MONITORING THE BEHAVIOR OF COPPER AND ZINC COMPLEXES IN SIMULATED STORMWATER DETENTION SYSTEMS

A Thesis in
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by
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ABSTRACT

Metals are one of the primary concerns regarding industrial stormwater discharge because of permit limits on their discharge. The formation of metal-ligand complexes in stormwater, particularly with copper and zinc, are not studied frequently, but they may have a large impact on the traditional processes used in stormwater treatment. In a historical study, it was anticipated that zeolite would achieve the best efficiency at removing dissolved copper from stormwater runoff, but the testing showed that the actual removal rate was rather underwhelming, and zeolite was ineffective. The formation of the metal-ligand complexes might result in a complex structure that no longer fits into the lattice space of the zeolite, as well as having a different valence charge since zeolite is best prepared for a valence charge of +2. In this experiment, a factorial design with three parameters including pH, dissolved organic matter, and chloride was used to examined the significance of each factor and their potential interactions that could impact the free and total metal concentration in simulated stormwater runoff. Differences were seen in recovered free copper due to pH. To further this investigation, a set of deep column experiments that simulated stormwater detention ponds and using the same experiment design were set up to observe the formation and kinetics of metal-ligand complexes. The results indicated that free copper and zinc concentration had a significant spike with the introduction of dissolved organic matter and salt. The formation of metal complexes was anticipated and observed when the concentration of copper and zinc went down significantly following the peak of spike, due to the decrease in amount of remaining available free metals in the columns.
# Table of Contents

LIST OF FIGURES ........................................................................................................... v

LIST OF TABLES ............................................................................................................... vi

Chapter 1 Introduction ................................................................................................. 1

1.1 Background knowledge ............................................................................................. 1
1.2 Research goals ............................................................................................................ 5

Chapter 2 Methodology ............................................................................................... 5

2.1 Sampling location ....................................................................................................... 5
2.2 Sample collection ....................................................................................................... 6
2.3 Total Cu, Total Zn and Free Cu determination ......................................................... 7
2.4 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matter as the Factors ......................................................................................................................... 8
2.5 Investigation of Metal Complexation Using Column Simulation ....................... 9
2.6 pH, Oxidation Reduction Potential Observation .................................................... 11
2.7 Dissolved Oxygen Observation .................................................................................. 11

Chapter 3 Results ......................................................................................................... 11

3.1 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matter as the Factors ......................................................................................................................... 11
3.2 Investigation of Metal Complexation Using Column Simulation ....................... 14
3.3 Investigation of Metal Complexation Using Column Simulation (Short term) .... 17
3.4 pH, Oxidation Reduction Potential Observation .................................................... 19
3.5 Dissolved Oxygen Observation .................................................................................. 21

Chapter 4 Discussion .................................................................................................... 22

4.1 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matters as the Factors ......................................................................................................................... 22
4.2 Investigation of Metal Complexation Using Column Simulation ....................... 23
4.3 pH, ORP, and DO Monitoring Results ..................................................................... 24

Chapter 5 Conclusions ............................................................................................... 25

5.1 Conclusions ................................................................................................................ 25

References ..................................................................................................................... 27
LIST OF FIGURES

Figure 1. Anticipated changes in precipitation as presented in the National Climate Assessment (Melillo, 2014). ........................................................................................................2

Figure 2. Anticipated increase in maximum dry days between storm events as predicted in the National Climate Assessment Report (Melillo, 2014) ........................................3

Figure 3: Geographical location of one of the sampling sites at Swatara Water Trail ........7

Figure 4: Experimental setup of Column Simulation .............................................................................................................10

Figure 5. Copper measurements as a function of 2^3 factorial design.................................................................12

Figure 6: Free copper concentration in mg/L without zeolite regeneration up to 700 hours ... 15

Figure 7: Free copper concentration in mg/L with zeolite regeneration up to 700 hours ........15

Figure 8: Zinc concentration in mg/L without zeolite regeneration up to 700 hours ..........16

Figure 9: Zinc concentration in mg/L with zeolite regeneration up to 700 hours .........17

Figure 10: Free copper concentration in mg/L without zeolite regeneration in the first 240 hours ..............................................................................................................................................18

Figure 11: Free copper concentration in mg/L with zeolite regeneration in the first 240 hours..................................................................................................................................................18

