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THE EFFECTIVENESS OF BIORETENTION STRUCTURES FOR METAL RETENTION AND TOXICITY REDUCTION OF COPPER ROOF RUNOFF

by

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THESIS APPROVAL PAGE

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ii

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Abstract

The Effectiveness of Bioretention Structures for Metal Retention and Toxicity Reduction of Copper Roof Runoff

Bill LaBarre

Concern has increased over the concentrations of copper in stormwater runoff from copper roofs due to its effects on sensitive aquatic biota. Stormwater control measures (SCMs) are being used as a way to treat effluent from various nonpoint pollution sources such as roadways and parking lots, but their efficacy has not been well demonstrated in the treatment of more concentrated sources such as copper roofs. Influent and effluent stormwater from a copper roof with two kinds of SCMs (bioretention planter boxes and biofiltration swales) were examined over a two year period to determine their ability to sequester copper and attenuate toxicity. The planter boxes averaged 93% copper removal and the swales averaged 97% removal. Effluent water toxicity was substantially decreased through water chemistry changes that reduce the bioavailability of copper as determined by the biotic ligand model and toxicity testing.

TABLE OF CONTENTS

List of Figures

List of Tables

List of Appendices

Chapter 1

Review of the Literature Regarding Copper Contributions to Stormwater Toxicity

1. STORMWATER

Stormwater is precipitation that falls as rain or snow and runs off impervious surfaces into streams and rivers. When these waters are absorbed into the ground they are subject to natural filtration and replenish aquifers or waterways in ways that are more in accord with natural flow patterns. However, municipalities have typically managed stormwaters by diverting them into storm drains, sewer systems, and drainage systems that contribute to downstream flooding, streambank erosion and channel incision, increased turbidity, habitat destruction, infrastructure damage, contamination, and overloading combined sewers (Schueler et al. 2009, Booth & Jackson 1997, Walsh et al. 2005, USEPA 2012b). The cost to manage stormwater from a single hectare of impervious surface ranges from ~ $5,000 to ~ $123,000 (Taylor & Wong 2002).

It has been estimated that 13% of rivers, 18% of lakes, and 32% of estuaries in the United States are impaired due to urban stormwater even though urban lands cover only about 3% of the land surface area (The National Academy of Sciences 2008). Stormwater has been shown to contribute many pollutants and adverse effects including metals (Pb, Zn, As, Cd, Cr, Ni, Zn, Hg, and Cu), nutrients (P and N), polycyclic aromatic hydrocarbons (PAH), total organics (pesticides phenols, phthalates, petroleum hydrocarbons) (Lefevre et al. 2012), temperature increases (Jones & Hunt 2010), readily soluble salts (Washington Department of Ecology 2012b, Lee et al. 2002, Göbel et al. 2008), and increased biological oxygen demand (BOD). A literature review has detailed the findings of many researchers who describe an increase in peak volumes, a decrease in the time of concentration of runoff to receiving waters, and a decrease in groundwater recharge with increased impervious area, contributing to a decline in ecosystem-level responses such as resilience (Shuster et al. 2005). However, the authors emphasize that a single impervious cover threshold cannot be easily obtained and should be site specific.

Impervious surface coverage from 12 to 20% has been shown to be detrimental to key macroinvertebrates from the Shannon diversity index (Ephemeroptera, Plecoptera, and Trichoptera) (Stepenuck et al. 2003). As little as 8% development showed negative impacts to amphibians, and an increase in invasive fish species that became more pronounced at 10 – 15% development (Riley et al. 2005). Various native fish species have shown declines above 10% impervious surface (Wang et al. 2001). Previous research has shown that areas with as little as 10% impervious surfaces or a large amount of effective impervious surface can have negative impacts on salmon populations (Schueler et al. 2009, Booth & Jackson 1997).

Two Federal Acts are generally related to stormwater management: The Federal Clean Water Act and The Water Pollution Control Act, although the Safe Drinking Water Act and Endangered Species Act may also play a role (Washington Department of Ecology 2012b). In the United States, urban stormwater is regulated as point source pollution through the United States Environmental Protection Agency (US EPA) National Pollutant Discharge Elimination System (NPDES) and enforcement is implemented by the states. Phase I of the program was issued in 1990 for Municipal Separate Storm Sewer Systems (MS4s) and requires medium and large cities to prevent harmful pollutants from being washed or dumped into MS4s under an individual permit. Phase II of the program came into effect in 1999 to regulate small urbanized areas under a general permit. This requires small to medium-sized municipalities to implement six minimum control measures: 1. Public education and outreach, 2. Public involvement and participation, 3. Illicit discharge elimination, 4. Construction site stormwater runoff control, 5. Post-construction stormwater management in new development and redevelopment, and 6. Pollution prevention / good housekeeping for municipal operations (EPA 833-F-00-002, 2005).

1.1 Stormwater Mitigation

Methods of mitigating the damaging effects of stormwater have typically used structural "end-of-pipe" designs that convey water off-site as quickly as possible directly to streams and rivers, into large stormwater management basins, or combined sewers where they flow into a wastewater treatment plant. Ponds have been the most common technique for treating stormwater. Wet ponds are designed to store stormwater, reduce peak flows, provide sedimentation, and provide some biological uptake. While they are reliable and can also provide some aesthetic and recreational value, they require large amounts of land (typically >5 ha), can increase water temperatures (Jones & Hunt 2010), may lead to mosquito habitat (Hunt et al. 2006), usually do not provide infiltration, and may be less suited to redevelopment. Dry ponds also provide for storage, help reduce peak flows, and facilitate sedimentation. They have less effect on temperatures as they are designed for infiltration and may be better suited to retrofitting from existing detention basins as they provide better groundwater recharge and pollution removal. Constructed wetlands provide many of the same benefits but require more land than wet ponds due to their shallow depths and typically do not have as great a storage capacity. Yet they can provide a great deal of habitat and can facilitate the biological uptake of contaminants. However, they may also increase water temperatures and provide mosquito habitat. Tank and tunnel systems or exfiltration trenches are used for both storage and water quality improvement using underground storage tanks that allow settling of sediments and conveyance of the less turbid water. The materials in the tanks must then be removed and treated. Exfiltration devices have the potential to contaminate groundwater. Sand filters can be placed either above or below ground usually as part of a treatment system that may direct the filtered water to an infiltration trench. Vortex treatment devices are high-flow chambers that settle particles and separate solids and floatables through an outlet pipe. Excess flows remove the solids and allow water to be conveyed to the receiving waters. Underground Oil and Grit separators or hydrodynamic separators capture sediment and trap hydrocarbons by skimming. Screens can also be installed upstream of storage and treatment facilities to remove floatable materials (Federation of Canadian Municpalities and National Research Council 2005). An Underground Injection Control (UIC) or a Class V injection well delivers water to the subsoil through slow filtration, though these have the potential for contaminating aquifers or drinking water wells (USEPA 2013b). Many of these techniques are costly and some do not provide on-site reduction, retention and infiltration of stormwater.

Stormwater Control Measures (SCMs) [also known as non-structural stormwater quality management measures or Best Management Practices, (BMPs)] are intended to minimize stormwater pollution and/or reduce volume using more flexible practices (Taylor & Fletcher 2007). Town and city planners can focus on education programs designed to change behaviors that may be damaging local waterways (such as over-application of fertilizer) (Taylor & Wong 2002). Sensitive or critical areas can be identified and set aside for non-development. Areas can also be revegetated or reforested. Building and development practices that focus on clustering and minimizing impervious surfaces maintain undisturbed areas thus reducing additional stormwater problems. Minimizing the disturbed area, avoiding soil compaction, and using erosion and sediment control on construction sites can substantially decrease pollutants in runoff (Taylor & Wong 2002). Street sweeping can remove potential pollutants before they enter treatment systems or waterways (Pennsylvania_DEP 2006).

1.2 Low Impact Development (LID)

LID [also known as sustainable urban drainage systems (SUDS) in the United Kingdom, water sensitive urban design or (WSUD) in Australia, green stormwater infrastructure (GSI) in Seattle, WA, and "onsite stormwater management" in previous documents published by the Washington State Department of Ecology] is a management approach to development (or re-development) that seeks to minimize stormwater as a waste product and manage it as close to the source as possible. It incorporates various designs that preserve the natural setting or landscape and minimize the effects of impervious surfaces. Tree box or planter box filters can be constructed over impervious surfaces or impervious surfaces can be removed below them to facilitate infiltration. Rain gardens are larger areas that provide aesthetic enhancement as well as the ability to retain contaminants. Vegetated Filter Strips (VFS) are used in narrow areas to treat sheet flow from adjacent areas such as parking lots. Bioretention structures are specifically designed for contaminant treatment. Green roofs do not generally treat contaminants but help to attenuate peak flows by temporarily retaining precipitation and through evapotranspiration. Permeable pavements and sidewalks allow for direct infiltration through the materials but must be maintained to prevent clogging. Soil amendments help to break compaction or heavy clay soils and increase infiltration. Rain barrels and cisterns are both appropriate for roof collection to attenuate peak-flows and allow for the reuse of the captured stormwater (USEPA 2012).

1.3 Bioretention

The focus of this project is on bioretention - a relatively new SCM; one of the earliest guidance documents was in the 1993 Bioretention Manual for Prince George's County, Maryland. Bioretention structures have various designs but can be thought of as shallow areas for water storage, treatment or conveyance. They contain a matrix of soils with mulch and drainage layers as well as plants. As a storage structure, they can temporarily absorb stormwater volumes that tend to peak from impervious surfaces and release them more gradually through exfiltration as well as evapotranspiration. These structures may or may not be intended for conveyance depending on the addition of subsurface drainage (Washington Department of Ecology 2012b). If native sub-surface soils are not adequately porous, drains can be installed, but if native soil infiltration rates are sufficiently high, water will percolate down through the matrix and into the soil. Bioretention structures therefore act as "filters" of stormwater before it reaches natural surface waters or groundwaters and are referred to as "biofiltration" structures. Systems are designed to be porous with a high concentration of sand-sized particles to allow for high flow and infiltration while minimizing clogging. In terms of texture, loamy sand to sandy loam is thought to be optimal for conveyance and sequestration of pollutants (Washington Department of Ecology 2012b) (Thompson et al. 2008). Organic matter (often composted fine material) can be incorporated into the sand matrix for its potential binding capabilities or other positive benefits. Sand-sized (or smaller) particles will help to bind metals especially when pH or soil organic matter (SOM) are low or SOM is saturated by metals (Weng et al. 2001). Biofiltration structures can be appropriately sized to treat a given volume of water. Like other filters, these structures will become "saturated" over time. Depending on the type of constituents removed from the stormwater, the media may need to be treated as a waste product and disposed of accordingly.

Apart from mitigating the stormwater surge, bioretention has been shown to decrease total suspended solids (TSS) (Trowsdale & Simcock 2011). Studies from the University of Maryland have found that particles larger than 1 µm will be filtered under typical conditions (50 mm hr^{-1} precipitation) (Li et al. 2009).

If the system is designed with internal water storage, the ability to remove total N has been shown. The installation of an upturned pipe (versus an elevated pipe) in the outlet can force a ponding depth to increase denitrification as well as assuring that waters that have had the longest residence times are forced out as new waters enter (Brown et al. 2011). Total P can be mitigated by adsorption to soil particles. Both N and P can also accumulate in vegetation and be mitigated if this vegetation is regularly harvested. Media selection should be done carefully to ensure that the initial conditions do not provide a source for either N or P. Though not much research has been done to establish the effectiveness of bioretention on hydrocarbons, there is some evidence of efficacy (DiBlasi et al. 2009). Also there is some evidence that pathogens can be somewhat (though not substantially) decreased by bacterial and protozoal mechanisms. Most evidence shows that bioretention is not effective for removing chloride.

Ultimately, the performance of SCMs should be tied to receiving water health (Winston, Hunt 2007). Tools such as the Relative Risk Model (RRM) that utilize Bayesian networks have been implemented to evaluate the effectiveness of SCMs on a regional level (Hines & Landis 2014). In this study, the authors noted that areas of the Pacific Northwest with the highest amount of development (more urbanized) had the highest risks to prespawning mortality (PSM) in salmonids but that LID could decrease the overall risks if implemented on a large scale.

The mechanism of bioretention treatment for dissolved metals is sequestration in the bioretention soil media (BSM) and modification of chemical speciation in water exfiltrating from the structure. For copper laden stormwater, it has been recommended that BSM be replaced after 2 or 3 years based on ecotoxicological values (Göbel et al. 2008), but other research has estimated BSM lifespans of 15 years (Davis et al. 2003) with Cu influent concentrations of 5 $\mu g\ L^{-1}$. Li and Davis found that most of the metals studied (Cu, Pb and Zn) were captured by organic components in the top surface of the media, though Cu had greater mobility than Pb or Zn due to its higher K_d (distribution coefficient) values. Lifespan can be increased by removing and disposing of the top layer (0 – 10 cm) of media (Li & Davis 2008). However the authors indicated that there exists the potential for Cu desorption from the lower layers. Lifespans of bioretention systems have also been estimated based on infiltration rate. Systems receiving city street and roof runoff were projected to last ~25 years (Paus et al. 2013).

A risk evaluation from 30 U.S. states was compiled that found the average representative regulatory limit for copper in soils to be 3,700 $mg\ kg^{-1}$ based on child soil exposure at home (Li & Davis 2008), however there are variations by several orders of magnitude with minimum and maximum values of 25 and 20,000 mg kg^{-1} respectively (Petersen et al. 2006). The Agency for Toxic Substances and Disease Registry (ATSDR) Cu levels for soil remediation were 2,800 mg kg^{-1} for residential and 63,000 mg kg^{-1} for non-residential/commercial based on the State of Arizona's limits (ATSDR 2004).

1.3.1 Design considerations

For bioretention SCM's such as rain gardens, pretreatment forebays can be constructed to remove coarse particles, debris and trash. If placed inside the cells, it is recommended they be lined, but if outside of the cells, unlined where they can become part of the infiltration system (Hunt & Lord 2004, Washington Department of Ecology 2012b). Pretreatment can also be done by a swale in an entry way, or by a vegetated filter strip, or a long, shallow, narrow gravel dissipation and infiltration structure known as a verge as on the edge of a parking lot or other impervious surface (Davis et al. 2009).

Biofiltration swales are commonly constructed alongside roadways or parking lots where long and narrow strips are most appropriate. They are meant to convey water when maximum ponding depth (15 – 30 cm) is exceeded. Most often they will support a vegetation of low grasses that can withstand flows and higher amounts of sediments (Washington Department of Ecology 2012b). Bioretention planter boxes are designed for a greater variety of plants and usually include an under-drain. They are typically deeper than swales and may be more appropriate for an urban setting such as near a building or on top of a sidewalk or street where spatial constraints are an issue. However they can also be constructed over native soils so to eliminate the need for an outflow if infiltration rates are high enough and groundwater contamination is not a concern (Athanasiadis et al. 2007).

Maintaining vegetation in bioretention systems helps to maintain porosity of the soils, penetrate confining layers, and increase evapotranspiration (Bartens et al. 2008). Some organic pollutants can also be transformed through plant root interactions (Lucas & Greenway 2009). Plants in bioretention systems have been shown to accumulate metals (0.5% - 3.3% of influent metals in a 230 d trial) and therefore must have substantial biomass to be used as a tool to prolong the lifespan of the media (Sun & Davis 2006). The use of hyper-accumulator plants enhanced with chelating agents has been suggested as a way to increase uptake of metals under high metal loading conditions (Salt et al. 1998) but this vegetation must be harvested and treated as a waste product.

There are many possible configurations for bioretention structures and a design should be constructed to treat the issues and contaminants of concern. A generalized design may feature a bowl that has been dug with the teeth of an excavator for the last part of subsoil roughening. It should contain 15 – 18 cm of gravel as the base layer with 90 cm of sandy loam and organic media preferred (60 cm minimum; marginal returns diminish after 120 cm). The top layer should be mulched inside of a 45 cm bowl depth (60 cm maximum; as little as 15 cm for small systems) as described in (Hunt & Lord 2004). There have been proposals to limit the number of rain events producing overflow to 10% of total rain events in the design criteria (Walsh et al. 2005). The Stormwater Management Manual for Western Washington (SWMMWW) (Washington Department of Ecology 2012b) Table 9.4.1 recommends a hydraulic residence time for swales at 9 minutes and swales should be sized with that goal in mind. In 2002 the capital cost estimate for grass swale construction was \$4.13 m^{-2} to \$8.75 m^{-2} and maintenance costs would be from 5% to 7% of the construction cost (Taylor & Wong 2002).

