LONG TERM PERFORMANCE OF A BIOINFILTRATION RAIN GARDEN WITH RESPECT TO METALS REMOVAL

BY

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DEDICATION

I dedicate my work in honor of my family and friends who have helped me find my path and supported me on the journey.

EXECUTIVE SUMMARY

The focus of this research was to quantify metals removal within a bioinfiltration stormwater control measure (SCM) with a focus on metals sorption to soil. The bioinfiltration SCM used in this study has been in operation since 2001. It was built into the traffic island of a parking lot and is referred to as the bioinfiltration traffic island (BTI). Its ability to treat stormwater runoff from a water quantity (i.e. volume reduction) perspective has been previously studied. However, the ability of the BTI to improve water quality has not been fully studied. Specifically, it is unknown as to what extent metals are removed as the stormwater is collected by the BTI and allowed to infiltrate into the ground instead of immediately entering the storm drain. This thesis analyzed metals (specifically copper, cadmium, chromium, lead, and zinc) concentrations entering and exiting the BTI, as well as the metals concentrations sorbed to soil, in order to determine a mass balance of metals in the system and to determine the removal rate of metals during the lifetime of the BTI. There had been 542 storm events greater than 0.25 inches (0.64 cm) that had occurred in the area since the BTI was put online in 2001. Surface and subsurface samples were collected during 95 of those events at the beginning, end, and throughout the duration of the storm event. Subsurface samples were taken from lysimeters which were located at 0 m, 1.2 m, and 2.4 m from the surface. All samples were tested for dissolved metals and all surface samples were tested for both dissolved and suspended metals.

An analysis of the mass in and mass out of the BTI showed that metals are removed in the infiltration media. All metals analyzed were removed at the surface of the BTI. Pore water samples collected below the surface did not show any measurable change in metals concentration with depth. This could partially be because most subsurface samples were at or below the

detection limit. Soil extractions performed in 2009 and 2013 confirmed the accumulation of metals on the soil at the surface of the BTI. Metals concentrations sorbed to the soil did increase for cadmium between 2009 and 2013 but did not change between 2009 and 2013 for the other metals. Accumulation of metals at the surface of the BTI demonstrates that this BTI system can remove metals found in stormwater. Also, measuring of metals sorbed to soil is a valid technique to quantify metals removal in bioinfiltration SCMs treating stormwater with metals concentrations below detection.

An analysis of the amount of metals currently sorbed to the soil, the rate of metals load into the BTI, and the maximum concentrations of metals allowed on soil to still be considered clean fill (based on PA Department of Environmental Protection regulations), indicated that the lifespan of the BTI will be limited by chromium accumulation and will need maintenance after 290 years of operation assuming that the soil could actually sorb enough of each metal to reach the clean fill limits. It is important to note that the above lifetime accumulation analysis is only an estimate due to the complexities of the system. However, the analysis does indicate that it is likely that metals will accumulate on the soils of this BTI to levels above that of PA Department of Environmental Protection clean fill standards during a reasonable (~30 year) time of operation. Copper sorption isotherm experiments were run on soil samples from the infiltration area of the BTI to determine the maximum amount of copper the soil can hold under equilibrium conditions similar to that experienced by the BTI. Copper was the only metal that was tested because it was the only metal in which a majority of the water samples were above the detection limit. The maximum amount of copper that can sorb to the surface of the infiltration basin varied throughout the BTI and ranged from 90-1080 μg/g. The maximum amount of copper that can sorb to the soil based on the sorption isotherms (1080 μg/g) was well below the maximum amount of copper allowed on soil to be considered clean fill (8200 μg/g) indicating that copper accumulation on the soil will never reach levels that exceed PA Department of Environmental Protection clean fill standards.

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Chapter 1 - Introduction

1.1 Problem Statement

The purpose of this thesis was to quantify the accumulation of metals on the soil of a bioinfiltration stormwater control measure (SCM) and to quantify the useful life of this system with respect to metals removal from stormwater. Stormwater management is a growing concern in the United States as runoff poses flooding problems and often contains many contaminants as sources of nonpoint pollution. Heavy metals are pollutants of great concern because they impose health risks on aquatic and human life. Some heavy metals are regulated in drinking water as well as in soils and therefore these metals should be of interest when designing SCMs so that they can be removed from the water before they enter the larger water systems such as rivers, lakes, streams, and groundwater.

Stormwater control measures include many types of control options that have been designed to reduce the volume of storm water as well as improve the overall quality of the water that is released into the environment. One type of SCM is a bioinfiltration rain garden which is an engineered system that allows water to infiltrate into the ground, evaporate into the air, and transpire while allowing time for pollutants to settle out or to be removed from the water before it reaches a larger body of water or the groundwater. Previous studies have found high removal rates for heavy metals in bioinfiltration and bioretention SCMs with the majority of the removal occurs in the top layers of the soil (Davis et al., 2003; Li and Davis, 2008). The removal mechanisms and rates will be investigated experimentally for a bioinfiltration rain garden on the Villanova University campus.

This research will investigate the water and soil quality of this SCM in order to quantify metals removal since this system was put online in 2001. Stormwater has been collected and measured for cadmium, chromium, copper, lead, and zinc since 2006. The results from the stormwater sampling will be analyzed to quantify the extent of metals removal from the influent stormwater within the infiltration bed. Soil samples were also collected in 2013 from the infiltration bed to determine the amount of metals that had sorbed to the media since the system was operational. The results from these extractions experiments were then compared to similar tests that were completed in 2009 in order to determine if metal concentrations on the soil have increased over time. The mass of metals that accumulated on the soils will then be compared to the mass difference of metals into and out of the BTI to determine if metals sorption to soil was a significant removal mechanism in this SCM. Copper sorption experiments were performed to determine the maximum amount of copper that could be sorbed which, combined with information about the rate of metals accumulation onto the soil, would allow for a basic analysis as to the lifetime of the SCM.

1.2 Research Goals and Objectives

1.2.1 Goals

The goals of this research were

- To understand the potential metal removal processes within the SCM
- To quantify the useful life of the SCM with respect to metals removal

1.2.2 Objectives

The objectives for this research were to

- Quantify the amount of metals entering and leaving the SCM during rain events
- Quantify the amount of metals sorbed to the soil throughout the lifetime of operation
- Determine the relationship of the sorbed metals with respect to depth and location within the SCM
- Determine the metal removal rates per year.

Chapter 2 - Literature Review

2.1 Presence of Metals in Stormwater

Heavy metals enter stormwater through a variety of sources. The main sources for lead before the phasing out of lead-based products included gasoline, gasoline by-products, combustion, and paints (Marsalek, 1986). Despite reductions in the concentrations of lead in gasoline and gasoline by-products, it is still present in these products. According to the USEPA, lead is also found in many household products such as ceramics, batteries and cosmetics (http://www2.epa.gov/lead/learn-about-lead#found). Davis (2003) found lead to have typical concentrations near 75 μg/L. Galvin and Moore (1984) reported lead concentration to be between 60-460 μg/L while Merrill (1984) typically found 57 μg/L for lead concentrations in the stormwater studied. The USEPA (1983) reported range for stormwater was 6-460 μg/L. Copper is a heavy metal that can be present in storm water due to erosion and corrosion of piping, algaecides, brake lines, and even pavement wear (Marsalek, 1986). Other sources of copper include brake pads, architectural pieces, wood preservatives and gasoline (Moran, 2004). Davis (2003) found copper to have typical concentrations near 80 μg/L. Galvin and Moore (1984) reported concentrations between 4-46 μg/L. The USEPA (1983) reported concentrations that ranged from 1-100 μg/L. Another study found copper concentrations that ranged from 7 and 49 μg/L (Bardin, 2001). Zinc is a highly abundant metal in storm water runoff and is typically sourced from corrosion processes, tires, exhaust, paints, and road salts (USEPA, 1983). Davis (2003) found copper to have typical concentrations of 700 μg/L. Galvin and Moore (1984) reported concentrations between 28 and 2500 μg/L (1984). The USEPA (1983) reported zinc concentrations between 10 and 2400 μg/L. Cadmium is a metal that can be found in stormwater through many different processes. Cadmium can be found in the air due to the combustion of fossil fuels as well as from metal smelting process (EPA 2013). This heavy metal is also found in cigarettes which is important to be vigilant of because the stormwater can easily transport discarded cigarettes or cigarette components into the BTI (EPA 2013). Davis (2003) found typical cadmium concentrations of 8 μg/L while other studies found cadmium concentrations to be significantly lower than that. Galvin and Moore (1984) reported concentrations between 0.2 – 1.9 μg/L, the EPA (1983) found concentrations between 0.1 – 0.14 μg/L, and Merrill (1989) found 0.8 μg/L as a typical value. Chromium has two states, the trivalent structure (chromium III) and the hexavalent state (chromium VI). Hexavalent chromium is considered to be more toxic to humans. Chromium can be found in dyes, preservatives, textiles, automobile brakes, as well as many industrial processes (EPA 2013). Galvin and Moore (1984) reported typical chromium concentration in stormwater that ranged from 2 – 19 μg/L while the EPA (1983) found concentrations from 1 to 90 μg/L. Merrill found a typical value of 6.2 μg/L.

Polluted stormwater runoff accounts for 13% of impaired rivers, 18% of impaired lakes, and 32% of impaired estuaries (USEPA, 2000a). There are many types of SCM systems, such as bioinfiltration and bioretention rain gardens. Bioretention is a type of SCM that allows runoff water to be ponded, or held, so that it can be slowly released into the storm water system or local rivers once a storm event has ended thus minimizing the effects of peak stormwater flow (Lord, 2013). In addition to ponding the water to reduce the peak volume of runoff that enters the sewer, this allows for certain contaminants including metals to sorb to the soil. Bioinfiltration, the SCM that this thesis investigates, allows for the stormwater runoff to pond so that the water can infiltrate into the ground rather than be slowly released into the stormwater system. This system also reduces the peak volume of runoff.

2.3 Metal Removal Processes

Stormwater can be polluted with many different metals, however the concentrations of these metals is typically in the μg/L range (Bardin, 2001; Davis, 2003; USEPA, 1983; Galvin and Moore, 1984; Merrill, 1989). Studies have shown that bioinfiltration and retention are an effective ways to remove heavy metals from runoff (Davis et al., 2003; Davis, 2007; Hunt et al., 2008; Jalali and Moharrami, 2007; Markiewicz and Patkowska, 2005; Yuan and Lavkulich, 1997). Mechanisms for removal of metals in a SCM include sorption to soil, filtration, metal precipitation, and biological treatment such as plant uptake (Davis et al., 2009; Dietz and Clausen, 2006; Pitt et al., 1995). It has been shown that plants have the ability to accumulate metals from water (Davis et al., 2003, Dietz and Clausen, 2006; Brown et al., 1995, Ebbs and Kochian, 1998; Sarret et al., 2001; Wu et al., 1999). The main removal mechanisms of metals in the soils of SCMs are adsorption (lead, copper), ion exchange (lead, zinc, copper), and precipitation (lead, zinc) (Pitt et al., 1995). Straining is a method of physical sorption that removes suspended metals by acting as a colander as the soil media traps large suspended particles that cannot pass through the spaces between the soil particles (Weiss et al., 2008). Suspended metals are a concern in SCMs due to the fact that as the suspended metals are removed from the water they can clog up the pore space in the soil media thereby reducing the area in which water can infiltrate into the system. Therefore, as the system clogs, it can increase the amount of time that there is ponded water and eventually reduce the amount of stormwater that can infiltrate into the SCM. Furthermore, a large fraction of most metals are usually bound to suspended soils (Davis and McCuen, 2005; Marsalek et al., 2001). Soil used for bioinfiltration media can effectively remove metals from storm water until the metals holding capacity of the soil is reached (Weiss et al., 2008).

Davis et al., (2003) determined that pH is a significant factor in the adsorption of metals to soil and that changes in the pH can significantly influence the sorbed concentration of metal to soil. Therefore, buffering capacity may play an important role in metal adsorption in soil. Other factors that have been found to impact adsorption of metals by soil are temperature, pressure, competing ions, counter ions, and loading rates of the metals (Harter and Naidu, 1998; Tsang et al., 2006). The organic matter content of soil can also be a very important factor in metal sorption within soils (Harter and Naidu, 1998). This would include natural organic materials in the suspended and dissolved form.

Some heavy metals are more easily adsorbed than others with preferential sorption to soil occurring in the order of lead, copper, nickel, cobalt, zinc, and cadmium (Pitt et al., 1995). It has been observed that metal accumulation on soil was highest at the soil surface and metals concentrations decreased with depth (Davis et al., 2003; Davis et al., 2008) with the majority of metals accumulation to soil occurring within the first 5 to 10 cm of depth of the bioretention media (Davis et al., 2003; Davis et al., 2008; Davis and Jones, 2013). Davis et al. (2003) also estimated how many years of accumulation could occur within a site before it reached the federal loading regulations for cadmium, copper, lead, and zinc. The useful lifetime of an infiltration SCM varied for each metal due to the different inflow loads and regulatory standards (Davis et al., 2003). Lead and zinc limited the useful lifetime to 16 years until the concentrations of these two metals surpassed the federal regulations (Davis et al., 2003).

Heavy metals are pollutants that are regulated in the state of Pennsylvania and therefore these regulations will also be considered in determining the useful life span of the rain garden. The Pennsylvania Department of Environmental Protection has limitations on the amount of metals that may be present in soil to be considered clean fill. The clean fill regulations from the PADEP for each of the metals are as follows: cadmium (38 mg/kg), chromium III (190,000 mg/kg), chromium VI (94 mg/kg), copper (8200 mg/kg), lead (450 mg/kg), and zinc (12,000 mg/kg) (PADEP, 2010).

Chapter 3 - Research Methods

3.1 Site Description

The Bioinfiltration Traffic Island (BTI) rain garden is located in a grassy traffic island in the parking lot of Villanova University's West Campus (Figures 1 and 2). The West Campus parking lot serves a dormitory complex and a recreation area. The BTI was retrofitted in 2001 into the shape of a shallow bowl, allowing the inflow of water to accumulate within. The drainage area is approximately 0.52 ha (1.3 acres) with ~35% directly connected impervious surface (Emerson and Traver, 2008). There has been no change to the watershed since BTI construction. The bioinfiltration area consists of a 1.2 m (4 ft) deep soil mixture containing a 1:1 ratio of excavated native soil from the traffic island (identified as silt according to USCS) with imported poorly graded sand. The average porosity of the bed was estimated to be 0.4 (Emerson, 2008). The approximate surface area and average depth of the infiltration bed when full is 144 m^2 and 25 cm, respectively (Emerson and Traver, 2008). The pond volume on top of the system was designed such that the runoff accumulates on top of the sand/soil fill area, thus allowing a maximum of ~36 m^3 of ponded water to accumulate at any given time and slowly infiltrate into the infiltration media. Rain events typically < 1.6 cm are completely infiltrated/evapotranspirated while rain events typically greater then this value completely fill the BTI resulting in stormwater exiting the system (the exact magnitude of rain event that resulted in overflow varied due to the moisture content of the infiltration bed and intensity and duration of the rain event). The recession rate was estimated to be 0.54 (± 0.20, n=123) cm/hr (Emerson and Traver, 2008). The BTI was initially planted with a variety of grasses, herbs and woody plants. A full list of these plants can be found in Emerson (2008). Vegetation in the BTI was periodically harvested as part of routine maintenance. Currently, the only maintenance that this site undergoes is trash removal, invasive species control and grass harvesting and no fertilization occurred at the site (VUSP). The groundwater is approximately 4.3 m below the infiltration bed (Emerson and Traver, 2008).

Figure 1: A photo of the traffic island from the south side of the island facing north.

Figure 2: A photo of the BTI from the western edge facing the southeast border.

3.2 Water Sampling Locations

The water quality for this SCM has been measured over time through the use of monitoring equipment and collected samples. Surface water samples were collected during and after storm events as well as subsurface water samples were collected through a series of pore water lysimeters located at various depths (0 m, 1.2 m, and 2.4 m) in and below the bioinfiltration systems (Figure 3). A lysimeter (Soilmoisture Equipment Company) is a porous device used to collect subsurface water samples by extracting the sample from the vadose zone (Komlos and Traver, 2012). The lysimeters were installed during the construction phase of the BTI. Two surface water samples were collected as 250 mL grab samples. The first sample was collected during a storm event, designated as ponded 1 and a second collected at the conclusion of the rain event (ponded 2). In addition to these samples, there was also an overflow, or "over" sample that was only taken when a storm event has enough runoff to fill the BTI to the point that water was released to the outflow drain near Location 3 in Figure 3a.

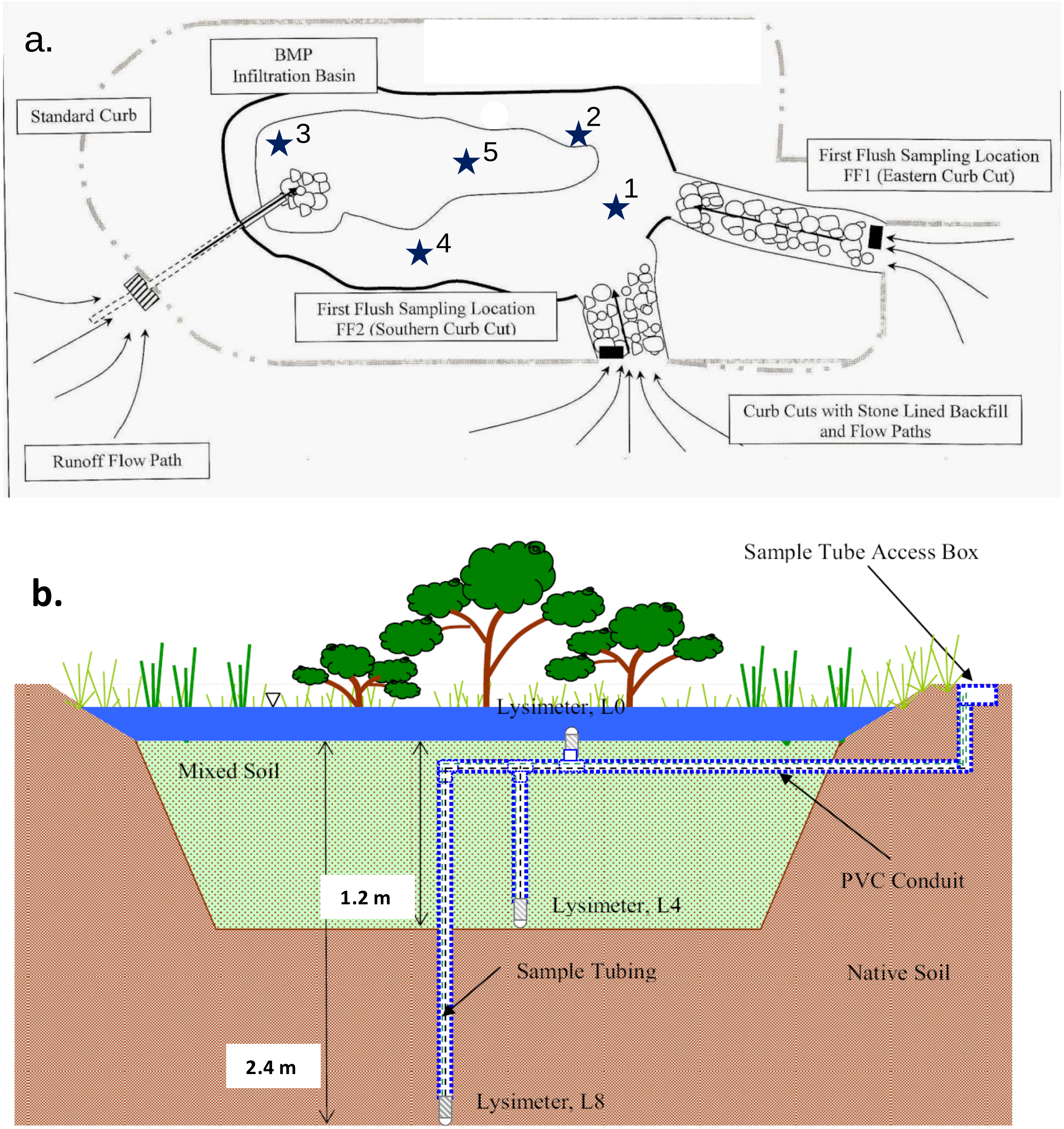

Figure 3: a) Aerial BTI schematic and soil sample locations b) Side profile of BTI and lysimeter locations (Image from Ermilio, 2005)

A mass balance of the metals into and out of the BTI was determined using the metals concentrations measured during storm events and the volume of water entering and leaving (overflowing) the BTI. Overflow samples were collected as grab samples when water was leaving the system via the outfall pipe. Grab samples collected at the beginning of the rain event (termed “ponded 1”) were used to estimate the metals concentrations entering the BTI. The mass of metals entering the BTI was quantified by multiplying the ponded 1 concentration by the volume of rainwater entering the BTI. The mass of metals leaving the BTI was quantified by multiplying the concentration leaving the BTI (termed “overflow”) by the volume of rainwater leaving the BTI. Grab samples collected from the ponded area toward the end of the rain event (termed ponded 2) were used to estimate the metals concentrations leaving the BTI when no overflow concentration was measured. The mass leaving the BTI was subtracted from the mass into the BTI to measure the amount of each metal removed per storm (eq. 1). Equation 1 was used to calculate the mass removed for dissolved metals and the suspended metals separately. The subsequent masses (dissolved and suspended) were then added together in order to determine the total mass removed.

$$\text{Mass removed} = (\text{Ponded 1})(V_{in}) - (\text{Over or Ponded 2})(V_{out}) \qquad \text{(eq. 1)}$$

In addition to the samples taken at the beginning of the rain event (ponded 1), the end of the rain event (ponded 2), and at the overflow, there were also additional ponded samples that were collected during the storm event. A composite sample was also compiled. This is a sample that was collected throughout the storm event and averaged to provide one sample to represent the entire storm event. The composite sample is in addition to the ponded 1, ponded 2 and overflow samples and was not a sample that was consistently collected until 2010 therefore the was not included in the full analysis but can be seen in section A of the appendix.

3.3 Soil Samples

3.3.1 Soil Sampling Location and Methodology

In late spring (June 4th 2013), soil samples were collected at five different locations in the BTI (Figure 3a) for metals extraction and metals sorption experiments. Metal extraction experiments were performed to determine the amount of metals that accumulated on the soil over time since the BTI was put online in August 2001. These five sites coincide with the same locations previously used to quantify the phosphate sorption to soil in the BTI (Komlos and Traver, 2012). Different locations within the BTI were analyzed to quantify how metal accumulation onto soil varied spatially. Samples were taken near the inlet (Location 1) and outlet (Location 3) as well as three samples (Location 2, 4, and 5) between these two locations (Figure 3a). The inlet area represented a control sample because it had a higher elevation than the rest of the bowl and thus received less infiltration. The other samples taken were analyzed individually as well as together to represent the area of ponding within the BTI.

Soil was collected from a depth of 0.025 meters (1 inch) from the surface (to avoid collecting materials that were not part of the soil makeup) as well as at a depth of 0.3 m (12 inches) for a total of ten sample locations. The soil was dug out using a plastic shovel and stored in sealed plastic 50 mL centrifuge tubes in a refrigerator at 4°C until they were analyzed. Enough soil was collected at each location to ensure that all extraction and sorption tests incorporated soil samples that were from the same collection time to allow for similar testing conditions. All large stones and roots (approximately larger than 2 mm) were removed but smaller media were left in the composition to provide for a more accurate understanding as to the actual field conditions. Before running any soil tests, the moisture content was determined for each sampling location by weighing a soil sample both before and after drying at 103°C for 24 hours (Komlos and Traver, 2012). Triplicate samples were run for each location.

3.3.2 Quantification of Metal Accumulation in the BTI Infiltration Media

Extraction experiments were performed in order to determine the amount of metals sorbed on the soil for each location. Extraction experiments were performed for each location in Figure 3a and soil depth of 0.25 m (1 inch) and 0.3 m (12 inches) in triplicates. This procedure involved measuring a known weight (approximately 3-4 grams, wet weight) of soil that was added to a 50 mL centrifuge tube. Then 25 mL of 0.5 M nitric acid was added. Each of the tubes was rotated at 100 rpm for 24 hours. After 24 hours, the vials were removed and allowed to settle for 15 minutes before filtration (Davis, 2007). The samples were filtered using a 10 mL syringe (Fischer Scientific) to extract the solution and then a 0.45 μm filter (Fischer Scientific) was attached to the syringe. This process was used in order to capture as much of the solution as possible (typically 20 mL was recovered). Due to the high nitric acid molarity used, the samples were diluted to ensure compatibility with the 0.3 M nitric acid standards used for detection (see below). The samples were then stored at 4°C until analysis for copper, chromium, lead, cadmium, and zinc concentrations. Moisture contents were obtained by weighing a sediment sample before and after drying at 103°C for 24 hours. The procedure used to extract metals from the soil was the same procedure that was used by another researcher to measure the sorbed metal concentrations in the same location back in 2008-2009. All of the metals besides the zinc were compared to the levels from 2009 to determine if metals accumulation over time could be quantified. The 2013 samples also underwent analyses to determine the organic content of the soil by heating a dried soil samples at 550°C for 1 hour. The organic content was assumed to be the volatile fraction of the soil (i.e. the difference between the soil mass before and after heating at 550 °C).

Statistical analysis was performed where indicated using paired t-tests. T-tests were performed to compare the 2009 and 2013 ponded area samples to one another. In addition, the metals concentrations sorbed to soil in the ponded area was compared to the control samples data for each location and year to determine if the ponded metal concentrations and the sorbed metals in the control section were statistically different. Data sets were considered significantly different if the p-values were lower than 0.05. Prior to the t-test, an f-test was performed in order to determine the correct parameters to use for the t-test.

3.3.3 Copper Batch Sorption Experiments

Batch sorption isotherm experiments were run to determine the maximum amount of copper the soil could remove at equilibrium with different dissolved copper concentrations. This experiment was performed using soil samples from locations 1, 3, and 5 (Figure 3a). A range of copper solutions were prepared in 0.01 M potassium nitrate in order to maintain a constant ionic strength (Davis et al., 2001). A known amount of soil (approximately 0.1 grams, weight wet) was added to a 50 mL centrifuge tube. Then 25 mL of a 0.01 M potassium nitrate solution containing copper concentrations of 0, 625 μg/L, 1270 μg/L, 2350 μg/L, and 6350 μg/L. These solutions were added to the tube and the initial pH was recorded. Duplicate experiments were performed for each metal concentration. The tubes were rotated at 100 rpm for 6 days. In addition to duplicate testing, experiments containing 635 μg/L and 2350 μg/L copper were run for 1, 3, and 8 days. This was done to ensure that equilibrium was reached within 6 days. All samples were removed on their designated day and allowed to settle for 15-20 minutes. The 20 mL of sample was filtered using a syringe and 0.45 μm filter (Fischer Scientific) into a bottle and then the final pH was measured (Chang and Wang, 2002). Then 0.4 mL of 1 M nitric acid was added in order to preserve the samples as well as ensure that they would be compatible with the standards used for analytical detection. The samples were sealed and stored at 4°C until analyzed.

Linear, Langmuir, and Freundlich isotherms were used to describe the copper equilibrium concentrations. The linear isotherm is provided in equation 2.

$$q_e = \frac{V(C_0 - C_e)}{M} \qquad \text{(eq. 2)}$$

Where: q_e = equilibrium adsorbent concentration of adsorbate, mass copper/mass dry soil

C_0 = initial aqueous phase concentration of adsorbate, mass of copper/volume

C_e = equilibrium aqueous phase concentration of adsorbate, mass of copper/volume

V = volume of aqueous phase added to bottle, L

M = dry mass of adsorbent, mass (soil)

The non-linear and linearized forms of the Langmuir isotherm are provided in equations 3 and 4, respectively.

$$q_e = \frac{Q_M K_{ad} C_e}{1 + K_{ad} C_e} \qquad \text{(eq. 3)}$$

$$\frac{C_e}{(q_e)} = \frac{1}{Q_M K_{ad}} + \frac{1}{Q_M} C_e \qquad \text{(eq. 4)}$$

Where: K_{ad} = Langmuir adsorption constant of copper (volume/mass copper)

Q_M = maximum soil-phase concentration of copper when surface sites are saturated with copper (mass copper /mass dry soil)

The non-linear and the linearized form of the Freundlich isotherm are provided in equations 5 and 6, respectively.

$$q_a = K_a C_a^{1/n} \qquad \text{(eq. 5)}$$

$$\frac{C_e}{(q_e)} = \frac{1}{Q_M K_{ad}} + \frac{1}{Q_M} C_e \qquad \text{(eq. 6)}$$

Where: K_a = Freundlich adsorption capacity factor [(mass of copper/mass of soil)*(Volume water/mass of copper)$^{1/n}$]

1/n = Freundlich adsorption intensity parameter

3.3.5 Analytical Methods

The water samples collected during rain events were immediately brought to the water quality lab where the water sample was passed through a pre-washed 0.45 µm membrane filter. The supernatant was analyzed as described below and the metals measured in the supernatant are defined as dissolved metals. The filter was dried and placed in a 250 mL beaker. Three mL of concentrated nitric acid (TM Grade) was added to the beaker, which was then covered with a pre-washed watch glass. The beaker was then slowly heated under reflux (250-300˚C). After the filter dissolved, the watch glass was removed and the heat increased to approximately 350˚C. Once most of the acid evaporated, the beaker was removed from the heat and an additional 3 mL of nitric acid (TM Grade) was added. The beaker was then heated under reflux again until the solution was a bright yellow color. The cover was then removed and the acid allowed to evaporate. The beaker was removed from heat and 0.5 mL of 1:1 HNO_3 added to the beaker. The beaker was warmed while swirling to be sure all residue was coated with the acid. The beaker was removed from the heat and any remaining particulates were filtered out. Distilled water was then added to bring the volume up to 50 ml. This digested filtrate was analyzed as described below. The suspended concentration of metals in the sample was determined by dividing the mass of each metal digested from the filter by the volume of water sample filtered (typically 300 mL).

Rainfall at the BTI was quantified using an American Sigma^{TM} tipping bucket rain gauge, level detectors to measure the depth of water within the basin, and a V-notch weir coupled with pressure transducers measuring overflow. Surface flow into the BTI was quantified using a calibrated hydrologic model that looked at different intervals of the storms, matched the runoff to the level changes within the bowl, and the overall recession limb infiltration after the rainfall stopped (Emerson and Traver, 2008, Komlos and Traver, 2012).

Cadmium, chromium, copper and lead concentrations were measured using a Perkin Elmer model AAnalyst 800 Graphite Furnace system according to EPA Method 7010a. Zinc was analyzed using a Perkin Elmer AAnalyst 800 Flame Atomic Absorption Spectrometer according to EPA Method 7000b. A value of ½ the concentration of the lowest standard was used for samples with readings below the lowest standard (hereby termed the detection limit) (Dietz and

Clausen, 2006; Smith, 2011). Furthermore, the detection limits varied over time for the metals. Tables 1-5 show the ranges of detection limits for each of the metals over time. These tables also quantify how many measured storm events corresponded to each lowest standard concentration that was used for the detection limit. These ranges represent the actual lowest standard concentration. The median lowest standard concentration for copper and lead was 5 µg/L. The median cadmium detections limits were 0.8 µg/L for both the dissolved and suspended samples. The median zinc detection limits were 50 µg/L for both dissolved and suspended samples. Lastly, the median dissolved chromium detection limit was 4.5 µg/L and the median suspended chromium detection limit was 5 µg/L.

Table 1: Dissolved and suspended copper lowest detection ranges and the number of storms that lowest concentration was used.

Dissolved Copper	
Detection µg/L	# Storms
0.46	2
0.51	2
0.55	2
0.56	1
1.7	3
1.723	2
3.041	6
4.5	15
5	46
5.01	8
5.1	5
5.8	3

Suspended Copper	
Detection µg/L	# Storms
2	1
4.5	12
4.91	4
5	40
5.01	12
5.4	10

Table 2: Dissolved and suspended chromium lowest detection ranges and the number of storms that lowest concentration was used.

Dissolved Chromium	
Detection µg/L	# Storms
0.45	3
0.5	4
0.64	1
0.65	5
0.66	2
1	2
2.5	1
2.51	1
3.25	2
4.4	9
4.5	15
5	35
5.015	2
6.5	2
8	1

Suspended Chromium	
Detection µg/L	# Storms
0.5	2
1	7
4.5	14
5	36
6.5	10
9.5	2

Table 3: Dissolved and suspended lead lowest detection ranges and the number of storms that lowest concentration was used.

Dissolved Lead	
Detection µg/L	# Storms
0.5	14
0.53	1
0.54	7
0.999	3
2.4975	1
2.5	1
2.7	3
4.91	6
4.995	1
5	47
5.4	1
6.3	9

Suspended Lead	
Detection µg/L	# Storms
0.47	2
1	9
4.91	4
5	48
5.4	1
9.6	9

Table 4: Dissolved and suspended cadmium lowest detection ranges and the number of storms that lowest concentration was used.

Dissolved Cadmium	
Detection µg/L	# Storms
0.04	2
0.05	1
0.1	4
0.38	2
0.4	10
0.6	5
0.8	33
0.88	4
0.96	7
1.1	4
2	2
5.03	7
6.8	5
11.7	9

Suspended Cadmium	
Detection µg/L	# Storms
0.05	1
0.4	1
0.6	5
0.8	24
0.87	5
0.88	4
6.8	2
11.7	4

Table 5: Dissolved and suspended zinc lowest detection ranges and the number of storms that lowest concentration was used.

Dissolved Zinc	
Detection µg/L	# Storms
10	7
50	48
53	7
57	5

Suspended Zinc	
Detection µg/L	# Storms
10	8
50	26
57	4
100	11

Chapter 4 - Results and Discussions

4.1 Quantification of Metals into and out of the BTI

On the basis of the Pennsylvania State Climate Office (http://www.stateclimate.org/state.php?state_id=PA) data from the Philadelphia International Airport sampling location as well as the Pennsylvania State Climatologist Data (http://climate.met.psu.edu/data/city_information/index.php?city=phl&page=dwa&type=big7), there were a total of 542 events with rainfall >0.64 cm (0.25 inches) in the Philadelphia area between when the rain garden was put online (August 2001) to the time samples were taken on June 4th, 2013 for soil associated metal concentrations. Ninety five storms were tested for the heavy metals of interest. The metals concentrations in samples collected in the ponded bowl at the beginning of the rain event (Ponded 1) and at the end of the rain event (ponded 2) were compiled for all metals and compared to determine if any metals were removed from the ponded area during storm events. The ponded 2 samples were also compared to the overflow samples from the BTI in order to determine if the ponded 2 could be used as an estimate of the overflow concentrations. The overflow concentration was only collected from certain storms when the BTI reached full capacity and water was released into the overflow drain (the metals concentration in stormwater that overflowed the BTI was not measured for all storms with overflow). Samples that were collected at the lysimeters at depths of 0 m, 1.2 m, and 2.4 m into the bed were also compiled and compared in order to determine if there was any relationship between metal removal and the infiltration bed depth.

The mass of each metal removed in the BTI was calculated using equation 1 which is the difference of the metal mass in and the metal mass out. The mass into the BTI was calculated by multiplying the ponded 1 sample by the volume that flowed into the BTI for each specific storm event. The mass out was determined in the same manner using the overflow (or ponded 2 concentrations) multiplied by the corresponding volume of water that flowed out of the BTI for that storm event.

4.1.1 Copper

There was no obvious trend when dissolved and suspended ponded copper concentrations were plotted over time (Figure 4) as storms varied with the amount of rainfall and metal concentrations that flow into and out of the BTI. Because the concentration versus time plots for the ponded samples (as well as for other sampling locations and for all other metals analyzed) did not show any particular trend, they will not be discussed further but can be found in Appendix A. All comparisons of concentrations and masess shown in the results section will be as exceedance probability plots.

The median dissolved copper concentrations for ponded 1 and ponded 2 samples (8.2 μg/L and 9.2 μg/L, respectively) were higher than the median overflow dissolved copper concentrations of 5.0 μg/L (Figure 5a). The median suspended copper concentrations for ponded 1 and ponded 2 samples (2.62 μg/L and 1.83 μg/L, respectively) were comparable to the overflow median concentration (2.43 μg/L)(Figure 5b). By using the ponded 2 samples when no overflow sample was available, the mass that can be removed by the BTI will be underestimated because the dissolved copper concentration in the overflow tended to be lower than the dissolved ponded 2 concentration (Figure 5a). As for the suspended, this will underestimate the removal by adding addition samples.

The metals were also analyzed in relation to the infiltration bed depth. The copper concentrations at the tested depths (0 m, 1.2 m, and 2.4 m) can be seen in Figure 6.