Figure 12: Zinc concentration in mg/L without zeolite regeneration in the first 240 hours .... 19

Figure 13: Zinc concentration in mg/L with zeolite regeneration in the first 240 hours ....... 19

Figure 14: Continuous monitoring data of pH for 4 columns in 30 days ..............................................20

Figure 15: Continuous monitoring data of oxidation reduction potential for 4 columns in 30 days ..................................................................................................................................................20

Figure 16: Dissolved Oxygen for 4 columns in the initial 240 hours ..............................................21
LIST OF TABLES

Table 1: Factorial design trails with each respected dosage ........................................8

Table 2: Relative impact of pH, chlorine and dissolve organic matter on copper and copper with zeolite regeneration at different timeframe ...........................................13
Chapter 1 Introduction

1.1 Background knowledge

The stormwater treatment systems that are designed to filter out target pollutants of concern largely rely on water retention which provides time for treatment reactions to occur. In the recent years, the impacts of climate change are closely monitored, and researchers predicted that an increase in the number of dry days is expected.

*Climate Change Impacts.* In Pennsylvania, climate change is predicted to result in limited changes in total precipitation compared to current conditions (Figure 1). For southcentral Pennsylvania, for example, winter precipitation is expected to increase by 10 – 20%, spring increases by 0 – 10%, and no anticipated changes in total precipitation for the summer and fall seasons.

What is predicted to change is the increase in the number of dry days between storms (Figure 2). For southcentral Pennsylvania, the anticipated change is between 5 – 10% in the maximum number of consecutive dry days, e.g., antecedent dry days between storms.

The increase in the number of dry days might create challenges in these treatment systems since multiple processes like sedimentation, coagulation, and sorption are involved to remove pollutants and since their effectiveness changes as the pH, dissolved oxygen, and oxidation-reduction conditions change in the systems. Two of the many problematic issues involving stormwater runoff are heavy metals, specifically, copper and zinc. Stormwater filters could potentially enter quiescent times when consecutive dry days occur more frequently, and no influent enters the filter which creates anaerobic conditions. Research suggested that for heavy
metals like copper and zinc, these pollutants tend to form complexes and causing filter media permanently retain these trapped pollutants even in anaerobic conditions (Clark & Pitt, 2009). Modeling has shown that metal complexes from copper and zinc are easily formed and might transform with changing conditions since copper and zinc are both transition metals with multiple possible charges. The form of these metals in stormwater is poorly understood, and their behaviors in different detention systems needs further investigation.

**Projected Precipitation Change by Season**

![Projected Precipitation Change by Season](image)

Figure 1. Anticipated changes in precipitation as presented in the National Climate Assessment (Melillo, 2014).
Metal complexes in stormwater could involve a combination of organic and inorganic ligands, including dissolved organic matter, nitrate, and phosphates, that come directly from stormwater runoff. Similarly, considerable amount of inorganic chlorides from snowmelt composites could be complexed through introduction in runoff, as well. The mechanism of metal-ligand complex in stormwater is still poorly understood with very limited data, mainly because multiple parameters could attribute to both forward and reverse kinetics of these complexations.

Change in Maximum Number of Consecutive Dry Days

Figure 2. Anticipated increase in maximum dry days between storm events as predicted in the National Climate Assessment Report (Melillo, 2014)

These parameters, such as temporal changes in pH, oxidation-reduction potential, dissolved oxygen, ion interactions, and ligands, each has potential to affect the behavior of metal
complex to some degree while a combination of selected few could result in more drastic change. An example was demonstrated by Clark and Pitt and their prior research on stormwater filters where changes in oxidation-reduction potential during quiescent times released the previously trapped metals, returning them to the porewater in the following event (Clark & Pitt, 2009). With a deeper understanding of metal removal in stormwater, the treatability of metal, particularly copper, might have largely different efficiency and which may be a function of the residence time in the filter. When trying to create a biofilter media to remove copper, Clark and Pitt noted a rather interesting issue where the surface modified zeolite did not achieve a satisfactory removal efficiency. In theory, zeolite should be the most optimal choice since it operates under the principle of ion exchange where the cation, in most cases sodium, binds weakly to the lattice structure and is easily exchanged by the pollutant of interest. The research pointed out that the zeolite might not be as effective since zeolite is most suitable for ion with a valence charge of +2, and many complexes will not fit into the lattice space of the zeolite because of their multi-valence charges (Clark & Pitt, 2010).