2. COPPER

2.1 Copper in the Environment

The use of copper dates back more than 10,000 years and it is one of the oldest metals in use. The word copper comes from *cypirum*, meaning “from the island of Cyprus.” Over 400 copper alloys are in use today to manufacture products for automobiles, appliances, electronics and communication, and a great range of other products (ICSG 2013). Building construction accounts for about 30% of the use of copper (ICSG 2013). Behind iron and aluminum, copper is the third most mined metal worldwide (Vale.com 2014).

Copper is a common element found throughout the biosphere. At low concentrations, it is an essential element for life. At high concentrations, it can be toxic to humans; at concentrations below that threshold it can be detrimental to sensitive aquatic life affecting growth, reproduction and survivability (Boulanger and Nikolaidis, 2003). The most toxic form of copper is the free-metal ion (Cu^{2+}) or cupric form (Wallinder & Leygraf 1997). When hydrated or dissolved in water it is represented as $Cu(H_2O)_6^{2+}$.

As of September 2014, the United States Environmental Protection Agency (US EPA) reports that 731 waterway segments of the United Sates are impaired with copper (US EPA, 2014). Copper can be toxic to sensitive organisms in the low µg L^{-1} (ppb) range (Bertling et al. 2006).

Copper enters the environment from architectural materials, automobile brake pads and fluids, coinage, fertilizers, copper-based pesticides, mining, municipal sewage plants, waste dumps, agricultural feedlot additives, sewage sludge applications, and other means (Berbee et al. 2014, Bertling, et al., 2006, Boulanger 2003). Copper is present in rainfall and as airborne particulates and has been estimated to deposit as much as 728 µg m^{-2} yr^{-1} as dry deposition and 130 µg m^{-2} yr^{-1} as wet deposition (Barron 2006). Barron's (2006) evaluation for the 15,000 ha service area of the Palo Alto Regional Water Quality Control Plant estimated that 136 kg yr^{-1} of dissolved architectural Cu was released at the source where there were 70 local homes and 100 large structures with copper roofs, 220 structures with copper gutters and downspouts, and 40 homes with copper containing algae-resistant singles (Barron 2006). A study in Texas of four different roofing materials (wood shingle, composition shingle, aluminum, and galvanized iron) obtained mean Cu concentrations of 29, 25, 26, and 28 µg L^{-1} in runoff respectively. However the study also found 43 µg L^{-1} in the direct rainwater which was an unusually high value. The authors noted that these values would have exceeded EPA freshwater standards more than 60% of the time (Chang et al. 2004). Usually, the concentration of Cu in rainwater is in the low, single digit ppb range (Pennington & Webster-Brown 2008, Chang et al. 2004, ATSDR 2004).

Both fresh and saltwater copper criteria are pursuant to section 304(a) of the Clean Water Act. Fresh water limits are derived using site specific water chemistry through the biotic ligand model and/or the hardness equation (details below). Therefore standards are set accordingly to individual water body segments (USEPA 2007a). Current salt water standards are set at 3.1 mg L^{-1} (3,100 µg L^{-1}) for the criterion continuous concentration (CCC) and 4.8 mg L^{-1} for the criterion maximum concentration (CMC) but allowance for the water effect ratio (WER – the ratio of the toxicity of metal in a site water to the toxicity of the same metal in standard laboratory water) in waters with high dissolved organic carbon (DOC) is permitted (USEPA 2014).

2.2 Copper Roofing Materials

Copper roofs have been used for centuries in various parts of the world. They are considered long lasting and require little maintenance. The copper that is made into roofing material is primarily pure copper (cold rolled 1/8" hard temper is 99.9% copper) (copper.org 2013). As it ages and is exposed to normal atmospheric conditions, it undergoes chemical changes that eventually form a greenish patina. The process starts by formation of copper oxides such as cuprite (Cu_2O) then later transitions to copper hydroxysulfates such as brochantite [$Cu_4SO_4(OH)_6$] and posjnakite [$Cu_4SO_4(OH)6{\cdot}H2O$], and also strandbergite [$Cu_{2.5}SO_4(OH)_3{\cdot}2H_2O$], langite [$Cu_4SO_4(OH)6{\cdot}H2O$], and antlerite [$Cu_3SO_4(OH)_4$] (Wallinder et al. 2007, Kratschmer 2002). Near marine environments there may be enough chloride present in air to cause formation of the copper chloride atacamite [$Cu_2Cl(OH)_3$] (Graedel 1987, He et al. 2001). These later conditions result in a roof texture with very high surface area and potential for flaking.

2.3 Stormwater Issues with Copper

Copper from copper roofs may be responsible for as much as 4 to 20% of the copper in stormwater (Arnold 2005) though there is tremendous variation due to factors such as precipitation rate, pH, roof angle, and dry deposition. Also important is not just the runoff rate or concentration from the roof itself, but what kind of attenuation processes take place between the roof outlet and the receiving water (Hedberg et al. 2014).

In freshwater systems, naturally occurring copper can vary between 0.2 and 30 µg L^{-1} (Bowen 1985). New roofs have been demonstrated to have 1000 to 14,000 µg L^{-1} of total Cu in runoff (Bertling, et al. 2006, and references therein) compared to some non-copper roof runoff concentrations such as 7.6 and 12.7 µg L^{-1} for tar felt and asbestos cement, respectively (Quek & Forster 2000). Algae-resistant asphalt roofing materials partly comprised of copper granules have been used for several decades (Jacobs & Thakur 1999). Their prevalence was estimated to be at 0.03% of home roof areas in one local study in the Palo Alto, CA area (Barron 2006). A more recent study (Velleux et al. 2012) estimated that 40% of homes would have algae-resistant shingles and found an expected Cu release rate of 160 µg L^{-1} at the shingle surface during rainfall.

States such as Washington and Oregon are seeking ways to mitigate potential harmful effects of diffuse and nonpoint sources of copper. Research in the Puget Sound Basin indicated that roofing materials account for 11% of copper releases (Ecology and King County 2011). By comparison, urban pesticides are listed as 29%, agricultural pesticides at 4%, plumbing as 16%, brake pad wear at 15%, and Army base sources at 10%. Other sources, including anti-fouling paint make up the remaining 15% (Ecology and King County 2011). In 2010, Washington State passed a law restricting and phasing out the use of copper in brake pads as a way to ameliorate copper pollution to waterways (Washington Department of Ecology 2012a).

Salmonids are a very important part of the economy, history and tradition of the Pacific Northwest but their numbers have been declining dramatically since the mid-19th Century and by 1933 they were estimated to be at about 1/5 of their previous levels (Lackey 2003). Salmon are anadromous fish that travel upstream to spawning grounds from the ocean. Some important salmonoids in the Pacific Northwest region include the spring and fall Chinook *(Oncorhynchus tshawytscha)*, summer and winter steelhead *(Oncorhynchus mykiss)* and Coho salmon *(Oncorhynchus kisutch)* (Helvoigt & Charlton 2009). They have been shown to be sensitive to copper in the low µg L^{-1} range. Thus regulators have paid particular attention to increased levels of copper in waterways where such sensitive species are of concern.

The revised Western Washington Stormwater Manual, released in 2012, documents details related to various Stormwater Control Measures (SCMs). This research was designed with these SCMs in mind, and to conform to the water quality requirements for the State of Washington.

2.4 Stormwater Contributions from Copper Roofing Materials

Previous research has shown that the initial concentrations of copper from copper roof effluent are highest during the first part of the storm due to varying environmental conditions (Athanasiadis et al. 2010). This first-flush effect is a product of local environmental conditions such as precipitation volume, pH and storm intensity as well as the porosity of the metal surfaces and how the length of the antecedent dry period (ADP) will permit corrosion products to be dissolved and re-precipitated (He et al. 2001). Precipitation volume is thought to be the most important factor in predicting the runoff quantity of copper.

The concentration of copper in copper roof runoff varies considerably. In terms of mass, average runoff contributions from copper roofing materials in the United States are estimated at about 2.12 g Cu m-2 yr-1 (Arnold 2005). Some research in Europe has found that copper roofs contribute from 1.0 to 3.9 g m-2 yr-1 (Athanasiadis et al. 2010) though some rates as high as 8.6 g Cu m-2 yr-1 were noted in Singapore for a patinated roof (Wallinder et al. 2007). Copper roofs in urban settings have shown runoff copper quantities and concentrations twice as high as rural settings (1.2 and 0.7 g Cu m^{-2} respectively); this has been attributed to increased deposition rates of corrosive species such as SO_2, NO_x, HCl, and aerosol particles. Marine settings have been even higher than urban settings (1.7 g Cu m^{-2}) attributed to increased Cl^- (He et al. 2001). He et al. (2001) also showed that decreasing pH increased Cu concentrations in runoff but it should be noted that they used artificial rainwater with a comparatively low pH (3.8, 4.3, and 4.8). Wallinder et al. (2007) and references therein, reported that the annual runoff rate for naturally patinated copper sheets in the Washington DC area was observed to be 3.3 g m^{-2} yr^{-1}. For the inland cities of Albany and the coastal city of Newport, OR, the rates were observed to be 1.7 g m^{-2} yr^{-1} even though annual precipitation is 1084 and 1822 mm yr^{-1} respectively.

Most research has found that Cu corrosion rates are highest in new copper with 70 to 90% of Cu leaving as the hydrated cupric ion $Cu_2(OH)_2^{2+}$ (Wallinder & Leygraf 2001). Aging copper roofs have been shown to affect the species of copper from cuprite [Cu_2O] in copper aged < 40 years to brochantite [$Cu_4SO_4(OH)_6$] in roofs > 40 years. Surface porosity also increases from 10% with 40 year old copper roofs to 25% for roofs aged 100 years (He et al. 2001).

Roof orientation may play a minor role in corrosion rates as north facing slopes may have a lesser drying period, however seasonal variation has not produced a significant effect unless related to precipitation volumes (Wallinder et al. 2000). The slope of the roof is an important factor since lower slopes increase contact time with stormwater (Wallinder et al. 2000).

An empirical model was developed (Wallinder et al. 2007) as a tool for estimating copper runoff from roofs under varying conditions. The model was derived using the observed runoff rate of copper roofs from 28 locations in Sweden, Switzerland, the USA, Singapore, and France where precipitation varied from 396 to 3,203 mm yr^{-1}; pH varied from 3.9 to 6.1; and SO_2 varied from an estimated 0.5 to 27 µg m^{-3}. Observed copper runoff rates used to derive the model ranged from 0.72 to 8.6 g m^{-2} yr^{-1}, with 19 of those values less than 2 g m^2 yr^{-1}. The model uses SO_2 (in ppb), precipitation (in mm), pH and roof inclination (θ) as input parameters to predict the release rate in g $m^{-2}yr^{-1}$ and is given as:

$$R = (0.37\,SO_2^{0.5} + 0.96\,rain10^{-0.62pH})\left(\frac{\cos(\theta)}{\cos(45°)}\right)$$

When the model was applied to European maps of rainfall pH, rainfall quantity, and SO_2 concentration, it predicted Cu runoff rates that varied between near zero to 3.0 g m^{-2} yr^{-1} with most predictions below 2 g m^{-2} yr^{-1} for the year 2000. If SO_2, precipitation, and pH are within certain parameters corresponding to greater weathering rates, the model could imply that the decision to install copper roofs in certain regions should include mitigation plans.

2.5 Copper Pollution Prevention

Research has shown that bioretention as a LID technique can be effective at treating many pollutants in stormwater including >92% of metals (Davis et al. 2001) though the researchers used relatively low concentrations of Cu (80 µg L^{-1} – more appropriate for urban street runoff) and slow infiltration rates (1 to 2 cm hr^{-1}) for the planter box. A literature review for pollution prevention SCMs reported that maintenance and cleaning of coarse sediments and litter in stormwater drainage in the San Francisco region could decrease annual copper loads to waterways by at least 3-4% (Taylor & Wong 2002), and that street sweeping could remove from 14% to 47% of metals dependent on particle size, timing and frequency of mechanical sweeping. Taylor and Wong (2002) also reviewed a comprehensive stormwater management program in Tulsa, Oklahoma that reduced Cu event mean concentrations by 56%.

Various materials have been examined and utilized for their ability to sequester metals in secondary treatment of stormwater. Previous research has shown the potential of using stormwater attenuation practices for copper roofs such as filtration tanks with zeolite, porous concrete with iron hydroxides, and commercial infiltration systems with removal rates greater than 90% of total Cu (Athanasiadis, et al, 2006; Athanasiadis, et al, 2007). Limestone has achieved retention of copper at lower (5-47%) rates (Bertling, et al, 2006). Trenches filled with granular iron hydroxide (GEH®) and calcium carbonate achieved removal efficiency of over 90% (Boller & Steiner 2002). One study examined 11 materials and found that among other metals, they adsorbed Cu in the following order: bauxsol-coated sand (BCS) > activated bauxsol-coated sand (ABCS) > fly ash (FA) > granulated activated carbon (GAC) > Alumina > granulated ferric hydroxide (GFH) > Spinel ($MgAl_2O_4$) > natural zeolite (NZ) > Sand > iron oxide-coated sand (IOCS) > bark with binding affinities (K_d) by Freundlich isotherms represented in that same order (Genç-Fuhrman et al. 2007).

Other methods of ameliorating copper runoff have been tried and tested on a limited basis such as clear coating copper roofs using a blend of polymer based resins that prevent corrosion and block UV light as a method of preventing corrosion and runoff from copper roofs (Everbritecoating.com n.d.) (Barron 2006). Neither the efficacy nor the durability of clear coating is well understood at this point but has been estimated to lessen Cu releases by 75% or more. However, they probably need to be reapplied about once per year (Barron 2006, copper.org n.d.). Runoff can also simply be diverted to already vegetated areas that could adsorb dissolved copper.

3. TOXICITY

As environmental conditions change, geochemical metal speciation as an equilibrium process will change dynamically. These conditions will determine the toxicity of metals in the environment. The presence or lack of ligands will ultimately be the most easily effective means of either immobilizing metals or making them less bioavailable to sensitive aquatic organisms (Rachou et al. 2007).

The biological receptor for metal toxicity is referred to as the biotic ligand. For aquatic organisms, biotic ligands are active ion uptake pathways (such as Na^+ and Ca^{2+} transporters) with an affinity (log K) and capacity B_{max} that can be quantified in 3 to 24 hour *in vivo* gill binding tests. A higher log K is correlated to greater toxicity of the particular metal (Niyogi & Wood 2004). The receptor binding affinities of metals such as Cu^{2+}, Ag^+, Cd^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+} are typically much higher than those of environmental cations such as Ca^{2+}, Mg^{2+}, and Na^+. Niyogi & Wood (2004), and references therein, reported log K of 7.4-8.0 affinity for Cu^+ [Cu^{2+} is apparently reduced to Cu^+ and generally crosses gills in the monovalent form (Campbell et al. 1999, Handy et al. 2002)] to Na^+ transport sites (the biotic ligand) where for Ca^{2+}, Mg^{2+} and Na^+, the log K constants were 2.3-3.6, 3.6, and 2.3-3.2, respectively. The main effect of Cu in fish is the alteration of Na homeostasis. At low Cu concentrations (~ 0.2 to 3.2 µg L^{-1}) there is an inhibition of Na^+ and Cl^- influx and a stimulation of Na^+, K^+ and Cl^- efflux (Meyer et al. 2007, and references therein). The LA_{50} (Lethal Accumulation – the short-term gill metal burden that is predictive of 50% mortality at 96 + hours) is generally predictive of the 96 hour LC_{50} (Lethal Concentration – concentration that causes 50% mortality) for fish and 48 hours for daphnids (Niyogi & Wood 2004). Juvenile fish are more sensitive to Cu toxicity (Welsh et al. 1996) and Na losses to rainbow trout fry have been reported to have high mortality rates due to decreased Ca deposition in the vertebrae when exposed to Cu. They also have exhibited disruptions to predator avoidance behaviors and effects on growth rate (Hecht et al. 2007, Hansen et al. 1999).