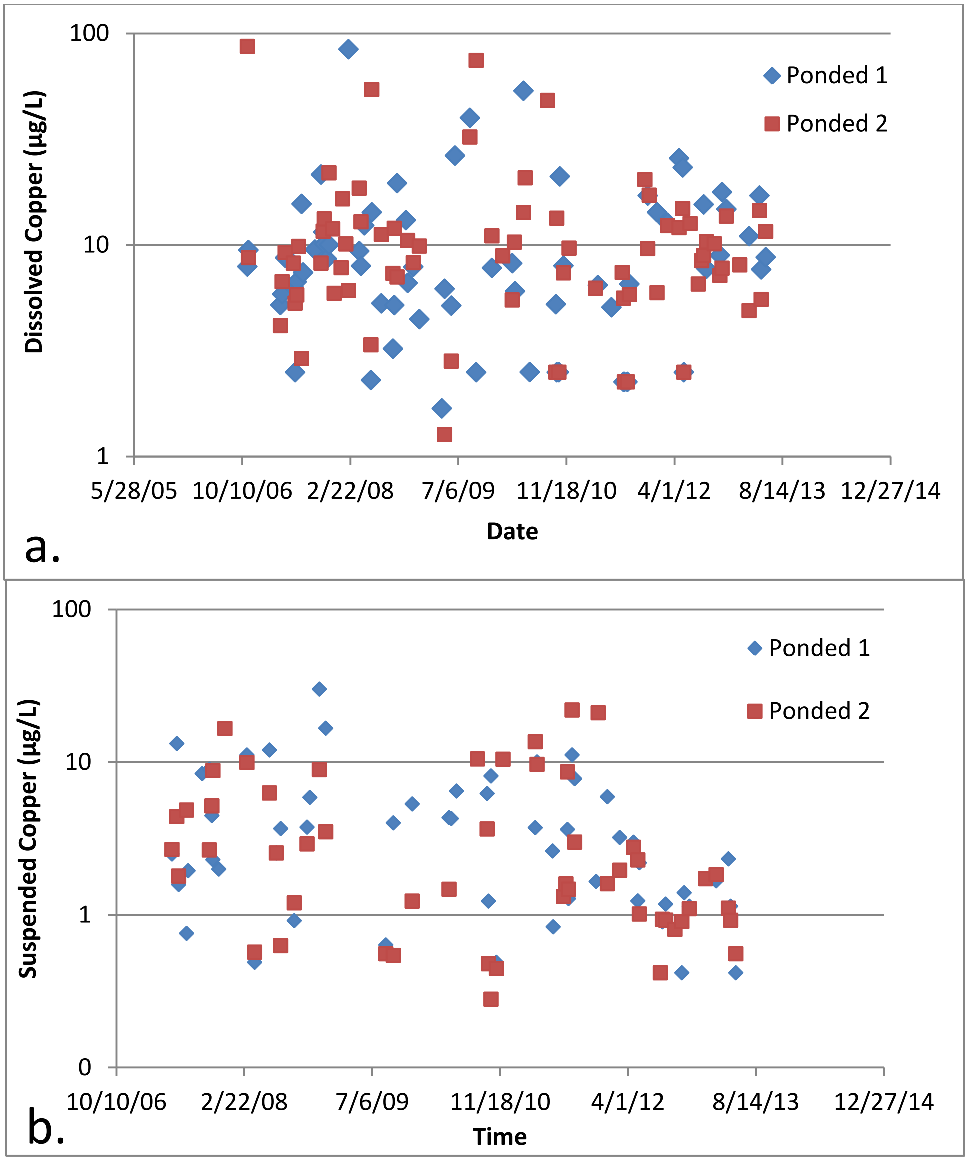

Figure 4: Concentration versus time plots for (a) dissolved copper and (b) suspended copper

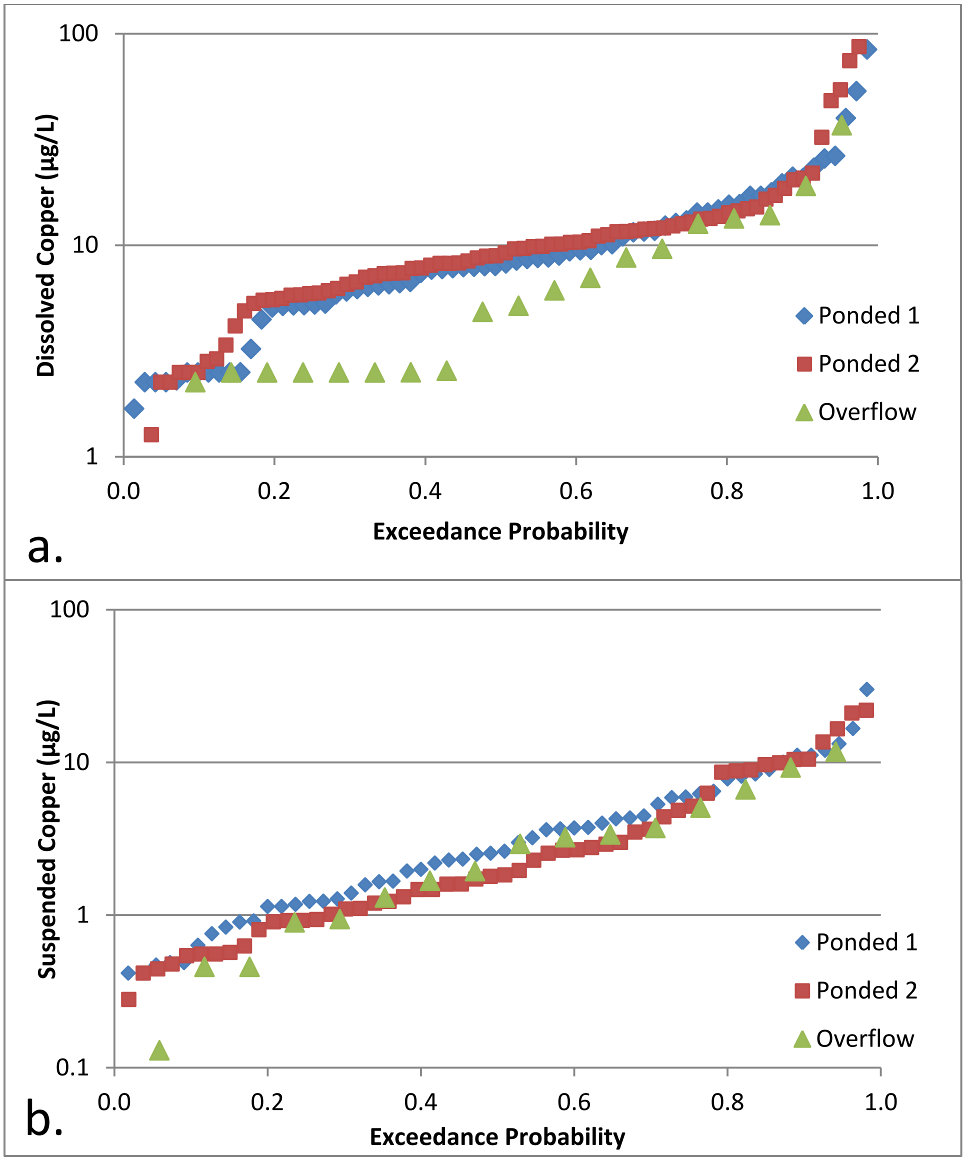

Figure 5: Ponded and overflow samples (a) dissolved and (b) suspended copper concentration

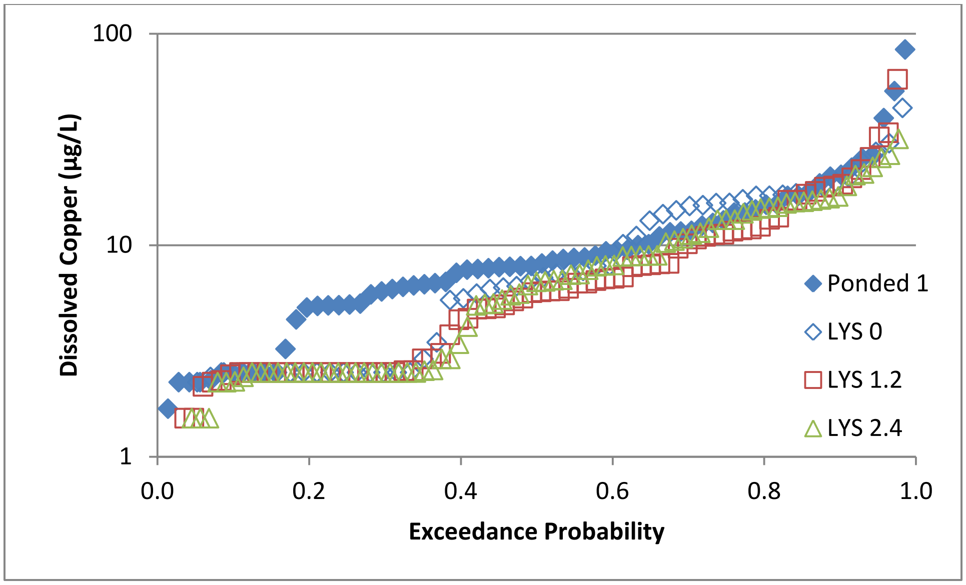

Figure 6: Concentration of dissolved copper within the soil at different depths and ponded all

The dissolved copper concentrations at different depths within the infiltration bed are similar (Figure 6) indicating that any copper removal occurred at the surface of the BTI infiltration media. The median ponded 1 dissolved copper concentration (8.2 µg/L) was higher than the dissolved copper concentrations at the surface (LYS0, 7.03 µg/L), 1.2 m below the surface (6.02 µg/L), and 2.4 m below the surface (6.71 µg/L) (Figure 6). It is important to consider that samples were below the detection limits and could be impacting the results seen for each of the metals as significantly more pore water lysimeter samples were below detection (~33%) than at the ponded 1 sampling location (11%) (Table 6).

Table 6: Percentage of copper samples below the detection limit

Copper	Ponded 1	Ponded 2	Overflow	LYS 0	LYS 1.2	LYS 2.4
Dissolved	11	6	45	33	33	34
Suspended	11	12	19	NA	NA	NA

There was a noticeable amount of dissolved and suspended copper removal that has occurred over time between the influent and effluent of the BTI (Figure 7). The median mass removed for dissolved copper was 295.6 mg while the suspended median was 44.3 mg.

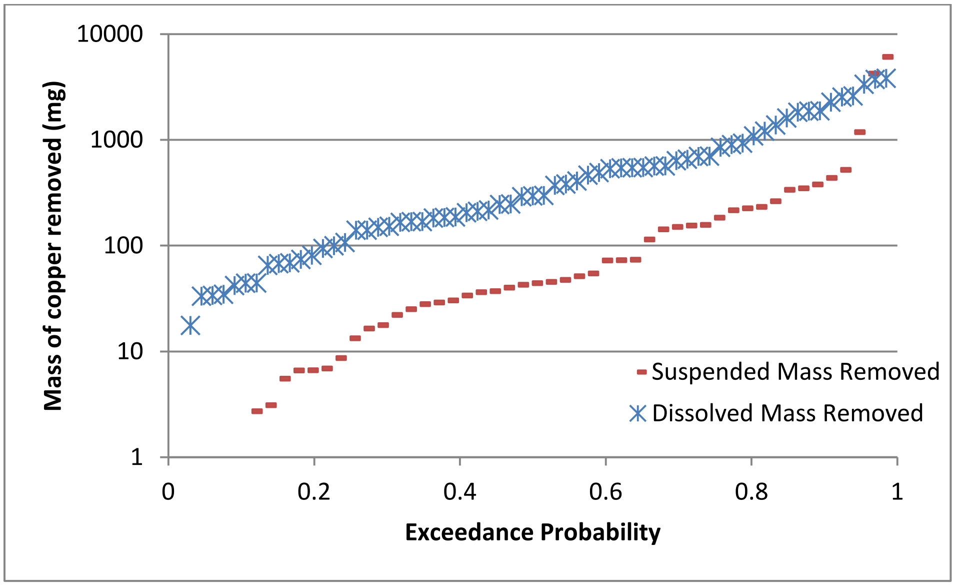

Figure 7: Mass removed for (a) dissolved and (b) suspended copper

4.1.2 Chromium

The ponded 1, ponded 2, and overflow chromium concentrations were compiled for the dissolved and suspended chromium in Figure 8a and 8b respectively. The median dissolved ponded 1, ponded 2, and overflow chromium concentrations were all 2.5 μg/L (Figure 8a). It is important to note that the majority of dissolved chromium concentrations were below detection (Table 7). The large number of dissolved cadmium concentrations at 2.5 μg/L in Figure 8a was due to the detection limit for dissolved cadmium being 5 μg/L for 35 of the 85 storms sampled (Table 2) and concentrations below detection were recorded as half of the concentration of the lowest standard used during testing. The suspended ponded 1, ponded 2, and overflow chromium concentrations were 2.4 µg/L, 2.4 µg/L, and 3.8 µg/L respectively (Figure 8b). There are similar concentrations of dissolved and suspended chromium entering the BTI. The dissolved chromium ponded 2 and overflow concentrations were comparable however the suspended chromium concentrations were not. The use of ponded 2 samples for storms where an overflow sample was not collected to determine metals removed by the BTI will underestimate the amount of suspended chromium leaving the system as the median suspended overflow chromium concentration was greater than the median suspended chromium ponded 2 sample.

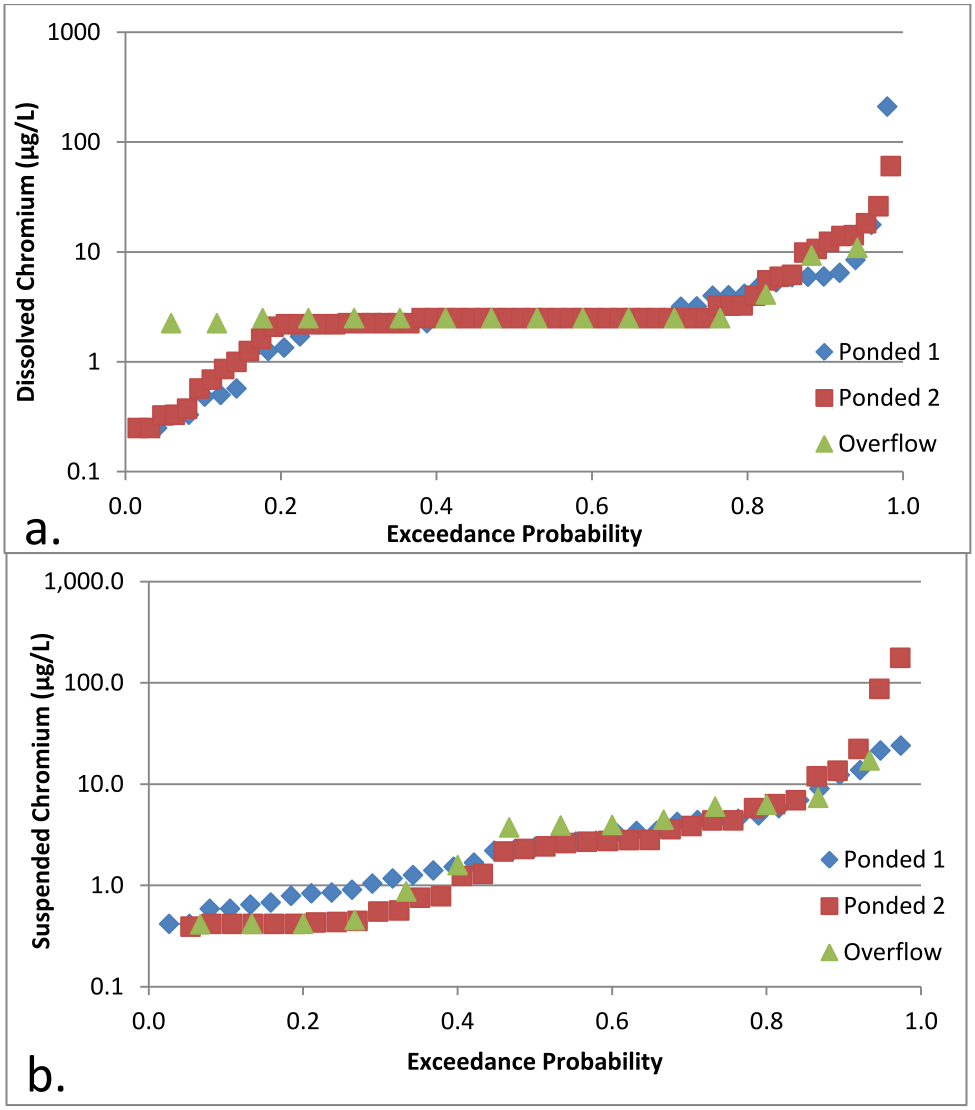

Figure 8: Ponded and overflow samples (a) dissolved and (b) suspended chromium

Figure 9 depicts the results for chromium in relation to the infiltration depth. The median dissolved chromium concentrations for ponded 1, LYS 0, LYS 1.2, and LYS 2.4 were 2.5 µg/L (Figure 9) due to the large number of samples at or below the detection limit (Table 7) (recall 2.5 µg/L is half of the median detection limit for dissolved chromium). The concentration of chromium did not change with depth however there was mass removal of chromium between the influent and effluent samples (Figure 10) due to the volume reduction as stormwater infiltrated into the ground. The median mass of dissolved chromium removed from the stormwater was 106 mg while the median suspended chromium was 25 mg.

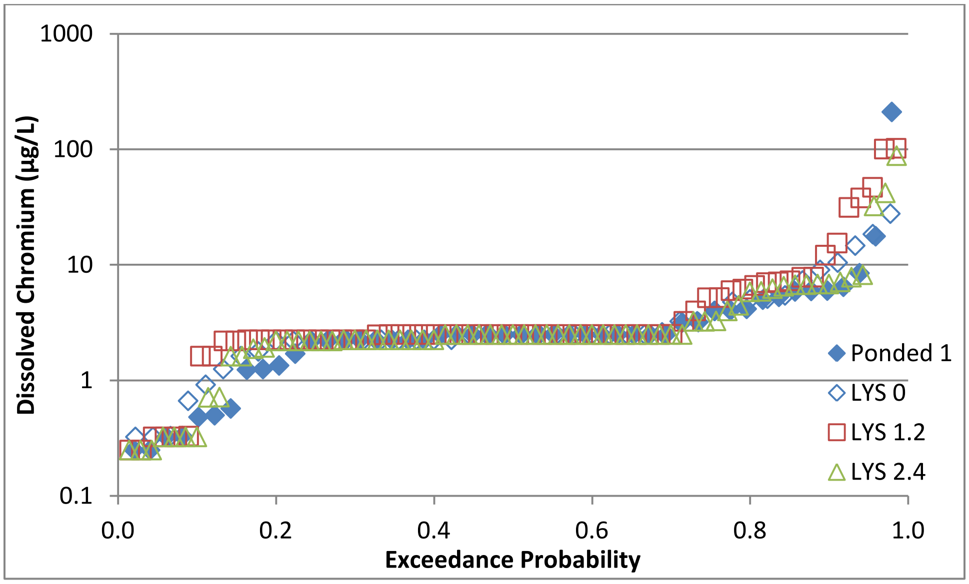

Figure 9: Chromium concentration in relation to infiltration bed depth

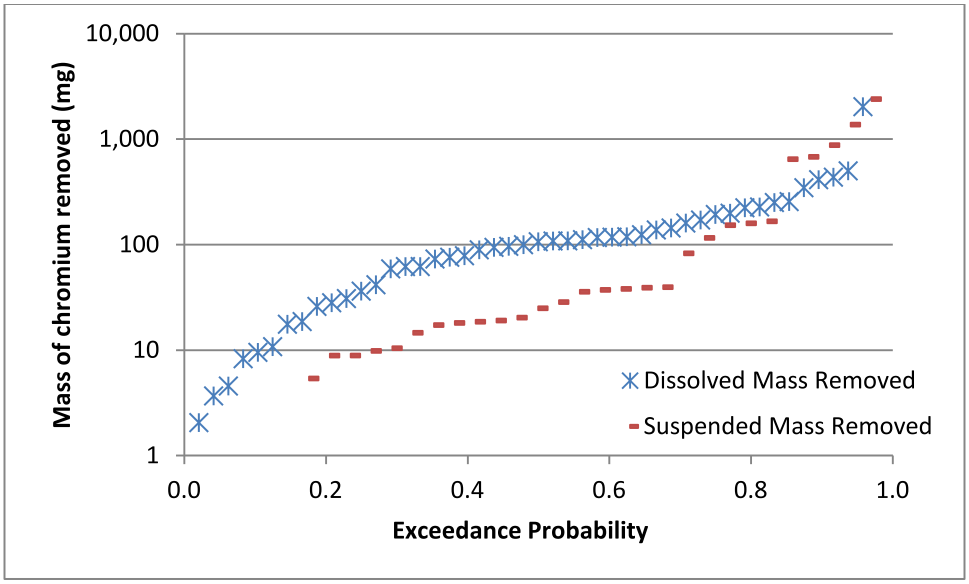

Figure 10 : Dissolved and suspended chromium removed

Table 7: Percentages of chromium samples below the detection limit

Chromium	Ponded 1	Ponded 2	Overflow	LYS 0	LYS 1.2	LYS 2.4
Dissolved	63	70	81	70	74	75
Suspended	11	31	36	NA	NA	NA

4.1.3 Lead

Figure 11 represents the exceedance probability of the ponded 1, ponded 2, and overflow samples for the (a) dissolved and (b) suspended lead concentrations. Similar to chromium, a majority (≥ 88% of all dissolved lead samples were below the concentration of the lowest lead standard (Table 8) and 47 of the 94 storms measured for lead had a detection limit of 5 µg/L (Table 3)). Due to the large number of samples below detection, the median dissolved ponded 1, ponded 2, and overflow lead concentrations were all 2.5 µg/L (i.e. half the detection limit most often used for the dissolved lead concentrations. The suspended lead concentrations for the ponded 1, ponded 2, and overflow concentration were 0.46 µg/L, 0.44 µg/L, and 0.73 µg/L.

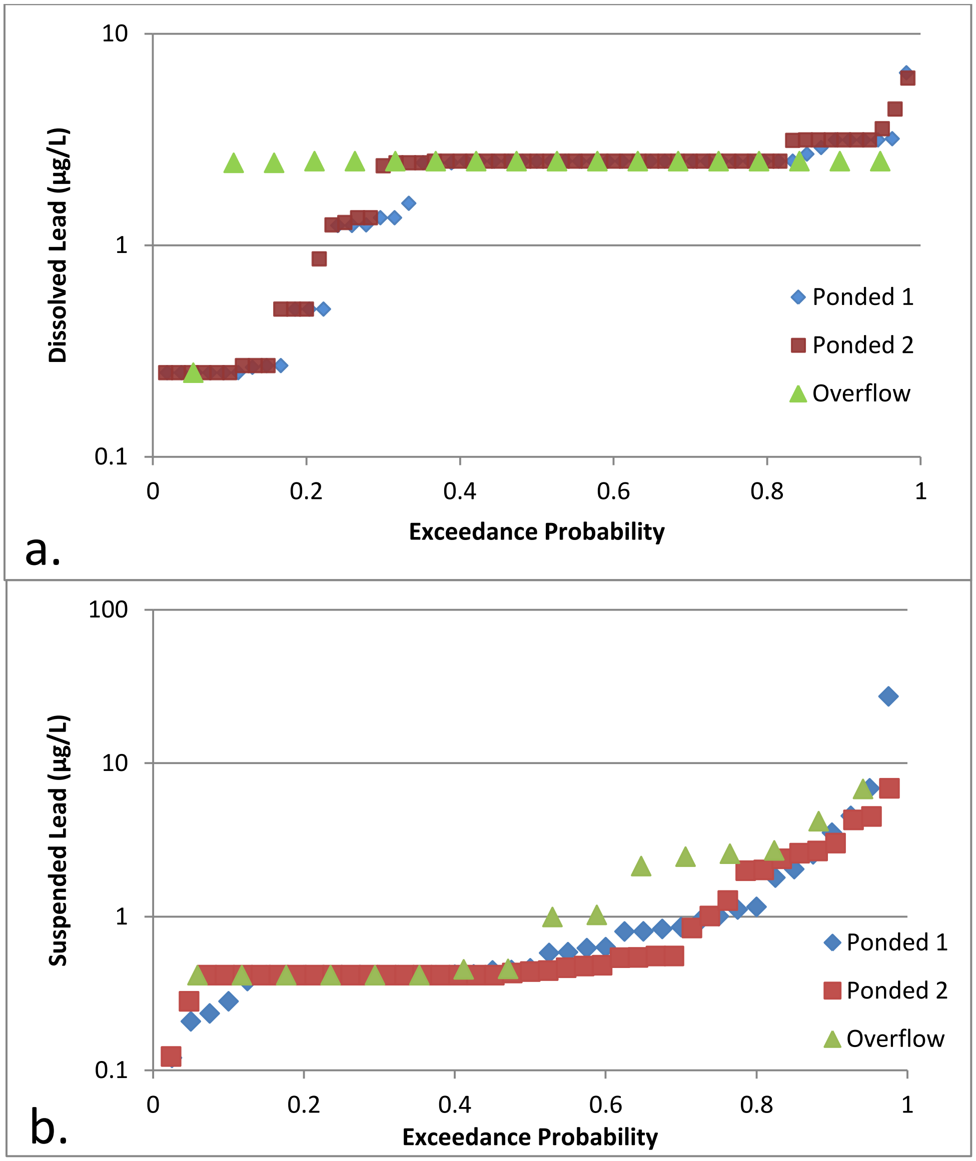

Figure 11: Ponded and overflow samples (a) dissolved and (b) suspended lead concentrations

Figure 12 depicts the concentrations of lead in relation to the bed depth. From this figure, it can be seen that again, there is no clear decreasing trend in the lead concentration as the infiltration bed depth increases due to the large number of samples at or below the detection limit. The median dissolved lead concentrations at all three lysimeters as well as for ponded 1 were all 2.5 μg/L (half of the detection limit). While the concentration of lead does not change with respect to depth, there was lead removed from the stormwater as can be seen in Figure 13. The median dissolved mass of lead removed mass was 52 mg while the suspended mass of lead removed was 14 mg.

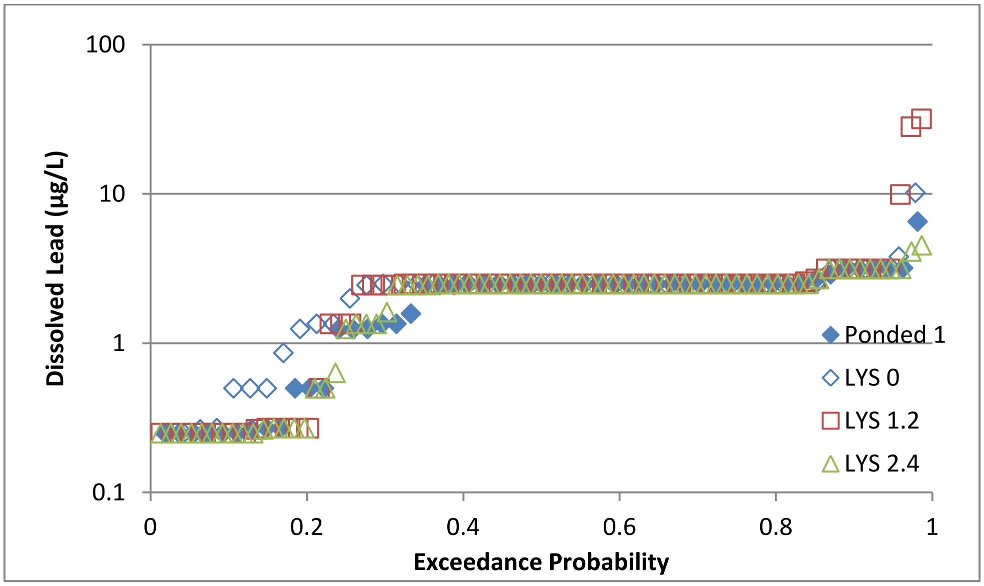

Figure 12: Exceedance probability of Ponded 1 and lead at various bed depths

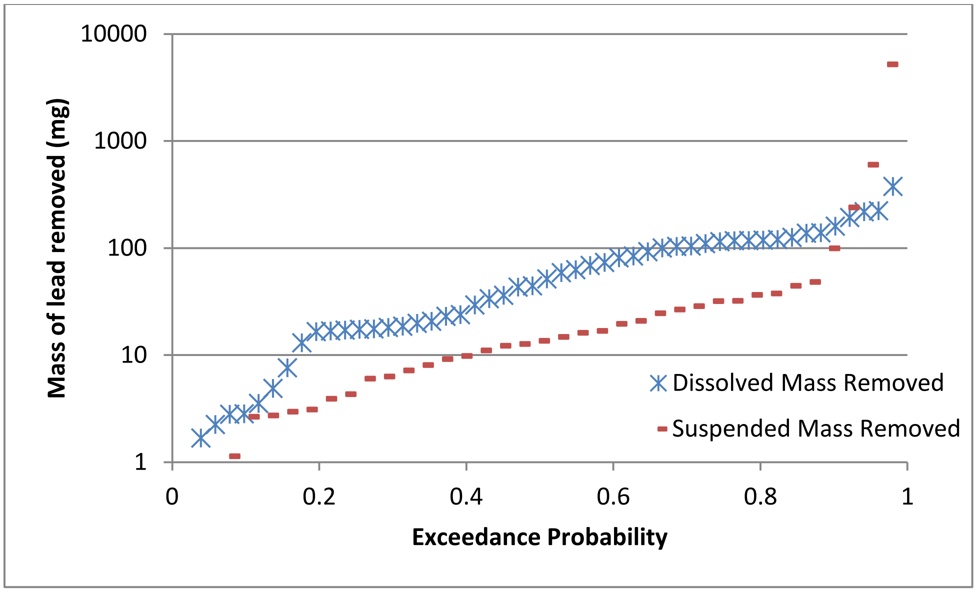

Figure 13: (a) Dissolved and (b) suspended mass of lead removed

Table 8: Percentage of lead samples below the detection limit

Lead	Ponded 1	Ponded 2	Overflow	LYS 0	LYS 1.2	LYS 2.4
Dissolved	89	88	100	91	95	95
Suspended	67	68	53	NA	NA	NA

4.1.4 Cadmium

Figure 14 represents the ponded 1, ponded 2, and overflow cadmium concentrations in the BTI. A majority (≥ 70% of all dissolved cadmium samples were below the concentration of the lowest cadmium standard (Table 9) and 33 of the 95 storms measured for cadmium had a detection limit of 0.8 μg/L (Table 4). Due to the large number of samples below the detection limits, the median dissolved ponded 1, ponded 2, and overflow concentrations were 0.4 μg/L, 0.4 μg/L, and 0.44 μg/L respectively. The median suspended concentrations for these samples were

0.067 μg/L for each the ponded 1, ponded 2, and overflow samples. Figure 15 depicts the results for the cadmium concentrations relative to the infiltration bed depth. The median dissolved cadmium concentrations for the all of the lysimeters (0 m, 1.2 m, and 2.4 m) were 0.4 μg/L. Again, this does not show any cadmium concentration decrease with bed depth since most of the samples were below detection (Table 9). There were noticeable masses of cadmium that were removed between the influent and effluent of the BTI for both dissolved and suspended cadmium (Figure 16) due to less volume leaving the BTI via the overflow as stormwater infiltrated into the bed. The median dissolved mass of cadmium removed was 18 mg while the median for suspended cadmium was 2 mg.

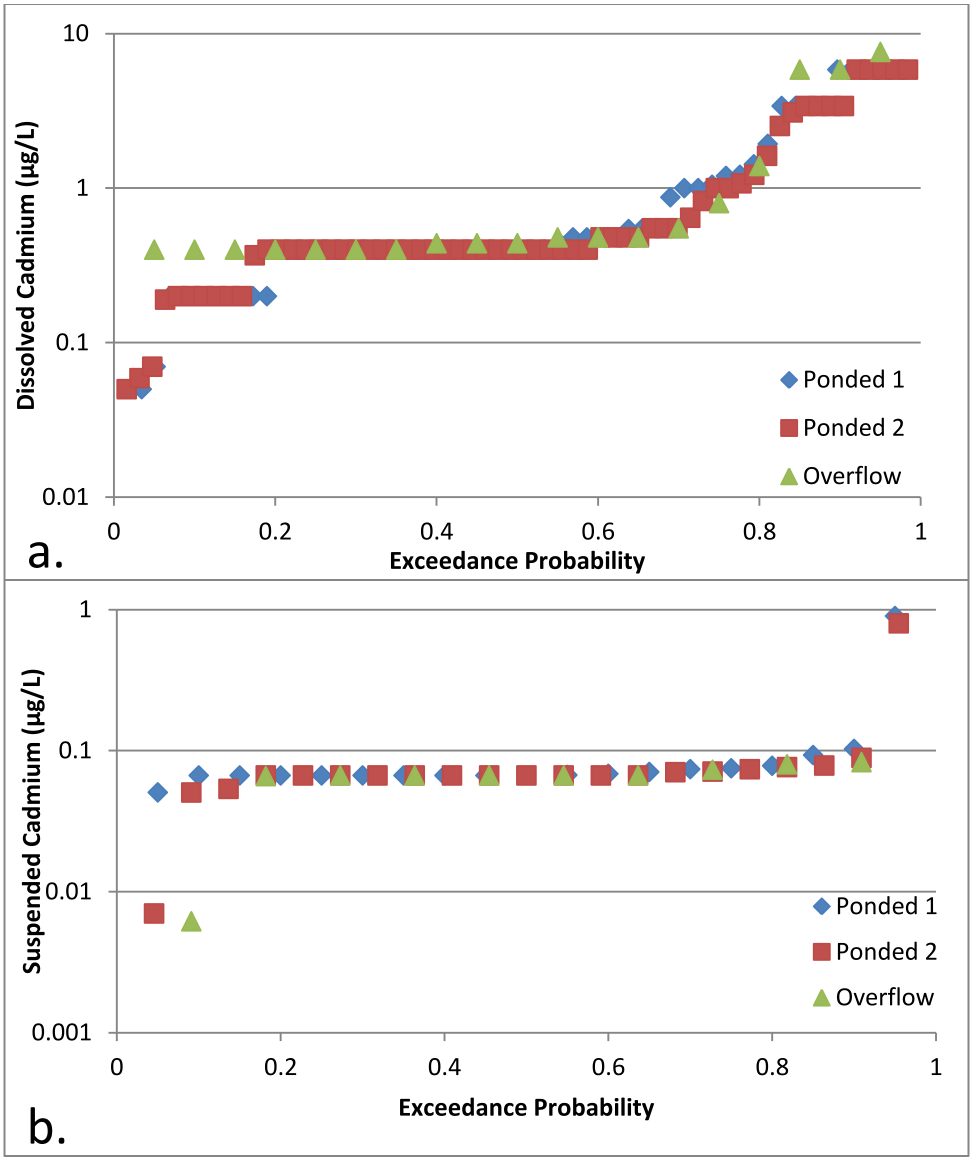

Figure 14: Ponded and overflow cadmium concentrations (a) dissolved and (b) suspended

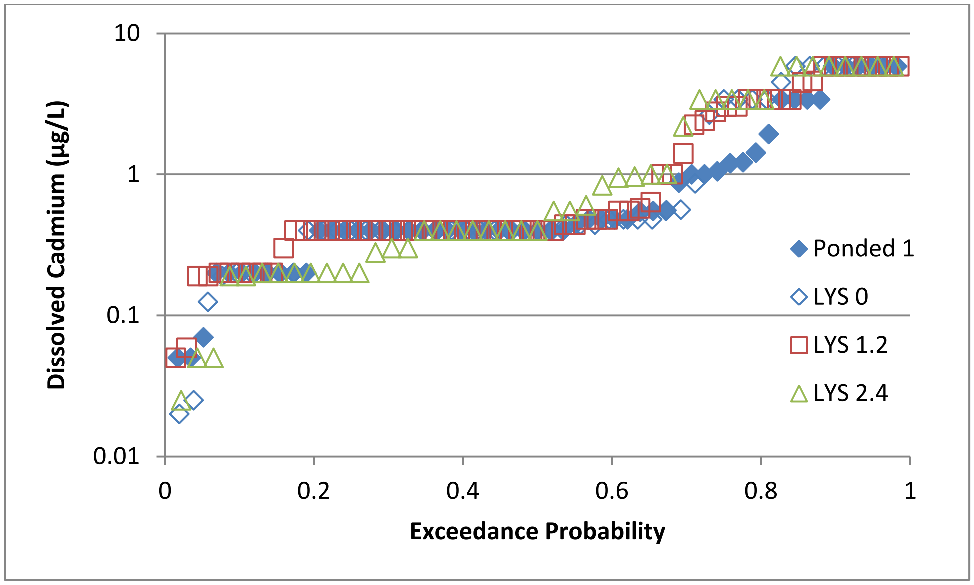

Figure 15: Relation between cadmium entering the BTI and removed at bed depths

Table 9: Percentage of cadmium samples below the detection limit

Cadmium	Ponded 1	Ponded 2	Overflow	LYS 0	LYS 1.2	LYS 2.4
Dissolved	84	85	89	70	74	75
Suspended	68	86	100	NA	NA	NA

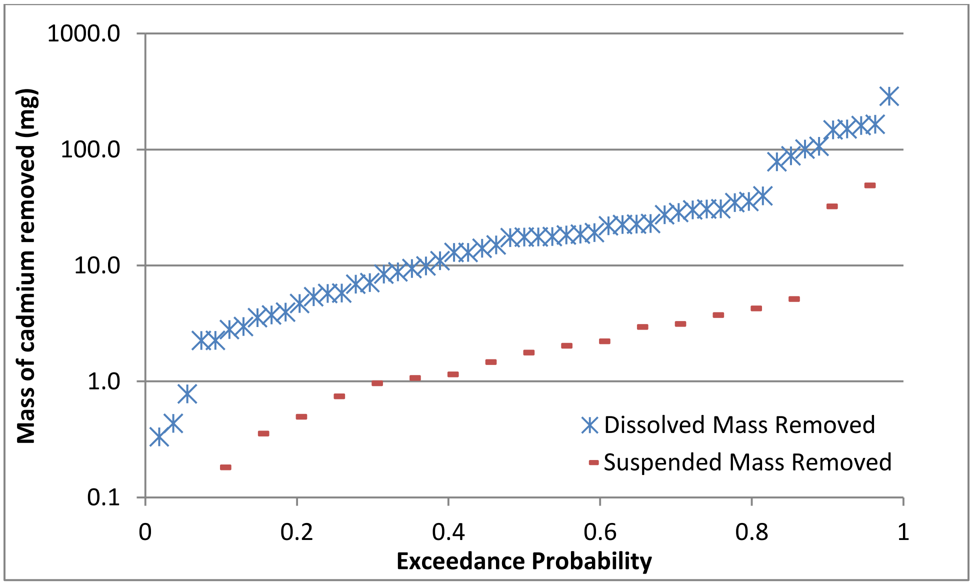

Figure 16: Mass of (a) dissolved and (b) suspended cadmium removed

4.1.5 Zinc

Figure 17 represents the ponded 1, ponded 2, and overflow zinc concentrations for (a) dissolved and (b) suspended samples. The median concentrations for those samples were 29 μg/L, 27 μg/L, and 48 μg/L respectively, for the dissolved zinc. The ponded 1, ponded 2, and overflow median suspended zinc concentrations were 15 μg/L, 18 μg/L, and 19 μg/L. Figure 18 depicts the results for the zinc concentrations relative to the infiltration bed depth. The median dissolved zinc concentrations for the all of the lysimeters (0 m, 1.2 m, and 2.4 m) were 25 μg/L. No changes in the median zinc concentrations with depth indicated that there was no measureable loss in the concentration as the water traveled down into the bed. It is important to note that no change in the median concentration could have been due to the large portion (≥ 46%) of the samples being below detection (Table 10). There was mass removed from the ponded stormwater for zinc in both the dissolved and suspended forms of zinc (Figure 19). The median dissolved and suspended masses of zinc removed were 996 mg and 212 mg, respectively.