In order to test this hypothesis, two experiments were performed. The first experiment, using a factorial design, evaluated the impact of various factors (pH, DOM, chloride) on free copper concentrations at 30 and 90 minutes. The water then was analyzed for copper and zinc, with zeolite used to separate free copper ions from complexes. The zeolite was regenerated using sulfuric acid to determine if additional free ions, and not complexes, were not measured in the initial water analysis.

Statistically, this experiment will analyze the system at four different conditions. This will correspond to a factorial analysis, because the factorial analysis can investigate interactions between multiple parameters (Berthouex & Brown, 1994). By assigning a high and low value to each parameter of interest, the model determines the relevancy of each parameter by conducting series of experiments concurrently. The impacts of each interactions are then calculated with
appropriate algorithm and analyzed statistically with a graphical representation. In this experiment, the parameter of interest such as pH, sodium chloride concentration, and dissolved organic matter would be selected for the factorial analysis to estimate the significance of each parameter to the overall free metal concentration.

A second experiment simulated a detention pond where water was allowed to sit in columns for up to 30 days with samples collected from the bottom of the column periodically. These tests were done at the natural pH of the water. This was a $2^2$ factorial experiment using DOM and chloride as the factors.

1.2 Research goals

The purpose of this research is to improve the understanding of zinc and copper metal complex with ligands in simulated stormwater detention pond conditions by monitoring the kinetics of these metal-ligand complexes over an extended period of time.

Chapter 2 Methodology

2.1 Sampling location

The initial factorial analysis was performed using distilled water. For the simulated detention pond, water samples were collected from the Pennsylvania State University Harrisburg campus creek and the Swatara Creek near the confluence with the Susquehanna River, south of campus. The local weather in Middletown, Pennsylvania was monitored throughout dry season, to track and prepare for a specific day with potential storm. All the samplings were done in a single day in August of 2019 which had substantial precipitation, to ensure that enough samples
were collected for the entire procedure. The purpose was to get test water that had been impacted by stormwater runoff.

2.2 Sample collection

Two 20 L buckets were brought to the sampling locations during the rainfall, one was used for sample collection at Penn State Harrisburg campus creek beside TL building, another one was used at boat launch location at the Susquehanna River. Equal amount (20 L) of natural rainfall water in the river and creek were collected, and the samples were stored at Penn State Harrisburg Pilot lab at room temperature for further mixing and usage. The samples were mixed in the lab and used to fill 4 columns that were used to mimic detention ponds.
2.3 Total Cu, Total Zn and Free Cu determination

Total copper, total zinc, and free copper were measured with HACH DR 6000 UV VIS Spectrophotometer (HACH, Inc.). The samples were tested for total copper and free copper with HACH CuVer 1 Copper Reagent Powder Pillows (Product # 2105869) and Free Copper Reagent
Powder Pillow (Product #2182369) respectively, according to USEPA Bicinchoninate Method 8506. The samples were also tested for total zinc with ZincoVer 5 Zinc Reagent Powder Pillows (Product #2106669) according to USEPA Zincon Method 8009.

2.4 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matter as the Factors

A $2^3$ factorial design with three parameters including pH, chloride, and dissolved organic matter was tested to see the impact and relevancy of each parameter on the overall concentration of the metal of interests. A series of deionized water samples were created in the specific conditions summarized in Table 1, varying with two pH values (7 and 9), two chloride values (10 mg/L and 30 mg/L) and two dissolved organic matter values (10 mg/L and 25 mg/L). The pH in each trial were calibrated as needed in each trial after mixing, but the actual pH readings were not continuously monitored. The high and low parameter values were used in combination with others to create a collection of samples, for a total of 8 trials.