3.1 Factors Affecting Copper Toxicity in Aquatic Organisms

The effect of pH on metal toxicity can vary and appear inconsistent even though toxicity usually increases as pH decreases since metals begin to form complexes with CO_3^{2-}, HCO_3^-, and OH^- at higher pH. However at low pH, H^+ ions can become more available to compete with metal (M^+) ions and at the same time metal-ligand complexes tend to dissociate at low pH. With a pH less than 4 to 4.5, H^+ can be present in toxic concentrations to make metals appear more toxic as pH decreases but there is a point at which the toxicity is due to H^+ ions and not the metal. In the acidic range less than 6 to 7, the toxicity of metals increases as pH increases since H^+ is less available to compete with M^+ for binding sites on the biotic ligand (Meyer et al. 2007). Working with various metals at low pH from mine runoff, one study found that decreasing pH from 4 to 3 in varying concentrations of copper (and other metals) had no statistically significant effect on the more metal tolerant Alderfly larvae (*Sialis spp.*) because of synergistic sublethal effects; this effect varies among different taxa (Last et al. 2002, Fulton & Meyer 2014). Cu toxicity is greatest at pH ~ 6 and decreases as pH increases in intermediate to high alkalinity waters, but toxicity only decreases above pH ~ 7 in low alkalinity waters (Meyer et al. 2007).

The effects of interacting metals and pH are highly complex. Toxicity to *D. magna* and fish by Cu, Cd and Zn can be decreased by acidity from pH 4 to 3 (Last et al. 2002 and references therein). The authors examined low pH mine drainage and alderfly and noted that Cu uptake occurs via both food and water for some taxa. Active transport of Cu and Zn across membranes is carrier-mediated as they are essential nutrients in trace amounts and in cytosol they are bound to metal-transporting proteins (metallothioneins). These proteins are inducible and appear to be an important mechanism of tolerance to some metals. The ability to sequester metals in intracellular granules also appears to be important for tolerance to Cu, Zn, Mn and Fe in several terrestrial insects (Landis et al. 1991). Tolerance to copper has been shown in *D. magna* over three generations up to 35 µg L^{-1} under environmentally relevant concentrations (5 mg L^{-1} DOC). Optimal copper concentration for *D. magna* were reported to vary from 1 to 35 µg L^{-1} depending on the conditioning of the test organisms and levels of DOC (Bossuyt & Janssen 2003).

Hardness (the sum of the equivalents of the divalent cations in solution) is usually dominated by Ca^{2+} and Mg^{2+} in freshwater. Both of these nutrients can be outcompeted by metal ions preferentially attached to gill surfaces, but passive body anion loss can follow if Ca^{2+} concentrations are low (Meyer et al. 2007). Ca^{2+} and Na^{2+} can compete directly with Cu^{2+} at biotic ligand sites and have a direct effect on toxicity. Alkalinity (the capacity to buffer the addition of acid to a solution) is usually dominated by HCO_3^-,

CO_3^{2-}, and OH^- and usually covaries with pH. Though these ions usually do not interact directly with fish gills, changes in alkalinity will affect metal speciation and thus the free metal concentration.

Dissolved organic matter (DOM) is a wide group of organic substances. In freshwater systems, the forms are usually the plant-derived polydentate humic and fulvic acids that bind free metal ions to functional groups such as hydroxyls and carboxylates, and are protective against metal toxicity since they are not permeable to membranes (Meyer et al. 2007). Up to 98% of Cu in circumneutral solutions has been reported to be complexed with DOM (Rachou et al. 2007). DOC is a term used to describe a large and heterogeneous group of organic molecules that are generally important for protection against metal toxicity and can act as a surrogate for DOM (Welsh et al. 1996). DOC has been found to be protective of Cu toxicity to *Daphnia magna* in a range of sources and concentrations from 0.9 – 22 mg L^{-1} (Kramer et al. 2004). If the DOC type is membrane-impermeable it can complex some of the free Cu provided that the binding affinity is higher for the DOC than for the gill and thereby decrease toxicity (Meyer et al. 2007). DOC is thought to bind Cu more strongly than other metals and may be especially important in sandy soils such as those used in bioretention (Weng et al. 2001). Using a Langmuir-Freundlich model Bertling et al. (2006) described the sequestering of leached hydrated Cu by DOC in soils. In their column experiment the authors found that retention was highest with an organic carbon content of 5.1% and pH of ~ 6. Furthermore they predicted that the time needed for Cu in runoff water to reach a depth of 50 cm varied between 170 and 8,000 years. For bioretention however, if the subground has a high permeability or is close to the saturation zone it is highly advisable to divert waters to a treatment facility (Göbel et al. 2008).

Concern has arisen over the effects of low concentrations of Cu on the olfactory responses of fish and invertebrates and in the Pacific Northwest, this particular response is driving regulatory concerns for Cu in stormwater. Concentrations of Cu in the single digit µg L^{-1} can cause avoidance to Cu-containing water when their olfactory system is not impaired, or when olfaction is impaired to lose important functions such as attraction to food and reproductive pheromones, and avoidance of predators (Hansen et al. 1999, McIntyre et al. 2012). Meyer & Adams (2010) and references therein, compared electro-olfactogram (EOG) responses to biotic ligand model (BLM) -based and hardness-based criteria for three salmonid fish and the fathead minnow (*Pimephales promelas*) and found 50% avoidance-based inhibitory concentrations (IC_{50}s) of 2.1 and 2.5 µg L^{-1} for rainbow trout and Chinook salmon respectively. However they noted that back-calculated IC_{20} values under their parameterized BLM under natural water conditions were always higher than the EPA's BLM based acute and chronic criteria demonstrating that the EPA acute and chronic criteria were protective for those sublethal endpoints (though hardness-based criteria were not).

Cu can affect the neurophysiological responses in fish by altering membrane potentials in the olfactory rosette resulting in an alteration to avoidance response to high Cu concentrations (Meyer et al. 2007). Short-term increases in ambient Cu concentrations (<3 µg L^{-1} for less than a week) have been reported to impair chemosensory systems in salmonids to a threshold from which they could not recover (Hecht et al. 2007). The authors also report that exposure times as little as 10 minutes could affect behaviors for hours to weeks depending on concentrations. It has also been demonstrated that with even shorter-term (4 hr) exposures of 3 – 58 μg L^{-1}, *Oncorhynchus keta* could recover within one day (Sandahl et al. 2006).

3.2 Biotic Ligand Model

The BLM is the basis for the EPA's national recommended water quality criteria (WQC) for copper (US EPA, 2007). It has been adopted by various states and is under consideration for adoption by Oregon and Washington for 2015/2016. The BLM is a quantitative model that takes chemical equilibrium, physiological and toxicological processes in to account (Paquin et al. 2002) and allows for the prediction of acute (criterion maximum concentration or CMC) and chronic (criterion continuous concentration or CCC) water quality criteria, and LC_{50} values for several fish and invertebrates.

The BLM calculates water quality criteria for the input water sample data as the predicted final acute value (FAV) (usually the normalized LC_{50} of the 5^{th} percentile most sensitive species of a genus mean acute value) (USEPA 2007b), criterion maximum concentration (CMC) (CMC = FAV/2) and the criterion continuous concentration (CCC) (CCC = CMC/ACR, where the ACR is the acute-to-chronic ratio). It also calculates acute toxic units (TU) as the ratio of Cu in the water to the CMC (TU = Cu/CMC) where TU values greater than 1 indicate a violation of the CMC (Paquin et al. 2005).

Before the development of the BLM, WQC were heavily based on hardness and the total amount of metals, or logarithmic regressions based on experimental LC_{50} data accumulated since the late 1970's; the BLM more fully incorporates influential factors such as pH and DOC and decreases the need for time-consuming site-specific modifications using the water effect ratio (WER) (Niyogi & Wood 2004). The BLM incorporates geochemical speciation algorithms similar to MINEQL and MINTEQA2 and thus calculates the effects of these other parameters and assigns toxicity given an abundance and speciation of the metals in question. It has been referred to as a computational equivalent of WER testing which itself was a site-specific deviation from the hardness equations (Niyogi & Wood 2004).

The BLM is based on the gill surface interaction model (GSIM) (Pagenkopf 1983) and the free ion activity model (FIAM) (Niyogi & Wood 2004, and references therein) and recognizes that toxicity is not entirely based on total aqueous metal concentration. The GSIM accounts for the effects of pH and alkalinity to influence metal speciation as well as the effects of inorganic ions in their ability to complex metals rendering them less bioavailable on the anionic "interaction sites" on gill surfaces while competing with protective cations. Though the focus of the FIAM was algae it recognized the critical importance of DOM and other competing metals in complexation reactions (Di Toro et al. 2001). Versions of chemical equilibria in soils and solutions (CHESS) (Santore & Driscoll 1995) and the Windermere humic aqueous model (WHAM) also provided a detailed model of proton binding and metal cation binding to DOM (Tipping 1993). Free metal ions are good competitors for essential elements required by aquatic organisms such as calcium, magnesium, and sodium that regulate bodily ionic composition. Free metals bind more easily to gill surfaces, and are thereby adsorbed by the organism, or can modify the ability of the organism to regulate the concentration of essential ions. For this reason hardness is an important factor in water quality as a simple quantity of essential and positively charged ions can out-compete metal ions for binding sites on the gill. Ligands in this case are functional groups that potentially bind free metal ions in a complex through the donation of one or more of the ligand's lone pairs of electrons. Ligands are usually negatively charged groups on natural organic matter such as humic and fulvic acids. However sulfides, carbonate, chloride, hydroxide, and ammonia can also serve as ligands. MacRae et al. 1999, state that "measurement of gill copper accumulation is an acceptable alternative for determining a toxicity-based gill copper binding affinity."

The BLM predicts the degree of metal binding at the site of the biotic ligand (Paquin et al. 2002). The BLM describes the relationship between metals, DOC, metal hydroxides and metal chlorides and their interface with gill surfaces. For this reason pH is a very important factor in water quality as more available hydroxide ions will also bind to metal ions making them less available for gill surfaces. Conversely, a greater abundance of hydrogen (H^+) ions will compete with metals for any available ligands thereby releasing more labile metals in the free metal form. DOM is usually also an important binder of metals especially when considering its natural abundance. However, if competing cations such as sodium, potassium, magnesium and calcium are more abundant they can more easily compete with metals for biotic ligands. But at the same time they can compete with metals for other ligands such as DOC. Thus the BLM predicts that given a constant concentration of copper, an increase of ligands, competing cations, and pH should decrease the toxicity of copper by lessening its bioavailability.

The mass balance with the biotic ligand was described by (Di Toro et al. 2001) as:

$$[L_b^-]_T = [L_b^-] + [HL_b] + \sum_{i=1}^{N_{M_i}} [M_i L_b^+]$$

“Where$[L_b^-]_T$ is the total binding site density of the biotic ligand (e.g. nmol of available sites/g of tissue), $[HL_b]$ is the concentration of protonated sites, and $N_{M_i}$is the number of metal complexes $[M_i L_b^+]$, e.g. CuL_b^+, CaL_b^+, etc., that form with the biotic ligand L_b^-.” Thus the BLM is based on the idea that mortality or toxic effects occur at a critical concentration established by the EC50 or LC_{50}. Much of the empirical work for the BLM has been based on Daphnids which generally have a high sensitivity to metals (about 5-10 times more sensitive than fish) probably since they have high surface area-to-volume ratios (Niyogi & Wood 2004). Using the BLM (Hecht et al. 2007, and references therein) found that the CMC range for salmonid impairment could be 0.34 to 3.2 µg L^{-1} compared to the EPA hardness-based criteria of 6.7 µg L^{-1} under the same conditions (pH 6.5 – 7.1; DOC 0.3 – 1.5 mg L^{-1}).

The input range for which the BLM has been calibrated is temperature (10 - 25 ° C); pH (4.9 - 9.2); DOC (0.05 - 29.65 mg L^{-1}); humic acid content (10 - 60%); Ca^{2+} (0.204 - 120.24 mg L^{-1}); Mg^{2+} (0.024 - 51.9 mg L^{-1}); Na^+ (0.16 - 236.9 mg L^{-1}); K^+ (0.039 - 156 mg L^{-1}); sulfate (0.096 - 278.4 mg L^{-1}); chloride (0.32 - 279.72 mg L^{-1}); alkalinity (1.99 - 360 mg L^{-1}); dissolved inorganic carbon (0.056 - 44.92 mmol L^{-1}); sulfide is not currently a calculated input (Paquin et al. 2005).

4. OBJECTIVES

The focus of this research was to quantify the ability of bioretention structures to mitigate the potential impacts of copper in stormwater originating from copper roofing materials. Stormwater sampling provided a means of determining copper quantity in roof runoff and bioretention structure effluent, and consequently the ability of bioretention structures to sequester copper. Biotic ligand modeling was used to provide information about chemical speciation and its relation to toxicity. Toxicity testing served to validate the model and quantify the potential impacts that pre and post-treatment stormwater runoff had on sensitive aquatic life. We hypothesized that the SCMs would decrease copper concentrations, increase copper binding ligands, and decrease toxicity in stormwater as it passed through the structures.

Chapter 2

Attenuation of Copper in Runoff from Copper Roofing Materials by Two Stormwater Control Measures

1. SUMMARY

Within the last 20 years, concerns have been raised by regulators over diffuse and non-point sources of metals including releases from copper roofs during storm events. A partitioned copper roof picnic shelter was constructed at Towson University in Maryland in August of 2012 along with two types of stormwater control measures (SCMs): two bioretention planter boxes and two biofiltration swales, and two roof reference structures (asphalt shingle and Plexiglas) in order to evaluate the ability of the SCMs to attenuate copper in stormwater from the roof. For both systems, copper in storm events was measured both before it entered the SCMs from the roof as influent as well as after it left the SCMs through their underdrains as effluent. The bioretention soil media (BSM) was composed of mineral matter and composted leaf-litter that constituted the primary organic component of the SCMs in the top 46 cm layer of the planter boxes, and mixed into the top 15 cm native soil layer of the swales.

Automated stormwater samples were collected from January 2013 through August 2014. Twenty-six storms totaling 223 samples were collected with flow-weighted composite sampling, and seven storms totaling 316 samples were collected with discrete time-resolved samplers. Lab analyses of stormwaters were performed for total and dissolved Cu, total N and P, and total suspended solids (TSS). Stormwater retention times in the SCMs were estimated using hydrograph analyses. A copper roof weathering

model (Wallinder et al. 2007) was used to calculate expected Cu runoff rates and compared to a copper loading estimation using data obtained from this site.

Total Cu in the influent waters from the roof ranged from 271 – 3192 µg L^{-1} and averaged 1,298 µg L^{-1} for the composite samples. Total Cu in the effluent waters from planter boxes ranged from 25 – 191 µg L^{-1}, with an average of 76 µg L^{-1}. Total Cu in effluent waters from swales ranged from 7 – 59 µg L^{-1} with an average of 29 µg L^{-1}. Attenuation in the planter boxes ranged from 82.6 to 99% with an average of 93% by concentration and in the swales ranged from 93 to 99% with an average of 97%. Several of the discrete samples showed a pronounced first-flush effect of Cu in SCM influent but planter outlets showed a more attenuated effect throughout the storm. Stormwater retention time in the media varied with antecedent conditions, stormwater intensity and volume with median values from 6.6 to 73.5 minutes. The Wallinder model gave an expected runoff value of 1.2 g m^{-2} yr^{-1} using runoff pH and 2.02 g m^{-2} yr^{-1} using the more appropriate precipitation pH. Estimation by loading gave 2.16 g m^{-2} yr^{-1} from the roof.

2. INTRODUCTION

It has been estimated that 13% of rivers, 18% of lakes, and 32% of estuaries in the US are impaired due to urban stormwater even though urban lands only cover only about 3% of the land surface (The National Academy of Sciences 2008). Many researchers have described impacts of urban stormwater including an increase in peak discharge, a decrease in the time of concentration of runoff to receiving waters, and a decrease in groundwater recharge related to increased impervious area, contributing to a decline in ecosystem-level responses such as resilience (Schueler et al. 2009, Shuster et al. 2005). Previous research has also shown that areas with as little as 10% impervious surfaces or a large amount of effective impervious surface can have negative impacts on salmon populations (Schueler et al. 2009, Booth & Jackson 1997). Methods of mitigating these damages have typically used structural "end-of-pipe" designs that convey water off-site as quickly as possible either directly to streams and rivers, into large stormwater management basins, or combined sewers where they flow into a wastewater treatment plant.

