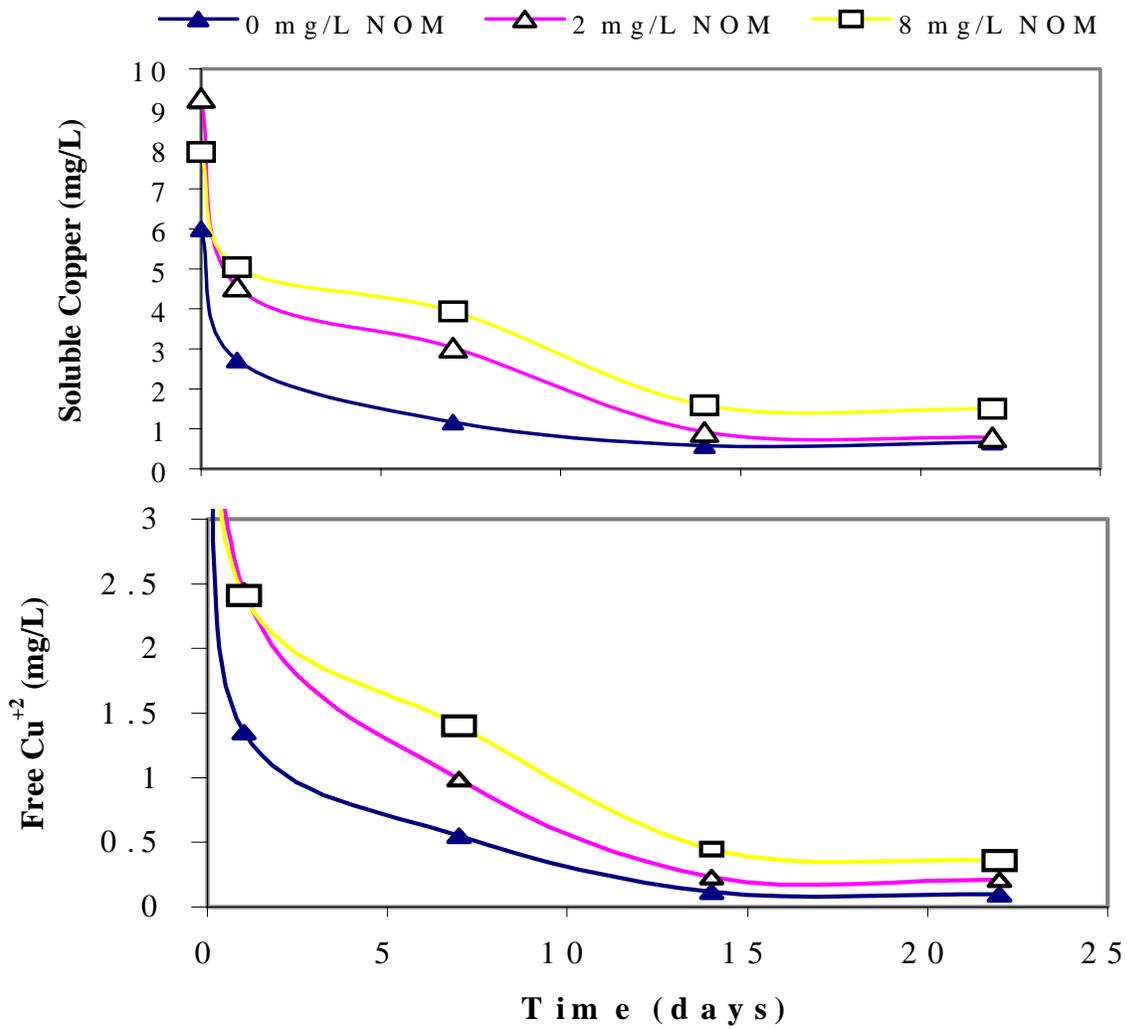


Figure 3-4: The presence of sorbed NOM interferes with aging of cupric solids, maintaining higher solubility (above) and higher Cu⁺² concentrations (below).