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</table>

For run number 1, 2, 5 and 6, to create the low Cl concentration, CuCl$_2$ was used as sole chloride component. For each trial, the samples were filtered through a Whatman membrane filter (0.45 um pore size) using Gelman filter apparatus which was filled up to half volume with zeolite.
For run number 3, 4, 7 and 8, the additional 20 mg/L NaCl was added to the original amount of CuCl$_2$ to increase the salt concentration but staying at levels to avoid interferences with the copper test. For each run, the concentration of total copper, free copper, and total zinc were measured respectively after 30 minutes and 90 minutes using a Hach DR6000 Spectrophotometer. A regeneration process was applied to each trial afterwards by flushing the zeolite pores with sulfuric acid, and the purpose of this process was to rinse out the weakly bound metals. 50 ml sulfuric acid (0.02 N) was diluted by half and filtered through Gelman filter apparatus to release the previously trapped metal ions. The readings of total copper and free copper with and without zeolite regeneration were recorded, respectively.

2.5 Investigation of Metal Complexation Using Column Simulation

Four large plastic columns were used to perform additional testing where there would be an overlayer of water and the potential for changing conditions in the column due to biochemical interactions. The goal was to simulate a shallow detention pond. Each column is a cylinder with roughly 8 L in volume, a diameter of 0.102 m, and a height of 1.016 m tall. The columns were setup as in Figure 3. There is a valve at the bottom of each column for sample collection.

The water samples collected and stored previously at PennState Harrisburg Pilot Lab were mixed as 50% creek water to 50% natural rainfall. All columns were filled with equal volume of mixed samples. In order to simulate the specific conditions that were selected for examination, 800 mg sodium chloride was added to column 2 to mimic the road salt concentration in detention ponds to achieve a salt concentration of 100 mg/L. Similarly, 800 mg humic acid was added to column 3 to represent pond bottom sediment to achieve a dissolved organic matter concentration of 100 mg/L. Next, 800 mg of both salt and DOM were added to
column 4 to understand the potential impact on the behavior of metal complexes. Column 1 remained free of salt and DOM as control.

For each column, 4 mg of copper and 8 mg of zinc were added to achieve an initial concentration of 0.5 mg/L for copper and 1 mg/L for zinc. A 100 ml sample was taken from each column at the following times and analyzed for free copper, and total zinc analysis using the
zeolite regeneration process: 0 min, 30 min, 1 hour, 2 hour, 5 hour, 12 hour, 24 hour, 48 hour, 120 hour and 240 hour.

2.6 pH, Oxidation Reduction Potential Observation

One pH probe and one oxidation-reduction potential probe were connected to a Logger Pro Interface. Both probes were submerged into each column for continuous measurements, the sample collecting rate was 1 collection per minute. This allowed trends to be observed. In this case, the parameters including pH, oxidation reduction potential, and dissolved oxygen were monitored and recorded continuously throughout 30 days.

2.7 Dissolved Oxygen Observation

The dissolved oxygen reading was taken for the first 240 hours using a Vernier Optical DO Probe.

Chapter 3 Results

3.1 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matter as the Factors

Figure 5 highlights the copper measurements at 30 minutes and 90 minutes as a function of the factors. Substantial differences in the measured copper concentration were visually seen as a function of pH. DOM and Salt concentration did not appear to have a substantial impact. Time also appeared to be an important factor for pH, even though it was not included in the analysis.
Figure 5. Copper measurements as a function of $2^3$ factorial design

The results were inputted into a model matrix that calculates the interactions between factors and the impacts of each factor on overall copper concentration (Berthouex & Brown, 1994). The effect values of each tested factor were arranged from smallest to largest for each data set and respected regeneration data set in Table 2. The highest probability of effect was interpreted as the most accurate interpretation of the interactions, as either parameter 1, 2 or 3 being the primary factor that were significant in that trial run. The result suggested that all 3 factors including pH, chlorine and dissolved organic matter were shown to have a significant impact on the amount of total copper and total copper with regeneration in 30 minutes. Chloride and dissolved organic matter had an impact on free copper and free copper with regeneration in 30 minutes. For experiments with extended time, all factors including pH, chlorine and dissolved organic matter were seen to have a significant impact on amount of total copper, total copper with regeneration, amount of free copper, and free copper with regeneration after 90 minutes.
Table 2: Relative impact of pH, chlorine and dissolve organic matter on copper and copper with zeolite regeneration at different timeframe

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3.2 Investigation of Metal Complexation Using Column Simulation