Stormwater control measures (SCMs) [also known as best management practices, (BMPs)] are intended to minimize stormwater pollution and/or reduce volume using flexible practices (Taylor & Fletcher 2007). Low impact development (LID) is a management approach to development (or re-development) that seeks to minimize stormwater as a waste product and incorporates various designs that preserve the natural setting or landscape and minimize the effects of impervious surfaces. Bioretention is a relatively new SCM that can have various designs but can be thought of as shallow areas for water storage, treatment or conveyance that contain a matrix of soils with mulch and drainage layers as well as plants. As a storage structure, they can temporarily absorb stormwater volumes that tend to peak from impervious surfaces and release them through exfiltration as well as evapotranspiration. These structures may or may not be intended for conveyance depending on the addition of subsurface drainage (Washington Department of Ecology 2012b). If native sub-surface soils are not adequately porous, drains can be installed, but if native soil infiltration rates are sufficiently high, water will percolate down through the matrix and into the soil. In this way, bioretention structures act as "filters" of stormwater before it reaches natural surface or groundwaters and are referred to as "biofiltration." Systems are designed to be porous with a high concentration of sand-sized particles to allow for increased flow and infiltration while minimizing clogging. In terms of texture, loamy sand to sandy loam is thought to be optimal for conveyance and sequestration (Washington Department of Ecology 2012b) (Thompson et al. 2008). Organic matter can be incorporated into the sand matrix for its potential binding capabilities or other positive benefits. Sand-sized (or smaller) particles will help to bind metals especially when pH or soil organic matter (SOM) are low or SOM is saturated by metals (Weng et al. 2001).

Biofiltration swales are commonly constructed alongside roadways or parking lots where long and narrow strips are most appropriate. They are meant to convey water when maximum ponding depth (15 – 30 cm) is exceeded. Most often they will support a vegetation of low grasses that can withstand flows of higher amounts of sediments (Washington Department of Ecology 2012b). Bioretention planter boxes are designed for a greater variety of plants and usually include an under-drain. They are typically deeper than swales and may be more appropriate for an urban setting such as near a building or on top of a sidewalk or street where spatial constraints are an issue. Maintaining vegetation in bioretention systems helps to maintain porosity of the soils and penetrate confining layers as well as increase evapotranspiration (Bartens et al. 2008). Ultimately, the performance of SCMs should be tied to receiving water health (Winston & Hunt 2007).

The mechanism of treatment for dissolved metals is their sequestration in the BSM and modification of chemical speciation in water exfiltrating from the structure. For runoff with elevated copper, it has been recommended that BSM be replaced after 2 or 3 years based on ecotoxicological values (Göbel et al. 2008), but other research estimated media lifespans of 15 years (Davis et al. 2003) with Cu influent concentrations of 5 μg L^{-1}. Li and Davis found that most of the metals studied (Cu, Pb and Zn) were captured by organic components in the top surface of the media, though Cu had greater mobility. In this way, lifespan may be increased by removing and disposing of the top layer (0 – 10 cm) of media (Li & Davis 2008). A risk evaluation from 30 U.S. states was compiled that found the average representative regulatory limit for copper in soils to be 3,700 mg kg^{-1} based on child soil exposure at home (Li & Davis 2008) however there are variations by several orders of magnitude with minimum and maximum values of 25 and 20,000 mg kg^{-1} respectively (Petersen et al. 2006).

Copper is common at low concentrations in soils and natural waters and is an essential element for life. At high concentrations it can be toxic to humans; at concentrations below that threshold it can be detrimental to sensitive aquatic life affecting growth, reproduction and survivability (Boulanger & Nikolaidis, 2003). The most toxic form of copper is the free-metal ion (Cu^{2+}) or cupric form (Wallinder & Leygraf 1997) represented as $Cu(H_2O)_6^{2+}$. Anthropogenic copper enters the environment from architectural materials, automobile brake pads and fluids, coinage, fertilizers, copper based pesticides, mining, municipal sewage plants, waste dumps, agricultural feedlot additives, sewage sludge applications, and other means (Berbee et al. 2014, Bertling, et al., 2006, Boulanger 2003). Copper is present in rainfall and as airborne particulates and has been estimated to deposit as much as 728 μg m^{-2} yr^{-1} as dry deposition and 130 μg m^{-2} yr^{-1} as wet deposition (Barron 2006). As of September 2014, the United States Environmental Protection Agency (US EPA) reports that 731 waterway segments of the United Sates are impaired with copper (US EPA, 2014). Both fresh and saltwater copper criteria are pursuant to section 304(a) of the Clean Water Act. Fresh water limits are derived using site specific water chemistry through the biotic ligand model and/or a hardness based approach.

Copper roofs have been used for centuries in various parts of the world. They are considered long lasting and require little maintenance. As they age and are exposed to normal atmospheric conditions, they undergo chemical changes that eventually form a patina (Wallinder et al. 2007, Kratschmer 2002). In terms of mass, the average contribution to runoff from copper roofing materials in the United States are estimated at about 2.12 g Cu m^{-2} yr^{-1} (Arnold 2005). Some research in Europe has found that copper roofs contribute from 1.0 to 3.9 g m^{-2} yr^{-1} (Athanasiadis et al. 2010) though some rates as high as 8.6 g Cu m^{-2} yr^{-1} were noted in Singapore for a patinated roof (Wallinder et al. 2007). Copper from copper roofs may be responsible for as much as 4 to 20% of the copper in stormwater (Arnold 2005) though there is tremendous variation due to factors such as precipitation rate, pH, roof angle, and dry deposition. It is important to note that attenuation processes that take place between the roof outlet and the receiving water are important factors to consider (Hedberg et al. 2014). Therefore, the Cu load from the roof is not necessarily what will reach the receiving water

In freshwater systems, naturally occurring copper can vary between 0.2 and 30 µg L^{-1} (Bowen 1985). New roofs have been demonstrated to have 1000 to 14,000 µg L^{-1} of total Cu in runoff (Bertling et al. 2006, and references therein) compared to some non-copper roof runoff concentrations such as 7.6 and 12.7 µg L^{-1} for tar felt and asbestos cement, respectively (Quek & Forster 2000). Algae-resistant asphalt roofing materials partly comprised of copper granules have been used for several decades (Jacobs &

Thakur 1999). One study of these algae resistant shingles (Velleux et al. 2012) used a modeled Cu release concentration of 160 µg L^{-1} at the shingle surface during rainfall based on literature values.

Previous research has shown that the initial concentrations of copper from copper roof effluent are highest during the first part of the storm due to varying environmental conditions (Athanasiadis et al. 2010). This first-flush effect is a product of local environmental conditions such as precipitation volume, pH and storm intensity as well as the porosity of the metal surfaces and how the length of the antecedent dry period (ADP) will permit corrosion products to be dissolved and re-precipitated (He et al. 2001). Precipitation volume is thought to be the most important factor in predicting the runoff quantity of copper.

Copper roofs in urban settings have shown runoff copper quantities and concentrations twice as high as rural settings (1.2 and 0.7 g Cu m^{-2} respectively); this has been attributed to increased deposition rates of corrosive species such as SO_2, NO_x, HCl, and aerosol particles. Most research has found that Cu corrosion rates are highest in new copper with 70 to 90% of Cu leaving as the hydrated cupric ion $Cu(H_2O)_6^{2+}$ (Wallinder & Leygraf 2001). Surface porosity also increases from 10% with 40 year old copper roofs to 25% for roofs aged 100 years (He et al. 2001). The slope of the roof is an important factor since lower slopes increase contact time with stormwater (Wallinder et al. 2000).

An empirical model was developed by Wallinder et al., (2007) as a tool for estimating copper runoff from roofs under varying conditions. The model was derived using the observed runoff rate of copper roofs from 28 locations in Sweden, Switzerland, the USA, Singapore, and France where precipitation varied from 396 to 3,203 mm yr^{-1};

pH varied from 3.9 to 6.1; and SO_2 varied from an estimated 0.5 to 27 μg m^{-3}. The model uses SO_2 (in ppb), precipitation (in mm), pH and roof inclination (θ) as input parameters to predict the release rate in g $m^{-2}yr^{-1}$ and is given as:

$$R = (0.37\,SO_2^{0.5} + 0.96\,rain 10^{-0.62pH})\left(\frac{\cos(\theta)}{\cos(45°)}\right)$$

When the model was applied to European maps of rainfall pH, rainfall quantity, and SO_2 concentration, it predicted Cu runoff rates that varied between near zero to 3.0 g m^{-2} yr^{-1} with most predictions below 2 g m^{-2} yr^{-1} for the year 2000. If SO_2, precipitation, and pH are within certain parameters, it could imply that the decision to include copper roofs in certain regions should include mitigation plans.

Because of the potential for adverse effects, states such as Washington and Oregon are seeking ways to mitigate potential harmful effects of diffuse and nonpoint sources of copper. Research in the Puget Sound Basin estimated that roofing materials ranked among the top seven sources of copper releases out of the 14 categories evaluated (Ecology & King County 2011). In 2010, Washington State passed a law restricting and phasing out the use of copper in brake pads as a way to decrease copper release to waterways (Washington Department of Ecology 2012a). Salmonids are a very important part of the economy, history and tradition of the Pacific Northwest but their numbers have been declining dramatically since the mid-19th Century (Lackey 2003). Some important salmonoids have been shown to be sensitive to copper in the low μg L^{-1} range. Thus regulators have paid particular attention to increased levels of copper in waterways where such sensitive species are of concern.

The revised Western Washington Stormwater Manual, released in 2012, documents details related to various stormwater control measures (SCMs). This research was designed with these SCMs in mind, and to conform to the water quality requirements for the State of Washington.

Research has shown that bioretention as a LID technique can be effective at treating many pollutants in stormwater including > 92% of metals (Davis et al. 2001) though the researchers used low concentrations of Cu (80 µg L^{-1} – more appropriate for urban street runoff) and slow infiltration rates (1 to 2 cm hr^{-1}) for the planter box.

The purpose of this project was to improve our understanding of the amount of copper released into runoff from copper roofing materials and to quantitatively evaluate the efficacy of two types of stormwater control measures (SCMs) for their ability to attenuate copper in copper roof runoff. Stormwater sampling provided a means of determining copper quantity in roof runoff and bioretention structure effluent, and consequently the ability of bioretention structures to sequester copper. We hypothesized that the SCMs would decrease copper concentrations in stormwater as it passed through the structures.

3. MATERIALS AND METHODS

In order to evaluate the effectiveness of bioretention for sequestering the relatively high concentrations of Cu in stormwater runoff from copper roofing materials, a copper roof was constructed along with two types of SCMs for evaluation. Stormwater runoff from the copper roof was evaluated both before entering the SCMs as influent and after exiting the SCMs as effluent. Additionally, two reference structures were built in order to compare atmospheric deposition and a common roofing material. Automated sampling was used to collect composite and discrete storm samples.

3.1 Site Design and Equipment

A 3 by 6 m picnic shelter was constructed in the summer of 2012 at Towson University, in Towson, Maryland. The shelter's roof was constructed of 16 oz. standing seam copper and was divided into four ~ 4.64 m^2 sections of equal area that total about 19 m^2. The pitch of the roof is 4:12.

3.1.1 Reference Structures

Two 1.22 x 2.44 m (about 2 m^2, 4:12 pitch) reference structures were built for a comparison of water quality collected from roofs constructed of other materials. Asphalt shingle was chosen to compare a common roofing material. Plexiglas was used to account for atmospheric deposition and to develop a reference for background copper levels. The reference structures were sited about 5 m from the picnic structure. Both structures drained separately via a rain gutter and downspout system, similar to the copper roof, and into a sampling box. Neither of these control structures was associated with SCMs.

The picnic shelter and control structures were constructed in a clearing of mixed hardwood near the center of the Towson University Campus, known as The Glen Woods. No trees directly overhang any of the structures. The site was built on a moderate slope that afforded easy draining of excess water from the treatments. The city of Baltimore (just south of Towson) receives 1064 mm average annual precipitation (National Oceanic and Atmospheric Administration 2014).

3.1.2 Grass Biofiltration Swales

The two grass swales were built according to the Stormwater Management Manual for Western Washington (SMMWW) (Washington Department of Ecology

2012b) BMP T7.30, and parallel the length of the picnic structure along either side. They were ~ 6.1 m long and ~ 0.9 m wide and were designed on a 1.5% longitudinal slope in a concave form with a ~ 15 cm bowl depth so that water would not to be able to sheet-flow either into or out of the swales. The top ~ 15 cm of compost-amended native soil (Glenville silt loam) sat above a ~ 25 cm limestone pea-gravel drainage layer which sat above a ~ 5 cm limestone drainage layer. In the center of the bottom drainage layer, a 4" perforated PVC pipe was designed to collect water that filtered through the soil and drain it to the end of the swale. The swales were constructed with a geotextile and an impermeable PVC liner on the bottom to collect as much water as possible (the liner is not part of a conventional design but was done only for the purpose of this project to facilitate sample collection). To capture surface sheet flow, surface drains were installed at the lowest points of the swale and connected to the subdrain to allow it to join the subsurface water collected via the underdrain. After construction, the swales were seeded with a Red Top and Tall Fescue blend (*Agrostis gigantea* and *Festuca arundinacea* respectively).

3.1.3 Bioretention Planter Boxes

The BSM used in this project was mostly sand mixed with composted leaf and yard litter as per specifications outlined in the Stormwater Management Manual for Western Washington (Washington Department of Ecology 2012b). The bioretention planter boxes were ~ 0.9 m x 0.9 m (length/width). The top layer was mulch over jute netting, overlying ~ 46 cm of BSM. Below that was a ~ 10 cm layer of limestone over ~ 15 cm of limestone pea-gravel. Each box had an impermeable liner and a ~ 5 cm perforated PVC sub-drain. To maintain complete vegetative cover, 3 containerized plants with a diversity of phylogenetics were planted – *Cornus sericea* 'Kelsey' (Kelseys' Dwarf Red Dogwood), *Polystichum acrostichoides* (Christmas fern), and *Pennisetum aloepecuroides* 'Little Bunny' (Dwarf Fountain Grass).

3.2 Stormwater Sampling

Each quarter of the copper roof drained (via rain gutters) to a separate downspout into a sampling box at each downspout where flow-weighted sampling took place (Figure 2.1). As water left the sampling box, an outlet pipe delivered the water to the top of the planter box (Figure 2.2), or to the high side of a bioinfiltration swale (Figure 2.3). These four sampling boxes were termed the "inlet" boxes. There were two swale treatments and two planter treatments. Water entering the SCMs percolated through the media and left the system via a perforated collection pipe in the subsurface. From there, it entered the outlet sampling boxes where flow-weighted sampling again took place.

The four downspouts from the copper roof were named as "inlets" thus "Planter Inlet 1" (PI-1) is the eastern most planter and "Planter Inlet 2" (PI-2) was the western-most of the two planters. The SCM outlets then were designated "Planter Outlet 1" (PO-1) (east) and "Planter Outlet 2" (PO-2) (west). This naming system also applied to the swales as swale 1 (SO-1) was the eastern-most swale and swale 2 (SO-2) was the western-most. The asphalt shingle reference structure was labeled "C-1" and the Plexiglas was "C-2.".

3.2.1 Sampling Equipment

Composite stormwater samples were collected approximately monthly from each sampling point. These composite samples were flow-weighted whereby an automatic sample was taken after a given volume of water passed through the sampling device, thus allowing the calculation of an event mean concentration (EMC). Due to the ability of both the planter boxes and the swales to absorb stormwater, high-volume rain events were preferentially collected since rain events less than five mm were unlikely to produce sufficient flow through the SCMs to result in an adequate sample volume for analysis. Before sampling, all sampling boxes were purged of residual water from previous events. Each sampling site was composed of an automatic sampler (WS750; Xylem Corporation; College Station, TX) and a flow gauge (6506h; Unidata Pty Ltd; O'Connor, Western Australia). All components of the sampling system were either plastic or stainless steel. All flexible tubing was either Mityflex® or Tygon® norprene, and all hard tubing was constructed of polyvinyl chloride (PVC). The sampling volume was set at 250 mL for each triggered event. The sample boxes were designed so that the low corner of the box would hold approximately 500 mL (Figure 2.4). The tipping bucket flow gauges measured the flow rate and triggered flow-weighted sampling events by coupling to a counter box relay. The relay had an adjustable counter that could be preset to collect a subsample for a given number of tips (1 - 99) from the flow gauges (1 tip per ~ 140 mL of flow). Thus for high-volume storm events, the counters were set higher so that the entire duration of the storm could be sampled; conversely they triggered at fewer tips for lower volume storms to provide sufficient sample collection for low flow events. Trigger events from the relays were recorded by HOBOware Pendant® event data-loggers (UA-003-64, Onset Computer Corporation; Bourne, MA) that could then be downloaded after each storm.