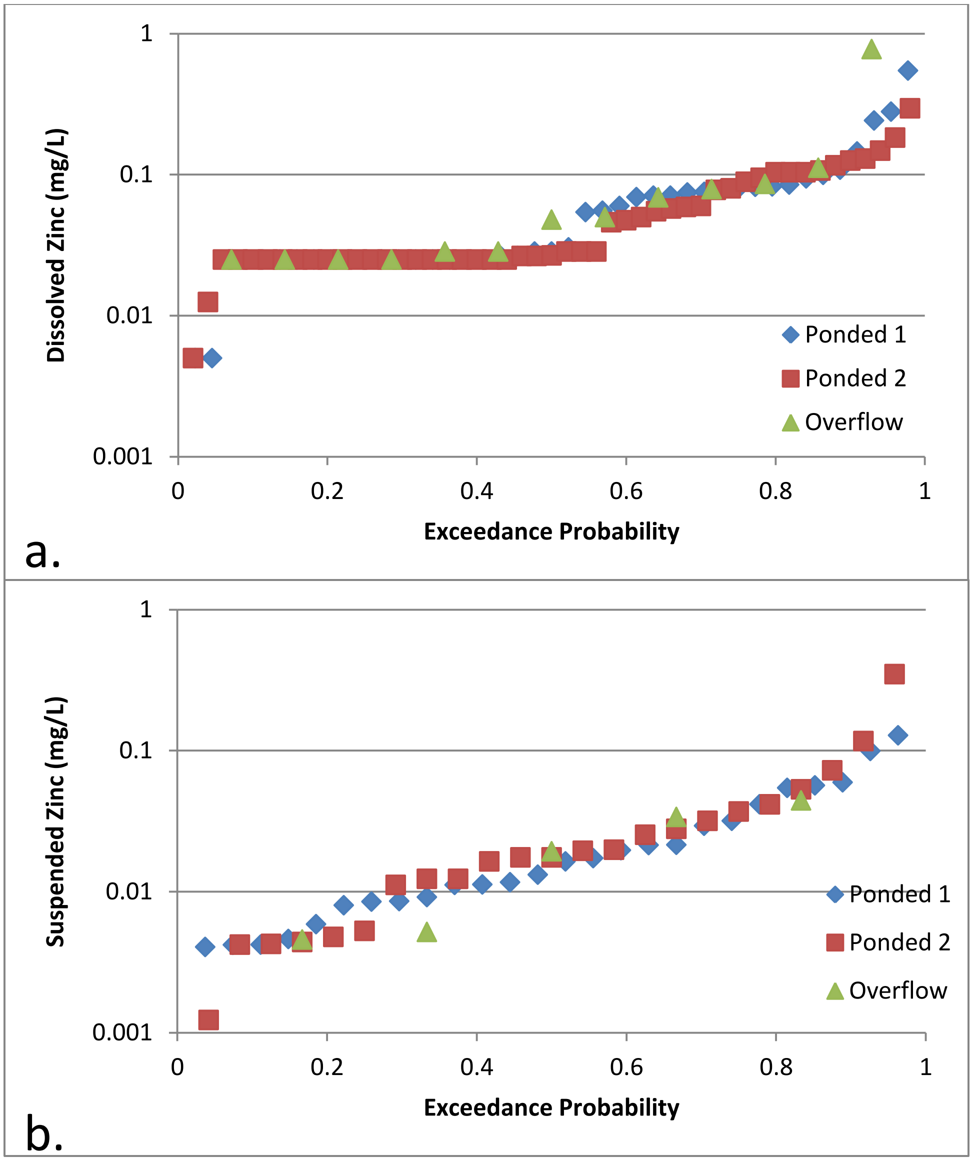

Figure 17: Ponded and overflow samples for (a) dissolved and (b) suspended zinc

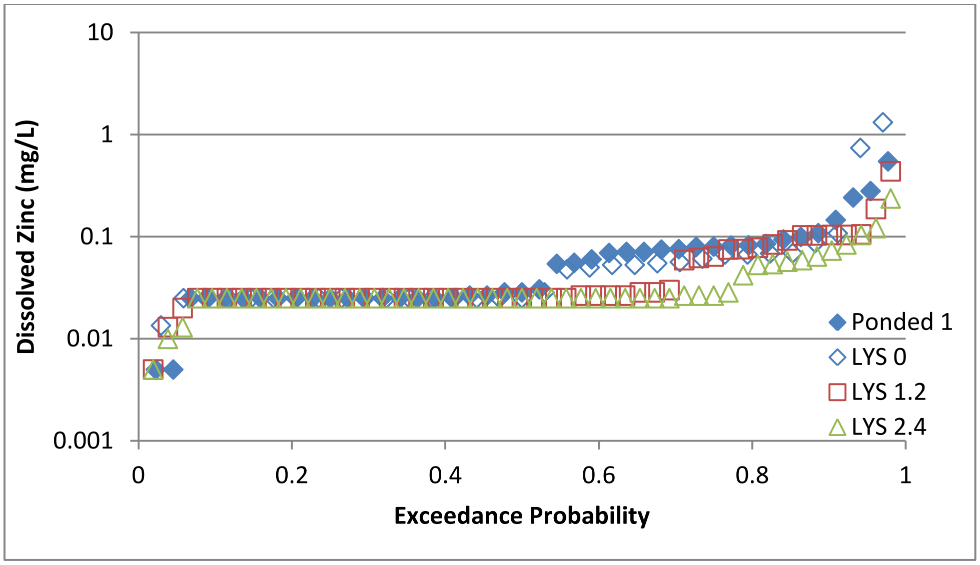

Figure 18: Influent and various bed depth dissolved zinc concentrations

Table 10: Percentage of zinc samples that were below detection

Zinc	Ponded 1	Ponded 2	Overflow	LYS 0	LYS 1.2	LYS 2.4
Dissolved	51	51	46	55	65	75
Suspended	27	22	40	NA	NA	NA

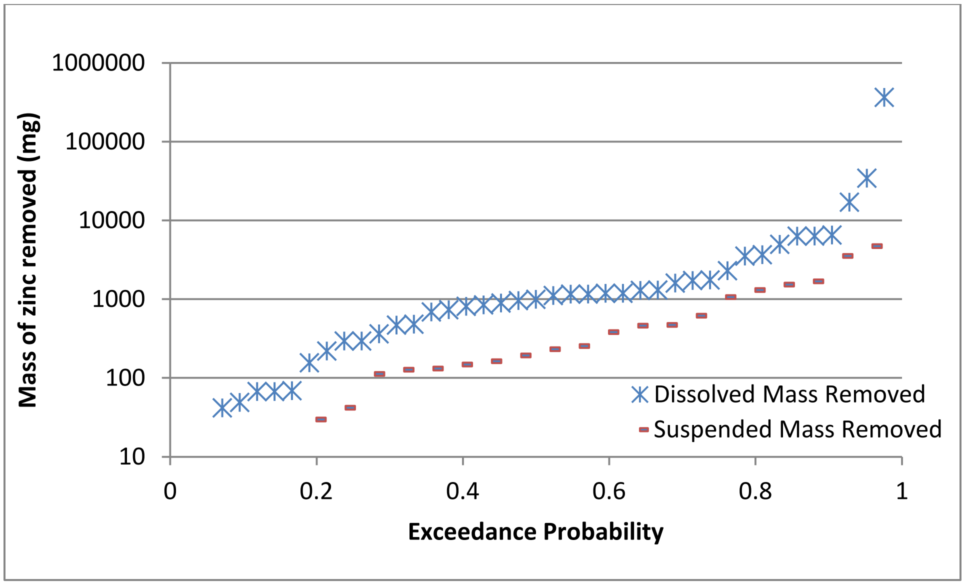

Figure 19: Mass of dissolved and suspended zinc removed by the BTI

4.1.6 Implications of the Analyzed Water Quality data

When there was no overflow sample measured during a storm event, grab samples collected toward the end of the storm event (ponded 2) were used to represent the concentration overflowing the BTI. The mass that can be removed by the BTI for all metals, except copper, was underestimated through this analytical assumption because the metal concentrations in the overflow tended to be higher than the ponded 2 concentrations.

Table 11 is a summary of the water quality for the stormwater ponded in the BTI. The dissolved and suspended median concentrations were summed and compared to measured ranges of metal concentrations found in the literature. From this table it can be seen that all metals, except for lead, in this BTI were recorded at levels that were within the typical range of measured concentrations for each respective metal. Table 11 also shows that the measured concentrations of dissolved metals were consistently higher than those of the suspended metals which may be true however could also be due to more dissolved concentrations at or below the detection limits compared to the suspended concentrations (Tables 6-10). This correlates to the dissolved mass of metals removed to being higher than the suspended mass removed as well. Furthermore, copper and (to a lesser extent) zinc were the only metals that showed consistent trends of dissolved concentrations in the ponded region that were higher than the concentrations measured with depth into the infiltration matrix below (Figures 6 and 18 respectively). None of the metals showed a strong trend of decreasing concentration with depth into the infiltration bed depth which could be attributed to the high number of samples being measured at or below the detection limits (i.e. any variations would have been below the detection limit of the analytical methods used for metals quantification). Each of the metals analyzed did have a measureable amount of mass that was removed from the stormwater but it is unclear from the above analysis alone if metals were removed in the infiltration bed or if the metals stayed in solution and passed through and down to the groundwater below. Straining or metal precipitation may be the dominant metals removal mechanisms as the stormwater infiltrations into the bed.

Table 11: Median metal concentrations ponded in BTI compared to ranges found in literature[a]

Metal	Dissolved	Suspended	Total	Literature
	ug/L	ug/L	ug/L	ug/L
Copper	8.2	2.6	10.8	1-100
Chromium	2.5	2.4	4.9	1-90
Lead	2.5	0.5	3.0	6-460
Cadmium	0.4	0.1	0.5	0.1-8
Zinc	28.5	16.4	44.9	0.7-117

[a] Bardin, 2001; Davis, 2003; USEPA, 1983; Galvin and Moore, 1984; Merrill, 1989

4.2 Quantification of Metals Accumulation onto BTI Soil

Soil samples were collected from different areas of the BTI in 2009 and analyzed to quantify the concentrations of metals that accumulated over time onto the BTI soil since the BTI was put online in 2001. Samples were again collected and analyzed in 2013 to determine how the sorbed metal concentrations changed with time. Samples were collected from approximately the same locations (Figure 3b).

4.2.1 Copper

Copper sorption onto the infiltration media was analyzed from five locations (Figure 3b) at both the surface (0.025 m, 1 inch) and at 0.3 m (12 inches) below the surface in 2009 (after 8 years of SCM operation) and in 2013 (12 years of SCM operation) (Figure 20). The influent samples were collected at location 1 (see Figure 3b). Location 1 was from an area at a higher elevation in the BTI and therefore received less ponding and was defined as the control area. The middle samples were collected from locations 4, 5, and 2 (see Figure 3b). The end samples were collected from location 3 (see Figure 3b). Locations 2 through 5 were lower in elevation and received the majority of ponding during storm events. Samples were not collected at the 0.3 m depth at location 1 in 2009. Although there were variations in sorbed copper concentrations throughout the ponded area, all ponded area concentrations were higher than the control area, indicating copper accumulation onto the soil due to stormwater infiltration (Figure 20). Sorbed copper concentrations were greater at the surface than those concentrations measured at a depth of 0.3 m into the infiltration basin.

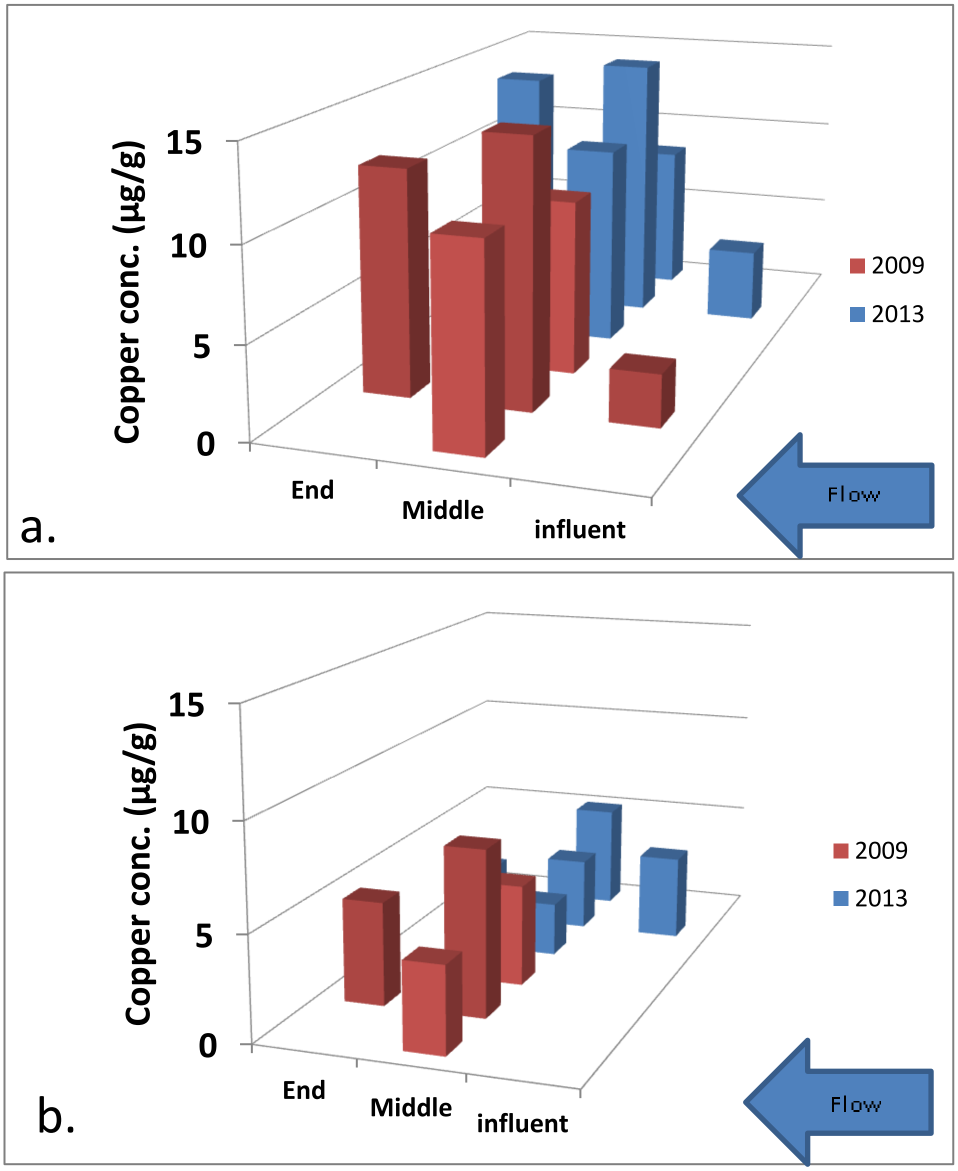

Figure 20: Copper concentrations sorbed to BTI soil at (a) 0.025 m and (b) 0.3m. Values are an average of triplicate soil samples collected from each location.

The average copper concentration sorbed to the soil at the surface (0.025 m) and at a depth of 0.3 m (12 inch) within the BTI for the ponded (locations 2-5) and control (Location 1) area is shown in Figure 21. It can be determined that the amount of copper sorbed to the soil decreased with depth. This coincides with what other studies found showing higher metal concentrations at the surface of the infiltration beds and decreasing with depth (Davis et al., 2003; Davis et al., 2008). A statistical t-test was performed to compare the 2009 and 2013 ponded data. The number of samples included for each set is given in Figure 21. The copper concentration sorbed to the soil in the ponded region (locations 2-5) at the surface was not significantly different ($p>0.05$ $n=30$) between the 2009 to the 2013 data indicating that there was no measurable accumulation of copper on the soil between 2009-2013. The copper concentrations sorbed to the soil in the ponded area were significantly higher ($p=0.0003$ and $p=0.0002$) than the copper concentrations sorbed to the soil in the control area at the surface (0.025 m) for 2009 and 2013 respectively thus indicating that more copper was sorbed in the ponded area. The copper in the ponded and control samples 0.3 m below the surface were not significantly higher ($p=0.07$) in 2013. The statistical test results are summarized in Table 12.

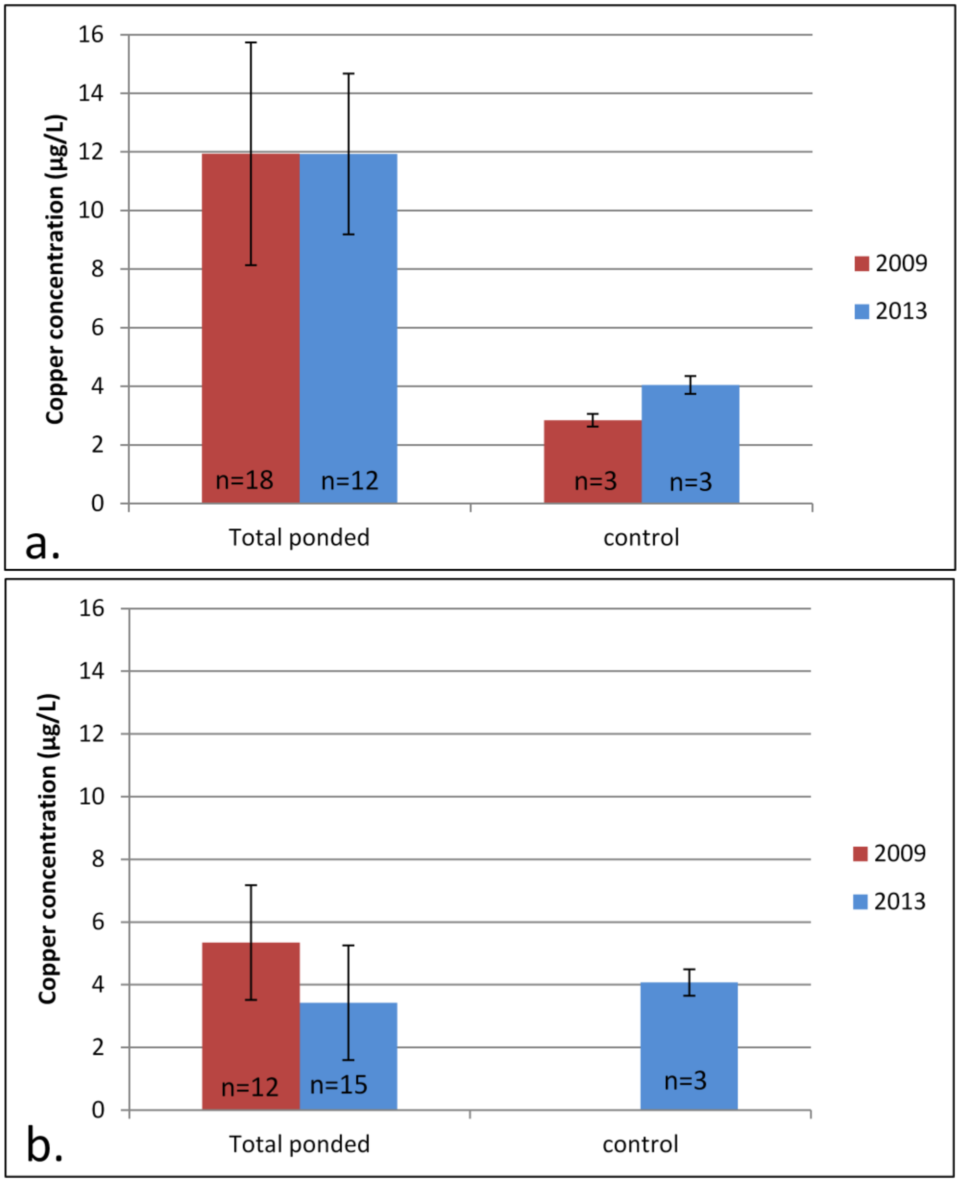

Figure 21: Average copper concentrations at a depth of (a) 0.025 m and (b) 0.3 m for the ponded area (locations 2 through 5) and the control area (location 1) (see Figure 3b).

Table 12: Copper Statistical Analysis Summary

Depth	Year	Ponded Area			Control			t-test
		avg (ug/g)	std	n	avg (ug/g)	std	n	p
0.025m	2009	11.93	3.80	18	2.84	0.22	3	0.00
	2013	11.93	2.74	12	4.05	0.31	3	0.00
0.3m	2009	5.34	1.83	15				
	2013	3.43	1.07	12	4.07	0.42	3	0.07

4.2.2 Chromium

The greatest concentration of chromium in the BTI was found to be in the center of the ponded area in both 2009 and 2013 (Figure 22). The concentrations of chromium at the surface are relatively the same between 2009 and 2013 (Figure 22a). At a depth of 0.3 m below the surface, the concentration of chromium sorbed to the soil has decreased over time in the center of the BTI while remaining relatively the same at the other locations. This may be due to slight variations in the testing location between 2009 and 2013. The chromium concentration sorbed to the soil in the ponded region (locations 2-5) at the surface was not significantly different (p=0.23) between the 2009 and 2013 data indicating that there was no measurable accumulation of chromium on the soil between 2009-2013 (Figure 23a). The chromium concentrations sorbed to the soil in the ponded area 0.3 m below the surface was also not significantly different (p=0.06) from 2009 to the 2013 data suggesting that the chromium concentration did not change from 2009-2013. The chromium concentrations sorbed to the soil in the ponded area were significantly higher than the concentrations from the control area at the surface for 2009 and 2013 (p=0.049 and p=0.048 respectively). Therefore, as expected, more metals are removed in the area that experiences ponding during storm events. However, the 2013 samples taken 0.3 m below the surface were not statistically different (p=0.16) than the chromium concentrations sorbed to the soil in the control area. There were not samples collected at this depth in 2009. The statistical test results are summarized in Table 13.

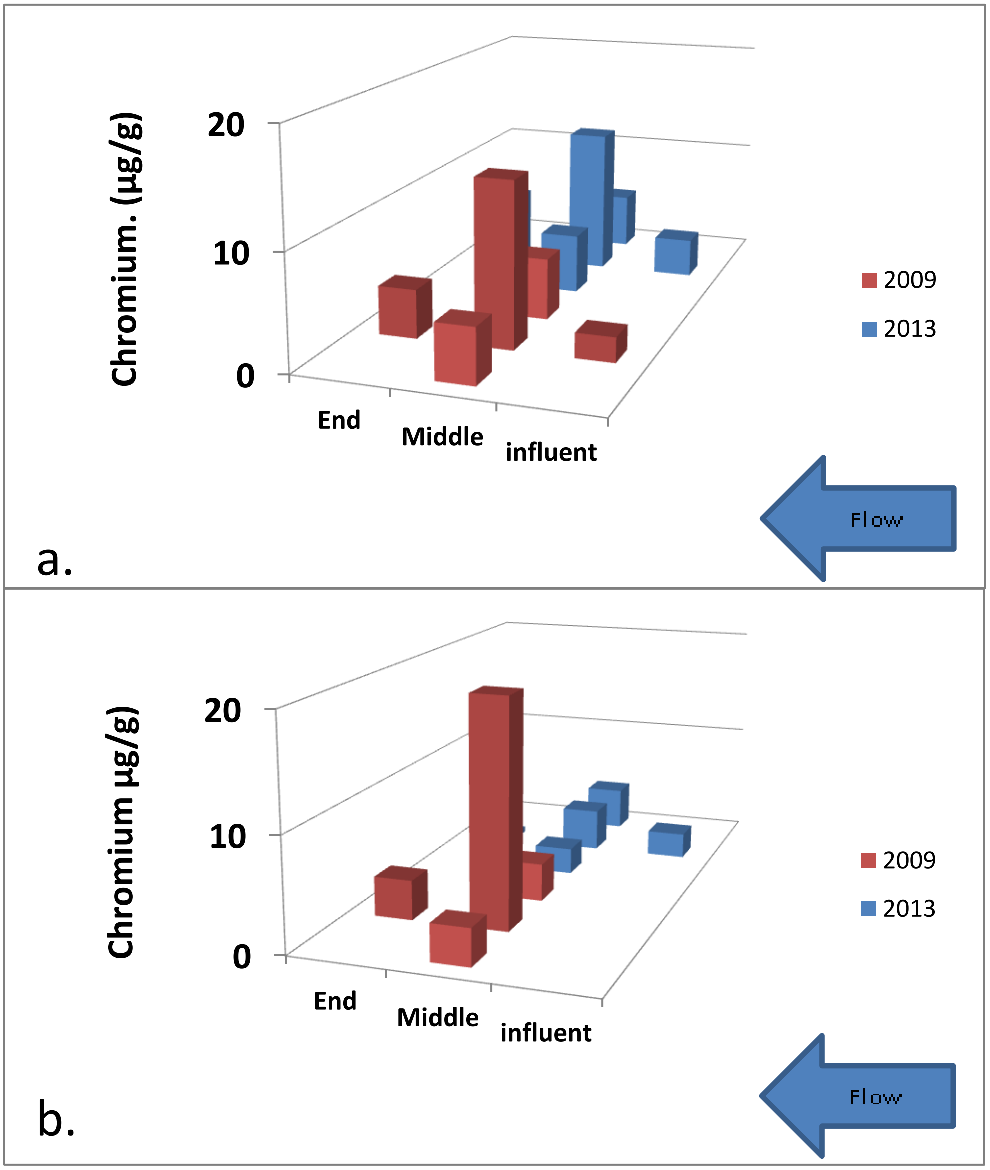

Figure 22: Sorbed chromium concentrations at (a) 0.025 m and (b) 0.3 m depths of the infiltration bed of the BTI. Values are an average of triplicate soil samples collected from each location.

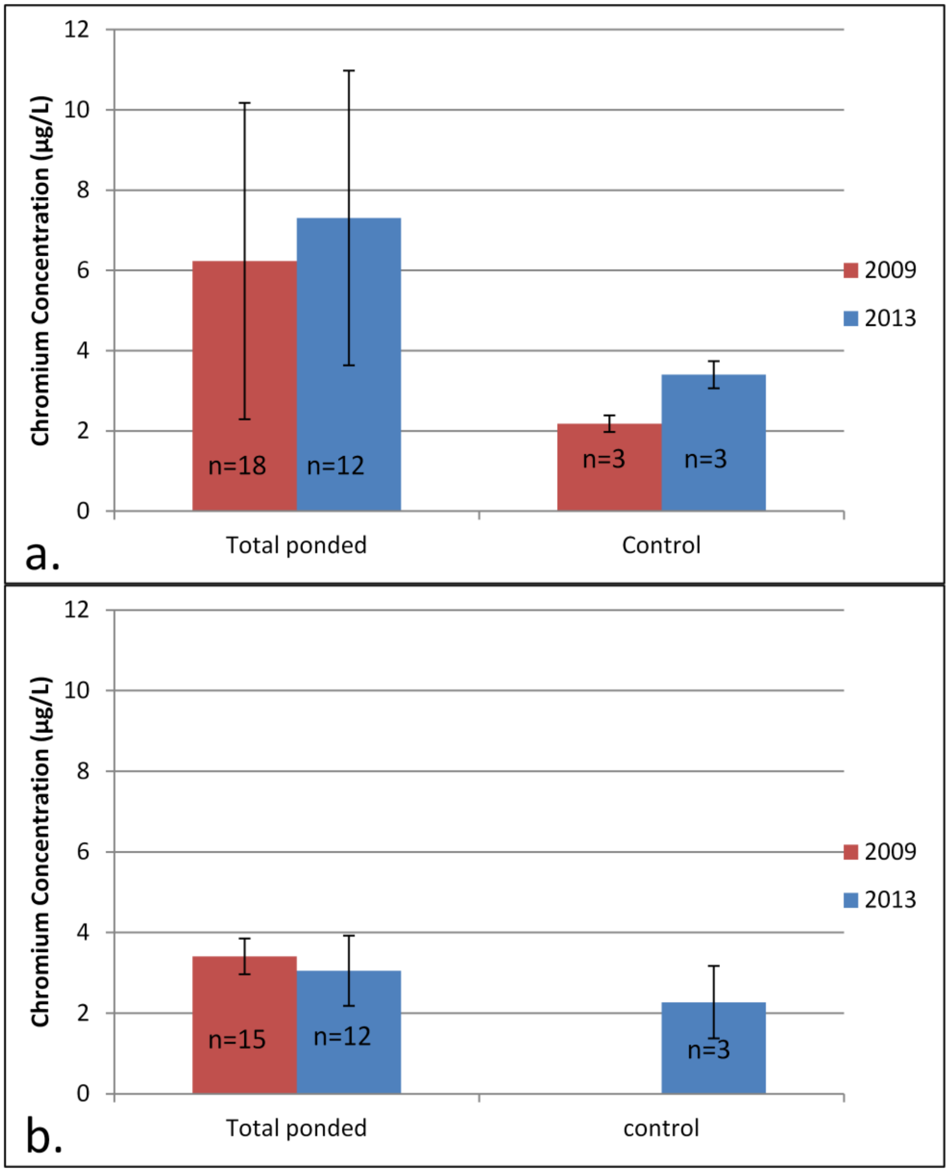

Figure 23: Average chromium concentrations in the ponded and control areas of the BTI at (a) 0.025m (1 inch) and (b) 0.3 m (12 inches) depths.

Table 13: Chromium Statistical Analysis Summary

Depth	Year	Ponded Area			Control			t-test
		avg (ug/g)	std	n	avg (ug/g)	std	n	p
0.025m	2009	6.23	3.94	18	2.18	0.21	3	0.05
	2013	7.31	3.67	12	3.40	0.34	3	0.05
0.3m	2009	3.41	0.44	15				
	2013	3.05	0.87	12	3.75	0.90	3	0.16

4.2.3 Lead

Figures 24 and Figure 25 are the results for the lead extractions from BTI soil collected in 2009 as well as in 2013. Figure 24a represents the lead found 0.025 m (0-2 inches) into the media for all five sampling location while Figure 24b is for the lead found in the soil 0.3 m (12 inches) down. The sorbed copper concentrations varied throughout the BTI with not all of the sorbed lead concentration in the ponded area higher than the control area. All samples except for the sampling location in the middle of the BTI had average lead concentrations that increased from 2009 to 2013. Sorbed lead concentrations at the surface of the ponded area data were not significantly different (p=0.16) from 2009 to the 2013 data (Figure 25) The ponded data 0.3 m below the surface was significantly higher (p=0.01) from 2009 to the 2013 data. The ponded data was significantly higher than the control samples at both the surface (0.025 m) for 2009 and 2013 (p=0.059 and p=0.002, respectively) however, samples at 0.3m below the surface were not significantly higher in 2013 for the ponded area compared to the control area (p=0.21) (Table 14). There was no control sample in 2009 to compare to the ponded.

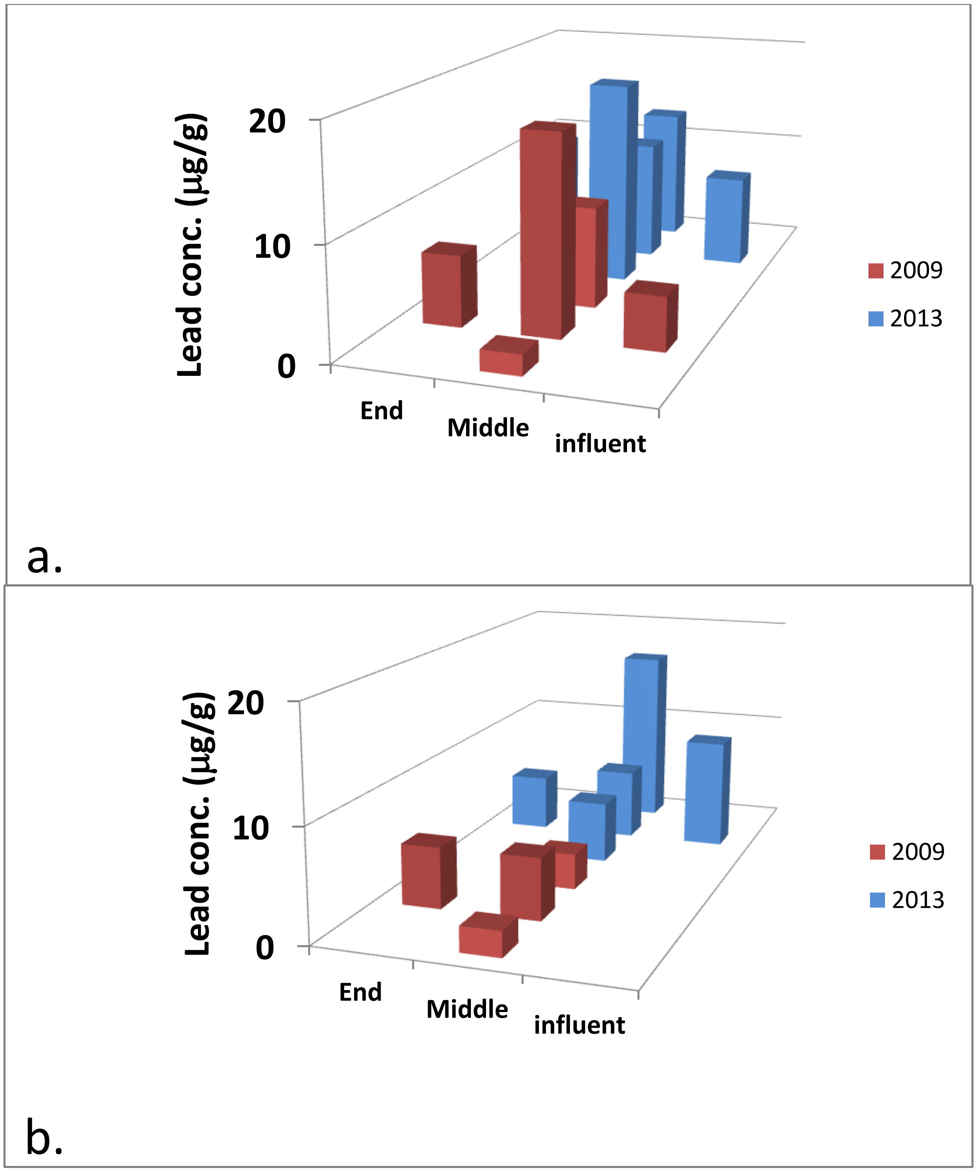

Figure 24: Lead concentrations at a depth of (a) 0.025 m (1 inch) and (b) 0.3 m (12 inches). Values are an average of triplicate soil samples collected from each location.

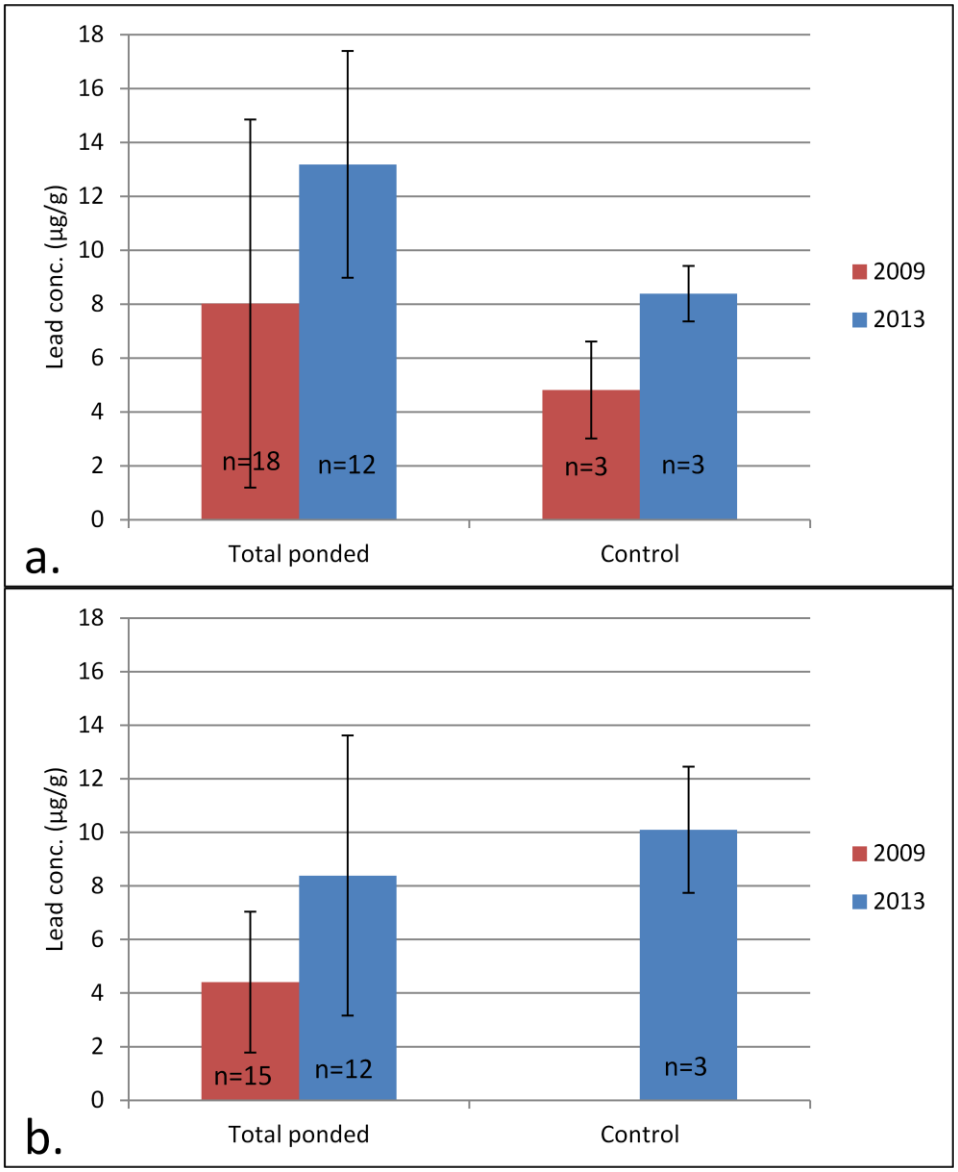

Figure 25: Average lead concentrations in the ponded and control areas of the BTI at (a) 0.025m (1 inch) and (b) 0.3 m (12 inches) depths.