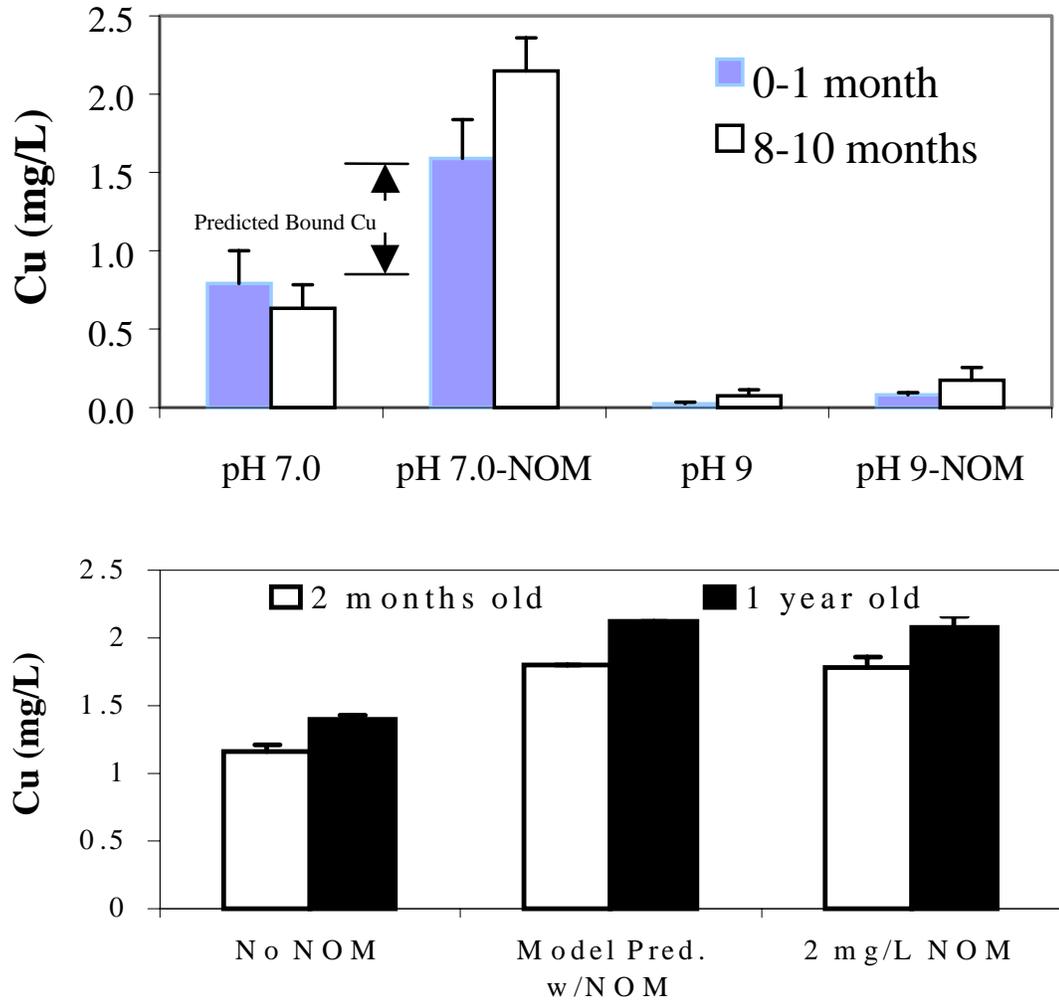


Figure 3-5: If NOM is present during aging, by-product release increases with time, whereas it decreases with time without NOM (above). When copper pipes are aged in the complete absence of NOM, increases in copper after NOM addition are consistent with complexation models alone (below).