A tipping bucket rain gauge (model 674, Teledyne ISCO; Lincoln, NE) was also connected to a separate data-logger to monitor storm events. Data from this gauge was used to determine rainfall for each storm event. All of the tipping bucket devices were calibrated prior to deployment in the field.

3.2.2 Sampling Adjustments

After sampling the first 11 storms, it was noted that the effluent volume from PO-2 was significantly less than the volume entering the SCM from PI-2. Excavation of the underside of the box revealed several leaks in the PVC liner. In December 2013, the materials from the planter were carefully excavated and segregated. The liner was replaced with a heavier gauge plastic and the media were returned to the structure. After replacement, the water balance between PI-2 and PO-2 improved.

Through the first 11 storms, the swales were consistently not producing effluent at the outlets except during very high intensity storm events. In August of 2013, excavation pits were made near the low end of each swale. It was determined that there was a design problem that hindered collection – the perforated, horizontal collection pipes were set too high (more than 30 cm) above the PVC liner, and the top edge of the liner was too low. Thus, stormwater would infiltrate into the gravel layer but not reach a high enough level to enter the PVC drain pipe before leaking around the liner. In order to capture swale water samples from a greater number of storm events, a screened PVC well with a float switch was installed into each excavation pit. The float switch was coupled to SHURflow 2088 Series Agriculture Diaphragm Pump powered by a 12V deep-cycle marine battery that purged the water from the swales into respective 40 L carboys. Each carboy then drained into the collection system for the outlet flow gauges. Because of this, the ability to collect samples from the swales was made possible for the remaining storms; however, flow times as recorded by the event data-loggers no longer realistically reflected the dynamics of the rain event. The swales were purged of residual water from previous precipitation before each sampling event.

The ISCO rain gauge became clogged with leaf debris several times throughout the collection period. Because of this, continuous rain gauge data are not available for the entire project duration and is also missing for several of the storm sample events. Several sources were used to estimate precipitation when data were not available from the ISCO rain gauge. Data from the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center's Record of Climatological Observations (station GHCND:US1MDBL0016, located less than one km from the study site) were used as primary backup. Local informal weather stations (Weather Underground and cocorahs.org) were also compared to NOAA data since both keep rain data from areas close to the Towson University Campus.

3.2.3 Composite Sampling

Acid washed 4 L Polyethylene collection vessels were used in the automatic samplers. Upon collection, an agitated subsample was then transferred to a 2 L HDPE sample vessel. Over the 2 year period, the goal was to sample approximately one storm event per month for a minimum of 24 sampled storm events.

3.2.4 Discrete Sampling

Discrete time-resolved samples were collected with ISCO samplers (models 6712 and 2700; Teledyne ISCO; Lincoln, NE) that contain 24 individual collection bottles. This method helped discern the composition of stormwater as it changed throughout a single storm event, especially as related to the characterization of any potential first flush effect. During storm events, one sampler was deployed at either PI-1 or PI-2 and one sampler each was deployed at the planter box outlets. Collection bottles were acid-washed before each sampling event. The ISCO samplers were connected to the sample tubing, control boxes and flow gauges used for composite sampling. Discreet and composite sampling was performed during separate storm events. Over the 2 year sampling period, discrete samples were collected approximately once per quarter (every 3 months).

3.2.5 Sample Labeling, Storage and Archiving

Composite storm events were labeled by a six digit storm code (yymmdd); discrete storm events were labeled by the sampling instrument and the order of the sampling event (e.g. ISCO 2). Samples were collected within 24 hours of the end of a storm event and stored at ~ 4 ˚C. While most samples were completely processed within 4 days, some were not completed until approximately 10 days later. After all processing had been completed, a subset of the remaining sample was archived. Archived samples were stored at approximately -17 °C in 50 mL polypropylene centrifuge tubes.

3.3 Sample Analysis

3.3.1 Quality Control (QC)

Recovery for standards is reported as % recovery, and duplicates are reported as % relative standard deviations (RSD). During analysis of QC data, all data points below the LOQ were replaced with half the LOQ.

Dilutions and cleaning were done using high-purity water (18.2 mΩ). For all sample preparation and analysis, one method blank (18.2 mΩ water) and one or more duplicates were run every ten samples to evaluate instrument reproducibility. Certified reference samples were also run to evaluate accuracy of the method.

3.3.2 Metals Analysis by ICP-MS

Preparation of samples for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was completed within 24 hours of sample collection. For dissolved metals, samples were passed through a 0.45 PTFE µm syringe filter then acidified to 0.2 M using trace metal grade 6 M HNO_3 for preservation. For total metals, samples were first acidified to 0.2 M with 6 M HNO_3, then agitated and allowed to stand for 5 minutes. This acidified sample was then passed through a 0.45 µm syringe filter. Indium was added to all samples at a concentration of one ppb as an internal standard. The metals Fe, Cu, Zn, Cd, and Pb were quantified on a Thermo (VG) PQ Excel ICP-MS using an external calibration curve. National Institute of Standards and Technology SRM (Standard Reference Material) 2709 San Joaquin Soil was used as a check standard and included in every sample analysis run. The limit of quantitation (LOQ) based on the average blank concentration was 1 µg L^{-1}.

3.3.3 Total Suspended Solids (TSS)

TSS was measured for composite storm event samples. Quartz filters (0.45 µm) were used to collect suspended solid residue through a vacuum flask. A sufficient amount of liquid was used to obtain residues heavier than 1 mg. Residues on the quartz filters were measured according to method 2540 D (APHA 2005) by mass along with a check standard [RICCA Chemical Company Total Suspended Solids (TSS) Non-filterable residue standard (100 mg L^{-1}) (Cat. No. 8672-16)].

3.3.4 Stormwater Nutrient Analysis

Selected storm events were analyzed for dissolved total N and total P content. For composite samples, filtrate from the TSS analysis were used. Discrete samples were filtered through glass fiber (0.45 µm) filters. Samples were analyzed for Total Nitrogen (TN), along with a 30 mg L^{-1} Nitrogen check standard using a Shimadzu TOC-VCPH Analyzer. The LOQ was 1 mg L^{-1}. Total phosphorus was measured by microwave digestion and the ascorbic acid spectrophotometric methods (Method 4500-PE, APHA 2005). The check standard was 75 µg L^{-1} PO_4^{3-} prepared from a commercially available 1 mg L^{-1} PO_4^{3-} (RICCA Chemical Company, Cat. No. 5826. 1-32). The LOQ was 5 µg L^{-1}.

3.4 Characterization of Bioretention Soil Media (BSM) and Soils

The BSM, BSM/native soil mixes, and a control soil obtained near the picnic shelter were analyzed for % total C using a TOC-VCHP Analyzer (Shimadzu Scientific). This was converted to % organic matter using the 1.72 Van Bemmelen conversion factor (Reijneveld et al. 2009). The SRM 8704 (Buffalo River Sediment; NIST) was used as a check standard. Particle size distribution was characterized with USA Standard soil sieves (sieve #'s 3/8, 4, 10, 40, 100, 200) (ASTM) with a shaker to analyze the BSM and swale soil / BSM materials by mass percent.

The BSM and BSM / swale soil mix cation exchange capacity (CEC) was determined by a method of barium chloride saturation and magnesium chloride extraction (Hendershot & Duquette 1986). BSM materials were taken from an archived pre-treatment sample. Planter box soils were determined from media taken from around the containerized plants. Swale soils were combined from two locations – an uphill location from near the entry point of roof influent, and a downhill location from near the lowest point of the swales at the opposite side.

3.5 Determination of the Acid Extractable Metal Content and pH of BSM, Soils, and Asphalt Shingle Reference Structure

Leachable metals in solid samples were analyzed by digesting approximately 50 mg of sample in a Teflon vial overnight with 7N HNO_3 at 120°C. Metals analysis of an archived (pre-treatment) sample of the BSM was performed in October 2014. In the same manner, planter box and swale media were analyzed in October 2013 and 2014. A portion of unused shingle was analyzed by ICP-MS to determine copper content. Six small portions (approximately 3 cm^2 each) were separated into 3 groups: the entire shingle; the base of the shingle; and the multi-colored granules that were on the base. There were 2 replicates in each group. The pieces were hand-chopped with a razor blade and digested. Samples were filtered through a 0.45 µm disposable filter, brought to volume using 1 ppb Internal Standard Solution (ISS), and analyzed by ICP-MS. One method-blank was also analyzed along with this set. Soil pH for each group was determined in October 2014 by combining a 1:1 dilution of soil by weight with a 0.01 M solution of $CaCl_2$ that was agitated overnight.

3.6 Media Lifespan Estimation

Using the soil Cu values obtained, a very rough graphical interpolation was used to make media lifespan estimations for the planter boxes, based on the State of Maryland's residential limits for soils Cu, by setting the base (year-zero) as Cu levels in the BSM and plotting trend lines with that point and levels at year-one and year-two.

3.7 Sampling Equipment Field Blank Assessment

A single field-blank experiment was performed on July, 29 2013 by first flushing 10 L of 18 mΩ water directly through the collection pipes and sampling boxes (i.e. not contacting the roof) and then running 2 additional sets of 10 L (each) and analyzing this effluent by ICP-MS using the methods previously described in order to determine residual Cu in the sampling equipment.

3.8 Precipitation Analysis

Rough Storm Intensity (RSI) was calculated by dividing the total rainfall depth in mm by the total duration of the storm in h. The flow gauge data were used to determine the volume of water that passed through the SCMs in order to calculate Cu loading when coupled with influent and effluent concentrations.

Regression analyses at the 95% confidence level were used to evaluate the relationship between pairs of variables. SCM influent total Cu was compared to planter box total Cu, time, ADP, total precipitation, and rough storm intensity. Planter box percent attenuation was compared to SCM influent total Cu, time, and total precipitation.

3.9 Estimation of Retention Time

By using the rain gauge data and setting the automated sampling control boxes to 1 tip/count, high-resolution data were obtained for about a one month period to estimate stormwater retention time in one planter box (PO-2) by hyetograph and hydrograph. Roof inlet times were subtracted from planter outlet times to determine the points at which 25, 50, and 75% of the stormwater had flowed through the SCM for 9 distinct precipitation periods.

3.10 Wallinder Copper Roof Weathering Model

The Wallinder Copper roof weathering model (Wallinder et al. 2007) was used to predict annual copper loading rates at the study site as a comparison to measured loading rates estimated using the roof runoff data. Data for rainfall from January 2013 through

August 2014 from NOAA was 1,210 mm yr^{-1}. Sulfur dioxide from an air monitoring station operated by Maryland Department of the Environment in Essex, MD gave an average value of 3.64 µg m^{-3}. For pH, an average value from the Plexiglas reference structure (C–2) was used (pH 6.12). Additionally, a pH value of 5.1 from the National Atmospheric Deposition Program (NADP) was evaluated. The equation is given as:

$$R = (0.37\, SO_2^{0.5} + 0.96\, rain 10^{-0.62pH}) \left(\frac{\cos(\theta)}{\cos(45°)}\right)$$

Where R is the predicted Cu runoff in g m^{-2} y^{-1}, SO_2 is in µg m^{-3}, rain is the amount of rain in mm yr^{-1}, pH is the pH of the rainwater, and θ is the roof angle in radians (Wallinder et al. 2007). The 0.37 coefficient considers the antecedent dry period (ADP) and first-flush effect. The 0.96 coefficient considers the rain events at steady state. The last term is the derivation of the roof angle from the horizontal.

The prediction from the Wallinder model was compared to measured values of copper loading estimates for this site. Loads from the roof inlets (in mg) were paired with total precipitation for each storm event (in mm) for all composite storm events (n = 92) to derive an estimate of loading per mm precipitation. This was multiplied by average annual precipitation for Towson, MD for the sampling period (1,210 mm yr^{-1}) and divided by the roof size (4.645 m^2) to give an average annual loading in g m^{-2} y^{-1}.

4. RESULTS

4.1 Characterization of Materials Used in SCM and Reference Structure Construction

The BSM contained an average of ~ 4% organic matter which is much less than the 40 % specified in the Stormwater Management Manual for Western Washington (SWMMWW). Analysis for CEC was also below the specified value of 5 cmol(+) kg^{-1}.

Leachable copper content for the BSM was 10 mg kg^{-1} by dry weight, which is much less than the 750 mg kg^{-1} by dry weight that was specified. pH was 6.7 which was between the specified 6.0 to 8.5 (Table 2.1).

Analysis of organic matter showed an average of 2.5% in the swale media which is less than the eight to ten % specified in the manual. Analysis of the reference soil showed 1.2%. The planter media contained a little too much fine and coarse material, but this lack of sand-sized material was more pronounced in the swales. The manual notes that existing soils may be amended (as these were).

Pieces of previously unexposed asphalt roof shingles were divided into 3 sections (entire pieces, the base of the shingle, and the granules) and analyzed by ICP-MS for metal content in duplicate; averaged results for these were 836, 405, and 3401 mg kg^{-1} for the entire shingle, base, and granules, respectively.

4.2 Sample Collection

According to NOAA's monthly climatological summary for Towson (National Oceanic and Atmospheric Administration 2014), approximately 442 mm of precipitation fell on the exposed roof over about three and a half months before the first sampling event. From the time of the first sampling through the last (20 months), approximately 2,016 mm fell on the exposed roof.

Twenty-six composite storm events were sampled over a 20 month period, totaling 226 samples. Additionally, 7 discrete events totaling 316 samples were collected within that same period. Two of the composite storm events (130607 and 140329) were 2 and 3 day long rain events respectively. In these events, composite samples were collected then the samplers were re-deployed for the remainder of the storm. These were treated as distinct events. Table 2.2 provides an overview of sample collection. Table 2.3 gives an overview of precipitation for each event.

For composite events, 95 samples were collected from the SCM inlets, 49 samples were collected from the planter box outlets, 37 were collected from the swale outlets, 22 were collected from C-1, and 23 from C-2. Equipment failures were responsible for 34 samples not being collected among the various attempts to sample. During 14 storm events, the regular collection vessels completely filled during the storm. However, there was no way to know the exact time at which they filled. Thus in these cases, the event mean concentration is for the portion of the storm that was sampled, although the exact fraction of the storm duration that was sampled may not be precisely known. Two samples (PO-2 and SO-2) for storm 130508 were taken 3 days after the main precipitation event but are presented as one storm set.

For discrete events, 133 samples were collected from the copper roof as influent, and 183 samples were collected from the planter boxes as effluent. Since only one ISCO sampler was connected to the planter box inlets, the 7 storm events were sampled either from the PI-1 (3 storms) or PI-2 (4 storms). Two ISCO samplers were connected to each planter outlet; however equipment failures prevented collection from both sites during all 3 of the storms. Thus, five storms were collected from PO-1 and six were collected from PO-2. For several collection points, the ISCO carousels filled completely. Thus there was likely additional precipitation that fell after collection.

4.3 Quality Control

All averaged SRM recoveries were between 90 and 110% except the analysis for total % C, which was 78.9%. Duplicate RSDs showed greater variation. Average duplicate % RSDs were 11.9 for Cu by ICP-MS, 41.9 for TSS, 45.0 for total N, 70.8 for total P, and 14.3 for % total C (Table 2.4).

4.4 SCM Copper Attenuation

Cu concentration was greatly attenuated by the SCMs with total Cu concentrations decreasing by one to two orders of magnitude on average (Figure 2.5 a). Attenuation occurred consistently over the 20 month period of sample acquisitions (Figure 2.6). Average total copper concentrations in the roof inlets, planter outlets, and swale outlets were 1298, 76, and 29 µg L^{-1} respectively. C-1 total Cu concentrations ranged from 10.2 – 377 µg L^{-1} with an average of 94 µg L^{-1}. C-2 total Cu concentrations ranged from below the LOQ to 15 µg L^{-1} with an average of 3.6 µg L^{-1}. Data for Cu concentration, as well as the concentrations of other stormwater analytes were not normally distributed and therefore the median is reported for analyte summary statistics.