Table 14: Lead Statistical Analysis Summary

Depth	Year	Ponded Area			Control			t-test
		avg (ug/g)	std	n	avg (ug/g)	std	n	p
0.025m	2009	8.02	6.83	18	4.82	1.80	3	0.06
	2013	13.18	4.21	12	8.39	1.03	3	0.00
0.3m	2009	4.41	2.63	15				
	2013	10.10	2.36	3	8.39	5.23	12	0.21

4.2.4 Cadmium

Figures 26 and 27 represent the concentrations of cadmium that were found to be sorbed to the soil in 2009 and 2013. Sorbed cadmium concentrations were only measured at two of the four ponded locations in 2009 (locations 3 and 5). The ponded cadmium concentrations were significantly greater (p=0.005 and p=0.004) than the control samples at the surface (0.025m) for 2009 and 2013 respectively. This suggests that cadmium was removed by sorption when a storm event creates a ponding effect within the SCM. Sorbed cadmium ponded concentrations at the surface increased significantly (p=0.000005) between 2009 and 2013. The ponded data 0.3 m below the surface also increased significantly (p=0.00005) between 2009 and 2013. Sorbed samples at 0.3 m below the surface were significantly higher (p=0.0008) in the ponded area than the control area in 2013. There was no control sample in 2009 to compare to the ponded area. The statistical test results are shown in Table 15.

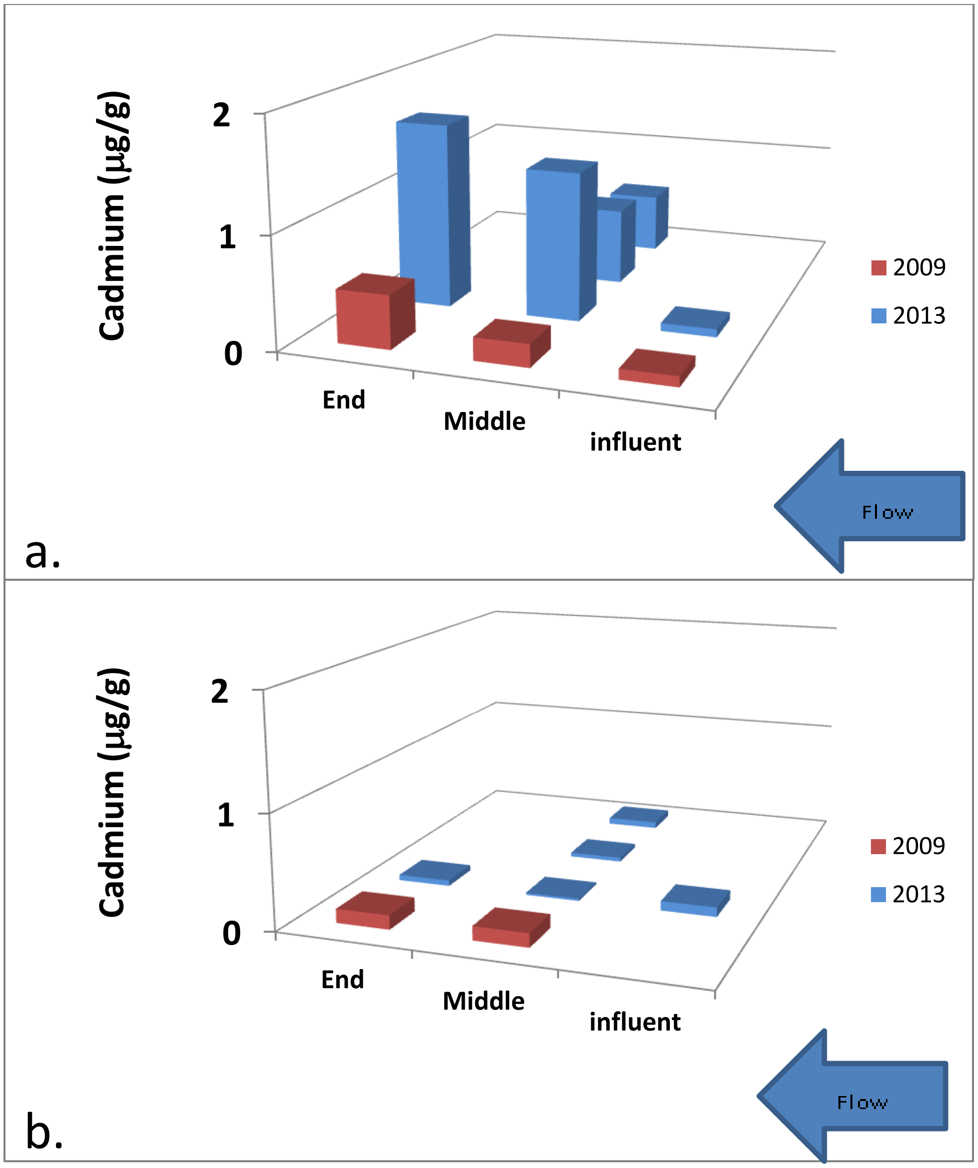

Figure 26: Cadmium concentration at (a) 0.025 m (1 inch) and (b) 0.3 m (12 inches). Values are an average of triplicate soil samples collected from each location.

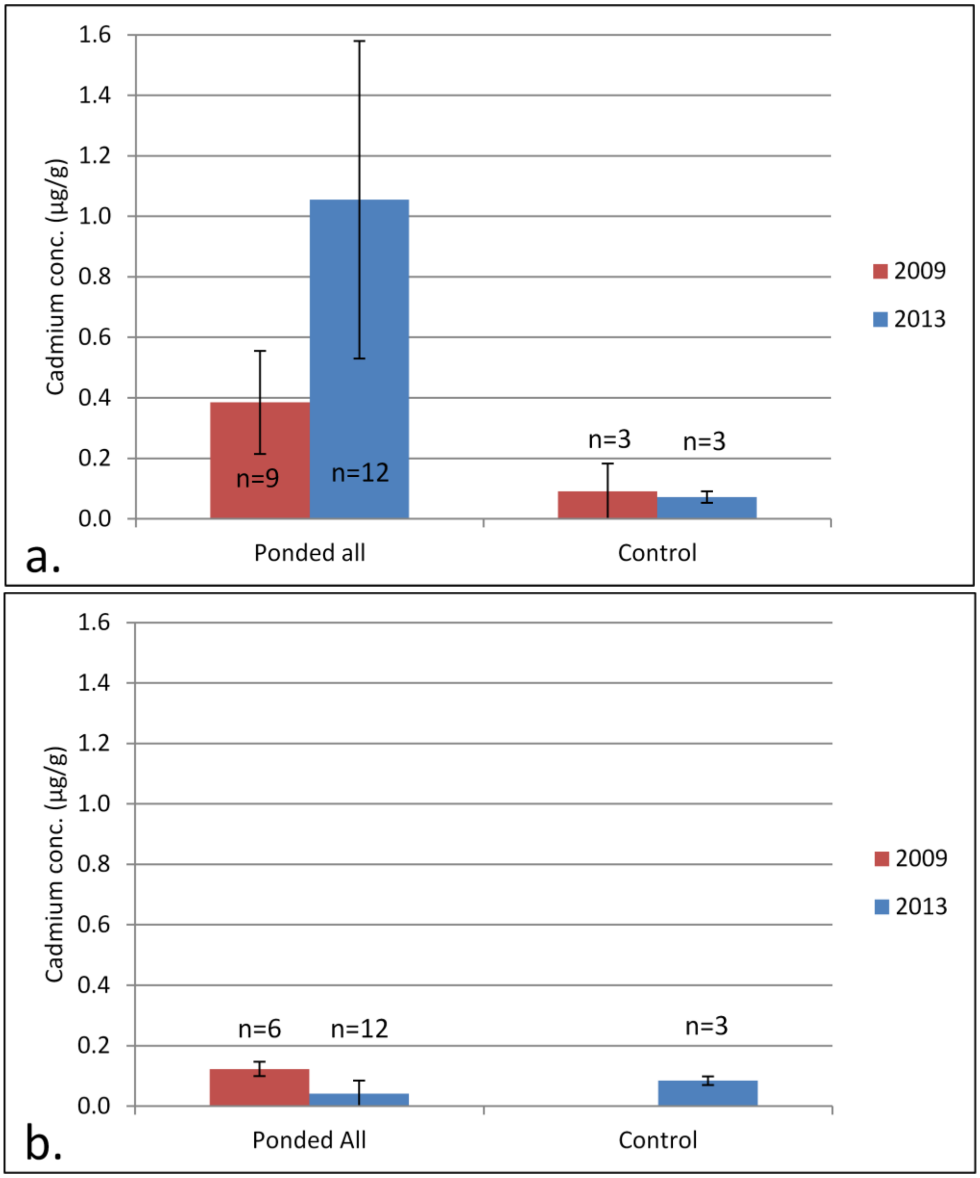

Figure 27: Average cadmium concentrations in the ponded and control areas of the BTI at (a) 0.025m (1 inch) and (b) 0.3 m (12 inches) depths.

Table 15: Cadmium Statistical Analysis Summary

Depth	Year	Ponded Area			Control			t-test
		avg (ug/g)	std	n	avg (ug/g)	std	n	p
0.025m	2009	0.29	0.09	6	0.09	0.01	3	0.01
	2013	1.06	0.52	12	0.07	0.02	3	0.00
0.3m	2009	0.12	0.02	6				
	2013	0.04	0.04	12	0.08	0.01	3	0.01

4.2.5 Zinc

Zinc concentrations sorbed to BTI soil were only analyzed in 2013. Although there were variations in sorbed zinc concentrations throughout the ponded area, all ponded area concentrations were higher than the control area, indicating zinc accumulation onto the soil due to stormwater infiltration (Figure 28). The average zinc concentration sorbed to soil on the surface of the BTI ponded area and at a depth of 0.3 m was significantly (p=0.0007 and p=0.00006) higher than the zinc concentration sorbed to soil in the control area at each respective depth (Figure 29).The statistical test results can be seen in Table 16.

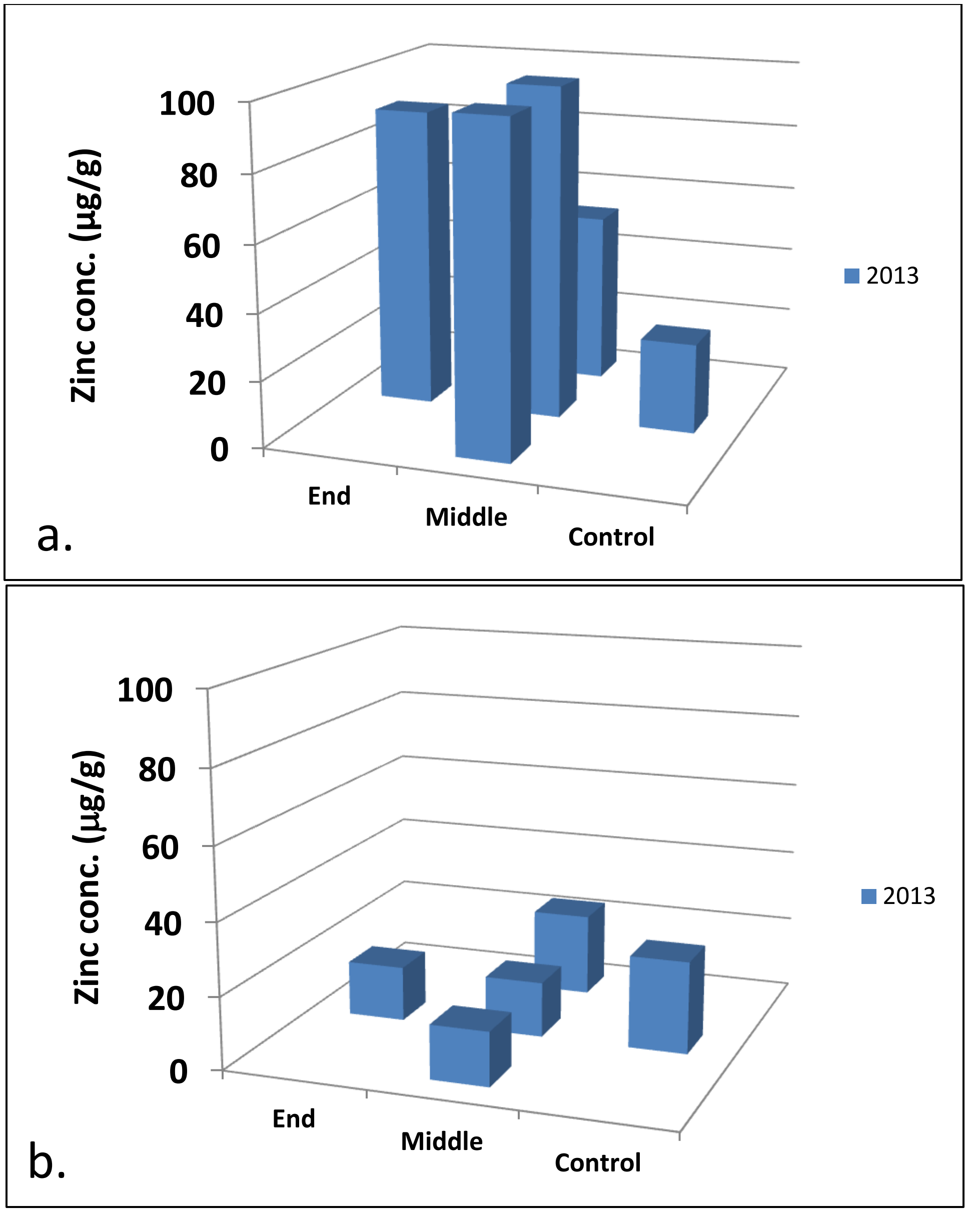

Figure 28: Zinc concentration at (a) 0.025 m (1 inch) and (b) 0.3 m (12 inches). Values are an average of triplicate soil samples collected from each location.

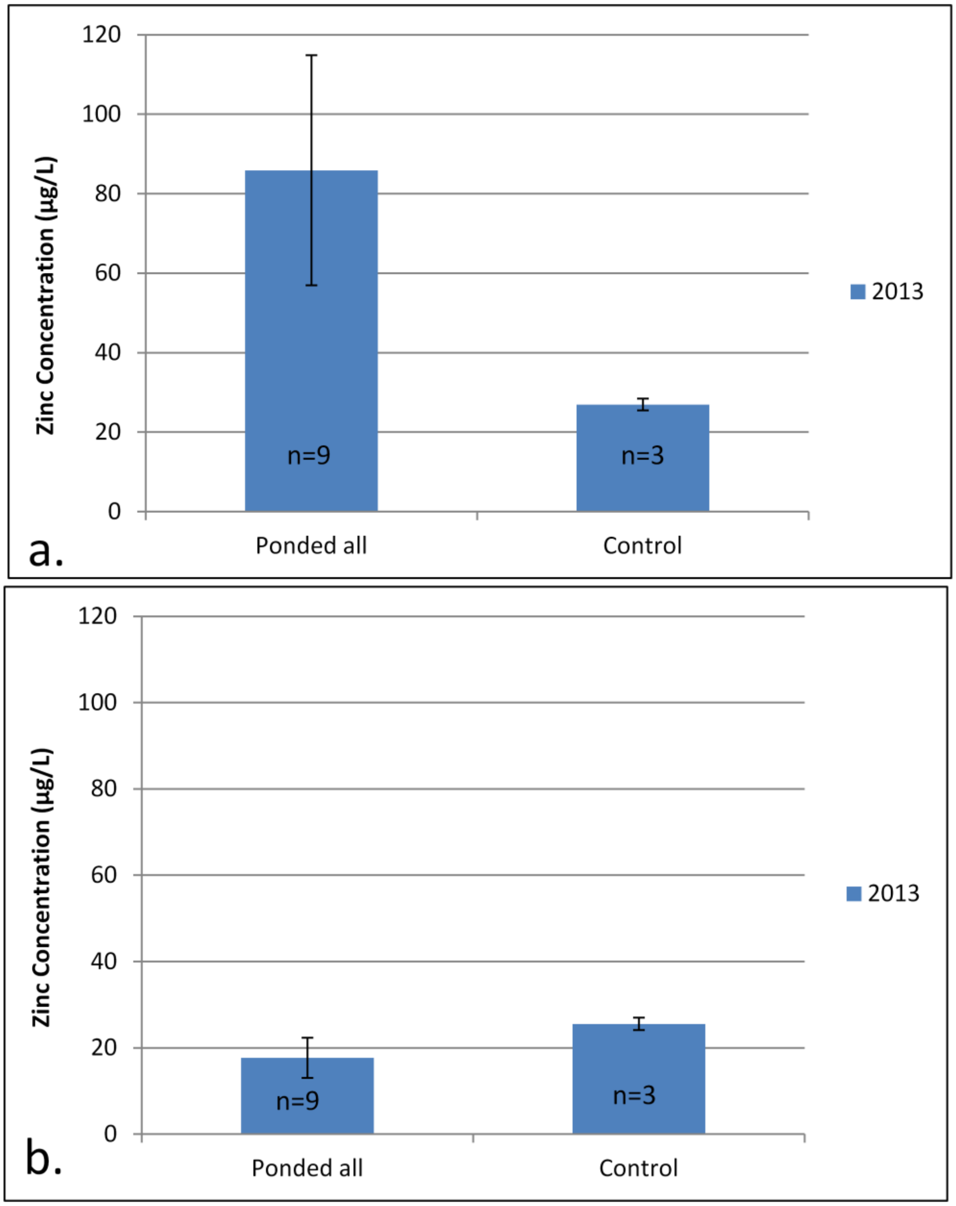

Figure 29: Average zinc concentrations in the ponded and control areas of the BTI at (a) 0.025m (1 inch) and (b) 0.3 m (12 inches) depths.

Table 16: Zinc Statistical Analysis Summary

Depth	Year	Ponded Area			Control			t-test
		avg (μg/g)	std	n	avg (μg/g)	std	n	p
0.025m	2013	86.91	25.03	12	26.95	1.45	3	0.0007
0.3m	2013	17.05	4.16	12	25.54	1.43	3	0.0001

4.2.6 Summary of Metals Accumulation onto the BTI media

As could be seen from all of the sorbed metals concentration profiles (Figures 20 - 29), generally the ponded area contained the highest concentration of metals. This was expected as the ponded area would receive the highest loads of metals from the stormwater runoff. The limits according to the PADEP (2010) regulations for the cadmium, chromium III , chromium VI, copper, lead, and zinc as mg/kg are 38, 190,000, 94, 8,200, 450, and 12,000 respectively. All five of the metals are currently far below the threshold levels allowed by the PADEP for residential fill (Table 17).

Table 17: Extraction summary for ponded samples and PADEP fill limits

Metal		Ponded Area						PADEP limits
		2009			2013			2010
(ug/g)	Location	average	std	n	average	std	n	ug/g
Copper	Surface	11.93	3.80	18	11.93	2.74	12	1080
	0.3 m	5.34	1.83	15	3.43	1.07	12	
Chromium	Surface	6.23	3.94	18	7.31	3.67	12	94
	0.3 m	7.37	10.03	15	3.05	0.87	12	
Lead	Surface	8.02	6.83	18	13.18	4.21	12	450
	0.3 m	4.41	2.63	15	8.39	5.23	12	
Cadmium	Surface	0.35	0.20	9	1.06	0.52	12	38
	0.3 m	0.12	0.02	6	0.04	0.04	12	
Zinc	Surface				86.91	25.03	12	1200
	0.3 m				17.05	4.16	12	

4.3 Metals Mass Balance in the BTI

The mass of each of the metals that infiltrated the BTI was estimated from the difference between the mass entering and leaving the BTI. The mass entering the BTI for different storms was calculated by multiplying the volume of water that entered the BTI over that storm event by the ponded water metal concentrations measured at the beginning of the storm event (Ponded 1). The mass leaving the BTI for different storms was estimated by multiplying the volume of water that overflowed the BTI (if any) by the ponded water metal concentrations either overflowing the BTI (when available) or measured at the end of the storm event. The median masses removed of each metal that infiltrated per rain event can be seen in Table 18 which is based on the exceedance probability plot of the mass removed (Figures 7, 10, 13, 16, and 19). On the basis of the Pennsylvania State Climate Office (http://www.stateclimate.org/ state.php?state_id=PA) data from the Philadelphia International Airport sampling location as well as Pennsylvania State Climatologist Data (http://climate.met.psu.edu/data/city_information/index.php?city=phl&page=dwa&type=big7), there were a total of 542 events with rainfall >0.64 cm (0.25inches) in the Philadelphia area between when the rain garden was put online (August 2001) to the time soil-associated metal concentrations that were determined in June 2013 in the extraction data. If it is assumed that the medium mass of each of the metals infiltrated per storm based on the storms sampled is representative for the entire number of storm events since the BTI was put online (542 events), then the approximate mass (g) of each of the metals can be determined as can be seen in Table 18. The last column in Table 18, the total combined, is the total dissolved plus suspended mass (g) of each metal that was removed between the influent and effluent throughout the lifetime of the BTI.

Table 18: Cumulative mass of each metal that infiltrated the BTI over the lifetime of the BTI

		Removed at Surface		total combined g
Metal		mg/storm	Total g	
Copper	suspended	44	24	184
	dissolved	296	160	
Chromium	suspended	25	14	71
	dissolved	106	58	
Lead	suspended	14	7.4	36
	dissolved	52	28	
Cadmium	suspended	2.0	1.1	11
	dissolved	18	10	
Zinc	suspended	212	115	655
	dissolved	996	540	

The concentration of metal that sorbed onto the surface of the BTI soil due to infiltrating stormwater was calculated by finding the difference between the average sorbed metals concentration in the ponded area (locations 2-5) and the average sorbed metals concentration in the control area (Location 1) . The total mass removed in the top 5 cm of the BTI was calculated by multiplying the difference in the ponded and control sorbed concentrations by the mass of soil in the top 5 cm (9.16×10^3 kg, determined under the same assumptions and conditions as Komlos and Traver (2012)) (Table 19).

The mass that was removed over the lifetime of the BTI (Table 18) was then compared to the mass that had sorbed to the soil (Table 19) in order to determine the percent of metals in the ponded water that the BTI effectively removed through means of sorption (Table 20). The first column represents the total amount of metals that did not overflow the BTI during storm events (from Table 18). The second column represents the total mass of metals that sorbed to the soil since the BTI was first operational (from Table 19).

Table 19: Estimate of the mass of each metal sorbed on the first 5 cm of BTI infiltration media after 12 years of operation.

Metal	Location	sorbed to soil since 2001		
		ug/g	ug/kg	g metal
Copper (ug/g)	Surface	7.88	7879	72
Chromium (ug/g)	Surface	3.91	3905	36
Lead (ug/g)	Surface	4.79	4794	44
Cadmium (ug/g)	Surface	0.98	983	9
Zinc(mg/g)	Surface	59.96	59958	549

Table 20: Comparison of mass of each metal that accumulated on the soil to the difference between the mass in and mass out of the BTI between 2001 and 2013.

Metal	Difference between mass in and mass out of the BTI (g)	Mass of metal that accumulated on the top 5 cm of the BTI (g)	% of metal removed in the BTI that sorbed to the top 5 cm
Copper	184	72	39
Chromium	71	36	51
Lead	36	44	122
Cadmium	11	9	82
Zinc	655	549	84

This mass balance shows that the mass of each metal sorbed to the top 5 cm did not exactly equal the mass of each metal that was removed between the influent and effluent since the BTI was put online. One possible reason for the discrepancy is that the metal extraction procedure may not have been strong enough to extract all of the metals that sorbed to the soil between 2001 and 2013. This would have caused an underestimation of the mass of metal that was sorbed to the soil. Another possible reason for the discrepancies is the high number of samples that were below the detection limit. The assumption of ½ the detection limit as the concentration for any non-detectable samples may have caused an overestimation of the mass in or out of the BTI. Lead, chromium, cadmium, and zinc all had significant numbers of samples (ponded 1, ponded 2, and overflow) that were below detection. The actual metals concentration may have been much lower. An overestimation of the ponded 1 concentration would have resulted in an overestimation of the mass removed. An overestimation of the overflow and ponded 2 concentrations would have resulted in an underestimation of the mass removed.

In addition to over estimating the mass out of the BTI, there may also be a discrepancy in using the ponded 2 concentrations when the metals concentrations were not measured in the water overflowing the BTI. There was a limited amount of overflow samples that were collected and these concentrations were typically greater than the measured concentrations of the ponded 2 samples. The use of the ponded 2 samples may have resulted in an overestimation of the amount of mass that the BTI removed during rain events. Furthermore, this paper only investigated sorption as a loss mechanism when in reality there are other possible metal removal mechanisms that could be taking place within this BTI. Plants that are in the system have the potential to uptake metals and those potentials were not considered in this analysis. The active metals sorption zone was estimated to be the top 5 cm of the BTI. The actual depth of the active sorption zone may have been shallower or deeper for each metal analyzed. Despite these discrepancies in the mass balance for the removal of metals within this BTI, the overall comparison does indicate that metal sorption to the soil is a major loss mechanism for the metals removed between the influent and effluent stormwater of this BTI.

Based on the mass balance, removal rates on a yearly basis were determined for each metal. This was done by dividing the total mass (g) of metals accumulated onto the soil (Table 19) by the number years in operation (12). This was then compared to the federal regulations (USEPA, 2000a) for metals present in soils (section 2.2). The federal regulations were converted from mg of metal/kg soil to gram of metal by multiplying by the mass of soil that was assumed to be at the surface of the BTI (9.16 x 10^3 kg) (Komlos and Traver, 2012) (see fifth column in Table 21). Lastly, column 5 was divided by the removal rate of the corresponding metal (column 3) in order to determine the years that it would take for the soil to reach the concentration of metal to be considered above the clean fill requirements. Table 21 depicts the time frame determined for each metal assuming that the soil would be able to sorb the metals to this extent. In all likelihood, these limits will not be reached due to factors that will hinder the soil to hold high concentrations of metals. Some factors include sorption capacity of the soil, selectivity factors for each of the cations present, and the overall concentration of cations present in the soil and stormwater.

Table 21: Time frame for metal concentration to reach the PADEP maximum loading rates

Metal	g metal	g/year	mg metal/kg soil	max g metal	Years to max
Copper	72	6	8200	75000	12500
Chromium	36	3	94	900	290
Lead	44	4	450	4200	1100
Cadmium	9	1	38	350	460
Zinc	549	46	12000	110000	2400

4.4 Estimation of the Copper Holding Capacity of BTI Soil

Batch sorption tests were performed on samples from locations 1, 3, and 5 (Figure 3a) in order to determine the maximum amount of copper that the soil samples could sorb. Copper was the only metal that was analyzed in order to form a base to begin competitive sorption experiments in the future. Furthermore, copper was the only metal in which the majority of the samples resulted in concentrations that were above detection and actually allowed for changes in concentrations at different sampling locations and depths to be observed. Results indicated that equilibrium was reached after 3 days (data not shown). Linear, Langmuir, and Freundlich adsorption isotherms were used as the methods to describe the copper sorption to the soil samples. The isotherm with the highest R^2 value was deemed the line of best fit. The sorption isotherms were used to estimate the maximum concentration of copper that the soil can hold when in equilibrium with dissolved copper concentrations typical of those experienced by the BTI (the median total copper concentration was used as the dissolved copper concentration). Figures that represent the isotherms with regards to the median concentration range of the stormwater that ponded in the system can be seen below. Section B of the appendix has Figures that represent all of the concentrations that were tested.

Figure 30 depicts copper sorption at the surface of location 1. Figure 31 represents the linear, Langmuir, and Freundlich isotherms 0.3 m below (12 inches) the surface of location 1. Figures 32 and 33 represent the same information for location 3. Figures 34 and 35 depict the same information for location 5.

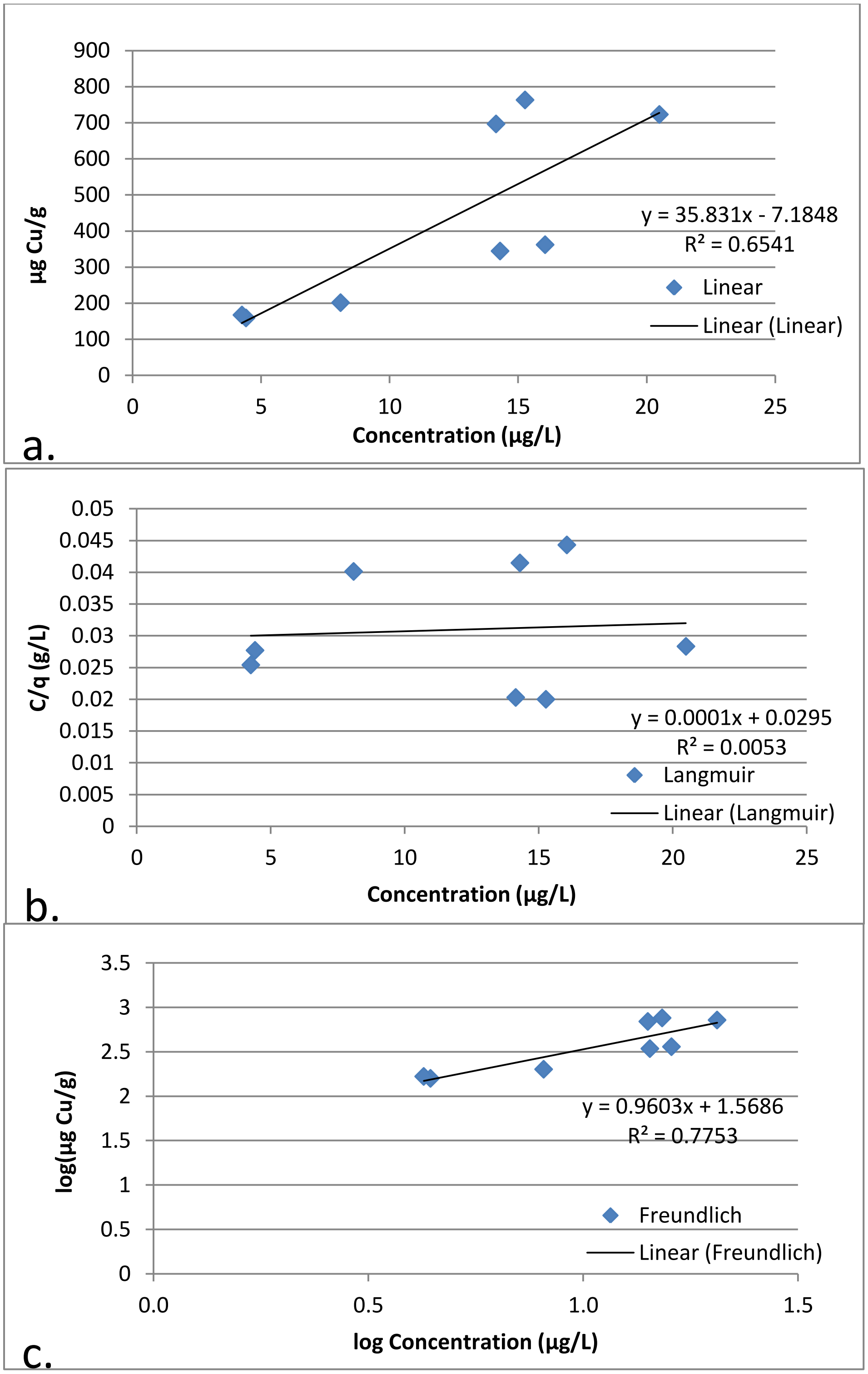

Figure 30: Sorption Isotherms for copper at the surface of Location 1
(a) Linear, (b) Langmuir, and (c) Freundlich Isotherms

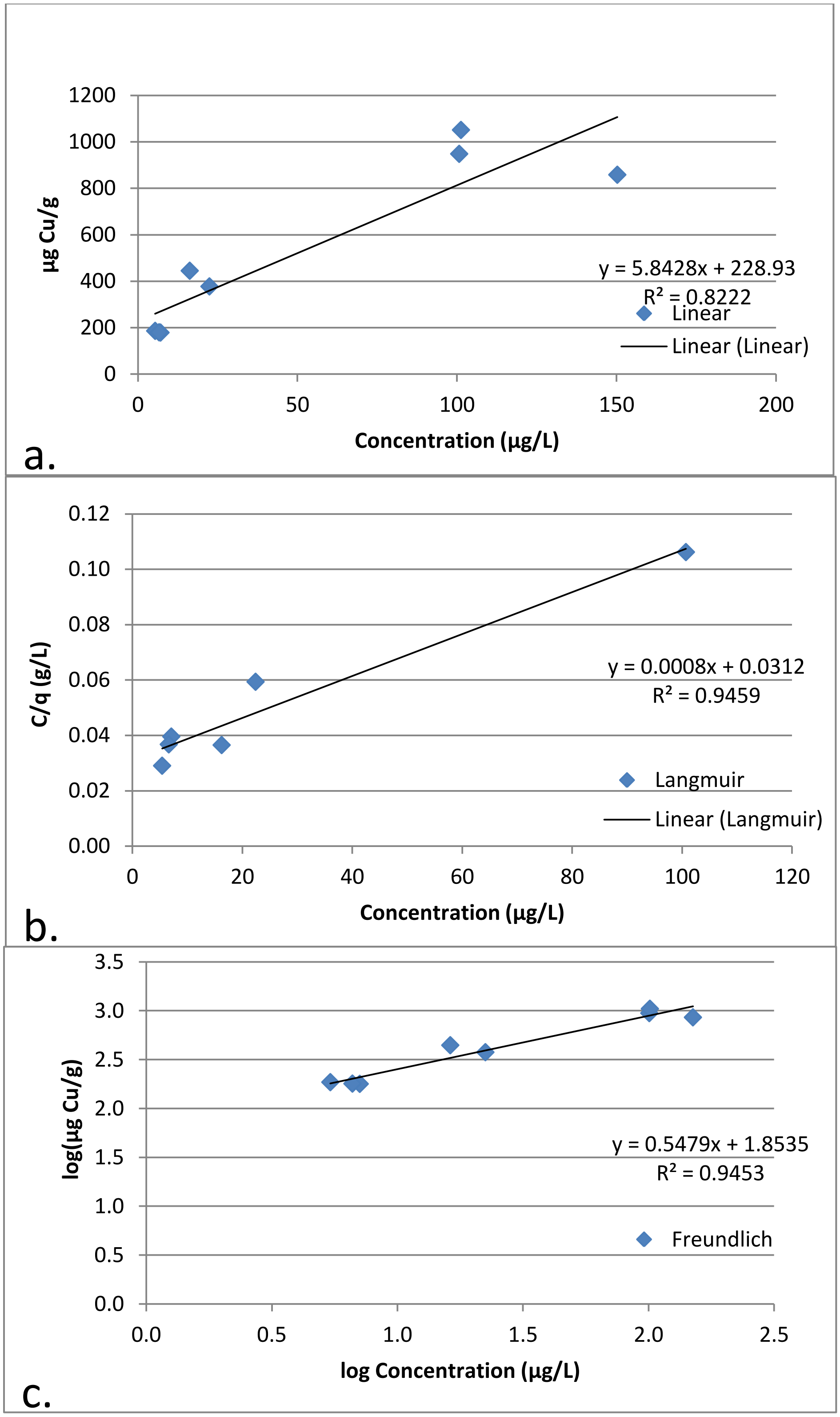

Figure 31: Sorption Isotherms for copper 0.3 m below the surface of Location 1
(a) Linear, (b) Langmuir, and (c) Freundlich Isotherms