Free copper and zinc concentration with and without zeolite regeneration were measured at each period as shown in Figure 4 and Figure 5. Free copper concentration without zeolite regeneration suggested a spike in all columns at approximately 10 hours and then a slow decrease back to base levels until 240 hours. The concentration increased from 0.1 mg/L to 0.5 mg/L for sample set “DOM, No Salt” and 1.2 mg/L for “DOM, Salt” in that initial 10 hours, for example. Free copper concentration in all the sample sets except the control (“No DOM, No Salt”) increased simultaneously from the base level of less than 0.1 mg/L in all sample groups to 0.8 mg/L in “No DOM, Salt”, 2.4 mg/L in “DOM, No Salt”, and 5.5 mg/L in “DOM, Salt” from 240 to 700 hours. Several of these concentrations were greater than the initial copper concentration in the columns, indicating potential contamination from the brass valve. Similar to the no-regeneration data, free copper concentration with zeolite regeneration showed a spike in 3 different sample sets: “No DOM, No Salt”, “DOM, No Salt”, and “DOM, Salt” in the first 10 hours and slowly drops back to base level, whereas data set “No DOM, Salt” had a slight drop in the free copper concentration. It was noted that different levels of background free copper concentration were observed at the beginning, indicating sorts of metal complexity or interference. A very similar observation was made that the free copper concentration in all sample sets started to increase at around 240 hours, from a base concentration of around 1 mg/L to 1.5 mg/L for “No DOM, Salt”, 2.3 mg/L for “No DOM, No Salt”, and 9 mg/L for “DOM, Salt” sample group. The control in this experiment which was represented by “No DOM, No Salt” suggested some abnormality or contamination throughout the experiment, rendering that it was not an accurate representation of control data. Another possibility would be an interference with the copper testing. Given that the testing was a free copper test, it was anticipated that the “No
DOM, No Salt concentration would be steady. Future work is needed to determine why this occurred, as well as why the final concentrations were greater than the spike concentration.

Figure 6: Free copper concentration in mg/L without zeolite regeneration up to 700 hours

![Figure 6](image_url)

Figure 7: Free copper concentration in mg/L with zeolite regeneration up to 700 hours

![Figure 7](image_url)

Zinc concentrations prior to the zeolite recovery step showed in Figure 6 were observed to be less than the initial concentration since sample groups other than control started with 0.2 to 0.7 mg/L zinc. Whether this is due to immediate interactions in the solution (in the few minutes prior to analysis) or to interactions in the column with the column walls cannot be determined. All sample groups, particularly the two groups with DOM, started to spike up to 1.4 mg/L in the initial 40 hours and return to around the base level until 240 hours. Zinc concentrations started to
increase from 0.3 mg/L to 0.9 mg/L for both “No DOM, Salt” and “DOM, No Salt” groups, and to 1.6 mg/L for “DOM, Salt”. The control remained at baseline despite the initial spike of zinc concentration at the 40 hours mark.

Zinc concentration with zeolite recovery in Figure 7 presented a very similar trend where the initial zinc concentration spiked in the first 40 to 100 hours from 0.2 mg/L to 0.5 mg/L in “No DOM, Salt” group, 1.7 mg/L in “DOM, No Salt”, and 2.4 mg/L in “DOM, Salt” with small amount of background noise in all groups. The zinc concentration drops down to base level except for “DOM, Salt” group which contained relatively higher amount of 1.2 mg/L at 240 hours. The zinc concentration in all sample sets except control started to increase consistently from 240 hours mark to 1.5 mg/L for “DOM, No Salt” group, 3 mg/L for “No DOM, Salt”, and 4.5 mg/L for “DOM, Salt” at 700 hours.

Figure 8: Zinc concentration in mg/L without zeolite regeneration up to 700 hours
Figure 9: Zinc concentration in mg/L with zeolite regeneration up to 700 hours