Individual composite storm events showed attenuation of total copper in the planter boxes from 82.6 to 99.2% (mean = 93.1%, n = 45), and from 93.3 to 99.3% (mean = 97.2%, n = 32) in the swales (Figure 2.5 c). For discrete events, attenuation by concentration ranged from 89.6% to 97.4% (mean = 93.5%, n = 6). Total copper attenuation by load was similar. For planter boxes, composite storm event load attenuations ranged from 76.2 to 99.0% (mean = 92%, n = 41), and from 89.4 to 99.9% (mean = 97.6%, n = 21) in the swales.

For discrete events based on averages of all sample bottles collected, the planter box inlet values ranged from 477 – 3958 µg L^{-1} for total Cu, with an average of 1634 µg L^{-1} (n = 7). The averaged planter outlet concentration was 101 µg L^{-1} (n = 11). The first bottle total Cu concentration from SCM influent was the highest of the set and well above the mean for four out of seven of the discrete events (ISCO 3, 5, 6, and 7); this appears to be consistent with a first-flush. For planter box effluent, the first flush seems to be a more minor component of the temporal dynamics (Figure 2.7).

Dissolved Cu also showed great attenuation in the SCMs. Inlet dissolved Cu from the roof quarters ranged from 203 – 2505 μg L^{-1} and averaged 1,038 μg L^{-1} for composite storms. Averaged outlet dissolved Cu concentrations ranged from 17.8 – 186 μg L^{-1}, with an average of 62.3 μg L^{-1} for planter boxes, and swales ranged from 3.7 – 48 μg L^{-1} with an average of 22.9 μg L^{-1} (Figure 2.5 a). The C-1 dissolved Cu concentrations ranged from 7.5 – 381 μg L^{-1} with an average of 75 μg L^{-1}. The C-2 dissolved Cu concentrations ranged from below the LOQ to 14.0 μg L^{-1} with an average of 3.1 μg L^{-1}. The dissolved portion of all composite storm events averaged 80, 82, and 78% of total Cu for the roof effluent, Planter Boxes, and Swales, respectively. The averages for C-1 and C-2 were 80 and 87%, of total Cu, respectively.

The difference between the total and dissolved Cu concentrations gives the particulate Cu concentration (Figure 2.5 b). For several inlet values, dissolved and total concentrations were close enough that instrument variations produced a lower total Cu concentration than dissolved concentration. These values were reported as a zero particulate concentration.

Copper loading from direct roof runoff ranged from 26 – 242 mg per storm, with an average of 120 mg. Average loading from planter box effluent ranged from 1.1 – 25 mg with an average of 9.5 mg. The swales ranged from 0.02 – 7.6 mg and averaged 2.2 mg (Figure 2.5 d).

4.5 Stormwater Nutrients and Total Suspended Solids (TSS)

TSS patterns were similar to particulate Cu. Levels showed high variation among storm samples but were generally higher in effluent, particularly in the swales (Figure 2.8). One value for SO-1 was more than an order of magnitude greater than the median value; one value for SO-2 was two orders of magnitude greater. It was noted that the sample water for that collection was particularly cloudy, as if a clump of collapsed soil had been drawn into the sample bottle.

Total P was analyzed for four storm sets from archived samples. The SCM influent inlets averaged 33 μg L^{-1}. The planter box effluent averaged 87 μg L^{-1}, and the swale effluent averaged 311 μg L^{-1}. Concentrations for the reference structures were 66 μg L^{-1} for C-1, and 24 μg L^{-1} for C-2. Total N was also analyzed for nine storms from both fresh and archived samples. Both roof inlets and planter outlets averaged 0.6 mg L^{-1} and swale outlets averaged 1.3 mg L^{-1} (Table 2.5).

4.6 Field-Blank Experiments

The field blank experiments for total Cu were performed on one planter box inlet (PI-1), one planter box outlet (PO-2), and one reference structure (C-2) in July of 2013. C-2 was below the LOQ for both flushes. PI-1 showed 85 and 35 μg L^{-1} on the 1^{st} and 2^{nd} flush respectively. PO-1 showed 5 μg L^{-1} in the 1^{st} flush, and was below the LOQ in the 2^{nd}.

4.7 Regression Analyses

For roof runoff, regression analyses found positive correlations between two factors related to total Cu concentrations – total precipitation and RSI. Two factors were correlated to planter box % attenuation – SCM influent total Cu and total precipitation. Planter box outlet total Cu was correlated to SCM influent total Cu (Table 2.6).

4.8 Retention Time Estimation

Retention times varied greatly with planter box media moisture conditions. Averages of 6 sets obtained from high antecedent moisture conditions showed 10.3, 12.8, and 22.6 minute retention times for the 25, 50, and 75% influent volumes respectively. Averages of 3 distinct precipitation periods with low antecedent moisture were 46.4, 73.5, and 51.8 minutes for the 25, 50, and 75% flow volumes respectively (Table 2.7).

4.9 Modeling

The Wallinder copper roof weathering model predicted a runoff rate of 1.2 g m^{-2} yr^{-1} using parameters measured at this site, including the roof runoff 6.12 pH from C-2. Estimates made for loading based on the measured Cu values from this site were 2.16 g m^{-2} yr^{-1}. Using the 5.1 precipitation pH data from the NADP in the Wallinder model from the study period gives a predicted runoff rate of 2.02 g m^{-2} yr^{-1}.

4.10 Media Lifespan Estimation

Planter Box 2 had the smallest increase in Cu levels from year zero through year two; this resulted in an estimation of approximately 16 years. In order to keep estimates conservative, a line was drawn between the points for years one and two for Planter Box 1, which resulted in an estimate of approximately seven years. Only planter box estimates were used since swale Cu levels in year two were lower than in year one.

4.11 Supplemental Information

Hyetographs from the ISCO rain gauge are given in Appendix A for all available storms. Appendix B shows the values for each sample for total Cu for composite storm events, including summarized data. Graphs for total and dissolved Cu for discrete events are presented in Appendix C. Appendix D shows detail for dissolved Cu for composite storm events along with summary information. Percent particulate concentration details for composite storm events are presented in Appendix E. Detailed TSS results are presented in Appendix F, along with summary information. Cu loading by storm is given in detail in Appendix G, including summary information for composite storm events. The hydrographs used to make the estimations for retention time can be found in Appendix H. The graphical estimates for media lifespan estimation are presented in Appendix I.

5. DISCUSSION

5.1 SCM Performance

Both bioretention structures were highly effective at treating copper roof runoff. Though there was some variation among individual storms, Cu attenuation by concentration and load was typically over 90% and there appeared to be no discernible trend suggesting a decrease in that ability over the 20 month period of sampling. Results from metal concentrations show substantial reductions in Cu in the SCM effluent, both in terms of total and dissolved Cu. Though there are variations in influent values from storm to storm, we did not detect a pronounced seasonal effect or any consistent changes over the study period.

Though a strong first-flush effect is less expected for new Cu roofs (He et al. 2001), the discrete events showed comparatively high concentrations in total and dissolved Cu in the earliest sample bottles in SCM influent for storm events ISCO 3, 5, 6, and 7, and trended toward lower levels as sampling progressed. While in most of the inlet data a first-flush can be seen, it is not clearly prevalent in all of the events. Planter outlet trends reflected the first flush from the inlets but were somewhat attenuated in magnitude. To some extent, lower levels observed in the early samples of the planter outlets could be attributed to the pre-event water being pushed out by the initial discharge. The planter boxes appeared able to buffer the strong first-flush observed in several of the discrete events.

A strong effect of seasonality was not noted during winter months, though this could be due to our limited sampling data. The results from 8 sampling periods from December through mid-March year 1 and year 2 storms averaged 1375 $\mu g\ L^{-1}$ compared to all other 18 events averaging 1236 $\mu g\ L^{-1}$. Corrosion rates from copper roofs are highly time-dependent and we should expect to see rates decrease after the first few years (Hedberg et al. 2014). However the particulate fraction many not change as patina formation occurs (Boulanger & Nikolaids 2003). Given the low levels of Cu we have seen on C-2, it is clear that copper does accumulate from atmospheric deposition on the roofs, probably from dry dust deposition.

Since high-volume storms were preferentially sampled, the performance of the SCM may be underestimated. Low-volume events likely produce similar or even higher concentrations of Cu influent (He et al. 2001) but result in little to no discharge from the SCMs due to their water holding capacity. In the absence of a bioretention system, these influents would have been released.

5.2 Nutrients and TSS

Elevated N and P effluent from bioretention SCMs has been reported at levels of 68.6 mg L^{-1} and 4,140 µg L^{-1} respectively (Herrera Environmental Consultants 2012). The levels from this study showed N levels that are two orders of magnitude below the aforementioned levels and P levels one to two orders of magnitude lower. Levels obtained from SCM effluent are in the same range as the levels obtained from the C-1. It needs to be emphasized that our results were based on a very limited number of samples. A TN:TP ratio of 5:1 to 10:1 would not be nutrient limiting, as is the case with planter box effluent. Because the total N in the swale effluent was so much lower, effluent would be P-limiting in surface water (Downing & McCauley 1992). It is believed that the source and quality of the BSM, being primarily a highly finished composted leaf litter, led to a stable C:N ratio (Barrington et al. 2002), thus showing little tendency to leach dissolved nitrogen. This is an important criterion for design specifications and QC. Levels of total N in the effluent do not appear to be a concern as influent and effluent concentrations show the system to be acting as an N sink.

TSS levels from the SCM influent were relatively low, so there is little surprise that levels were raised by the SCMs. The majority of values from planter box effluent were in the low double-digit mg L^{-1} range and should not be a concern since this is near target level for treatment (Washington Department of Ecology 2012b). There were some outlier values in the swale effluent however. These appear to be isolated to the swales and could be attributed to singular events were sloughing soil was drawn into the sample equipment (though this is not certain). However, it needs to be kept in mind that a swale is normally designed to infiltrate into the ground, where for collection purposes, this system was designed with an impermeable liner.

5.3 SCM and Reference Structure Materials

Analysis of the pretreatment BSM for metal content showed it to be low in Cu content. Per specifications, it should have had less than 750 mg kg^{-1} and ours was 10 mg kg^{-1}. BSM pH was within the specified range.

Analysis of the BSM showed that it was quite low in organic matter compared to the specifications. Assuming organic matter (OM) contains 58% organic carbon, and using a 1.72 conversion factor, the BSM would have only 4% OM by our single test. Interestingly, the analysis of the planter soil (which should be the same material as the BSM, only having been aged in the planter box) would have an approximate organic content of 4.6%. These values are only about half of the organic content specified by design. While it would be expected to have lower values in the swales, 2.5% OM is still very low for a bioretention system. It is probable that our SCMs would have performed better with a higher OM content (Bertling et al. 2006) and a higher CEC.

Textural analysis of the planter box soils shows good agreement with the design specifications. However, the swale analysis shows that there were both too many coarse particles as well as too many fines. This may be expected since these were amended native soils that were not analyzed before construction. Coarse particles (greater than sand-sized) would not be expected to contain the surface area nor cation exchange capacity to enable soil absorbance of Cu. Small particles (fine silt-sized or smaller) may have a great surface area, but they may reduce the lifespan of a SCM due to clogging.

Early in the sampling period, unexpectedly high values of Cu from the asphalt shingle reference structure (C-1) were noted. It was thought that this was not an asphalt shingle embedded with copper granules and the packaging did not indicate algal resistance. However, when the shingles were tested for Cu, high values were found, indicating the presence of copper granules. A conversation with a manufacturer informed us that copper granules can be left in the hopper from a previous batch of algae-resistant shingles. It should be noted that some of the highest effluent values from C-1 contained about the same concentration of Cu from some of the lower values of the copper roof. Asphalt shingles may therefore be contributing substantial amounts of copper given their greater prevalence as a roofing material.

5.4 Field-blank Experiments

Field-blank experiments showed that residual Cu in the SCM outlet boxes was negligible. Although there was some residual Cu in the inlet boxes, typical stormwater concentrations were greater than an order of magnitude higher. This is understandable since the sample boxes were not washed or flushed between each collection. With a long ADP between collections, evaporation from residual waters in the boxes could have deposited Cu that could have contributed to a subsequent sample, especially if the subsequent sample was of a low volume. However, any sample box contributions from pre-event deposition were likely minimal in comparison to contributions from the rest of the system, including Cu that precipitated and re-dissolved from roof gutters, downspouts and other parts of the experimental system (Li & Davis 2008).

5.5 Regression Analyses

5.5.1 *SCMs*

No trend of SCM saturation by Cu has been shown after the two year exposure since there has not been a statistically significant decline in attenuation over time. The positive correlation between total Cu in SCM influent and planter box percent attenuation suggests that more diluted stormwaters (lower Cu concentration from the roof) were not as easily adsorbed by the SCM media. The lack of correlation between planter box attenuation and RSI further suggests that the SCMs maintain their functionality with heavier precipitation events. Copper attenuation in the planter boxes was negatively correlated with total precipitation. As total precipitation increased, attenuation decreased again showing the importance of retention time or treatment capacity.

The positive correlation between total influent roof Cu and total effluent Cu in planter boxes is not remarkable. It may suggest that the media is only capable of sequestering a finite amount of copper as a function of mass loading per unit time.

5.5.2 *SCM Influent*

There was no correlation between elapsed time and SCM inlet concentration and it probably should not be expected given the relatively short duration of sampling. The positive correlation between particulate Cu for the PI-1 roof quarter may also be the cause for the increased particulate Cu in PO-1. That there was no statistically significant effect between Cu influent concentration and ADP was unexpected since it has been widely reported, and the Wallinder model takes this into consideration. It is possible that the characteristic frequent precipitation events in Maryland did not allow sufficient weathering between events. The simple RSI as mm hr^{-1} did show a correlation with SCM influent Cu concentration that suggests dilution throughout the storm. This effect was also seen in most of the discrete sampling events since Cu concentrations in influent became more dilute as the sampling series progressed. Along with RSI, total precipitation captured a similar metric (though storm length was not factored) since Cu concentrations decreased with total storm volume from the roof.

5.6 Flow

The high-resolution flow data suggest that retention time in the planter box is dependent on several factors such as moisture content of the media as well as total amount and intensity of precipitation. The lowest retention time was 4.2 minutes for the first 25 % of storm flow during an intense period of precipitation. In fact 28% of estimated retention times (n = 18) during back-to-back precipitation periods were less than the recommended 9 minutes. When BSM moisture was lower, retention times increased substantially. All retention times (n = 9) during these periods were 18 minutes or longer with some of the longest times greater than 1 hour. However, these retention times may be an underestimation, especially for the earlier (25%) periods since residual water from a previous event is being pushed out by the incoming water. Thus that earliest effluent could have been sitting in the BSM for substantially longer than the estimated times.

5.7 Modeling

The Wallinder copper roof weathering model has predicted 76% of all reported runoff rates within 35% of their measured value. In 2007 Wallinder et.al found that runoff rates were less than 2 g $m^{-2}yr^{-1}$. Estimation using the model gave a lower predicted weathering rate (R = 1.2 g m^{-2} yr^{-1}) when using runoff pH from C-2 than our measured value (R = 2.16 g m^{-2} yr^{-1}). When precipitation pH data from the NADP was used instead, agreement was very good. Since we preferentially sampled high-volume storms, this value could be a slight underestimation if low volume storms produce greater loads in relation to storm volume from the roof due to increased concentrations. It should be noted that there are other factors that are unaccounted for in the model, such as the quantity, duration, frequency and intensity of rain events, as well as environmental pollutants (such as synergistic effects between SO_2 and NO_2, or between SO_2 and O_3), humidity and temperature, as well as ADP (Hedberg et al. 2014). This new roof may be weathering at a higher rate than the aggregated data set from which the Wallinder model was generated since it included a much older overall distribution of roof ages (Wallinder et al. 2004, Hedberg et al. 2014, Boulanger 2003, Pennington & Webster-Brown 2008). The predicted runoff rates coincided much better when pH from the NADP was used, and since the Wallinder model was based on precipitation pH, this is probably a more accurate reflection.

5.8 Media lifespan estimations

The graphical extrapolations were conservatively drawn and it should be noted that Maryland's acceptable residential Cu levels are one of the lowest in the United States. The SWMMWW accepts initial BSM levels at more than double this level. Second year measured levels of soil Cu are below the State of Maryland's cleanup standards for soil of 310 mg kg^{-1} for residential and 4100 mg kg^{-1} for non-residential (State of Maryland DoE 2008). Nevertheless, the estimates were made to obtain a "ball-park" time-frame for Cu soil levels. Though these values are consistent with the research presented by Paus et al. (2013) based on lifespans estimated by hydraulic conductivity, the results should be viewed with caution.