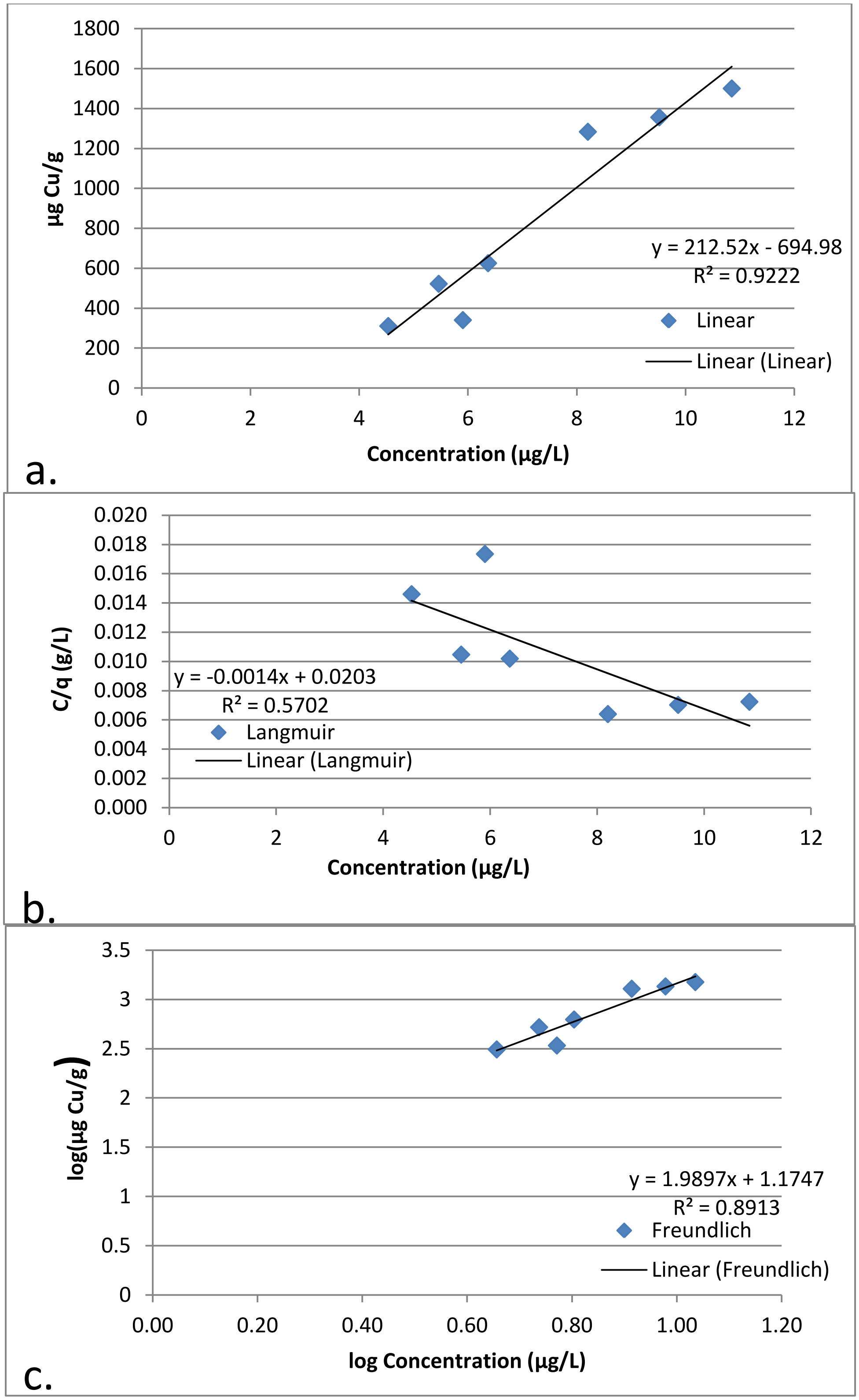

Figure 32: Sorption Isotherms for copper at the surface of Location 3
(a) Linear, (b) Langmuir, and (c) Freundlich Isotherms

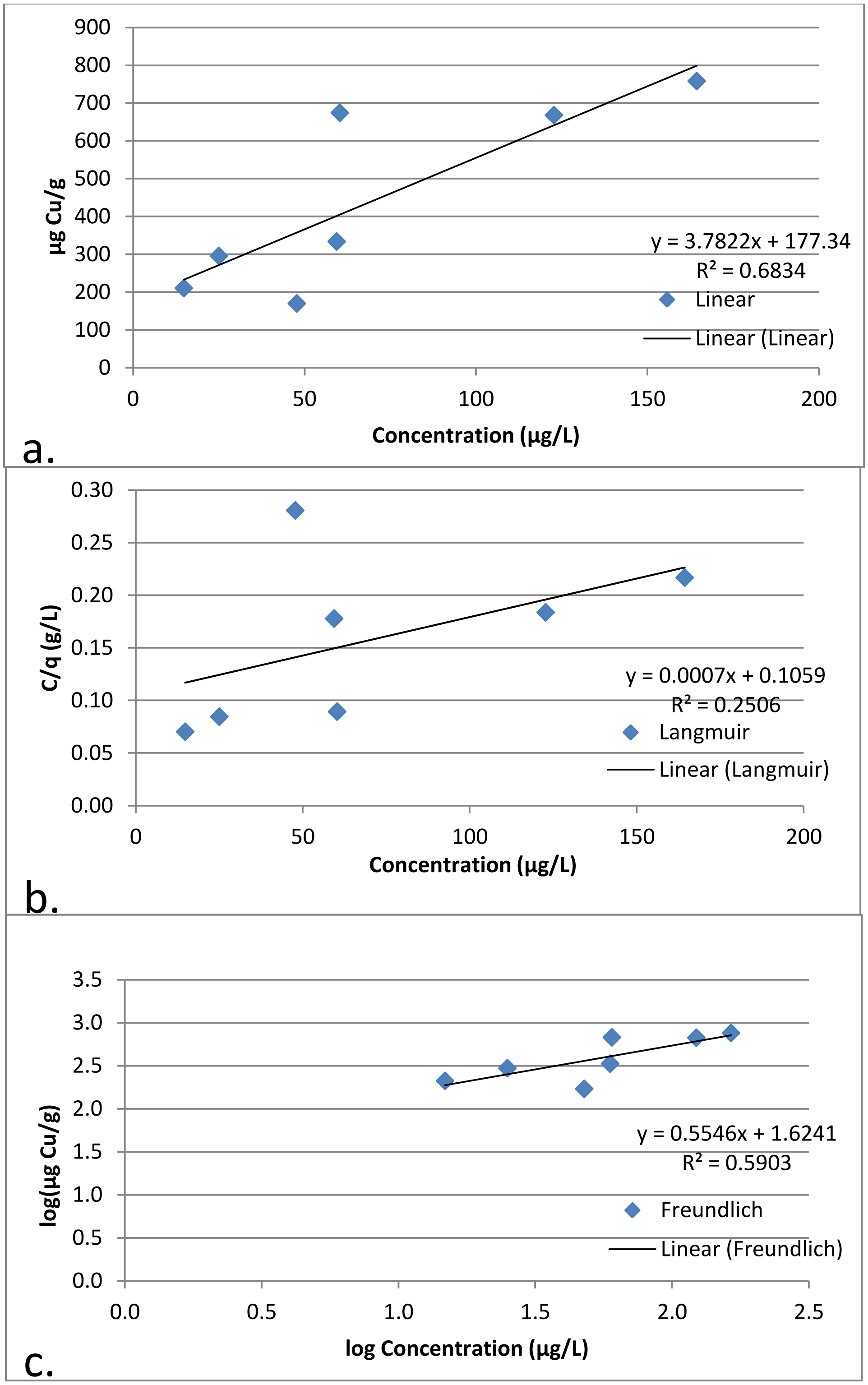

Figure 33: Sorption Isotherms for copper 0.3 m below the surface of Location 3
(a) Linear, (b) Langmuir, and (c) Freundlich Isotherm

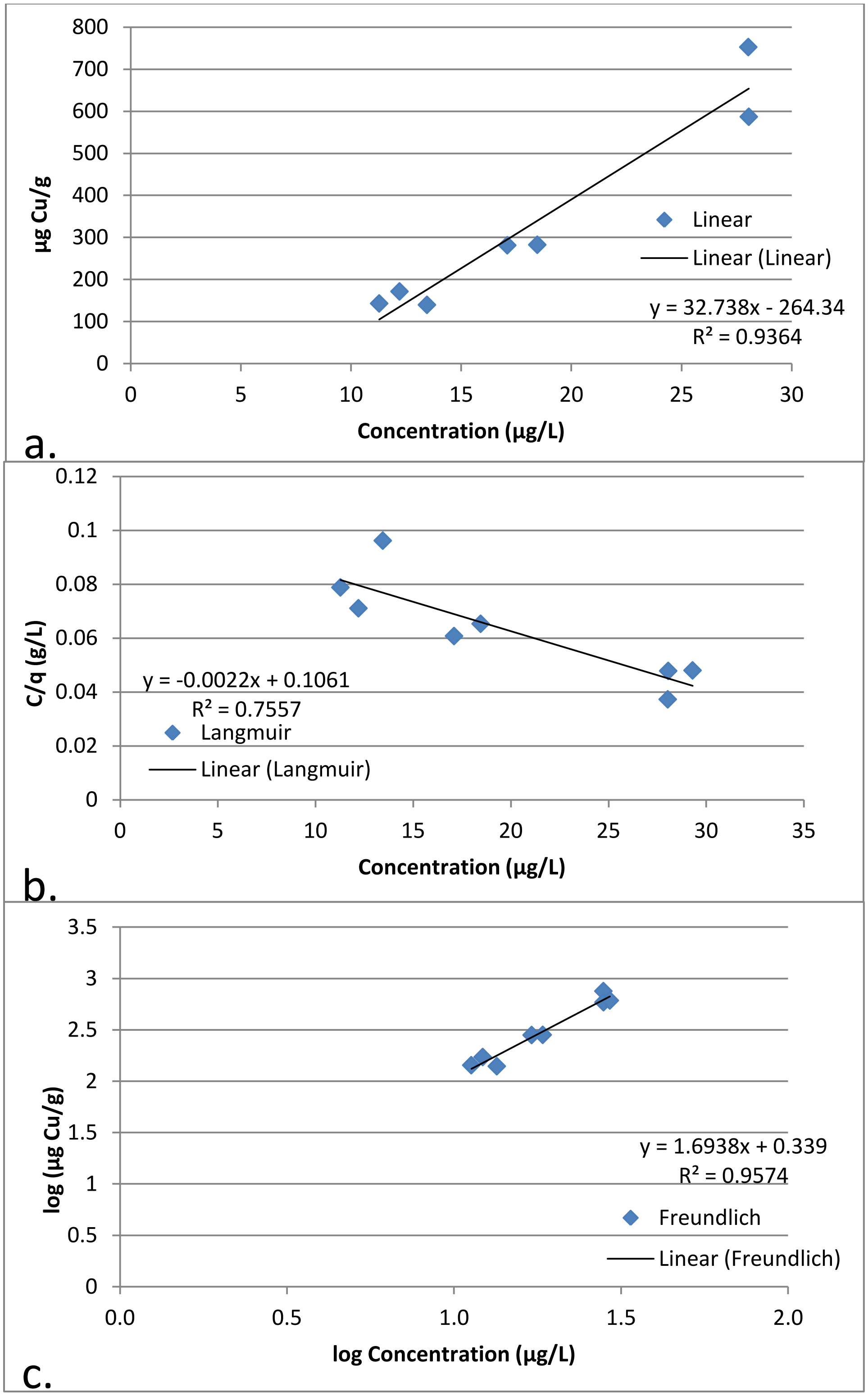

Figure 34: Sorption Isotherms for copper at the surface of Location 5
(a) Linear, (b) Langmuir, and (c) Freundlich Isotherm

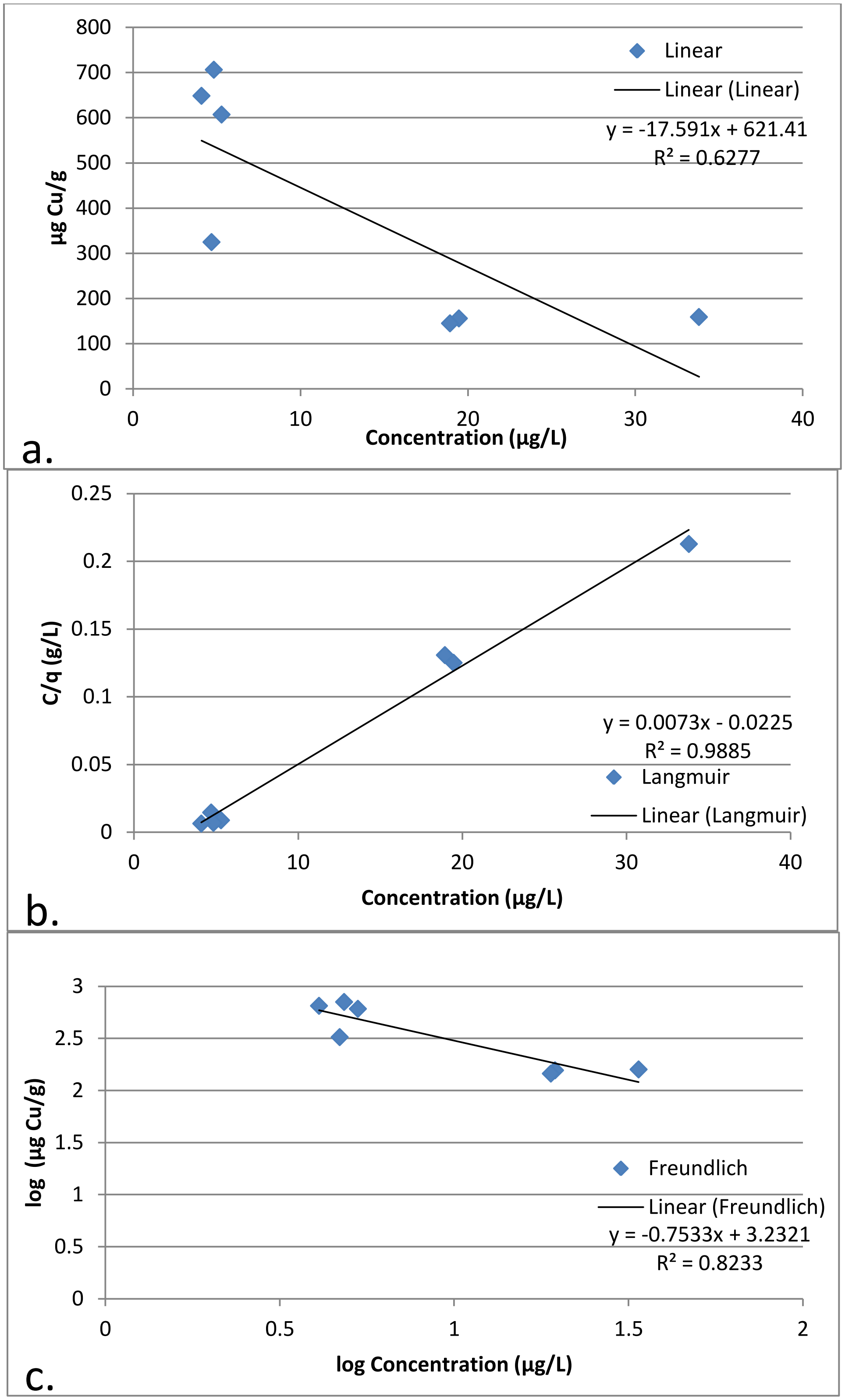

Figure 35: Sorption Isotherms for copper 0.3 m below the surface of location 5 (a) Linear, (b) Langmuir, and (c) Freundlich Isotherm

The isotherm figures were adjusted to represent the range of ponded concentrations seen in the rain garden. This was done in order to be able to directly compare the isotherms to the conditions that the BTI experiences during storm events. The median dissolved copper concentration (ponded 1) was 8.2 μg/L and for suspended copper was 2.6 μg/L (Figure 5). The isotherms that best fit the data can be seen in the Figures 31-35. The Freundlich isotherm was either the best isotherm or the second best isotherm for each sampling site and therefore was used as the general isotherm, therefore in Figures 31-35 all of the graphs labeled "c" were used for further analysis when applicable. This was done under the assumption that the soil makeup is the same throughout the BTI.

The maximum amount of copper that could sorb to the soil at each of the locations tested can be seen in Table 22. The maximum amount of copper that is allowed to be present in residential soils is 8200 μg/g (PADEP, 2010; EPA, 2000a) and these levels according to this analysis will never be reached. Therefore, this soil will not be deemed hazardous under the Federal regulations as this soil cannot hold that amount of copper based on the isotherm tests that were performed.

Table 22: Maximum copper that can sorb to the soil

Location	Top (μg/g)	Bottom (μg/g)
	Dissolved	Dissolved
1	364	263
3	1702	157
5	123	284

The maximum amount of copper that can sorb to the soil should be used to determine that lifespan of the BTI with respect to copper rather than using the limits from PADEP. The lifespan of the BTI with respect to copper are 556 years, 2600 years, and 188 years at locations 1, 3, and 5 respectively.

The results of the sorption tests do not consider the field conditions of the BTI. The actual conditions will result in different equilibrium copper concentrations sorbed to the soil that are expected to be lower due to other cations that are present in the soil that will compete with the copper for sorption sites. The selectivity coefficients for cations that are present would need to be investigated in order to determine which cations are most likely to sorb to the soil. Other parameters to consider are the presence of natural organic matter, temperature, pressure, counter ions, loading rates, and pH of the stormwater. The sorption values determined from this analysis therefore are an overestimation as to the true amount of copper that can sorb onto the soil.

Chapter 5 – Conclusions & Recommendations

5.1 Conclusions

An analysis was performed on the water and soils within a bioinfiltration raingarden to determine the effectiveness of metals removal through sorption processes. In addition, copper sorption experiments were performed in order to determine the maximum amount of copper that the soil could sorb. The following summarizes the research results:

- The BTI was effective at reducing stormwater volume as well as stormwater pollutants (copper, chromium, lead, cadmium, and zinc) entering the system.
- Copper concentrations decreased between the ponded water samples and samples collected in the infiltration bed. Whether the metals concentrations decreased between the ponded water and the infiltration bed was inconclusive for cadmium, chromium, lead, and zinc because the majority of dissolved concentrations for these metals were below detection.
- Even though metals removal based on surface and pore water metals concentrations were inconclusive for most metals analyzed, metals accumulation onto soils was measured in the active infiltration area of the BTI for all metals analyzed.
- The copper sorbing capacity of the soil was significantly lower than the regulated 8200 μg/g soil maximum allowed by the PADEP for the soil to be considered clean fill.

- Based on the amount of metals currently present in the soil, the median ponded concentration, and the maximum concentrations of metals allowed, chromium will limit the lifespan of the BTI.

5.2 Recommendations

The following are recommendations for future research topics in relation to this BTI and the metals that are present:

- An investigation of vegetation uptake of metals should be performed as it was neglected for this analysis. It is possible that the plants could be removing a portion of the metals present in the BTI.
- Competitive cocktail sorption experiments should be run in order to determine which metals have the highest selectivity coefficient. This will also aid to determine the competiveness of cations within the BTI as well as determine a more accurate maximum sorption capacity for each of the metals in the infiltration media.
- A cation exchange capacity experiment and analysis on the soil media would aid in understanding the sorption capacity of this BTI as this experiment would take into account all cations that are present in the stormwater.
- This analysis was limited by detection limits, specifically for quantifying the concentrations of lead. Therefore it would be advantageous to try to maintain a consistent lowest detection limit as well as potentially reducing this lowest detection.
- A similar analysis should be conducted in the future in order to determine the mass removed over an even longer time span and to determine if any of the metals are near the corresponding sorption capacity.

- A study should be performed to determine the source of these metals within the BTI. The main goal is to reduce pollutants present in the water (and increase infiltration) and the most effective way to reduce those concentrations is by removing the sources so that they do not enter the water cycle in the first place.

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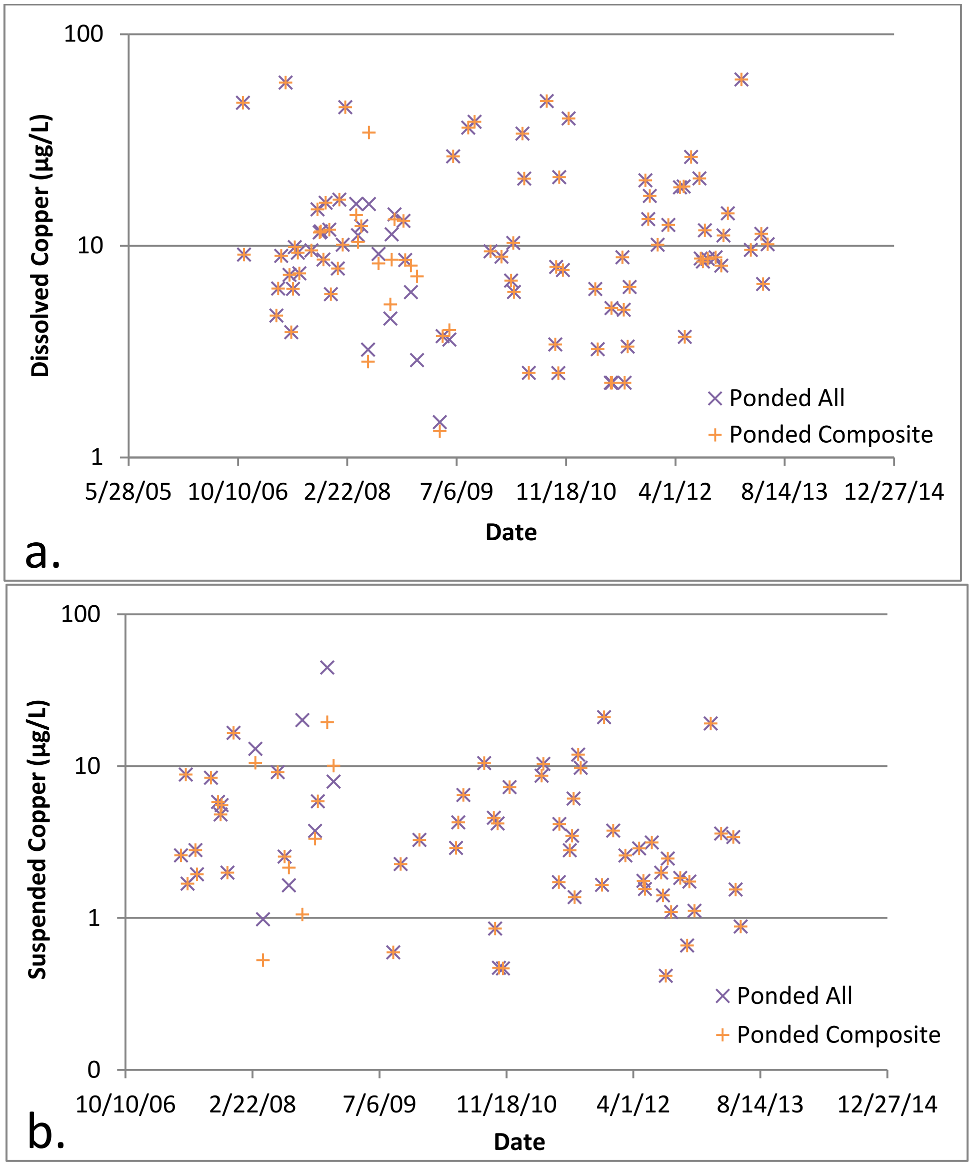
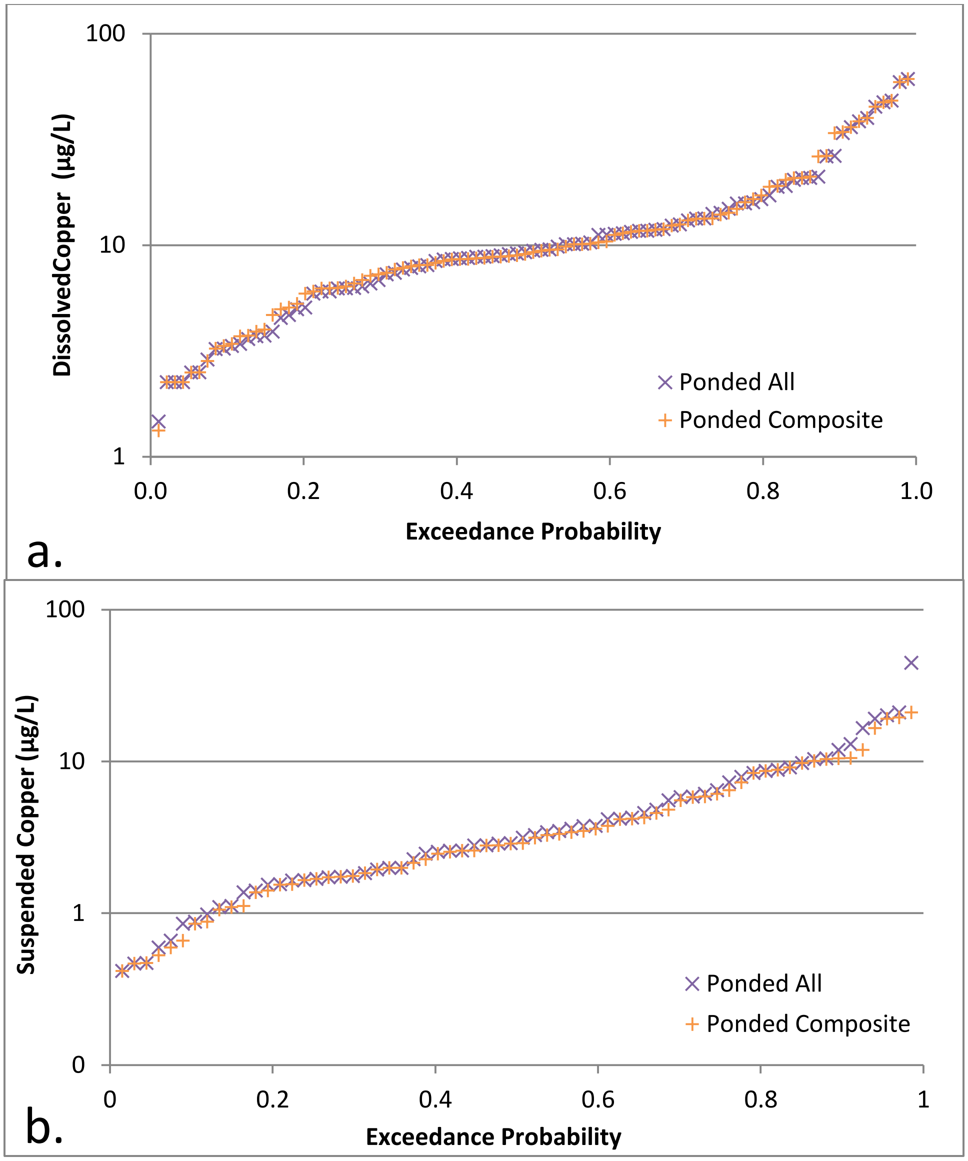
Appendices

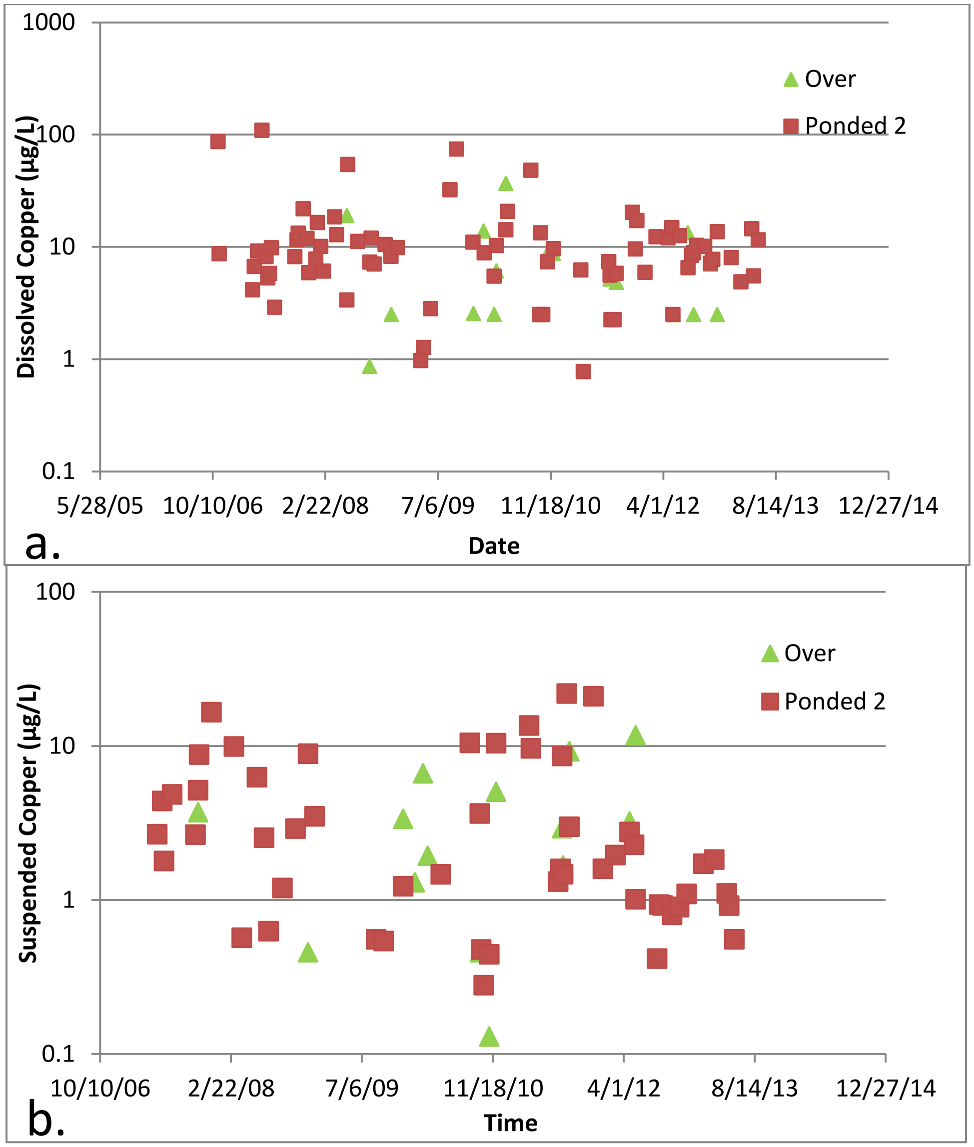
Appendix A : Dissolved and Suspended metals concentrations over time



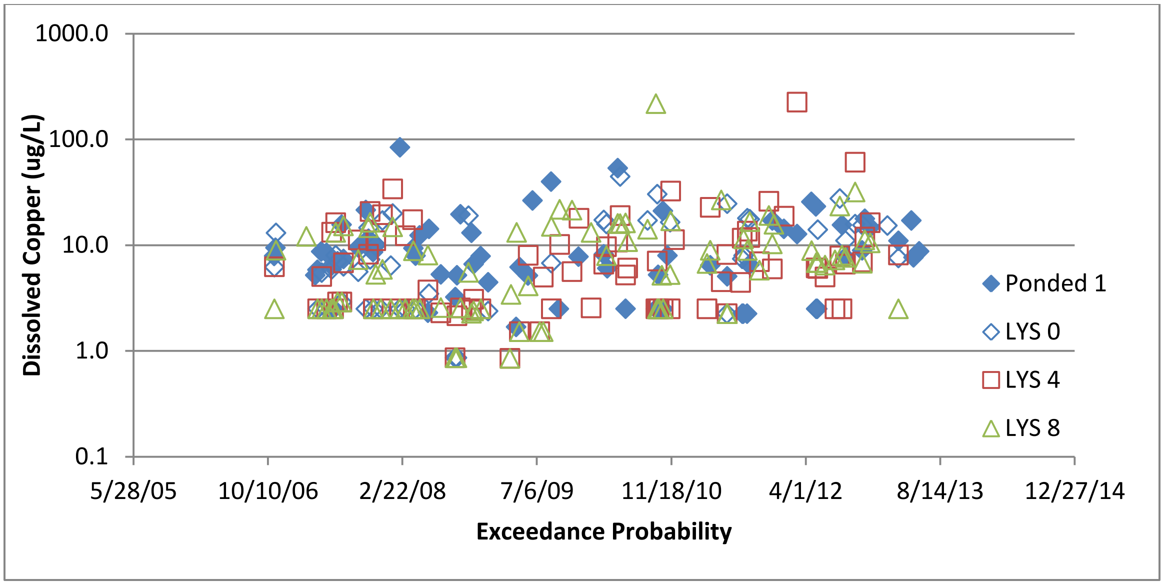
A1: Concentration vs. time for (a) dissolved copper and (b) suspended copper ponded all and the ponded composite samples



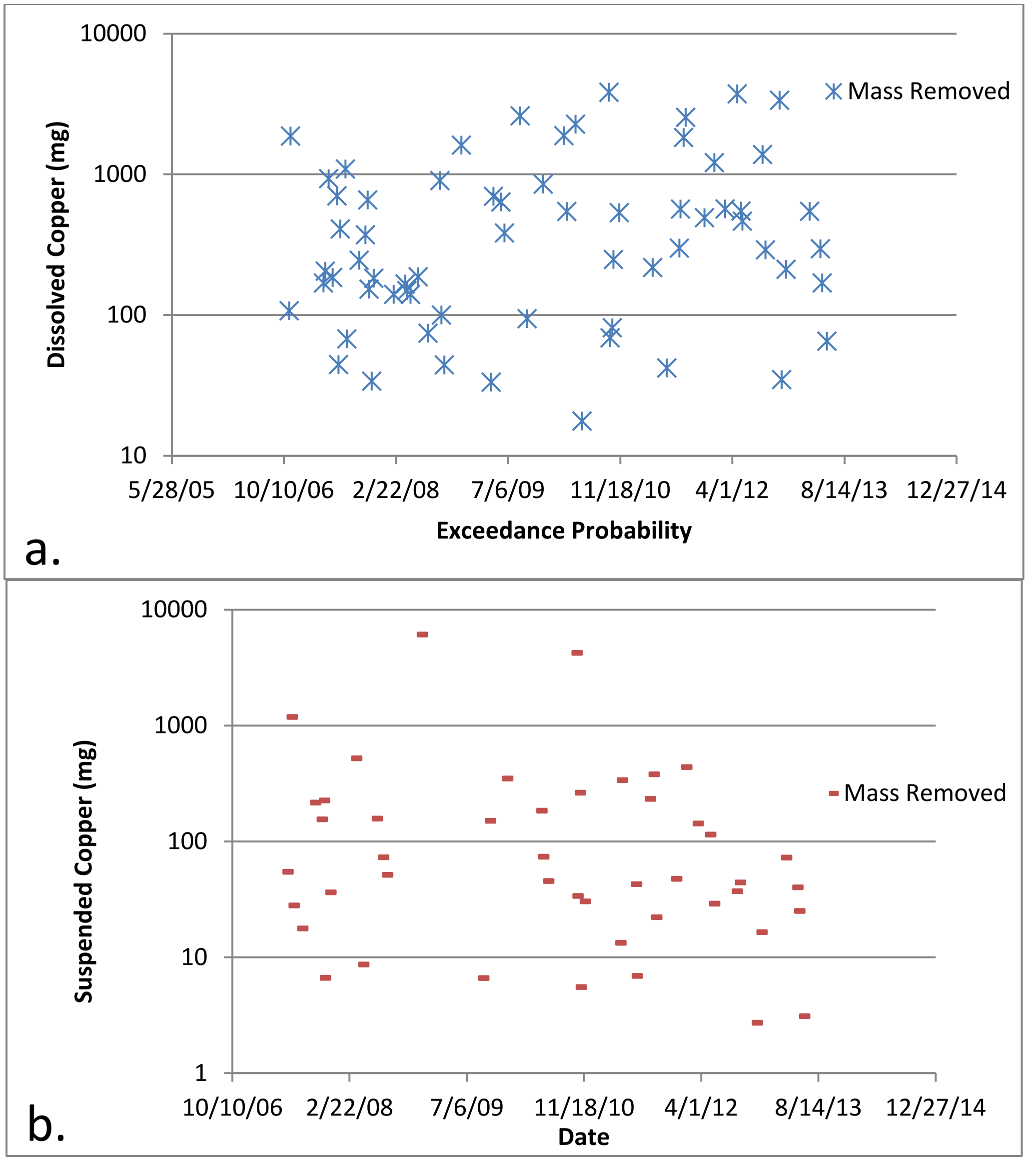
A2: Exceedance Probability for (a) dissolved copper and (b) suspended copper ponded all and ponded composite samples



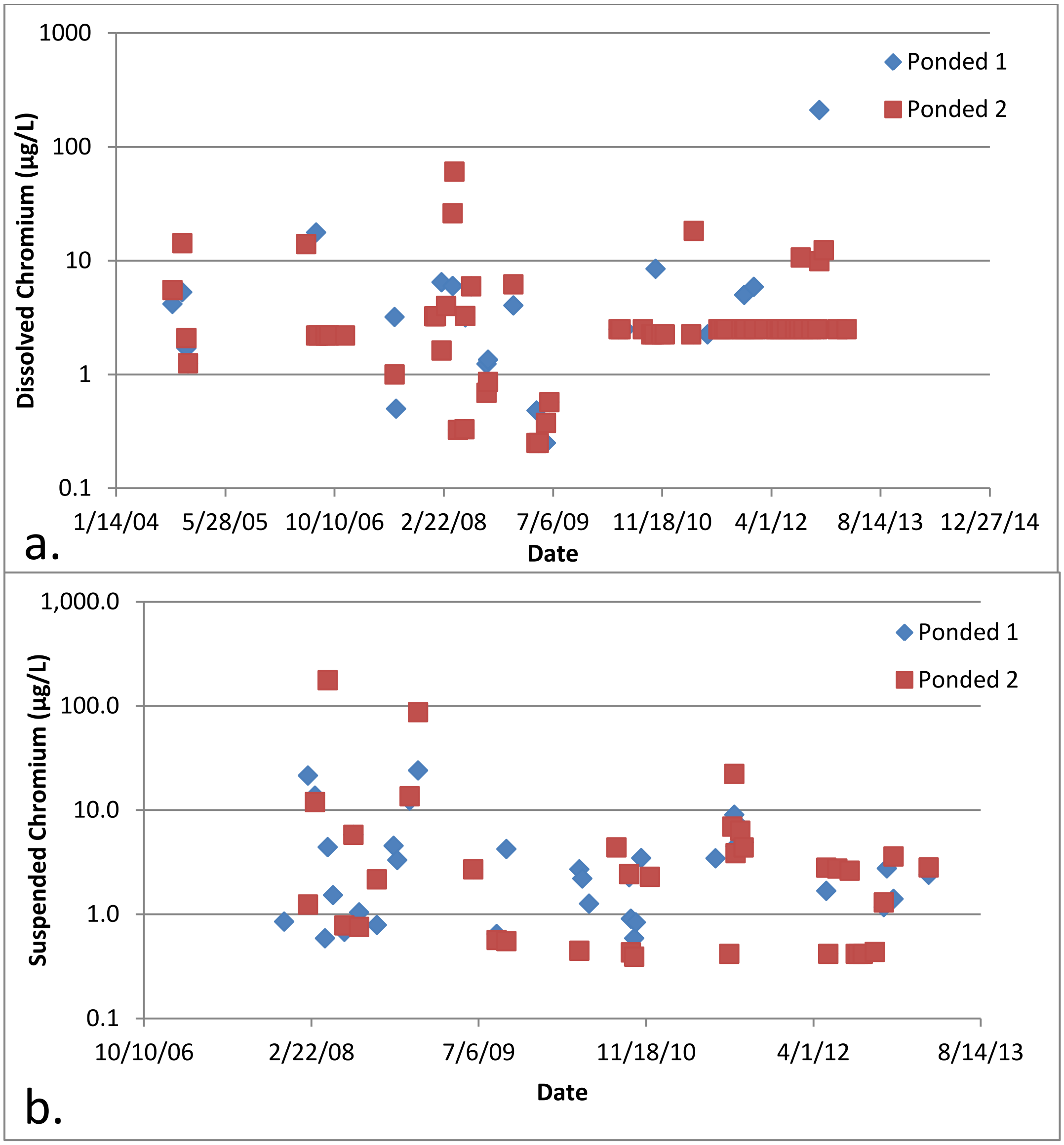
A3: Concentration vs. time for (a) dissolved copper and (b) suspended copper over and the ponded 2 samples