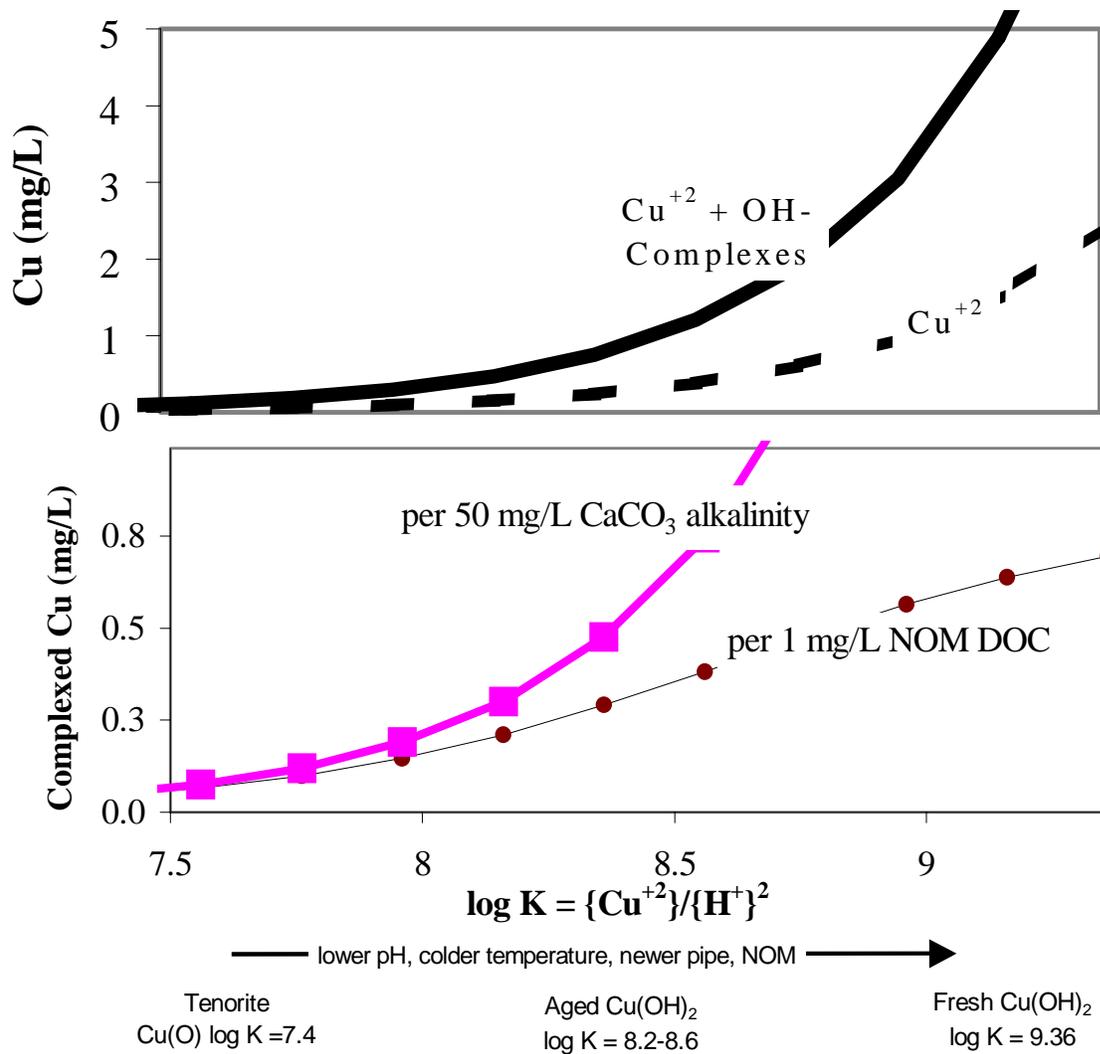


Figure 3-6: Predictions for soluble copper in the presence of various cupric hydroxide phases (above) and in the presence of key complexing agents in drinking water (below). Model prediction: 20° C, I = 2 mM.