6. CONCLUSIONS

The SCMs are able to sequester Cu from copper roof effluent. While Cu concentrations in influent water were very high, this study demonstrated that the SCMs can retain greater than 90% of that Cu on average. Precipitation intensity and volume were found to be some of the strongest factors predicting the Cu concentration in SCM influent and SCM effluent, as well as the ability of the SCMs to attenuate Cu. These results are likely conservative given the low organic matter content and CEC compared to specifications. Given the loading rates seen thus far the SCMs should last years to decades based on conservative estimates. Using the Wallinder model for copper roof weathering can provide a good estimation for even new roofs, depending on the parameters used in the model.

Figures

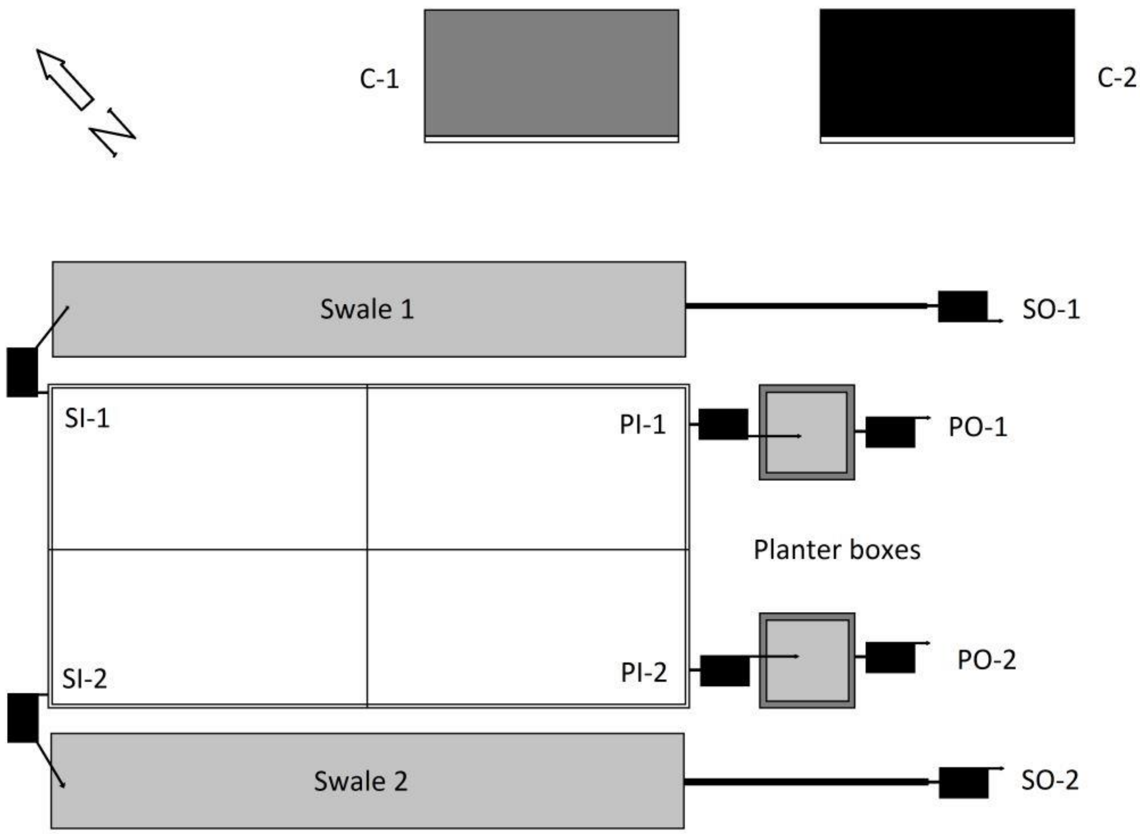


Figure 2.1 - Plan view of the study site. The copper roof is partitioned into 4 quarters. Each drains to a SCM. The small black boxes represent the sampling boxes. The grey squares are the planter boxes where PI-2 and PI-2 influent enters the planter boxes. PO-2 and PO-2 are the effluent sampling boxes. SI-1 and SI-2 influent flows into the high side of the swales (left side of drawing) and drain to the effluent sampling boxes (SO-1 and SO-2).

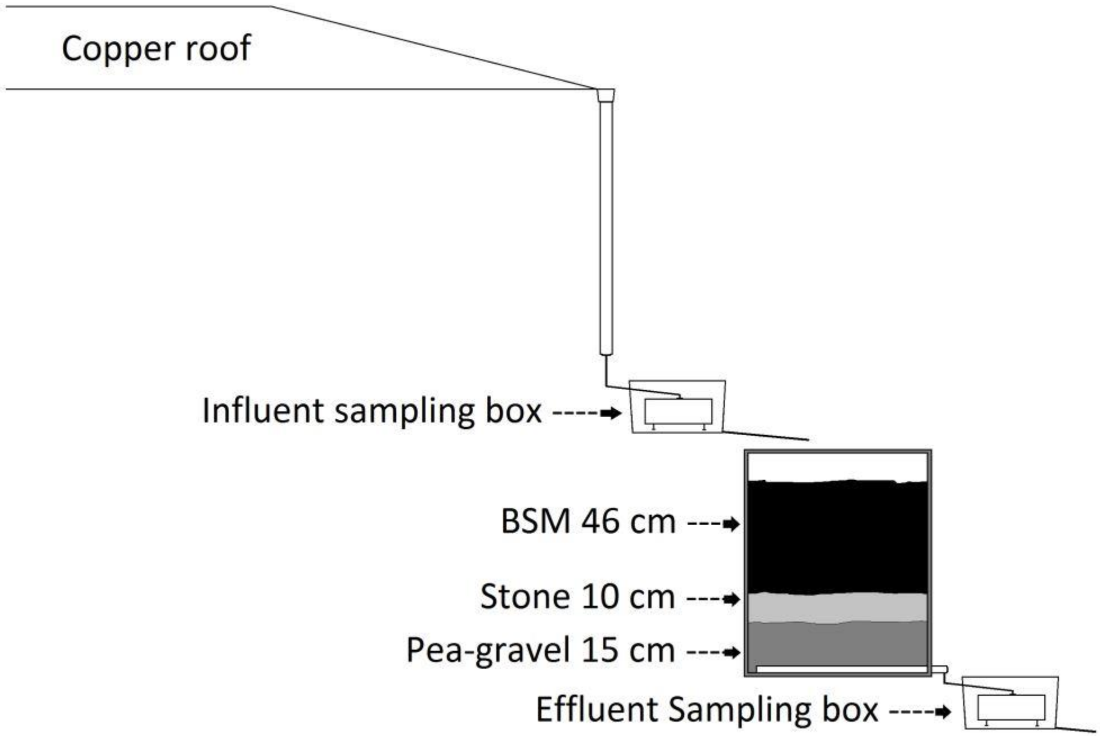


Figure 2.2 - Side view of copper roof, and transparent views of bioretention planter box and sampling boxes. Stormwater flows from the roof into the influent sampling box flow gauge via the gutter and PVC pipes. The flow gauges are located inside the sampling boxes. Samples are drawn from the lowest corner of the canted boxes (sampling equipment not shown). The stormwater then flows out of the box and into the planter box where it percolates through the media. Effluent is collected via a perforated collection pipe that drains to the flow gauge in the effluent sampling box. (Note: diagram is not to scale).

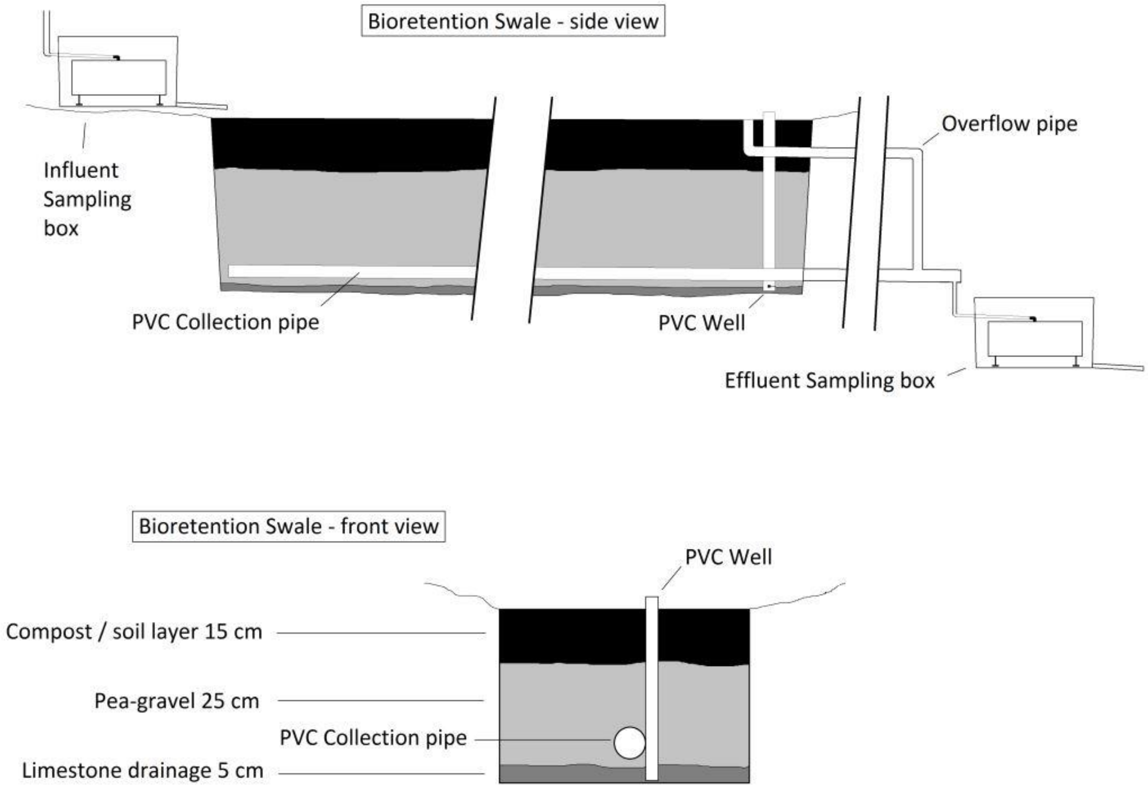


Figure 2.3 -Transparent side and front views of biofiltration swale and sampling boxes. Stormwater flows from the roof and into the higher sampling box flow gauge via the gutter and PVC pipes. The flow gauges are located inside the sampling boxes. Samples are drawn from the lowest corner of the canted boxes (sampling equipment not shown). The stormwater then flows out of the box and into the high side of the swale where it percolates through the media. Effluent is collected via a PVC well and pump system that drains to the flow gauge in the effluent sampling box via the overflow pipe (see the text for more detail). (Note: diagram is not to scale).

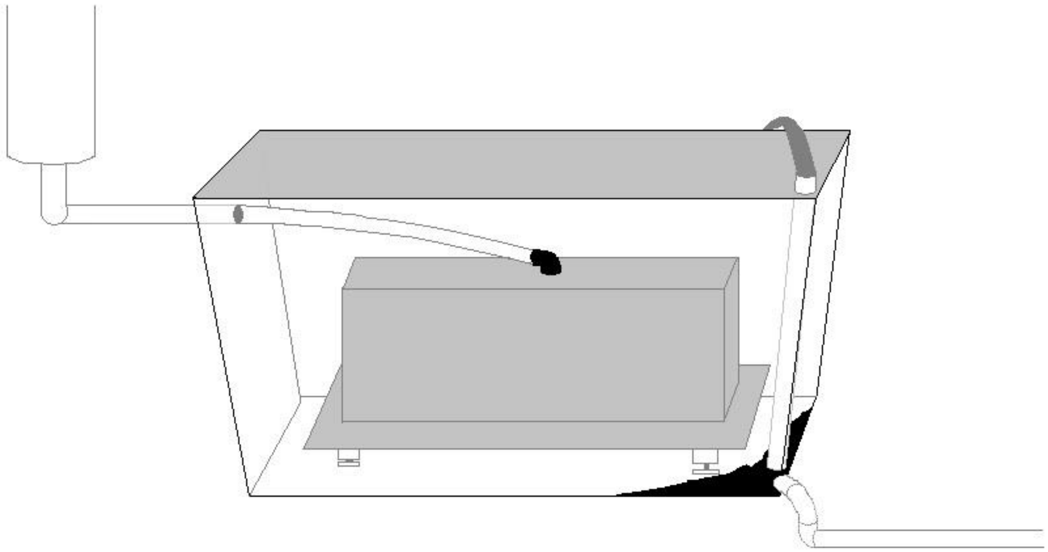


Figure 2.4 - Detail of sampling box. Stormwater flows into the box through the PVC pipe (left) and into the flow gauge. The box is canted to allow ~ 500 mL of water to pool in the low corner where the sampling tube draws water. Excess water flows out of the low corner (right). The flow gauge feet were height-adjustable to allow leveling of the flow gauge.

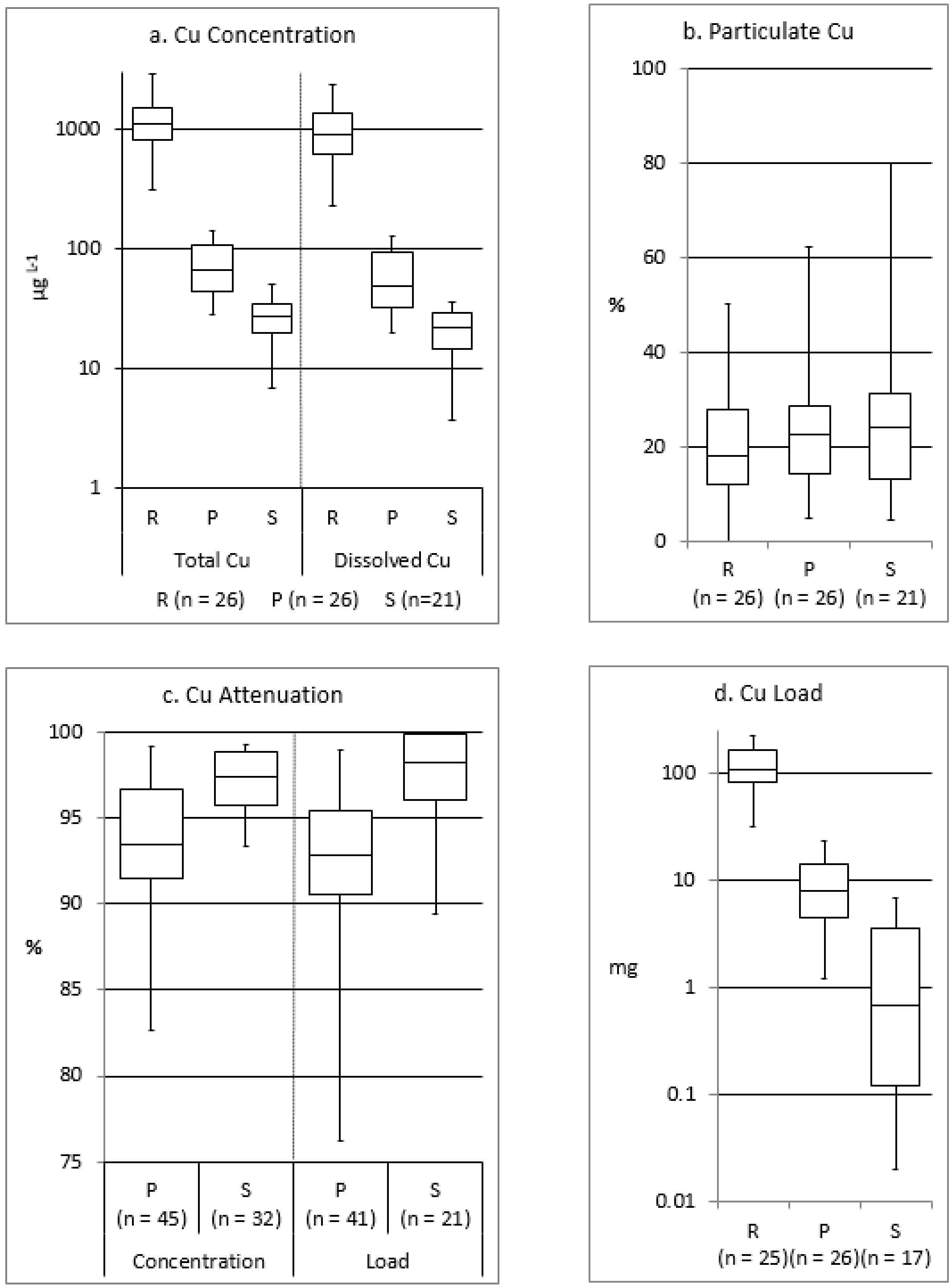


Figure 2.5 (a-d) – Cu Concentration, % Particulate, Attenuation, and Loading for composite storm events. R = Copper Roof; P = Planter boxes; S = Swales. The middle bars are the median value; the boxes represent 25th and– 75th percentiles; bars represent the range of the data. Note that the panel c y-axis is truncated.