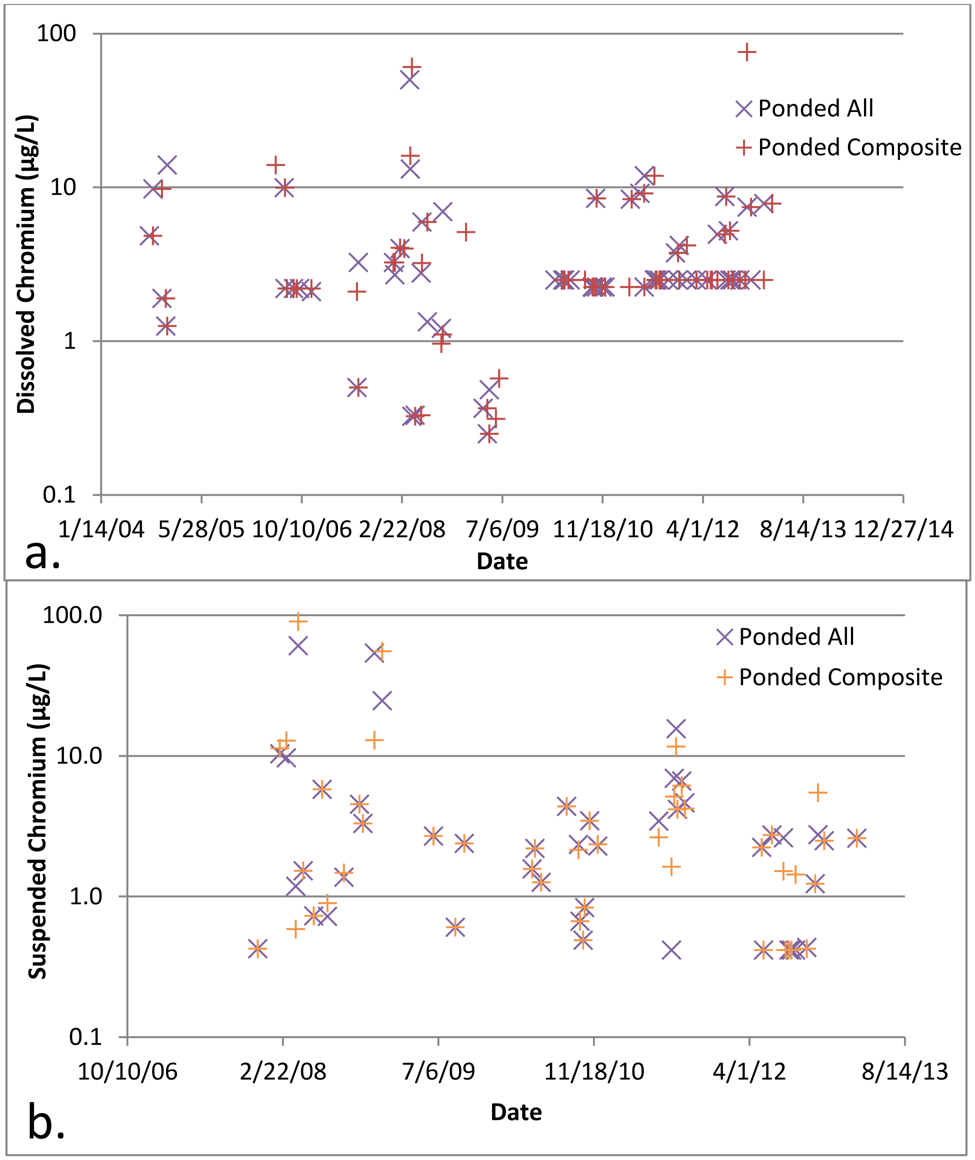
A4: Concentration vs. time for dissolved copper at various depths and the ponded all samples



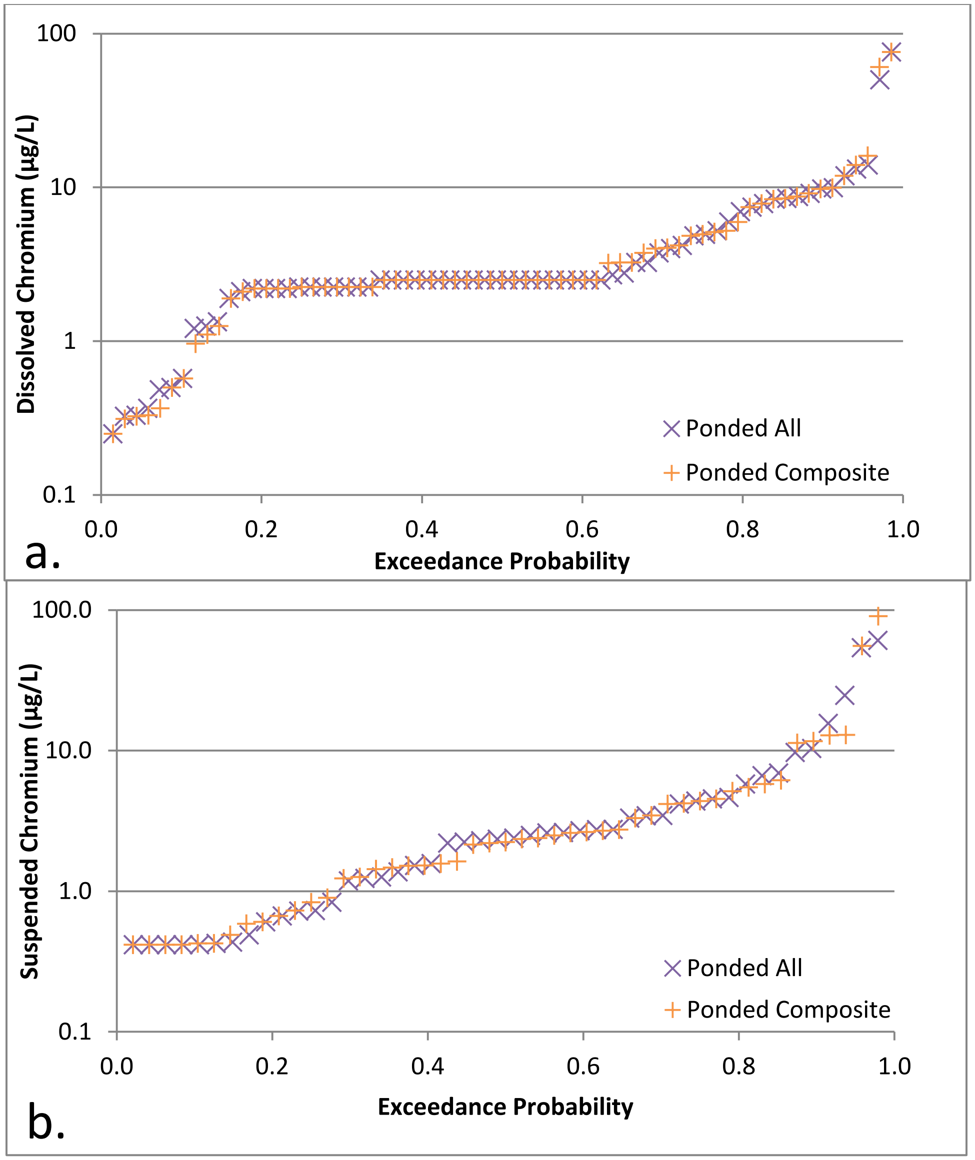
A5: Mass removed (mg) vs. time for (a) dissolved copper and (b) suspended copper



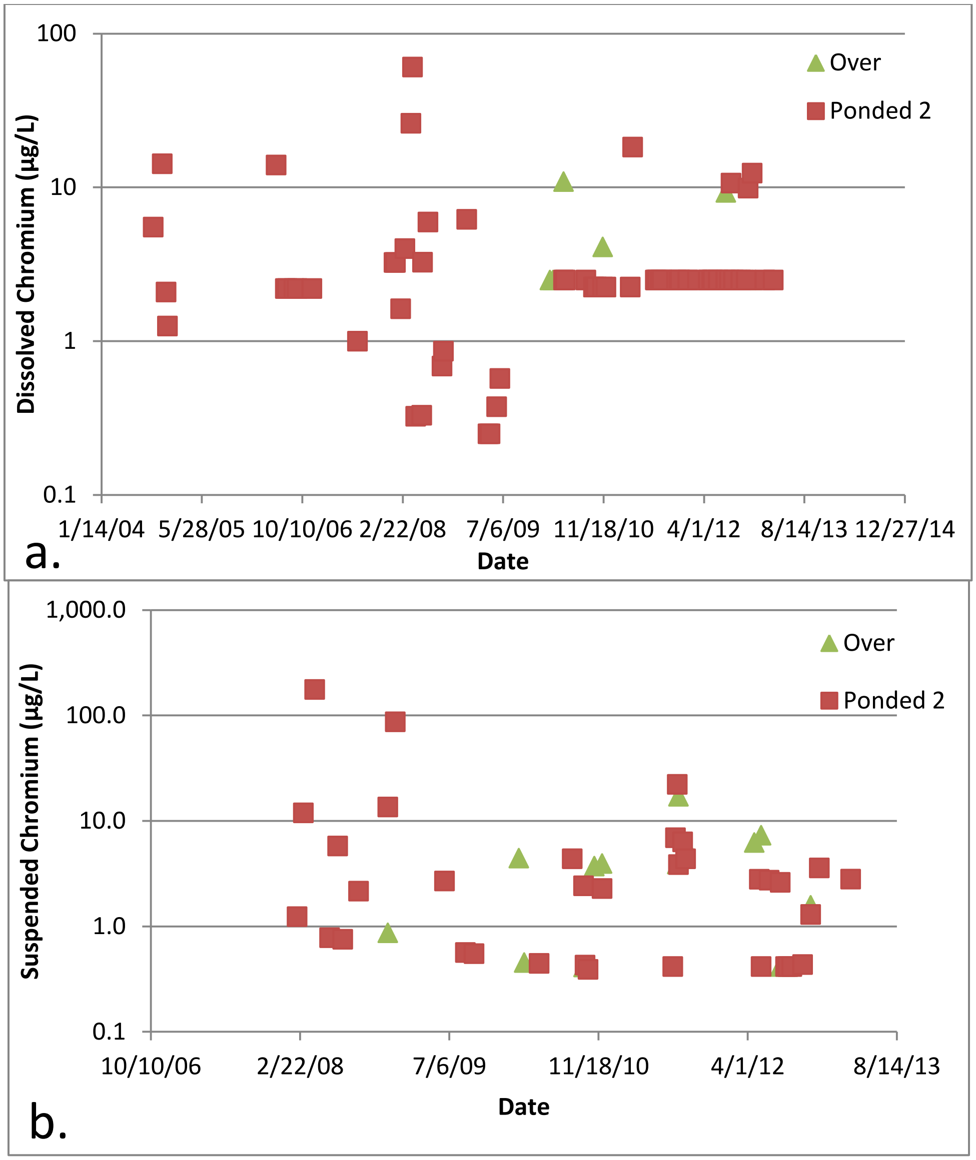
A6: Concentration vs. time for (a) dissolved chromium and (b) suspended chromium ponded 1 and ponded 2 samples



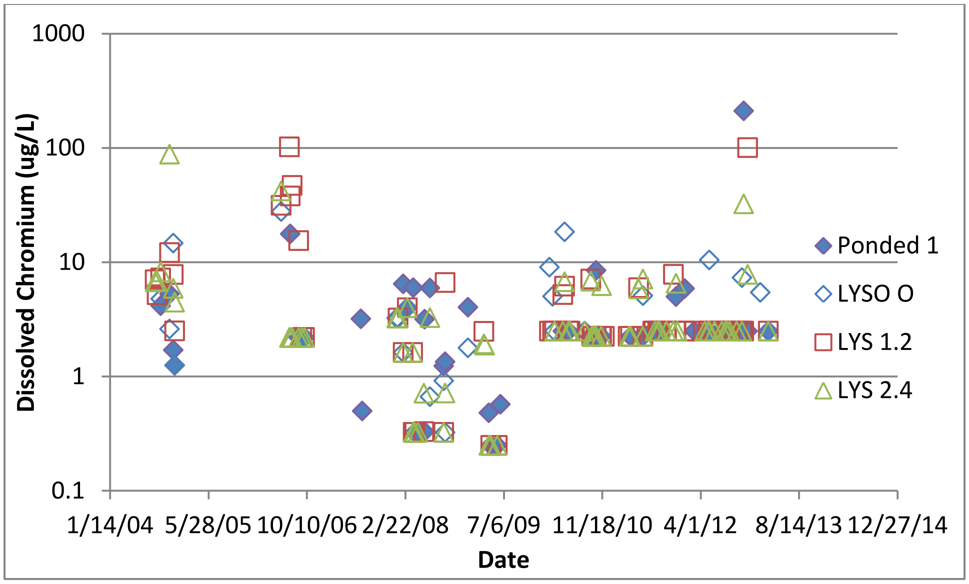
A7: Concentration vs. time for (a) dissolved chromium and (b) suspended chromium ponded all and the ponded composite samples



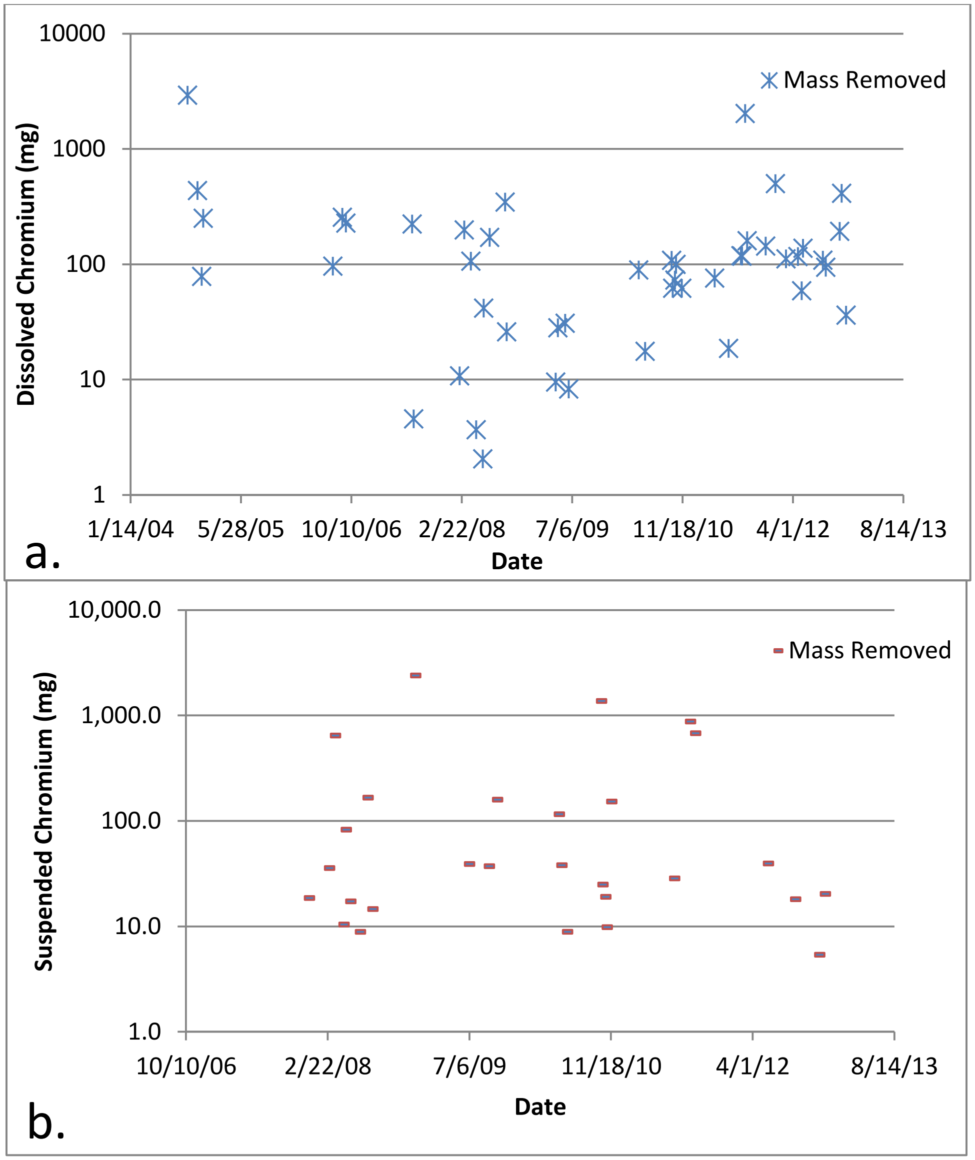
A8: Exceedance Probability for (a) dissolved chromium and (b) suspended chromium ponded all and ponded composite samples



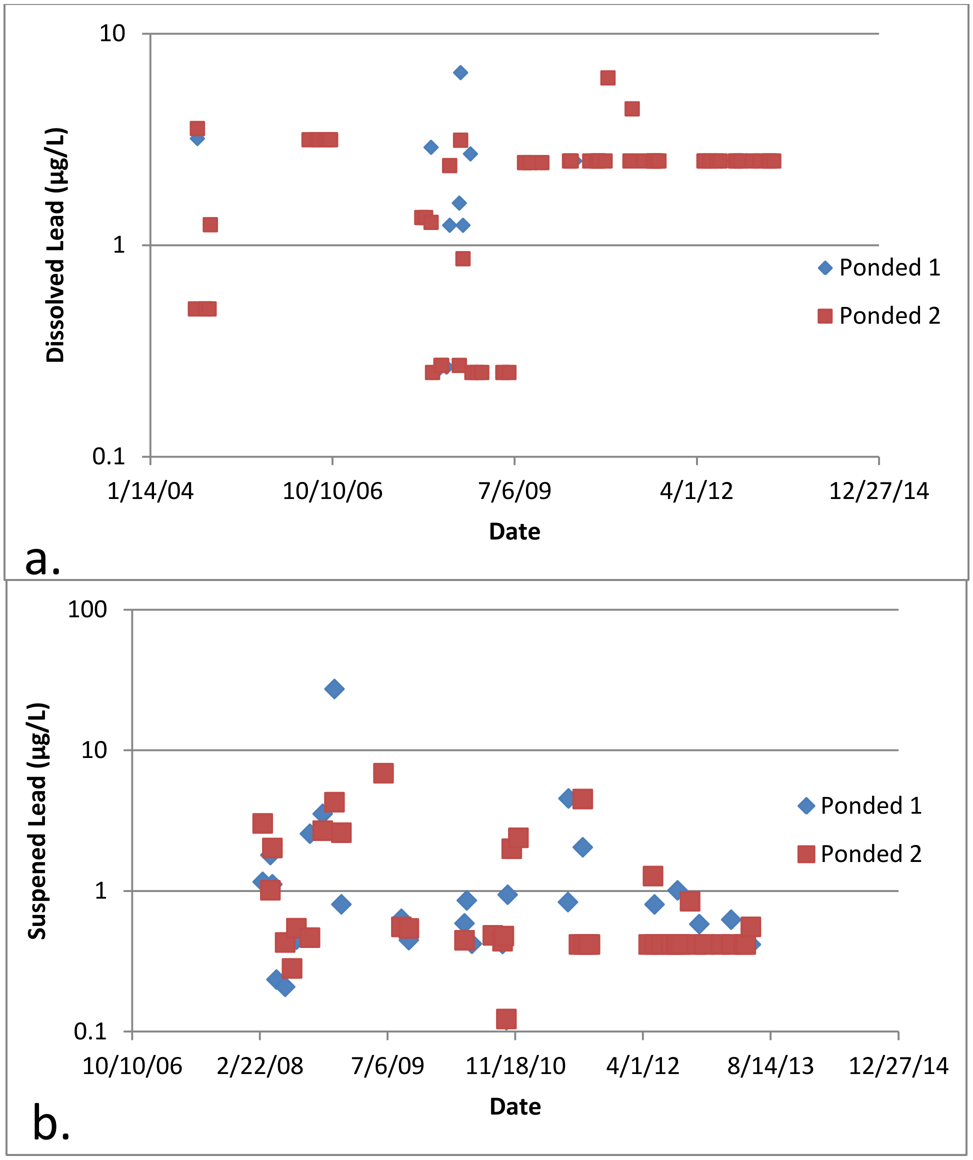
A9: Concentration vs. time for (a) dissolved chromium and (b) suspended chromium over and the ponded 2 samples



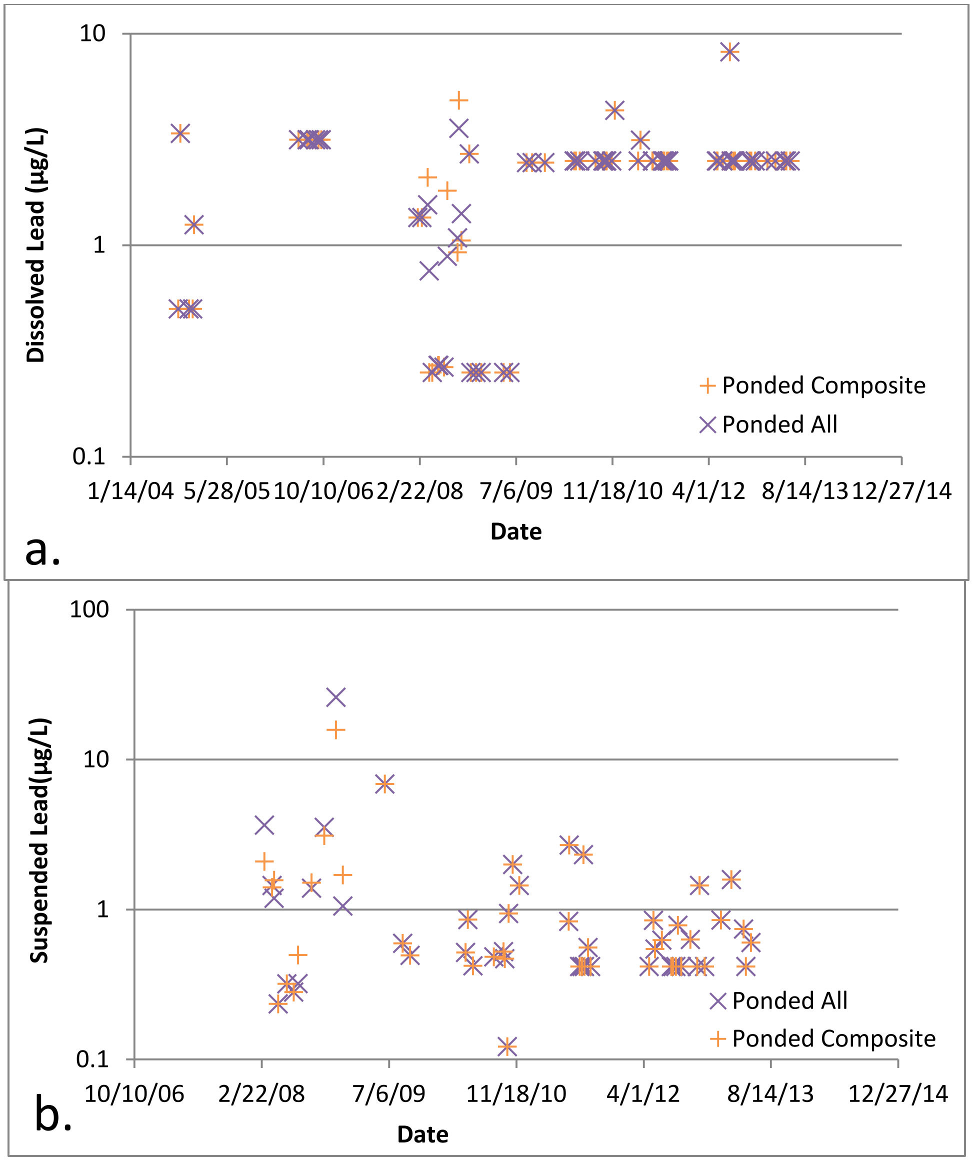
A10: Concentration vs. time for dissolved chromium at various depths and the ponded all samples



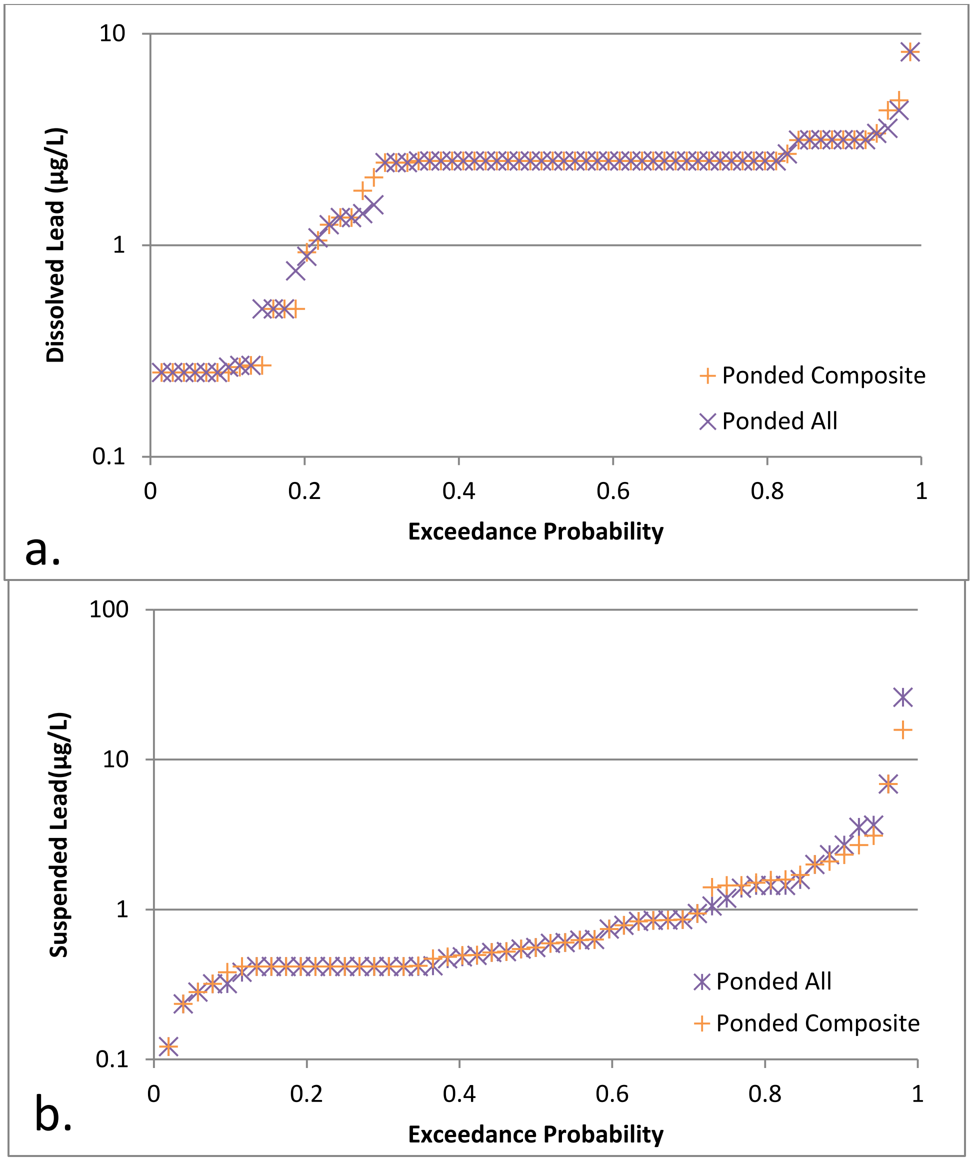
A11: Mass removed (mg) vs. time for (a) dissolved chromium and (b) suspended chromium



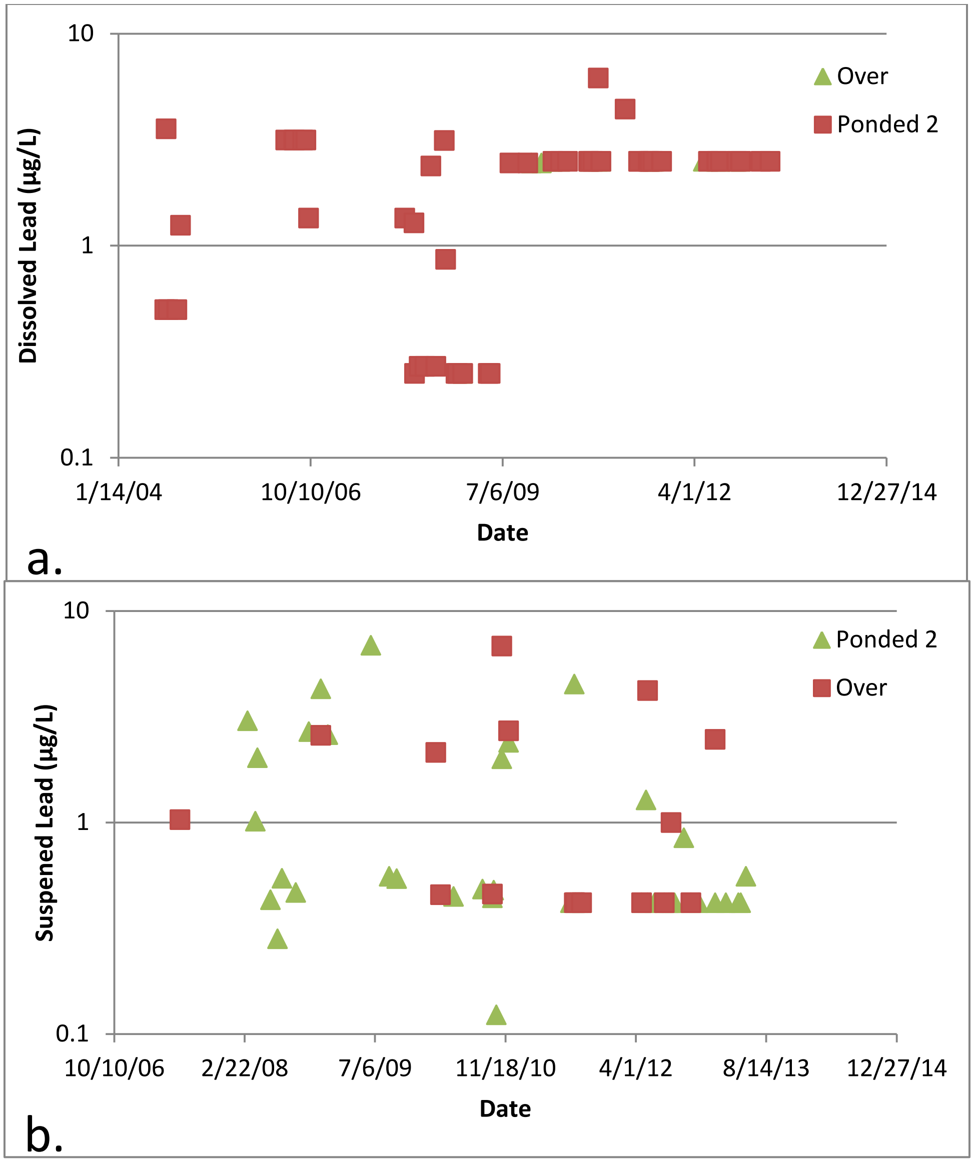
A12: Concentration vs. time for (a) dissolved lead and (b) suspended lead ponded 1 and ponded 2 samples



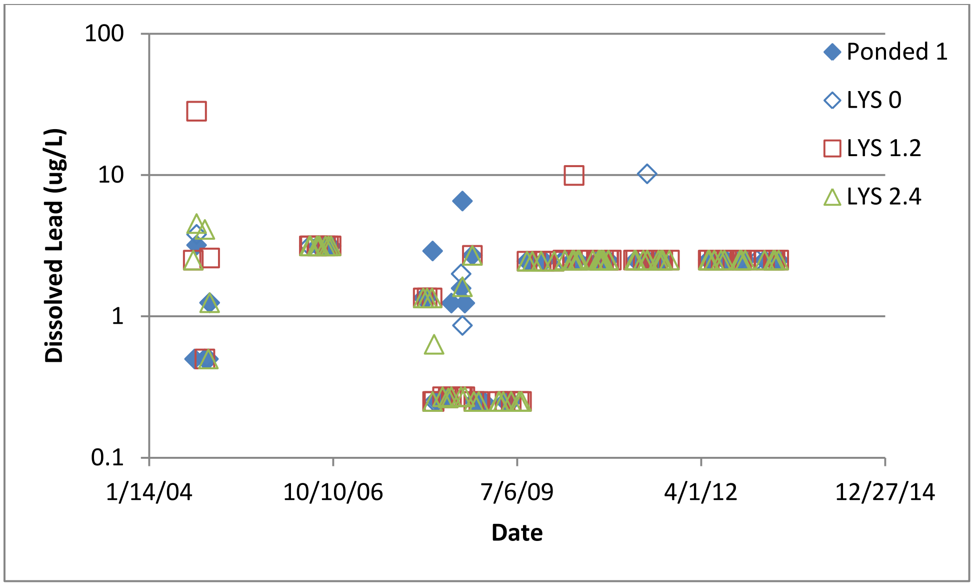
A13: Concentration vs. time for (a) dissolved lead and (b) suspended lead ponded all and the ponded composite samples



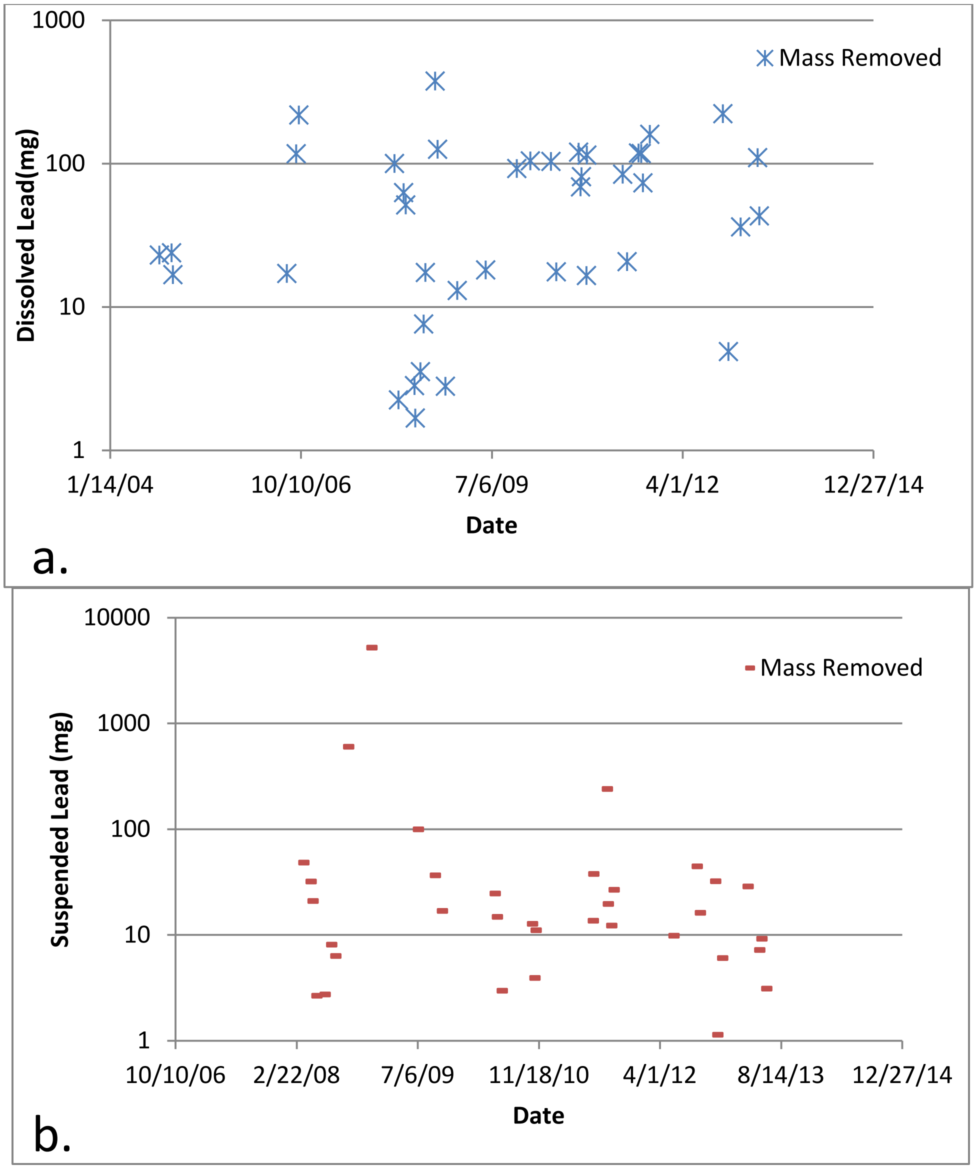
A14: Exceedance Probability for (a) dissolved lead and (b) suspended lead ponded all and ponded composite samples