3.3 Investigation of Metal Complexation Using Column Simulation (Short term)

Free copper and zinc concentration from Figure 4 to Figure 7 highlighted a very similar trend across all sample sets where a noticeable spike of metal concentration was observed within the initial 100 hours, but a significant increase in concentration after 240 hours. The brass valve at the bottom of each column was suspected to be the primary source of contamination since it was made of copper and zinc. Therefore, the focus of the investigation must be shifted to monitoring in shorter timeframe. Data within 240 hours were plotted in Figure 8 to Figure 11 accordingly. The initial concentration for free copper was 0.5 mg/L and the small amount detected in both copper sample sets suggested the results were relatively consistent. Free copper concentration started to fluctuate and incline until a peak where sample group “DOM, Salt” showed a noticeable higher level of increase in concentration than other groups at the peak of 25 hours. The initial zinc concentration was 1 mg/L and the collected data were within the range. Zinc concentration in both sample sets had a significant reduction in the initial 25 hours. Two sample groups “DOM, No Salt” and “DOM, Salt” started to increase rapidly after 25 hours and reached a peak at 50
hours mark, where the other two groups “No DOM, No Salt” and “No DOM, Salt” remained below input level during the same timeframe.

For both copper and zinc, the test kits did not indicate an interference at the concentrations of chloride or DOM used. However, the increase in concentration above the initial spike concentration indicates a concern about the tests or a contamination in the system.

Figure 10: Free copper concentration in mg/L without zeolite regeneration in the first 240 hours

Figure 11: Free copper concentration in mg/L with zeolite regeneration in the first 240 hours
3.4 pH, Oxidation Reduction Potential Observation

The pH and oxidation reduction potential data were constantly monitored within the timeframe of 30 days. The columns were categorized as “pH1” for “No DOM, No Salt” column, “pH2” for “No DOM, Salt” column, “pH3” for “DOM, No Salt”, and “pH4” for “DOM, Salt” in figure 3. The columns were also labeled as “ORP1” for “No DOM, No Salt”, “ORP2” for “No
DOM, Salt”, “ORP3” for “DOM, No Salt” and “ORP4” for “DOM, Salt” sample group respectively in figure 4. Data was collected at a fixed rate of one sample per minute.

For pH, little change was seen over the 30 days. The greatest fluctuation was seen in the “Salt, No DOM” column, but it was approximately 0.4 pH units.

![Figure 14: Continuous monitoring data of pH for 4 columns in 30 days](image)

![Figure 15: Continuous monitoring data of oxidation reduction potential for 4 columns in 30 days](image)
The two lowest ORP values over the monitored time period were associated with the No-DOM columns, including the No-DOM, No-Salt which showed the greatest decrease over time.

3.5 Dissolved Oxygen Observation

The dissolved oxygen was monitored for the initial 240 hours for all columns. Monitoring equipment was not available for the last 480 hours for dissolved oxygen. All sample groups resembled a trend of constant and slow reduction within the given timeframe in Figure 14, where the “No DOM, Salt” sample group had a more significant drop.

![Figure 16: Dissolved Oxygen for 4 columns in the initial 240 hours](image-url)
Chapter 4 Discussion

4.1 Factorial Design Using pH, Sodium Chloride, and Dissolved Organic Matters as the Factors

The evaluation of interactions using factorial design provided an estimation of the impacts of changes in one or multiple factors on the overall system. The factorial design results indicated that multiple parameters including pH, chloride concentration and dissolved organic matter had significant impacts on the concentration of total copper in 30 minutes, total copper in 90 minutes and free copper in 90 minutes with and without zeolite regeneration. Differences were noted in fractional recoveries of copper as a function of time, indicating that time was important, even though time was not included as a factor in the analysis. All of the lower pH samples (pH = 7 versus 9) had lower free copper concentrations, indicating the impact of pH on the results (as supported by the factorial results where X1 was a factor in all analyses). However, chloride and dissolved organic matter contributed to free copper concentration with and without zeolite regeneration in 30 minutes, which is the only sample set that did not involve pH as a primary factor. The concept of this quick test was not to examine the interactions between parameters with extreme accuracy, but rather to diagnose whether the impact of each factor on copper were sufficiently significant to affect the overall metal concentration and to help plan the Phase 2 experiments. Most sample groups consistently showed, in addition to time, that pH, chloride concentration, and dissolved organic matter should all be considered when further examining the formation of copper and zinc complexes.
4.2 Investigation of Metal Complexation Using Column Simulation

The samples consisted of natural rainfall combined with creek water, where copper and zinc were added. In the full duration of the experiment, the deep column system seemed to initiate a significant release of metal at around 240 hours due to possible corrosion of brass valve at the bottom, which is consisted of copper and zinc. This release was particularly high in the columns with salt. The sodium chloride in the sample was sufficiently high to promote the acceleration of corrosion process after extended period. The sample “DOM, Salt” showed the greatest increase of copper and zinc concentrations at the end of 700-hour tracking period, suggesting that the corrosion happens the most severely with the introduction of both dissolved organic matter and sodium chloride. The differences between the usage before and after zeolite regeneration is subtle but noticeable since the final concentration of free copper and zinc at 700 hours are generally slightly higher with zeolite recovery.