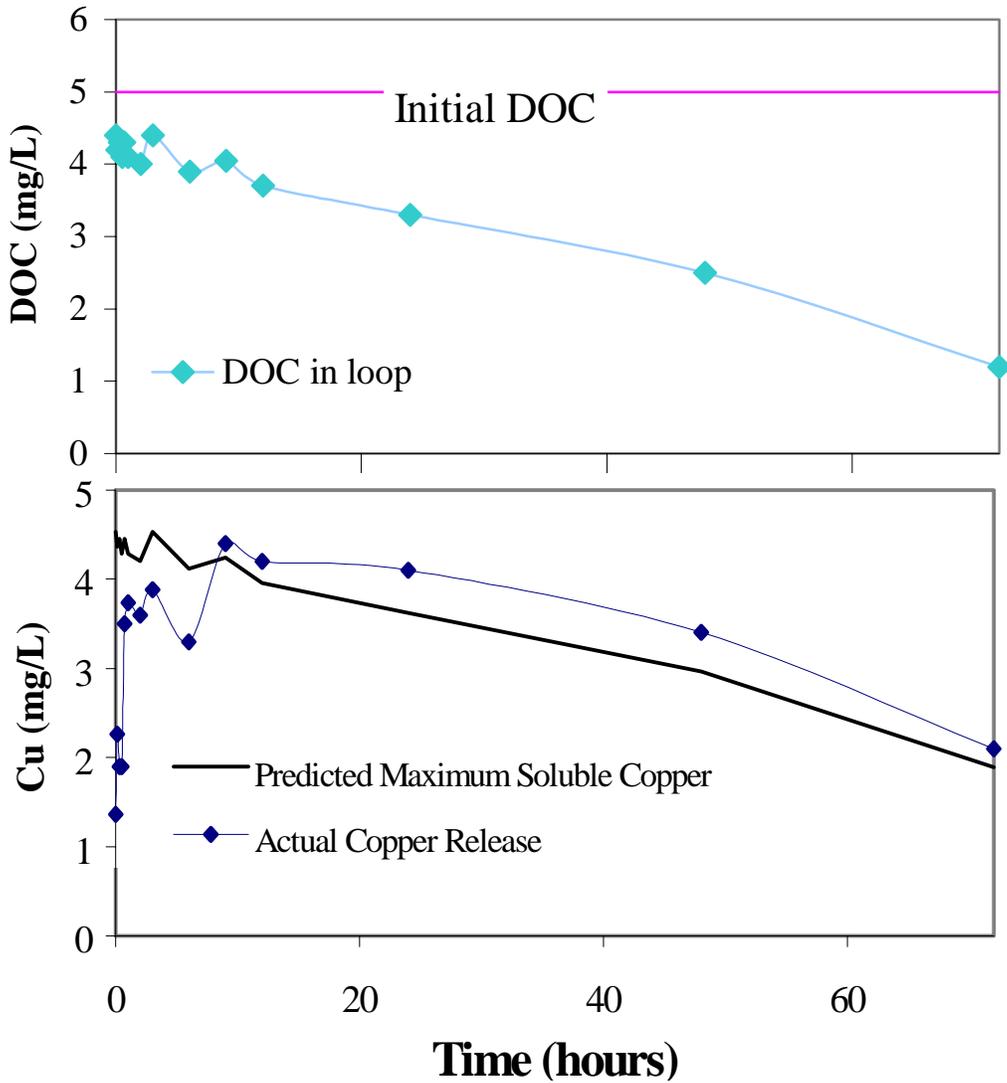


Figure 3-7: As water is recirculated through the pipe, DOC is removed from solution (above). This decreases complexation capacity (below), and ultimately decreases soluble copper release. Conditions: constant pH 7.2, alkalinity 5 mg/L, 1 year pipe age.