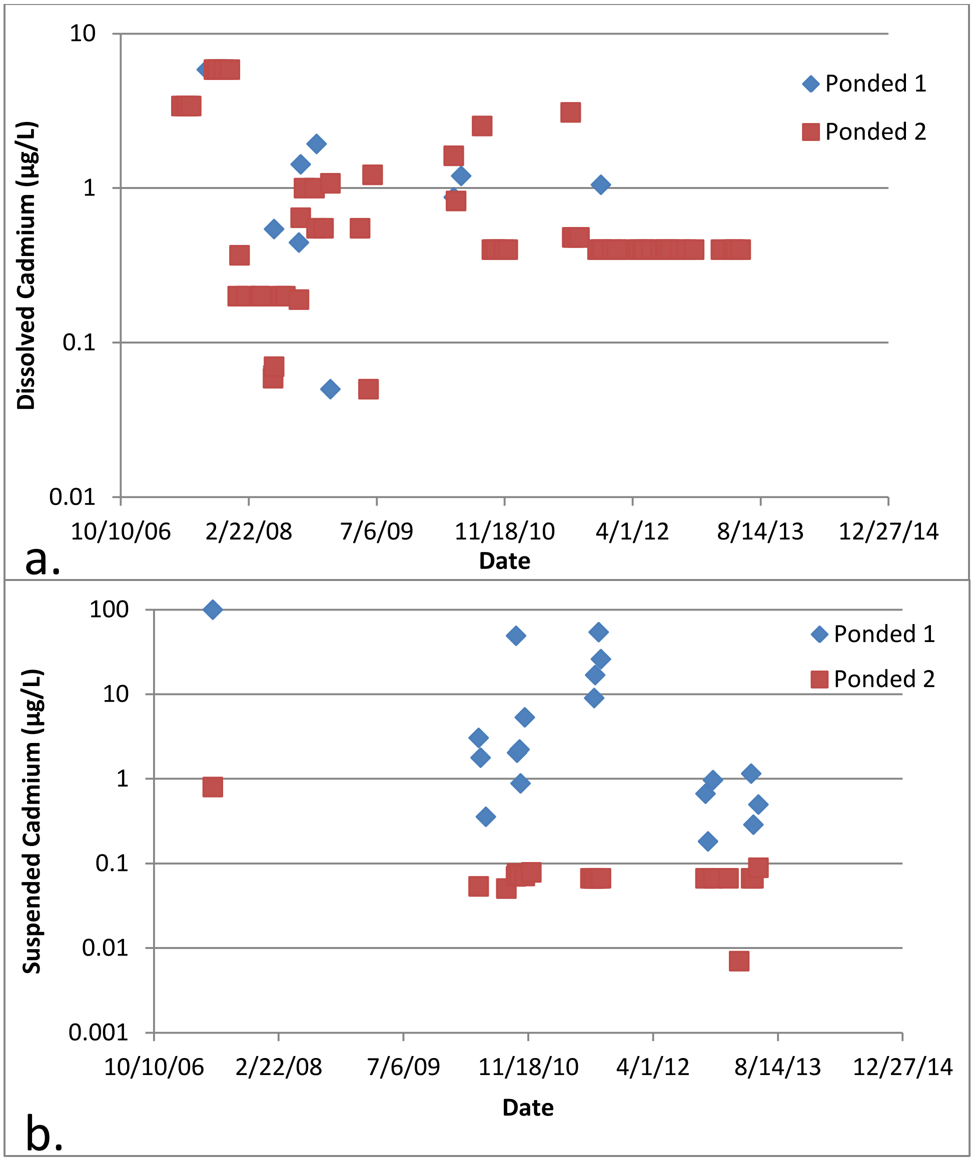
A15: Concentration vs. time for (a) dissolved lead and (b) suspended lead over and the ponded 2 samples



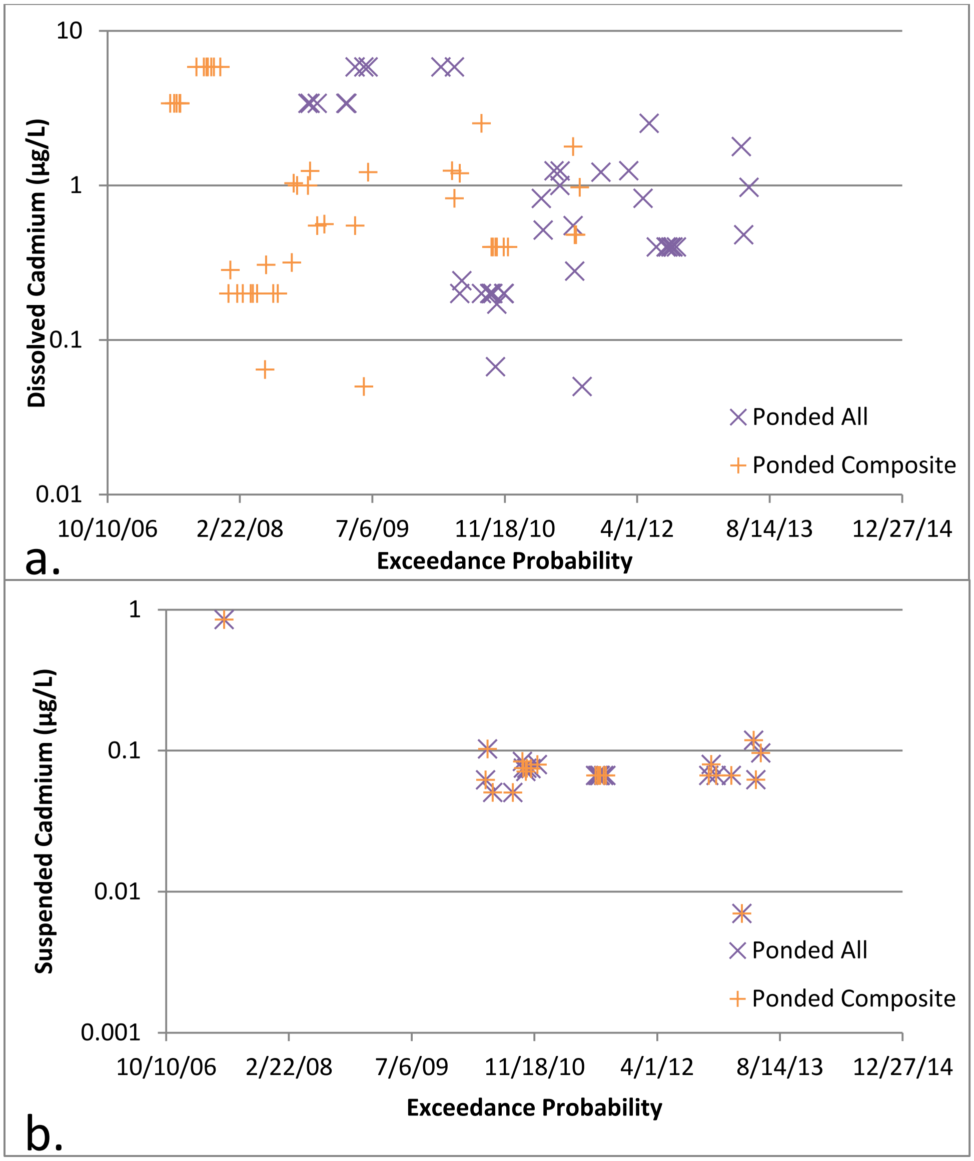
A16: Concentration vs. time for dissolved lead at various depths and the ponded all samples



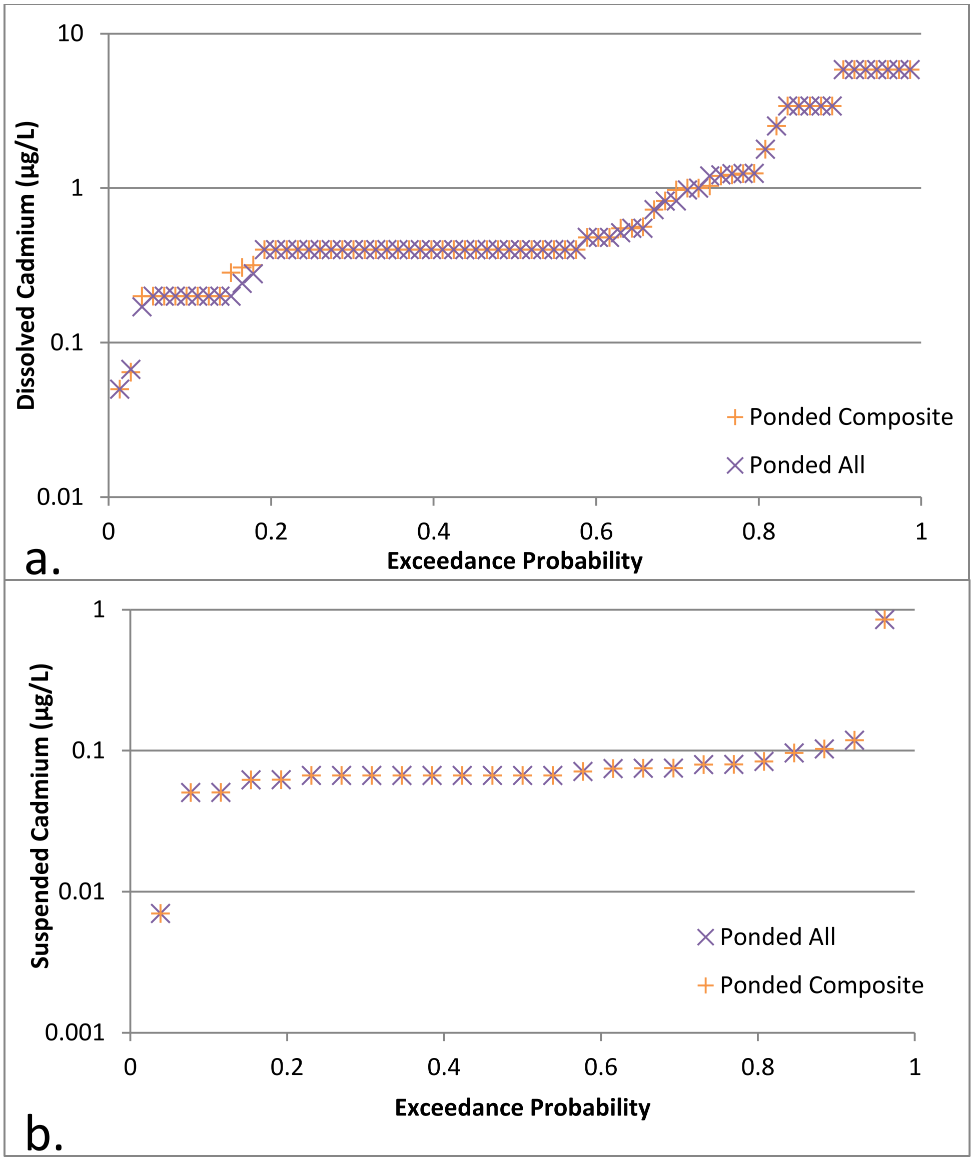
A17: Mass removed (mg) vs. time for (a) dissolved lead and (b) suspended lead



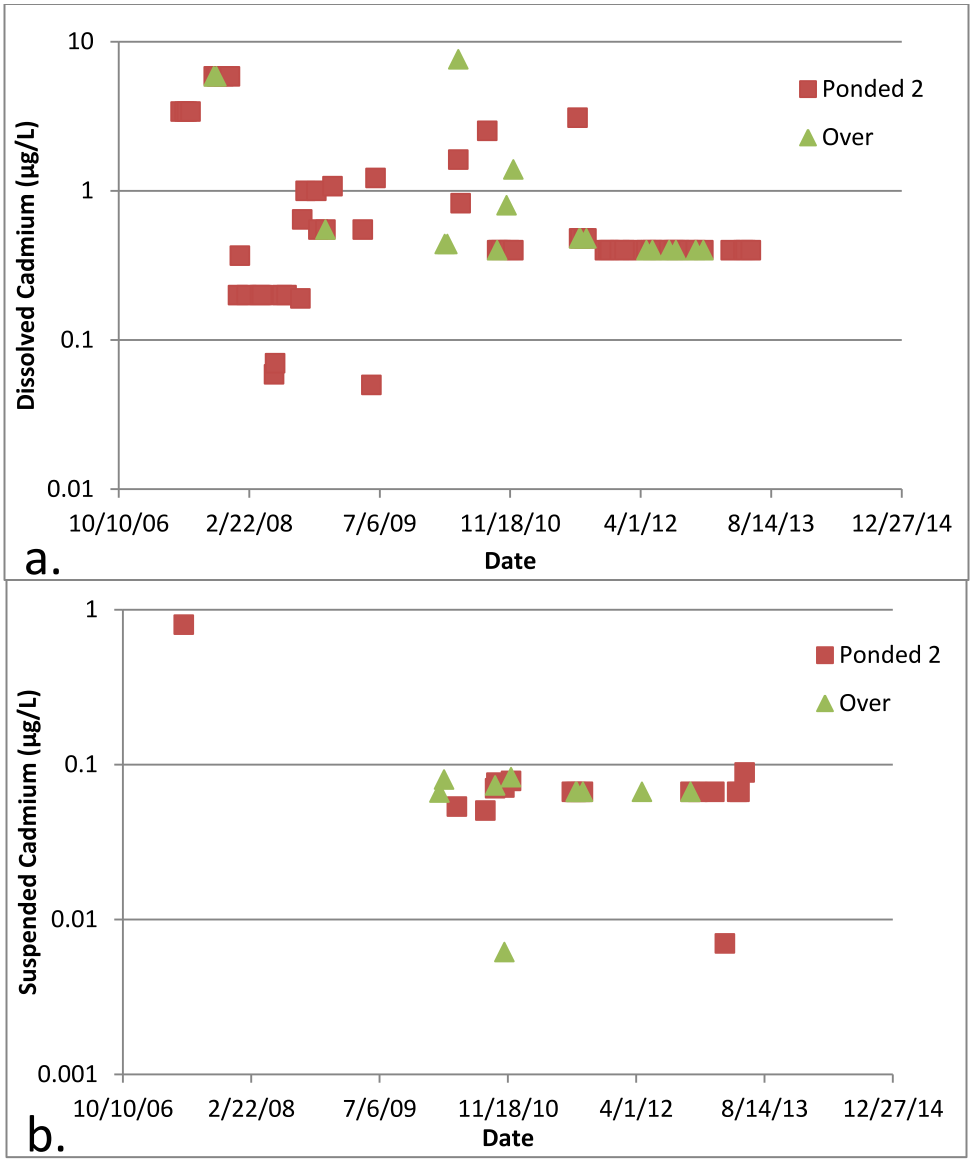
A18: Concentration vs. time for (a) dissolved cadmium and (b) suspended cadmium ponded 1 and ponded 2 samples



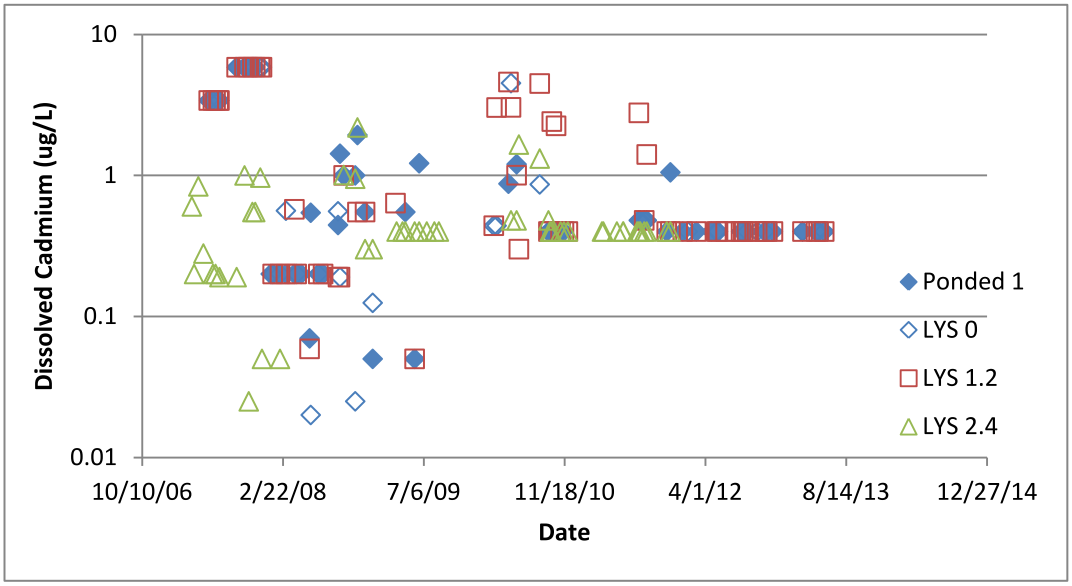
A19: Concentration vs. time for (a) dissolved cadmium and (b) suspended cadmium ponded all and the ponded composite samples



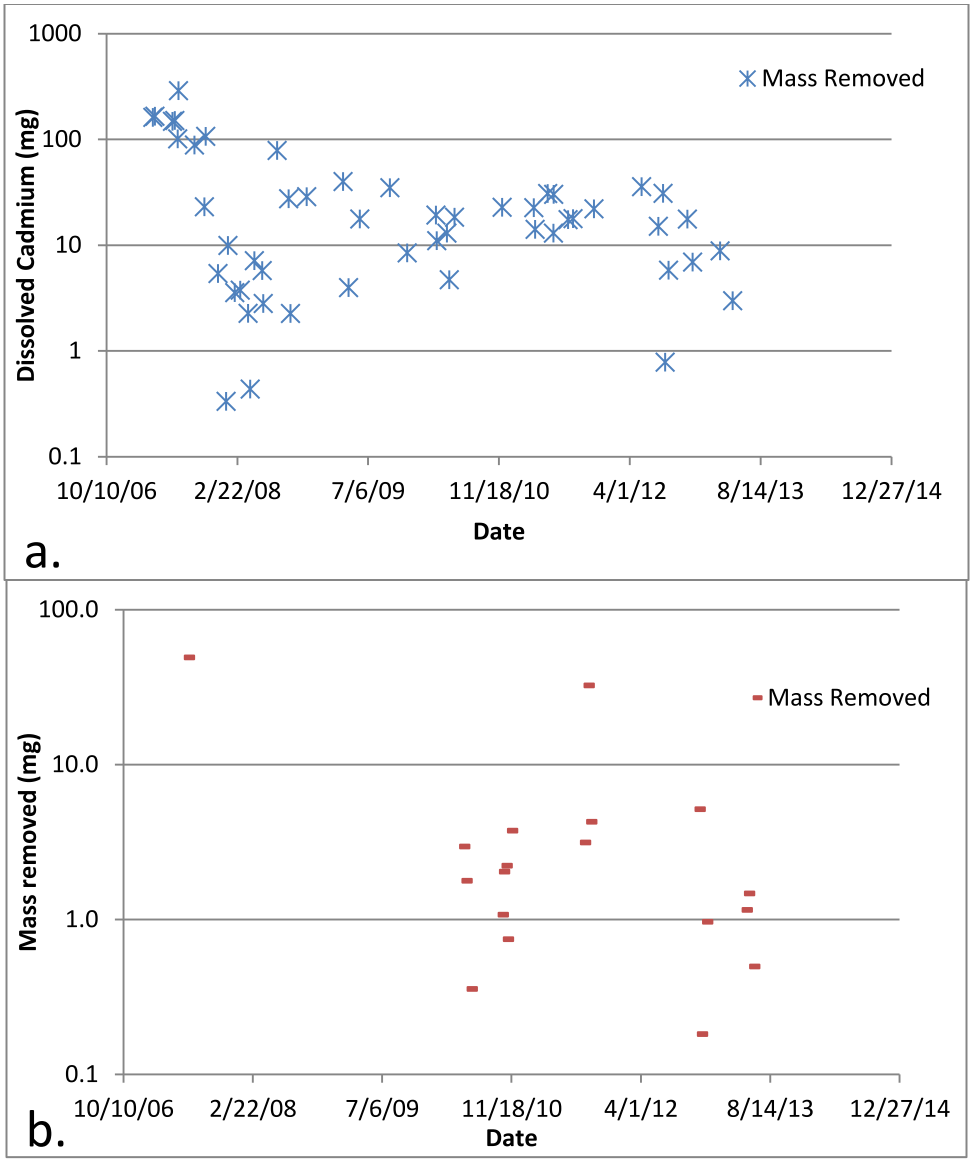
A20 : Exceedance Probability for (a) dissolved cadmium and (b) suspended cadmium ponded all and ponded composite samples



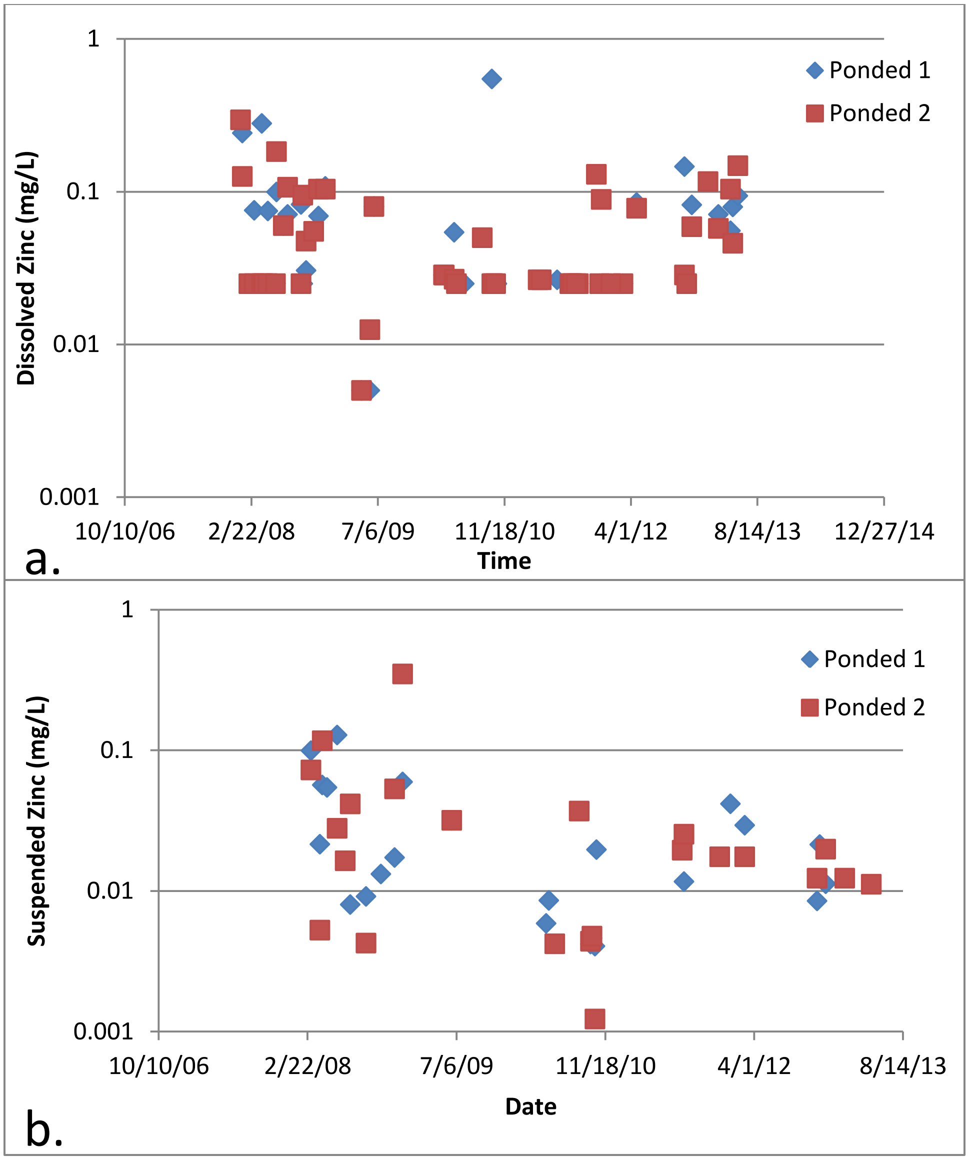
A21 : Concentration vs. time for (a) dissolved cadmium and (b) suspended cadmium over and the ponded 2 samples



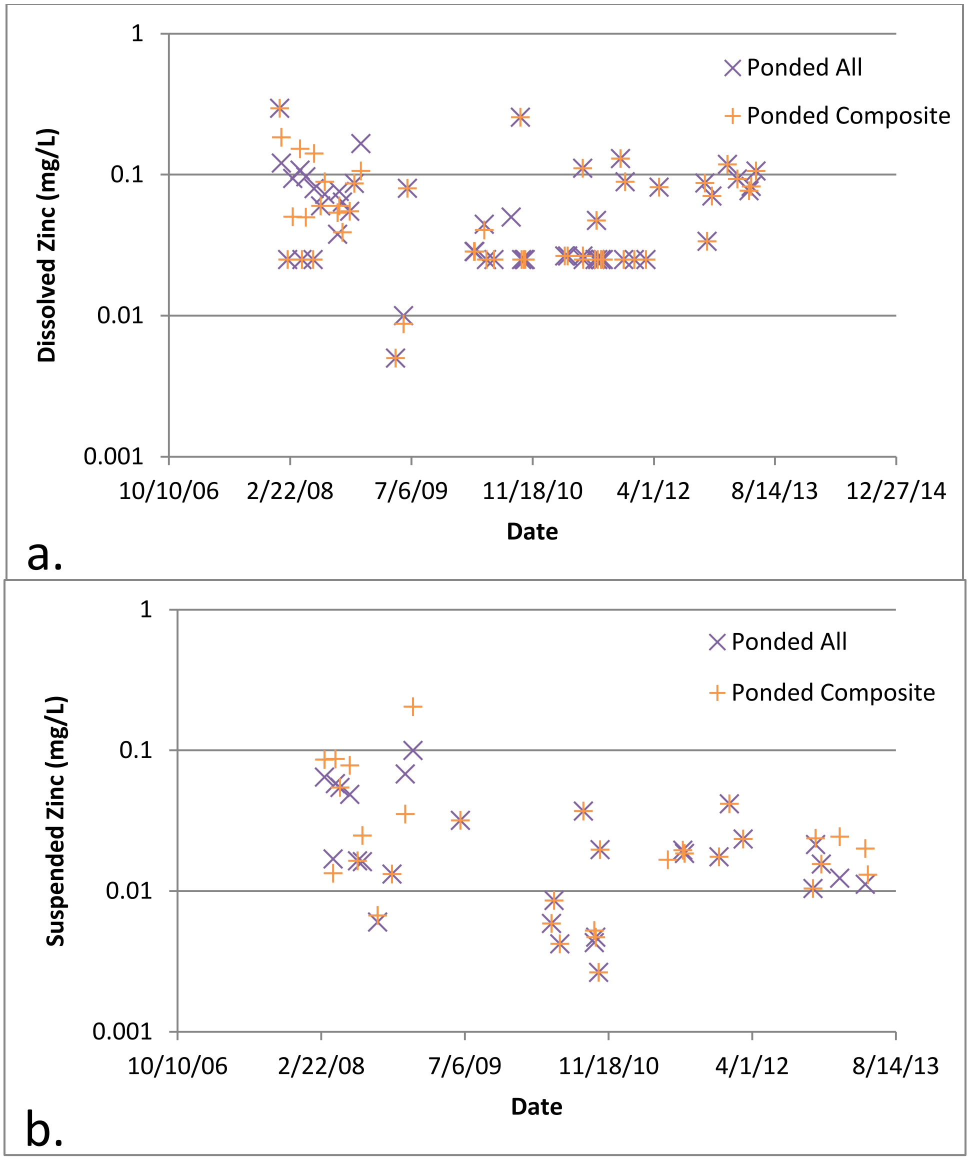
A22: Concentration vs. time for dissolved cadmium at various depths and the ponded all samples



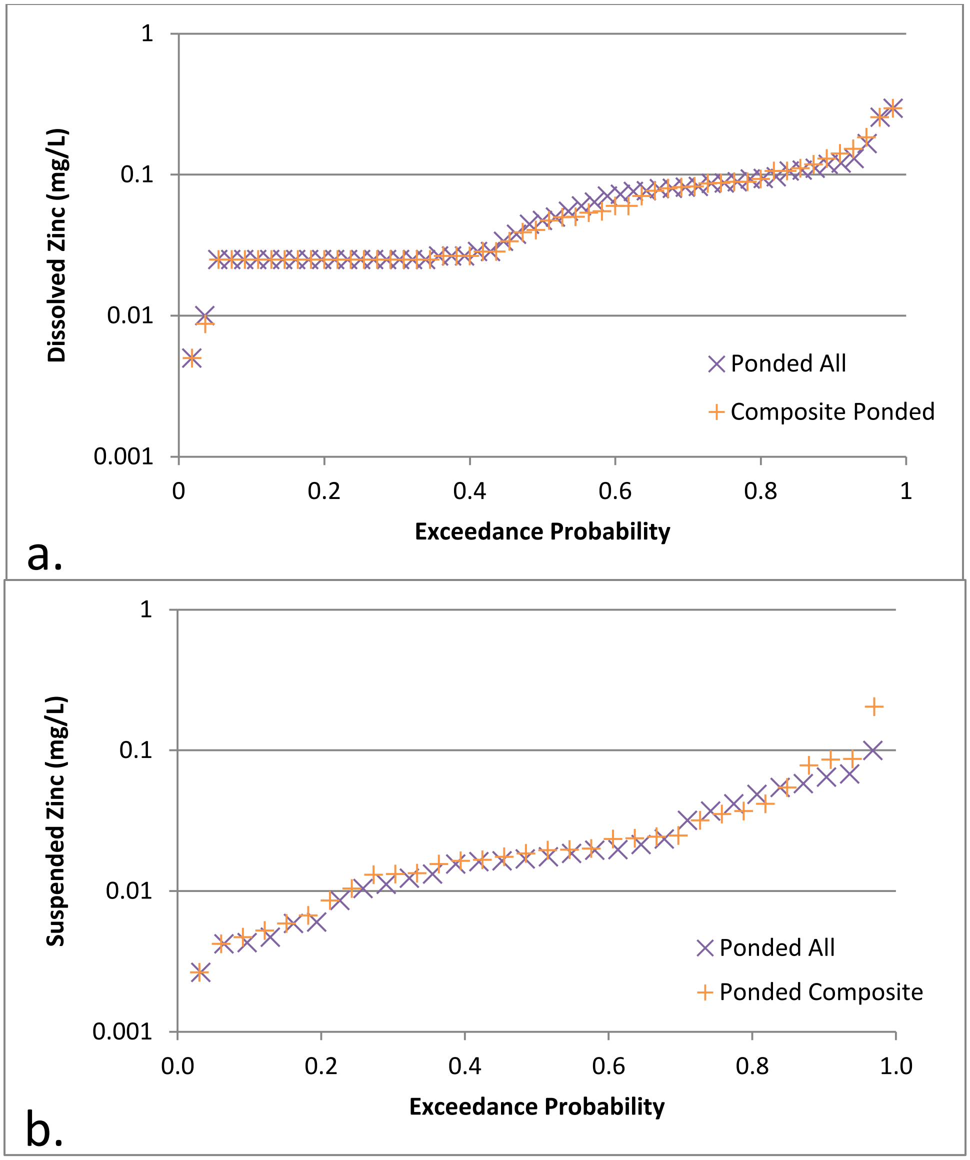
A23: Mass removed (mg) vs. time for (a) dissolved cadmium and (b) suspended cadmium



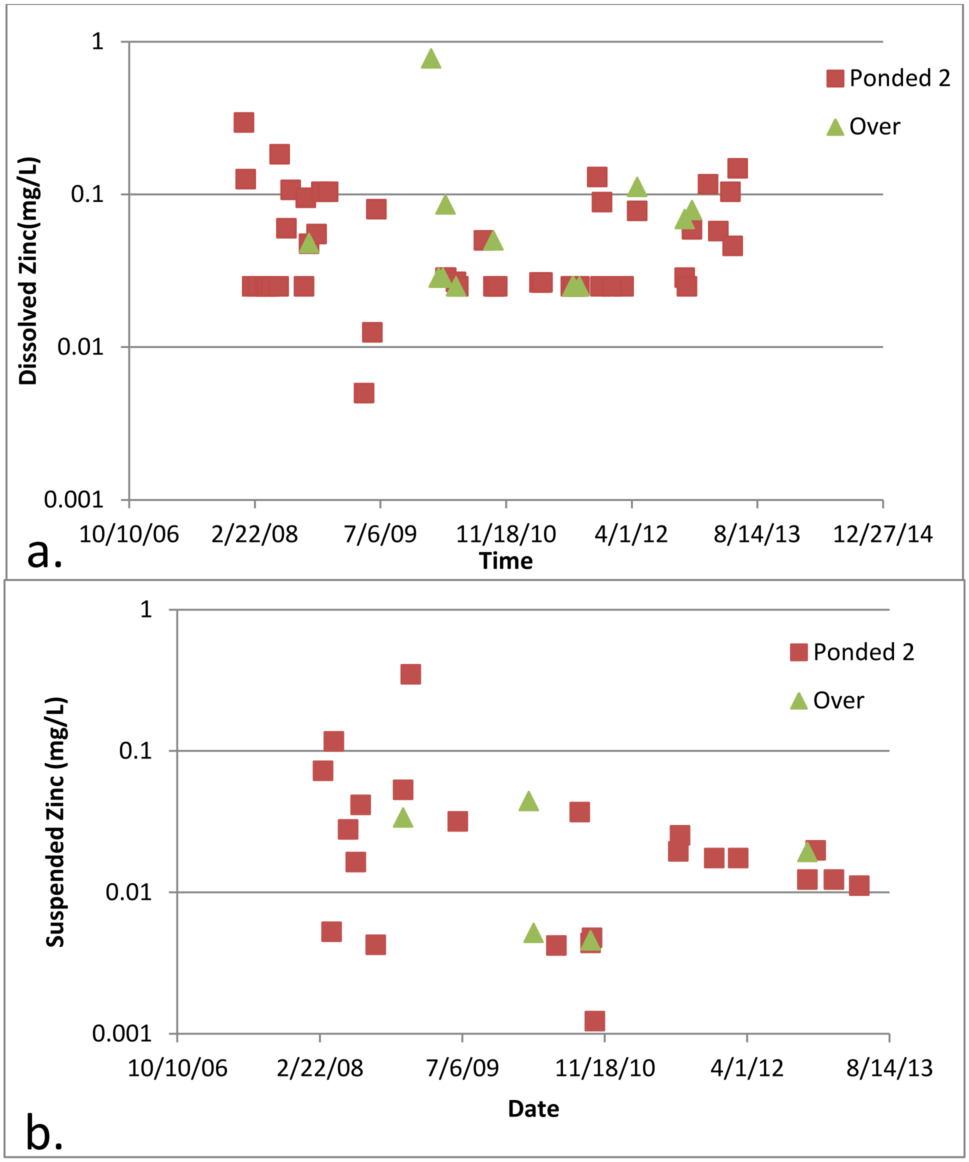
A24: Concentration vs. time for (a) dissolved zinc and (b) suspended zinc ponded 1 and ponded 2 samples



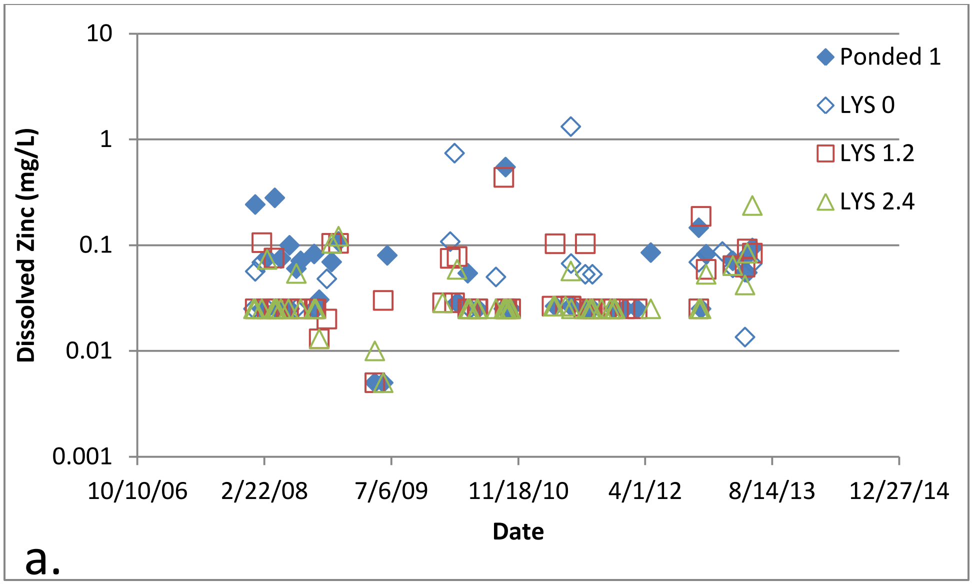
A25: Concentration vs. time for (a) dissolved zinc and (b) suspended zinc ponded all and the ponded composite samples