Since significant corrosion seemed to occur after 250 hours, the focus of the discussion must be shifted to short-term release of zinc and copper. Initial concentrations of copper and zinc in most sample sets were slightly below respected base level concentration. The fluctuation with concentration was consistent in the first few hours in columns, but a significant spike of concentration was observed in all samples at around 20 hours for copper and 50 hours for zinc, but it was temporary. For free copper, the spike increases the concentration up to 2.5 times the initial concentration, whereas the spike increases the concentration of zinc up to 2 times. The question that cannot be answered in this data set is the potential interference with the analytical method, even though the method does not report that these concentrations should cause an interference.

Free copper concentration, with or without recovery, both showed the spike with the introduction of sodium chloride and dissolved organic matter. For second and third sample sets,
namely “No DOM, Salt” and “DOM, No Salt”, these two columns had only one element of interest introduced, and the trend indicated a mild spike in the concentration. It is worth noting that zeolite regeneration process netted more free copper in general. This would be expected since the zeolite would extract free copper, which would fit into the zeolite lattice, and then would be rinsed out by the sulfuric acid solution. In comparison, the fourth sample group “DOM, Salt” had both parameters of interests in the column, and the spike in copper concentration is significantly higher than the previous sets. Assuming no interference, which also is possible, in the presence of both dissolved organic matter and sodium chloride, large amount of copper metals were released at around 20 hours at first and likely from the column itself, and these copper metals quickly bonded with ligands to form a variety of metal complexes, directly resulting as a dramatic decrease in the available free copper.

Zinc concentration with and without zeolite recovery, on the other hand, showed a more noticeable spike with sample groups that had only dissolved organic matter involved in “DOM, No Salt” and “DOM, Salt” at 50 hours. Again, the zeolite regeneration flushed out a bit more zinc metals that might have been previously trapped, resulting a high concentration of zinc with recovery. Significant amount of zinc metals was released after dissolved organic matter was reacted in the deep columns, some of the zinc started to bind with ligands to form complexes. However, the formation of complexes was not as aggressive as seen with free copper complexes, due to possible copper complexes structures and valances charges.

4.3 pH, ORP, and DO Monitoring Results

pH values and oxidation reduction potential data were monitored continuously for 30 days. The pH values fluctuated slightly but were kept relatively consistent around 7 with a slight fluctuation (±0.6). The oxidation reduction potential values were also kept consistently in
respected sample sets. The dissolved oxygen level for columns remained stable and follow a trend of decreasing overtime, except for the second column with no dissolved organic matter and with salt. There is a noticeable dip in both pH and oxidation reduction potential for the second column with “No DOM, Salt”, because the brass valve at the bottom of the column was leaking and dripping sample water at an almost unnoticeable rate. The logger pro interfaces were restarted a few times and most probes were re-calibrated during each restart in the collection phase, it is possible to cause some of the irregular fluctuations in the trends.

Chapter 5 Conclusions

5.1 Conclusions

The factorial experimental design concluded that all three factors including pH, chloride concentration and dissolved organic matter had significant impact on copper concentrations. All three factors should be considered when further examining the formation of copper complexes.

The deep column simulation indicated that with the addition of sodium chloride and dissolved organic matter, the free copper and zinc were initially released with a spike in concentration. These free metals then bonded with ligands in the columns to form a variety of metal complexes, resulting in a decrease in remaining available free metals. The copper concentration was more impacted by both sodium chloride and dissolved organic matter, whereas zinc seemed more sensitive to dissolved organic matter. The brass valve is likely the primary source of contamination, but it is also likely that the analytical method caused interference that might need future investigation.
The pH, oxidation reduction potential and dissolved oxygen were kept relatively consistent during the long-time investigation, but future studies can focus on testing one of these specific factors in larger scope.
References