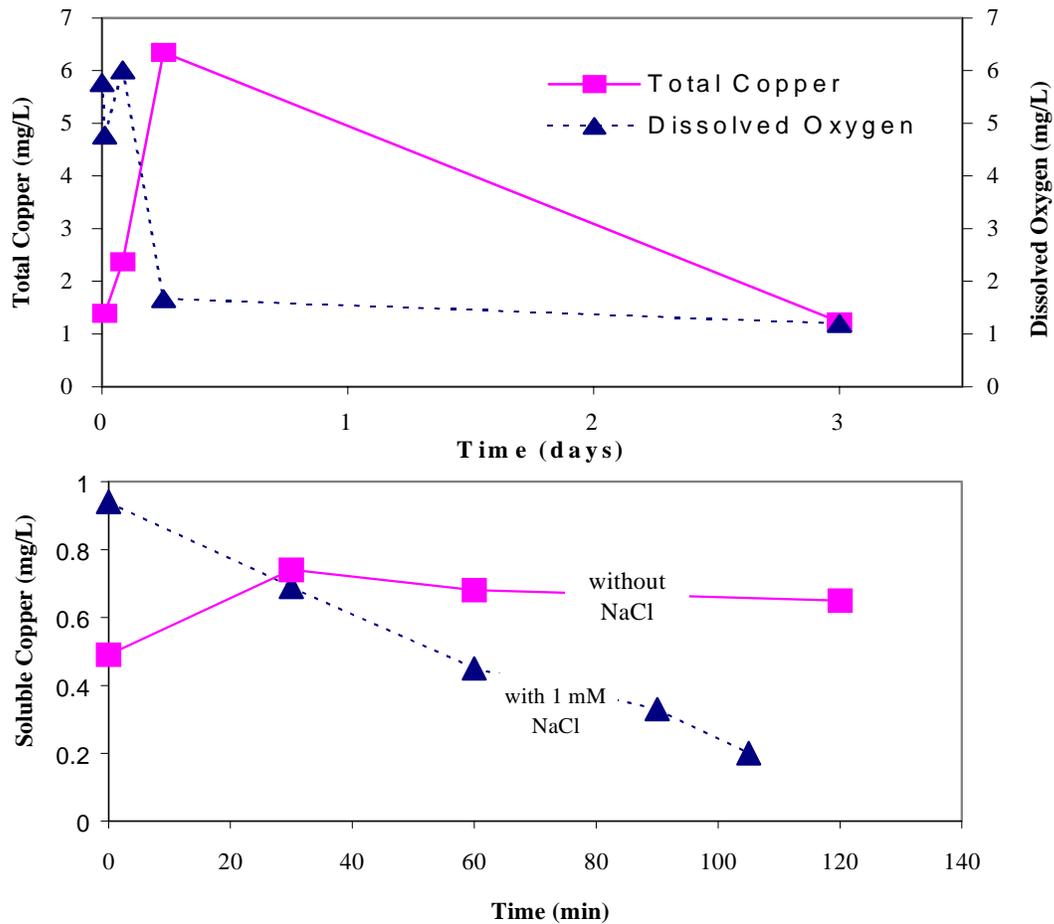


Figure 3-8: During stagnation in pipes containing high concentrations of biodegradable organic matter (2% alginate), copper levels peak after about 6 hours and then plummet after DO is completely consumed (above). The same trend was reproduced in batch tests, but only copper metal and chloride were present (below).

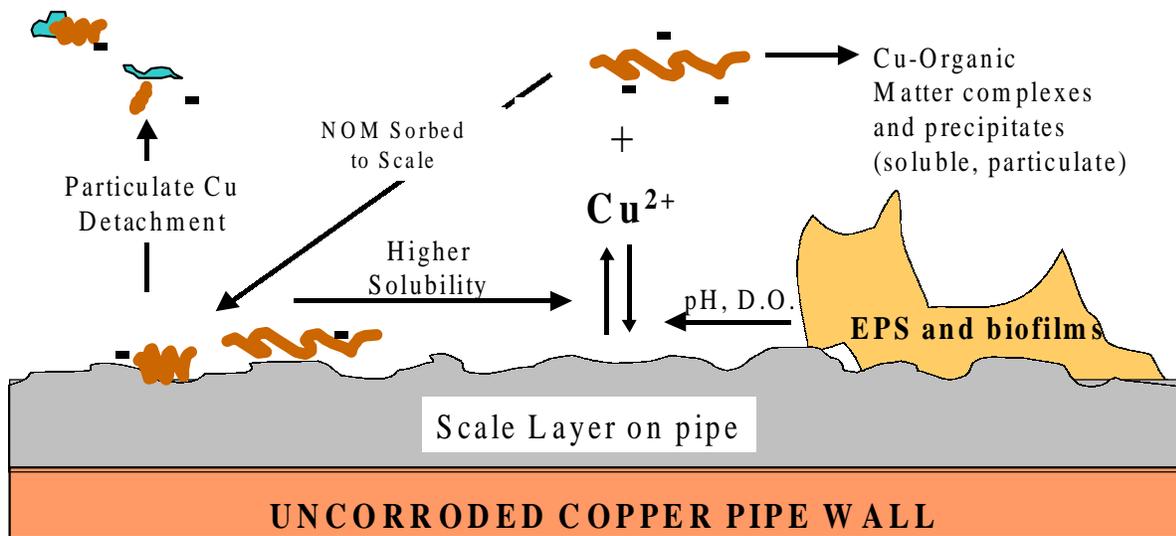


Figure 3-9: Mechanisms by which organic matter influences copper corrosion by-product release.