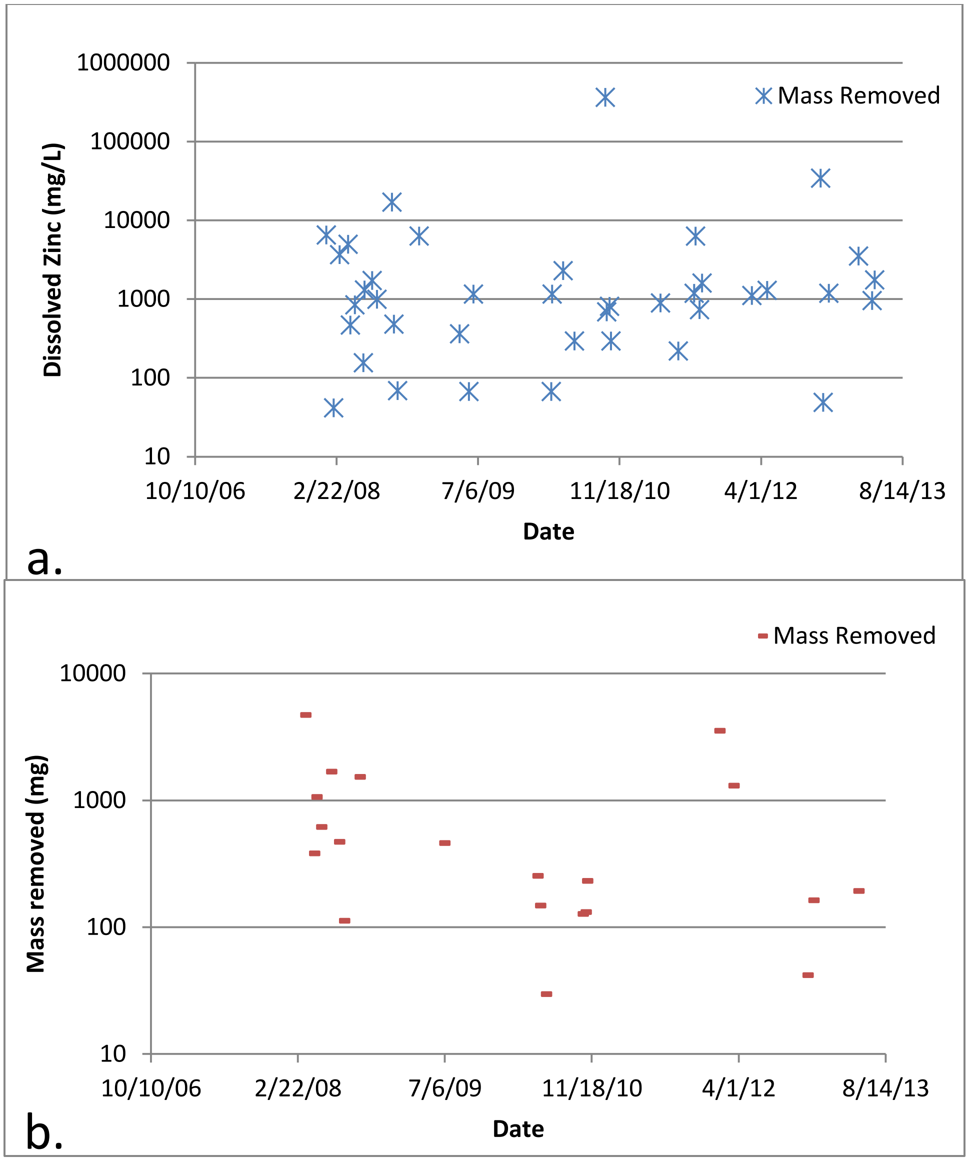
A26: Exceedance Probability for (a) dissolved zinc and (b) suspended zinc ponded all and ponded composite samples



A27: Concentration vs. time for (a) dissolved zinc and (b) suspended zinc over and the ponded 2 samples



A28: Concentration vs. time for dissolved zinc at various depths and the ponded all samples



A29: Mass removed (mg) vs. time for (a) dissolved zinc and (b) suspended zinc

Appendix B : Soil Bound Metals

B1: Copper bound onto the surface of the soil samples in 2009

Copper	µg/g	Surface 0 m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
Oct-08	a		3.06		16.87				
	b		2.62		15.01				
	c		2.83		8.45				
Nov-08	a	3.15		11.68	6.79				
	b	2.16		18.84	7.26				
	c	2.69		12.79	7.20				
Apr-09	a				16.30	11.21	10.15	Total middle	Total Ponded
	b				15.68	11.12	10.31	area	area
	c				16.80	10.15	8.20	(middle, left	all middle
								and right)	and effluent
average		2.67	2.84	14.44	12.26	10.83	9.55	11.6	11.93
std		0.50	0.22	3.85	4.64	0.59	1.17	3.0	3.80
n		3	3	3	9	3	3	9	18

B2: Copper bound onto the soil samples taken at the surface in 2013

Copper	µg/g	Surface 0m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	11.79	4.05		12.93				
	b	11.69	4.35		14.35				
	c	11.97	3.74		13.69				
6/4/2013	a			13.66					
	b			15.5					
	c			15.29					
6/4/2013	a					10.89	8.34	Total middle area	Total ponded
	b					10.47	7.29		
	c					11.58	9.12	(middle, left	all middle
								and right)	and effluent
average		11.82	4.05	14.82	13.66	10.98	8.25	11.35	11.93
std		0.14	0.31	1.01	0.71	0.56	0.92	2.95	2.74
n		3	3	3	3	3	3	9	12

B3: Copper bound onto the soil samples taken 0.3m below the surface in 2009

Copper	µg/g	0.3 m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
10/1/2008	a								
	b								
	c								
11/1/2008	a	5.61		6.39	5.10				
	b	7.20		11.43	4.16				
	c	6.29		5.84	5.98				
4/1/2009	a				4.91	4.26	4.76	Total middle area	Total ponded
	b				4.53	3.82	4.62		
	c				4.93	4.28	5.14	(middle, left and right)	all middle and effluent
average		6.36		7.89	4.94	4.12	4.84	5.62	5.34
std		0.80		3.08	0.62	0.26	0.27	2.33	1.83
n		3		3	6	3	3	9	15

B4: Copper bound onto the soil samples taken at 0.3m below the surface in 2013

Copper	µg/g	0.3 m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	5.36	4.48						
	b	5.89	4.1						
	c	5.11	3.64						
6/4/2013	a			3.58	2.47				
	b			3.49	2.64				
	c			3.35	2.9				
6/4/2013	a					2.53	4.21	Total middle area	Total ponded
	b					2.4	5.63		
	c					2.77	5.13	(middle, left and right)	(middle, left and right)
average		5.45	4.07	3.47	2.67	2.57	4.99	3.68	3.43
std		0.40	0.42	0.12	0.22	0.19	0.72	1.13	1.07
n		3	3	3	3	3	3	9	12

B5: Chromium bound onto the soil samples taken at the surface in 2009

Chromium	µg/g	0 m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
10/1/2008	a		2.41		5.81				
	b		2.01		6.57				
	c		2.11		2.58				
11/1/2008	a	3.73		15.45	2.86				
	b	2.66		13.23	2.46				
	c	3.60		14.40	2.72				
4/1/2009	a				5.17	4.91	4.81	Total middle area (middle, left and right)	Total ponded all middle and effluent
	b				5.13	5.11	5.77		
	c				5.11	4.42	5.65		
average		3.33	2.18	14.36	4.27	4.81	5.41	8.19	6.23
std		0.59	0.21	1.11	1.60	0.35	0.52	4.67	3.94
n		3	3	3	9	3	3	9	18

B6: Chromium bound onto the soil samples taken at the surface in 2013

Chromium	µg/g	0 m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a		3.73		5.77				
	b		3.41		6.54				
	c		3.06		6.2				
6/4/2013	a	6.19		15.57					
	b	6.18		13.65					
	c	6.11		9.5					
6/4/2013	a					5.55	5.2	Total middle area (middle, left and right)	Total ponded area all middle and effluent
	b					4.81	5.08		
	c					5.37	4.42		
average		6.16	3.40	12.91	6.17	5.24	4.90	7.68	7.31
std		0.04	0.34	3.10	0.39	0.39	0.42	4.23	3.67
n		3	3	3	3	3	3	9	12

B7: Chromium bound onto the soil samples taken 0.3m below the surface in 2009

Chromium	µg/g	0.3m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
10/1/2008	a			38.33					
	b			23.52					
	c			7.77					
11/1/2008	a	2.81			3.38				
	b	2.81			3.77				
	c	2.45			4.31				
4/1/2009	a				3.11	3.06	4.07	Total middle	
	b				3.23	3.65	2.86		Total ponded
	c				3.31	3.08	3.13	(middle, left and right)	all middle and effluent
average		2.69		23.21	3.52	3.27	3.35	9.94	3.41
std		0.21		15.28	0.45	0.34	0.64	12.55	0.44
n		3		3	6	3	3	9	15

B8: Chromium bound onto the soil samples taken 0.3m below the surface in 2013

Chromium	µg/g	0.3m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a				2.41				
	b				2.33				
	c				2.08				
6/4/2013	a	6.50	4.54	4.40					
	b	8.76	3.94	3.70					
	c	5.42	2.77	3.26					
6/4/2013	a					2.27	3.31	Total middle	Total ponded
	b					2.76	4.36	area	
	c					1.96	3.78	(middle, left and right)	all middle and effluent
average		6.89	3.75	3.79	2.27	2.33	3.82	3.31	3.05
std		1.70	0.90	0.57	0.17	0.40	0.53	0.86	0.87
n		3	3	3	3	3	3	9	12

B9: Lead bound onto the soil samples taken at the surface in 2009

Lead	µg/g	0 m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
10/1/2008	a		5.98		17.69				
	b		5.73		11.11				
	c		2.75		2.02				
11/1/2008	a	10.37		12.20	5.02				
	b	6.90		21.50	4.85				
	c	8.48		19.86	4.71				
4/1/2009	a				1.42	1.82	5.19	Total middle area	Total ponded
	b				8.92	2.03	5.67		
	c				2.03	1.65	16.68	middle, left and right	all middle and effluent
average		8.58	4.82	17.85	6.42	1.83	9.18	9.62	8.02
std		1.74	1.80	4.96	5.32	0.19	6.50	8.06	6.83
n		3	3	3	9	3	3	9	18

B10: Lead bound onto the soil samples taken at the surface, 0m, in 2013

Lead	µg/g	0m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a		7.77		6.82				
	b		9.58		8.87				
	c		7.82		16.47				
6/4/2013	a	11.77		11.77					
	b	13.42		10.57					
	c	11.59		10.84					
6/4/2013	a					20.11	13.60	Total middle area (middle, left and right)	
	b					18.11	14.66		Total ponded all middle and effluent
	c					17.44	8.95		
average		12.26	8.39	11.06	10.7	18.55	12.40	14.0	13.2
std		1.0	1.0	0.6	5.1	1.4	3.0	3.9	4.2
n		3	3	3	3	3	3	9	12

B11: Lead bound onto the soil samples taken 0.3m below the surface in 2009

Lead	µg/g	0.3 m	2009						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
10/1/2008	a								
	b								
	c								
11/1/2008	a	6.23		8.35	6.47				
	b	6.37		4.43	7.79				
	c	6.72		3.90	10.44				
4/1/2009	a				3.66	2.10	2.93	Total middle area (middle, left and right)	Total ponded all middle and effluent
	b				2.40	2.02	2.54		
	c				2.30	2.67	4.21		
average		6.44		5.56	5.51	2.26	3.22	3.68	4.41
std		0.26		2.43	3.28	0.35	0.87	1.96	2.63
n		3		3	6	3	3	9	15

B12: Lead bound onto the soil samples taken 0.3m below the surface in 2013

Lead	µg/g	0.3 m	2013						
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a				4.55				
	b				5.53				
	c				5.28				
6/4/2013	a	6.88	11.24	7.21					
	b	9.98	11.67	5.55					
	c	8.62	7.39	6.53					
6/4/2013	a					5.45	12.95	Total middle area (middle, left and right)	Total ponded all middle and effluent
	b					5.51	21.21		
	c					5.71	15.15		
average		8.49	10.10	6.43	5.12	5.56	16.44	9.47	8.39
std		1.55	2.36	0.83	0.51	0.14	4.28	5.67	5.23
n		3	3	3		3	3	9	12

B13: Cadmium bound onto the soil samples taken at the surface in 2009

Cadmium		ug/g	0 m	2009					
Location in Figure 3a			1	5	3	2	4		
		background	control	middle	effluent	left	right		
10/1/2008	a		0.09		0.39				
	b		0.11		0.36				
	c		0.08		0.36				
11/1/2008	a			0.20					
	b			0.17					
	c			0.24					
4/1/2009	a							Total middle	Total ponded
	b								
	c							(middle, left and right)	all middle and effluent
avg			0.09	0.20	0.37			0.20	0.29
std			0.01	0.03	0.02			0.03	0.09
n			3	3	3			3	6

B14: Cadmium bound onto the soil samples taken at the surface in 2013

Cadmium		µg/g	0 m	2013					
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	0.12	0.08		1.25				
	b	0.12	0.09		1.87				
	c	0.10	0.05		1.87				
6/4/2013	a			1.26					
	b			1.40					
	c			1.33					
6/4/2013	a					0.71	0.14	Total middle (middle, left and	Total ponded all middle and effluent
	b					0.67	0.73		
	c					0.69	0.75		
avg		0.11	0.07	1.33	1.66	0.69	0.54	0.85	1.06
std		0.01	0.02	0.07	0.36	0.02	0.35	0.40	0.52
n		3	3	3	3	3	3	9	12

B15: Cadmium bound on the soil samples taken 0.3m below the surface in 2009

Cadmium		ug/g	0.3	2009					
Location in Figure 3a			1	5	3	2	4		
		background	control	middle	effluent	left	right		
10/1/2008	a				0.11				
	b				0.10				
	c				0.16				
11/1/2008	a			0.12					
	b			0.13					
	c			0.12					
4/1/2009	a							Total middle	Total ponded
	b								
	c							(middle, left and right)	all middle and effluent
avg				0.12	0.12			0.12	0.12
std				0.01	0.04			0.01	0.02
n				3	3			3	6

B16: Cadmium bound onto the soil samples taken 0.3m below the surface in 2013

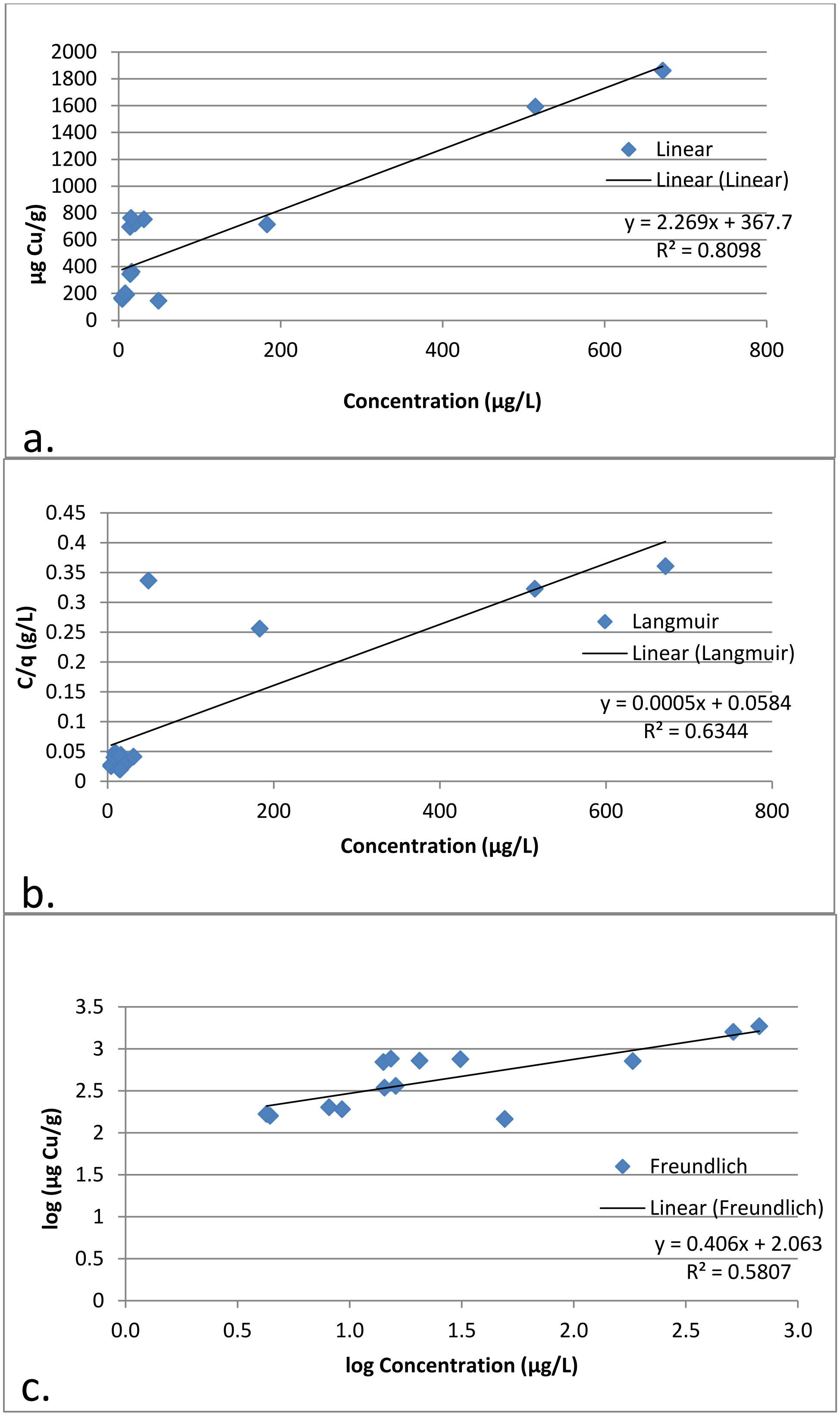
Cadmium		µg/g	0.3	2013					
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	0.11	0.09		0.05				
	b	0.09	0.10		0.06				
	c	0.07	0.07		0.04				
6/4/2013	a			0.01					
	b			0.05					
	c			0.01					
6/4/2013	a					0.04	0.01	Total middle	Ponded All
	b					0.04	0.17		
	c					0.04	0.01	(middle, left and	all middle and effluent
avg		0.09	0.08	0.02	0.05	0.04	0.06	0.04	0.04
std		0.02	0.01	0.02	0.01	0.00	0.09	0.05	0.04
n		3	3	3	3	3	3	9	12

B17: Zinc bound onto the soil samples taken at the surface in 2013

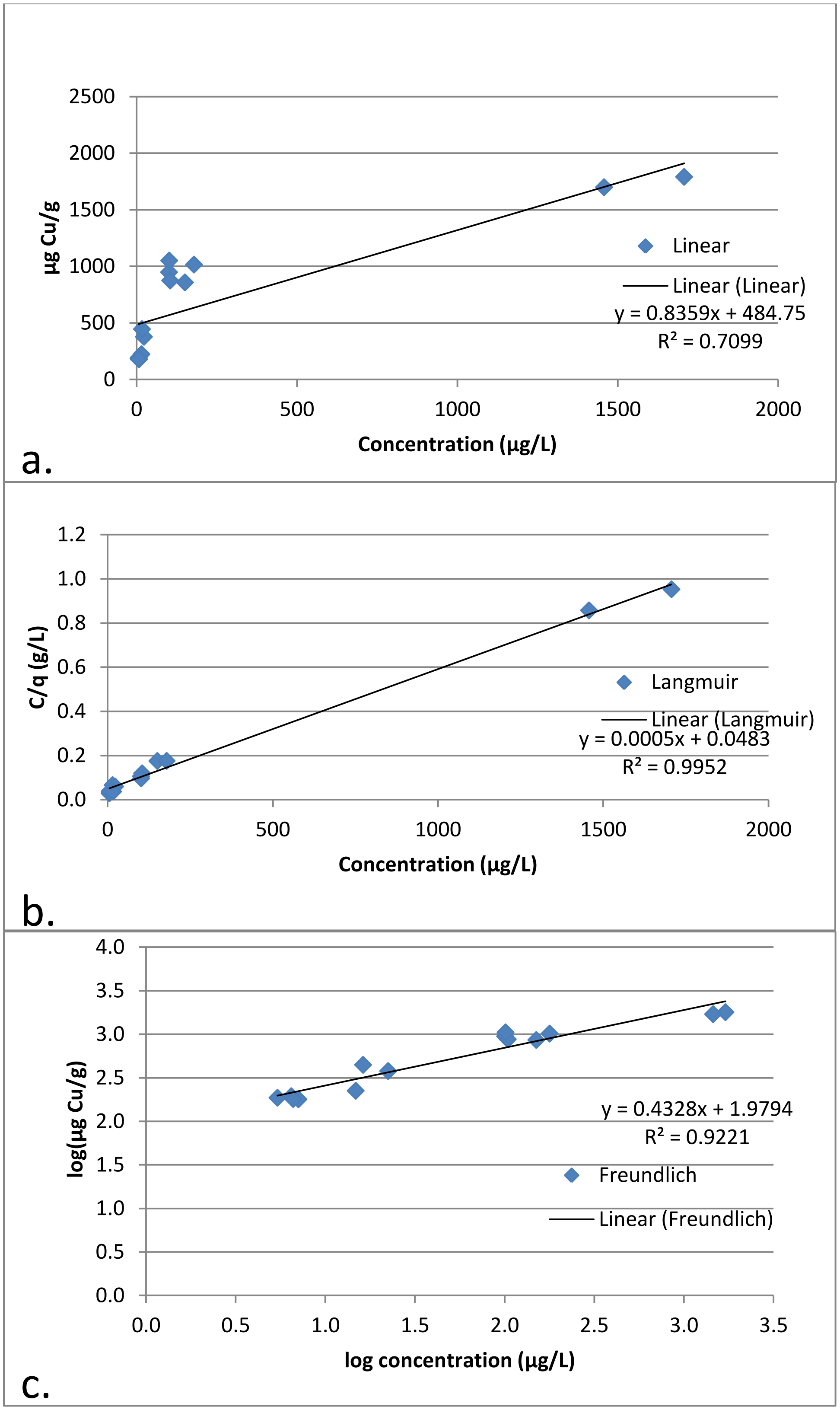
Zinc (mg/g)	0m	2013							
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	0.027	0.025		0.098				
	b	0.027	0.028		0.081				
	c	0.026	0.027		0.091				
6/4/2013	a			0.096					
	b			0.134					
	c			0.093					
6/4/2013	a					0.099364	0.045	Total Middle (middle, left and	Total ponded (eff, middle,
	b					0.096903	0.045		
	c					0.098531	0.065		
average		0.027	0.027	0.108	0.090	0.098	0.052	0.086	0.09
std		0.001	0.001	0.023	0.009	0.001	0.012	0.015	0.025
n		3	3	3	3	3	3	9	12

B18: Zinc bound onto the soil samples taken 0.3m below the surface in 2013

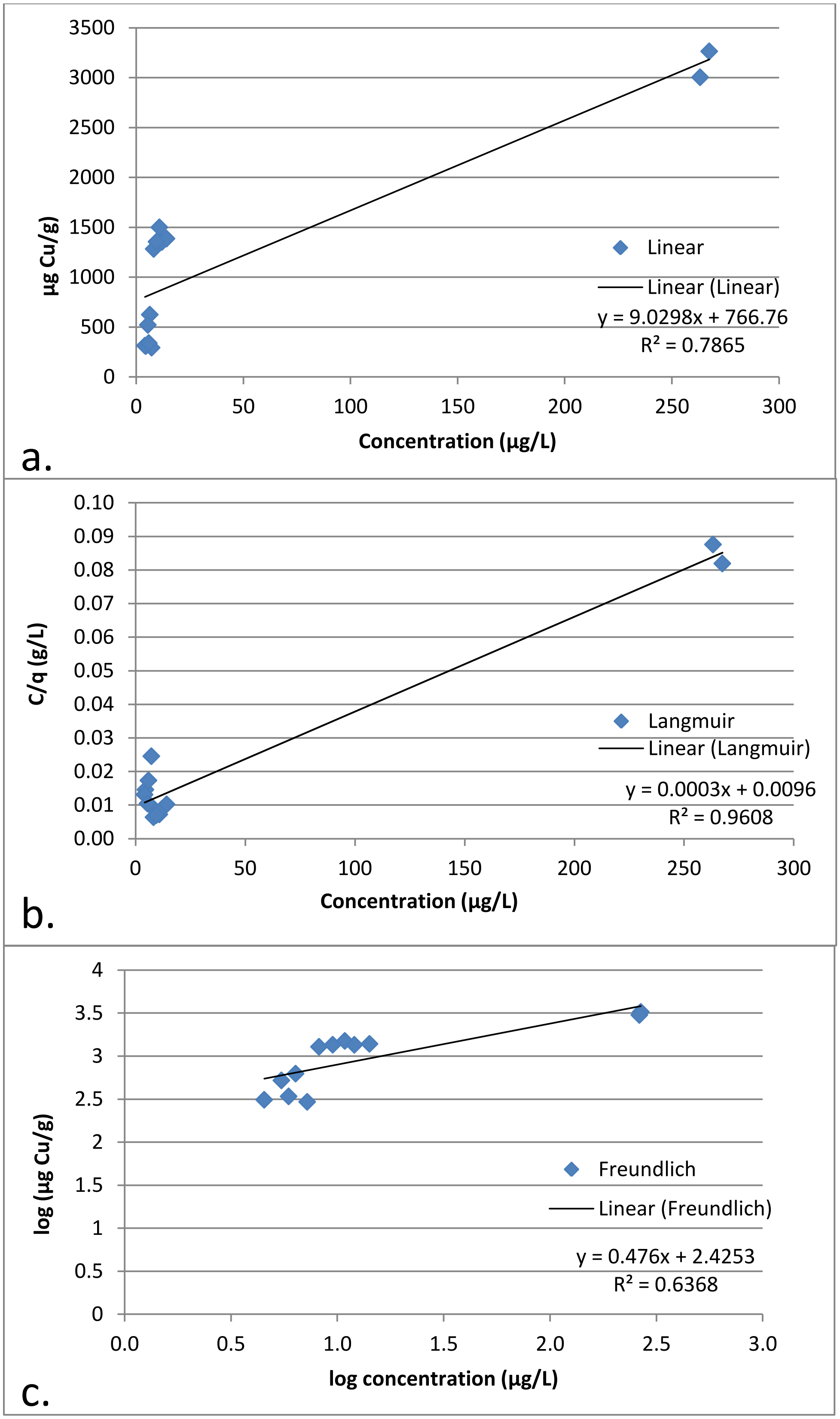
Zinc (mg/g)	0.3 m	2013							
Location in Figure 3a			1	5	3	2	4		
		Background	Control	Middle	Effluent	Left	Right		
6/4/2013	a	0.017	0.027		0.014				
	b	0.019	0.025		0.016				
	c	0.018	0.024		0.016				
6/4/2013	a			0.018					
	b			0.013					
	c			0.015					
6/4/2013	a					0.014	0.019		
	b					0.016	0.027	Total Middle (middle, left and	Total ponded (eff, middle,
	c					0.015	0.022		
average		0.018	0.026	0.015	0.015	0.015	0.023	0.018	17.050
std		0.001	0.001	0.003	0.001	0.001	0.004	0.004674	4.160
n		3	3	3	3	3	3	9	12



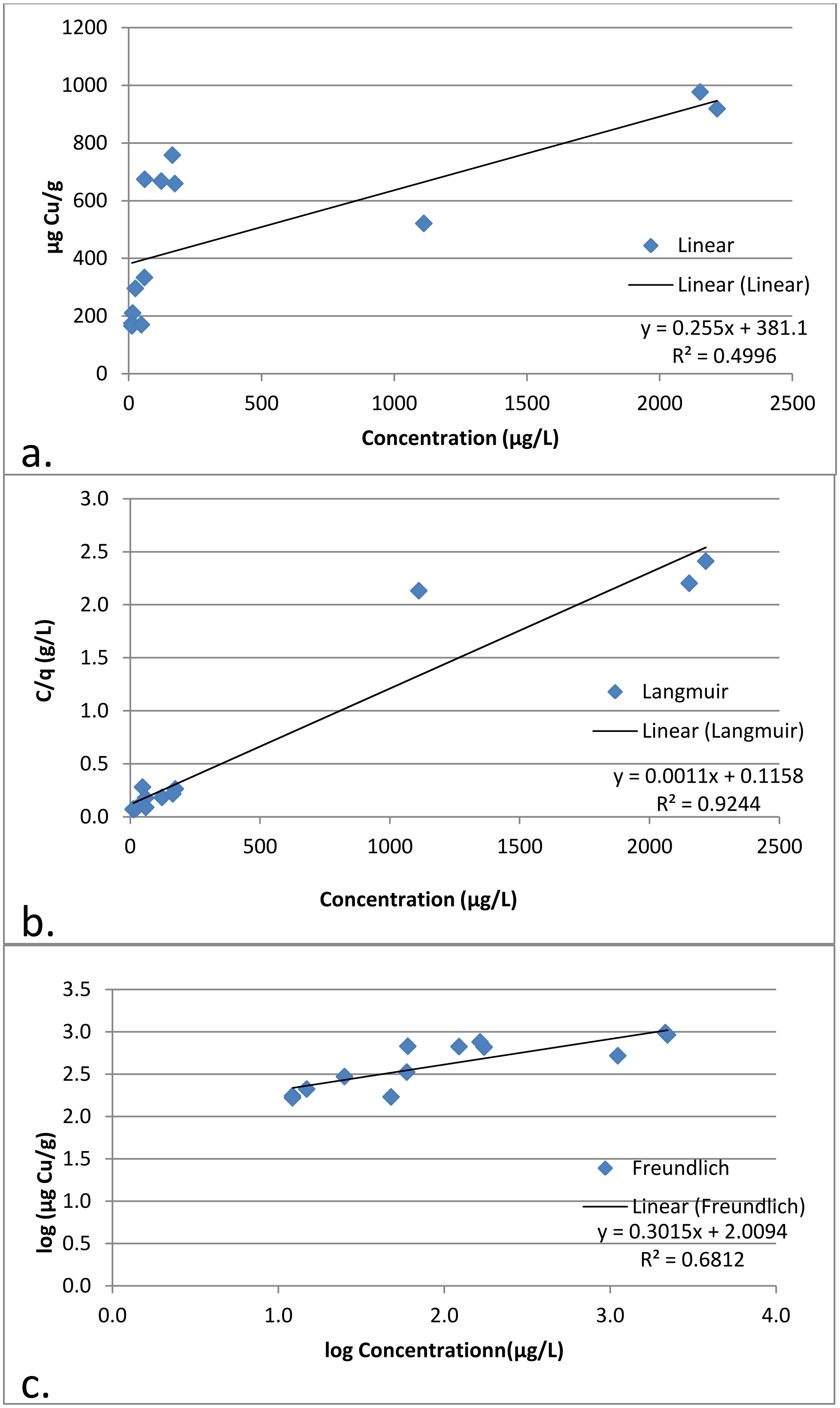
B19: Isotherms including all copper concentrations at the surface of Location 1



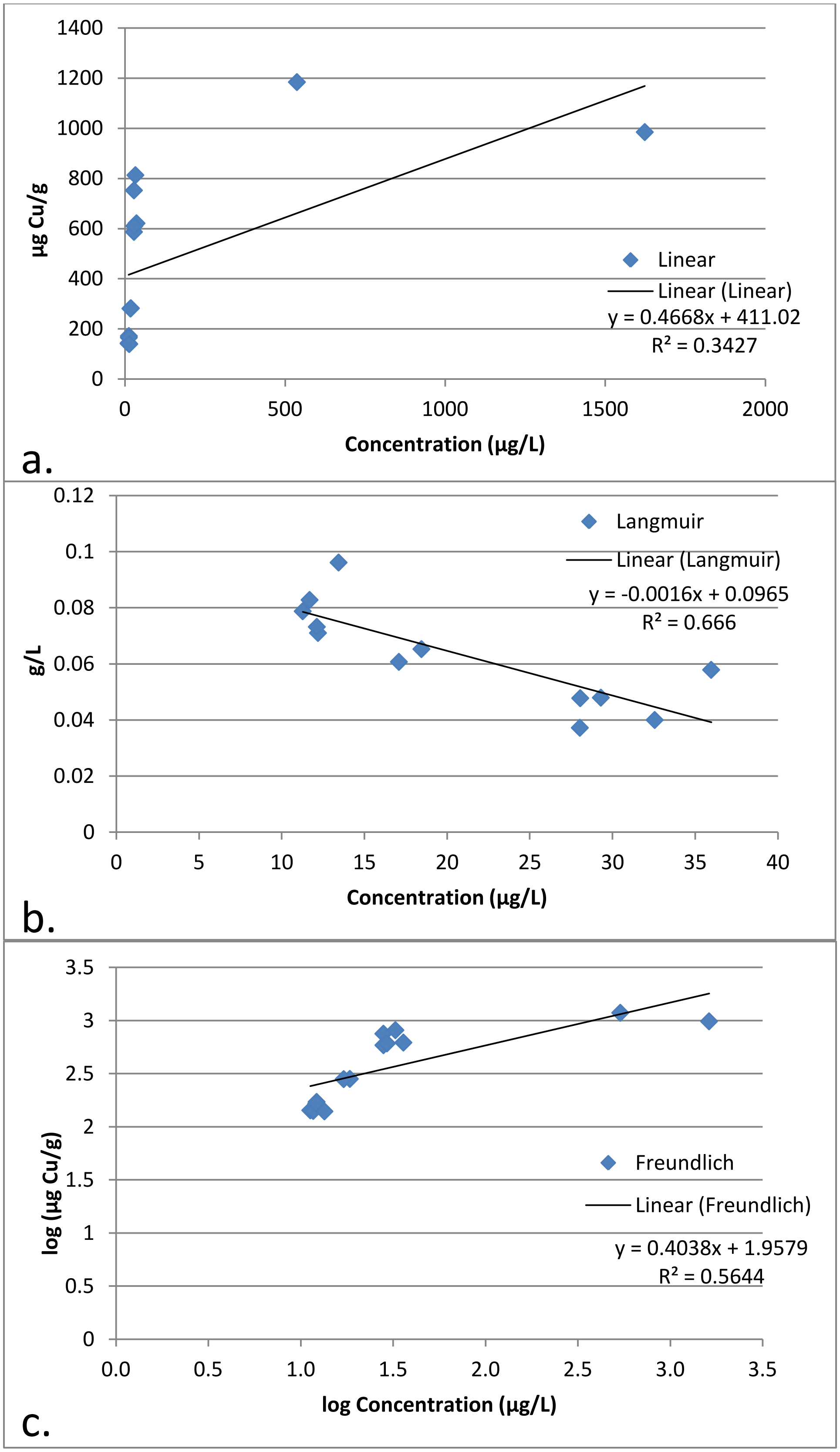
B20: Isotherms including all copper concentrations 0.3 m below the surface of Location 1



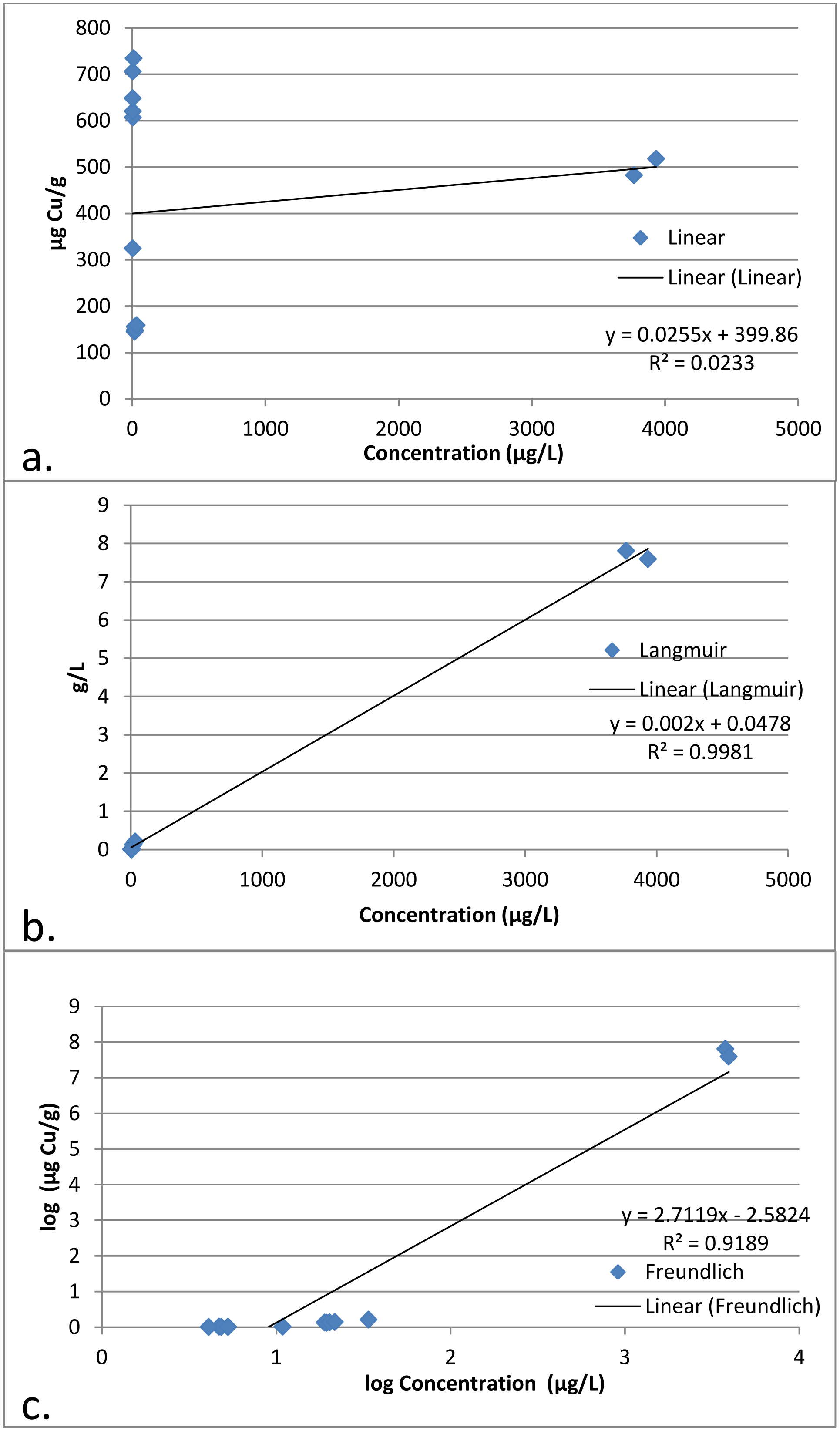
B21: Isotherms including all copper concentrations at the surface of Location 3



B22: Isotherms including all copper concentrations 0.3 m below the surface of Location 3



B23: Isotherms including all copper concentrations at the surface of Location 5



B24: Isotherms including all copper concentrations 0.3 m below the surface of Location 5