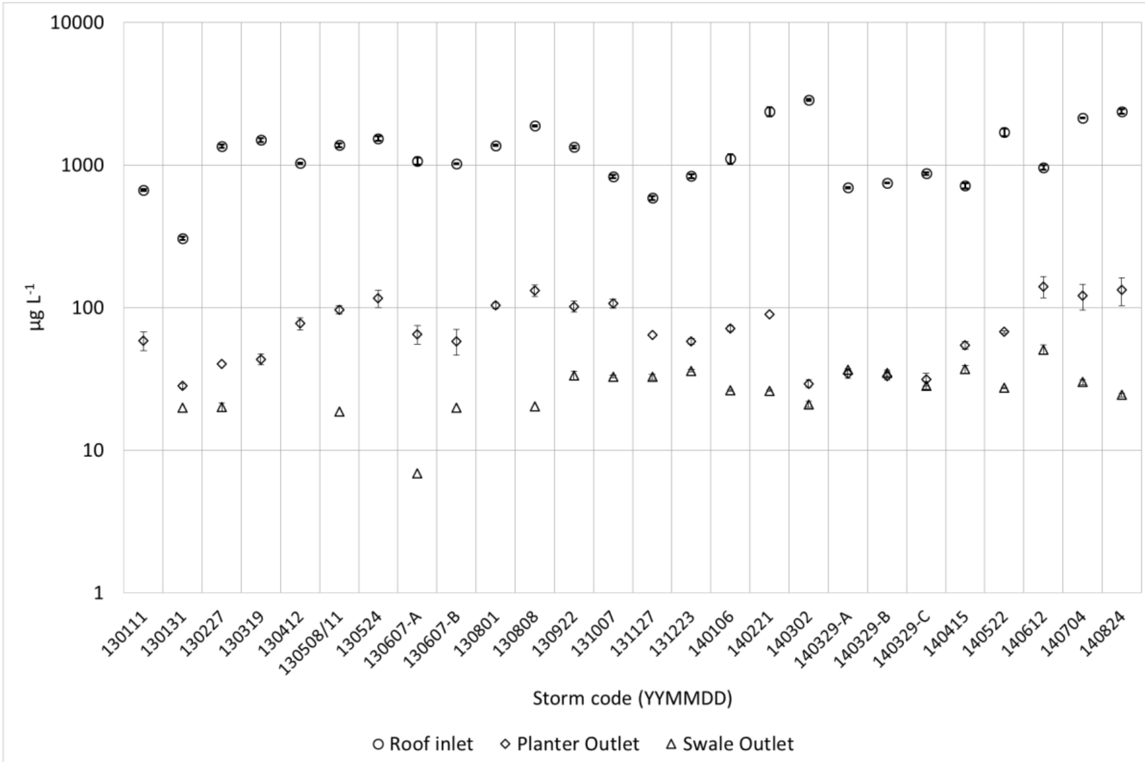
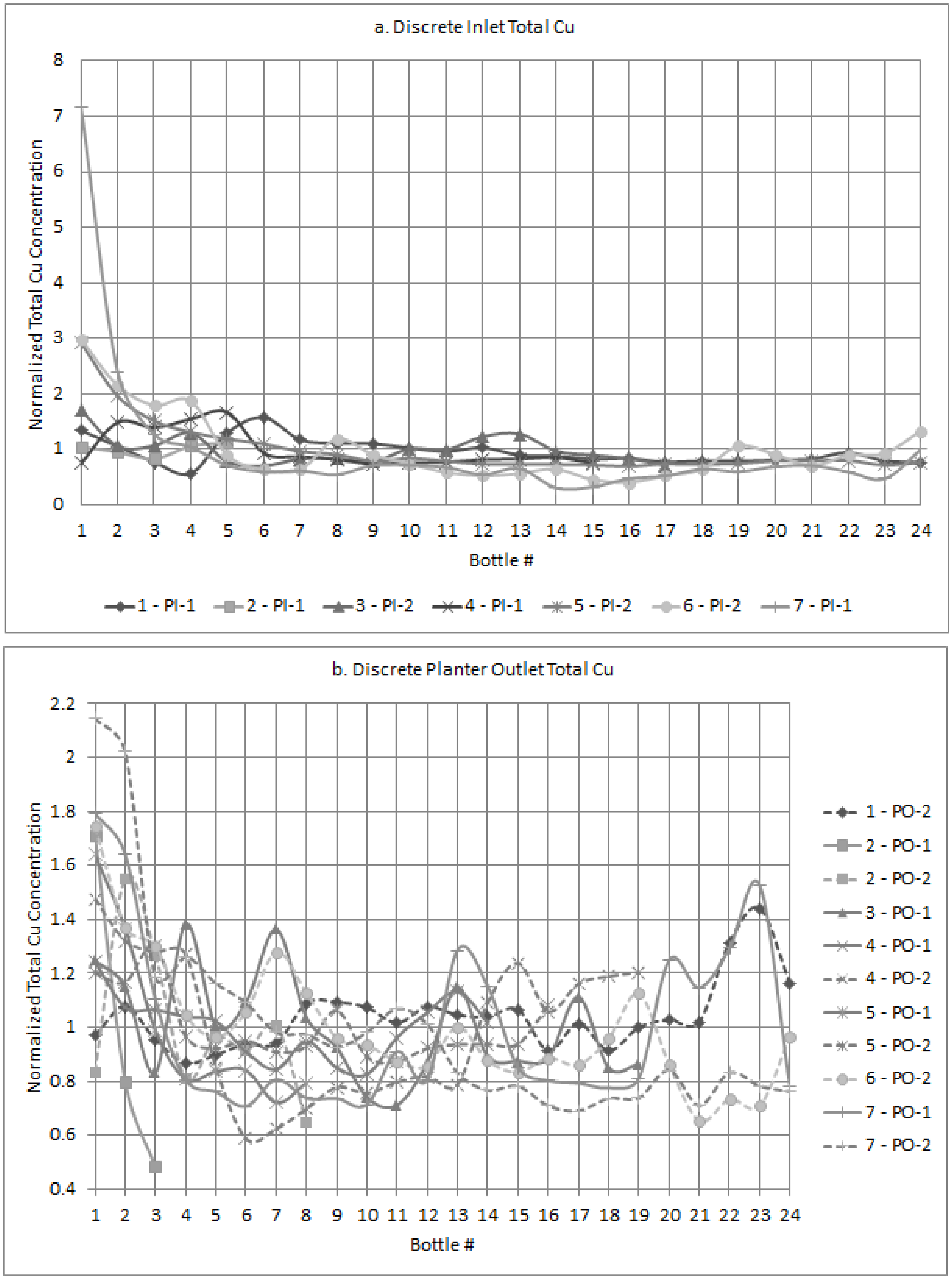


Figure 2.6 - Total Cu for 26 averaged composite storm inlet and outlet values by ICP–MS. Roof inlet mean = 1,279 µg L^{-1}, Planter Outlet mean = 75 µg L^{-1}, Swale Outlet mean = 28 µg L^{-1}. Many of the standard error bars are too small to be seen within the data points. Note that the y-axis is logarithmic.



2.7 (a-b) – Normalized Total Cu for Discrete Events. Values for each storm were divided by the mean value for that storm so that the average total Cu concentration was set to 1.0 for all storms. Note that the Y-axis values are different for each graph.

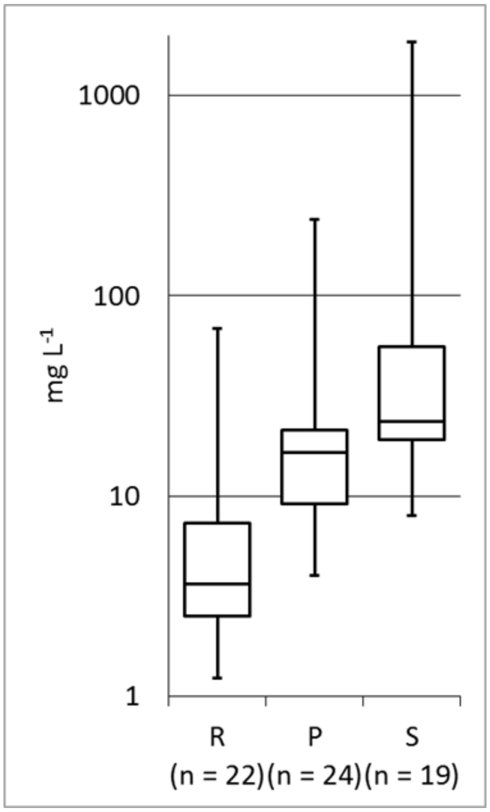


Figure 2.8 - TSS for SCM influent and SCM effluent averages for composite storm events. R = Copper Roof; P = Planter boxes; S = Swales. The middle bars are the median value; the boxes represent 25th and– 75th percentiles; bars represent the range of the data.

Table 2.1 – Analyses for planter and swale soils. Nominal % pass is the general guideline for mineral aggregate gradation per design specification in the SWMMWW; percentages given under each SCM are the results from our analysis. Planters are presented as averages of the two BSMs; swale averages are given by their profile depths.

Sieve # (size)	Nominal %	Planters	Swale (0-10 cm)	Swale (10-20 cm)	BSM
3/8 (9.5 mm)	100%	100%	100%	71.9%	
4 (4.75 mm)	95-100%	92%	94.5%	70.5%	
10 (2.00 mm)	75-90%	71.2%	71.3%	61.7%	
40 (425 µm)	25-40%	35%	36.7%	34%	
100 (150 µm)	4-10%	11.7%	19.8%	17.3%	
200 (15 µm)	2-5%	7.1%	12.6%	10.8%	
OM	40%	4.6%	2.5%		4%
Cu	750 mg kg^{-1}				10 mg kg^{-1}
pH	6 – 8.5				6.7
CEC [cmol(+) kg^{-1}]	5	2.0	0.9		1.7

Table 2.2 - Number of samples collected from the 10 sample locations for composite and discrete storm events. Note the “key” at the bottom of the table. Check marks indicate a sample collected for composite storm events. The number of bottles collected in each ISCO sampler are indicated for each discrete event. Full bottles and grab samples for composite events indicates that the sample may not represent a true EMC.

Storm Code	C-1	C-2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					Composite Storm Events					
130111	✓	✓	✓		✓	✓	✓	✓		
130131	✓	✓	✓f	✓	✓f	✓	✓	✓		✓
130227	✓	✓	✓		✓		✓	✓	✓gs	✓gs
130319	✓	✓	✓	✓	✓	✓	✓	✓		
130412	✓	✓	✓	✓	✓	✓	✓	✓		
130508/11	✓	✓	✓	✓	✓	✓f, 11	✓	✓		✓11
130524	✓	✓	✓	✓	✓	✓	✓	✓		
130607-A	✓	✓	✓f	✓	✓f	✓f	✓	✓		✓
130607-B	✓	✓	✓	✓	✓	✓	✓	✓	✓	
130801	✓	✓	✓	✓	✓	✓	✓	✓		
130808	✓	✓	✓f	✓f	✓f	✓f	✓f	✓f		✓
130922	✓	✓			✓	✓	✓	✓	✓	✓
131007	✓	✓	✓	✓	✓	✓	✓		✓	✓
131127	✓	✓	✓f	✓		✓			✓	✓
131223	✓	✓	✓		✓	✓	✓	✓	✓	✓
140106			✓	✓	✓	✓	✓	✓	✓	✓
140221	✓	✓	✓	✓	✓		✓	✓	✓	✓
140302			✓	✓	✓	✓	✓	✓	✓	✓
140329-A	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
140329-B	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
140329-C		✓	✓	✓	✓	✓	✓	✓	✓	✓
140415	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
140522	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
140612	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
140704	✓	✓	✓	✓	✓	✓		✓	✓	✓
140824			✓	✓	✓	✓	✓	✓	✓	✓
total	**22**	**23**	**25**	**22**	**25**	**24**	**24**	**24**	**17**	**20**
					Discrete Storm Events					
ISCO 1				24		24				
ISCO 2			5		3	8				
ISCO 3				17	19					
ISCO 4			15		14	19				
ISCO 5				24	8	16				
ISCO 6				24		24				
ISCO 7			24		24	24				
total			**44**	**89**	**68**	**115**				
Key	Blank = no sample			f = full bottle		gs = grab sample			11 = 130511	

Table 2.3 - **Precipitation information for each storm event.** For calculations during the 130508/11 storm, the initial total precipitation measurement was used for the 2 sample points collected on May 11th. Discrete Events were often collected during long-duration storms. In order to discern the sampling period, the hydrographs should be consulted. ADP is the antecedent dry period.

Storm Code	Total precip. mm	ADP days	Storm duration hours	Rough Storm Intensity mm hr^{-1}
Composite Storm Events				
130111	7.0	13.0	2.8	2.5
130131	59.3	3.0	11.5	5.2
130227	16.1	3.0	18.5	0.9
130319	10.9	6.0	5.5	2.0
130412	14.0	7.0	2.7	5.2
130508/11	24.6/15.5	7.0	12.5	2.0
130524	25.9	7.0	17.0	1.5
130607-A	44.5	3.0	9.4	4.7
130607-B	19.1	0.0	15.2	1.3
130801	12.7	1.1	20.4	0.6
130808	4.6	1.2	22.4	0.2
130922	22.4	5.0	6.8	3.3
131007	20.8	15.0	3.5	5.9
131127	51.4	8.0	17.6	2.9
131223	21.8	1.9	27.9	0.8
140106	6.6	4.0	18.2	0.4
140221	5.5	0.5	1.0	0.6
140302	6.2	5.0	9.7	0.6
140329-A	19.2	0.4	11.9	1.6
140329-B	31.5	0.0	16.6	1.9
140329-C	22.6	0.0	16.2	1.4
140415	31.5	8.0	14.5	2.2
140522	4.9	5.0	22.4	0.2
140612	40.6	0.4	29.1	1.4
140704	22.9	7.0	24.2	0.9
140824	10.7	6.5	90.1	0.1
Average	**21.3**	**4.5**	**17.2**	**1.9**
Discrete Events				
ISCO 1 (12 July, 2013)	22.4	9.0	28.5	0.8
ISCO 2 (13 Sept. 2013)	6.5	15.0	5.5	1.2
ISCO 3 (5-7 Dec. 2013)	27.2	8.0	37.3	0.7
ISCO 4 (13-14 Jan. 2014)	6.8	1.8	27.5	0.2
ISCO 5 (12-13 Mar. 2014)	7.0	7.0	1.7	4.1
ISCO 6 (16 May 2014)	57.5	6.0	10.2	5.6
ISCO 7 (12 Aug 2014)	56.2	6.5	26.9	2.1
Average	**26.2**	**7.6**	**19.7**	**2.1**

Table 2.4 - Quality Control for analytes.

	% recovery SRM	n	% RSD Duplicate	n
ICP - MS				
Total Cu	102.0	32	13.1	39
Dissolved Cu			10.6	38
TSS	99.0	11	37.6	16
Total N	98.4	8	45.0	5
Total P	107.7	3	70.8	6

Table 2.5 – Stormwater nutrients - Total N (mg L^{-1}) by C/N analyzer for limited storm events. Values for ISCO 6 are an average of all sample vessels. Total P (µg L^{-1}) by spectrophotometric methods.

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Total N					mg L^{-1}					
130131					0.6	1.2				
130808			0.3	0.3	0.4	0.5	0.3	0.2		5.3
131127						0.1			0.4	2.7
140415	0.6				0.2	0.6			0.5	0.4
140522	1.3	1.5	0.9	1.1	0.8	0.9	0.8	1.0	0.3	0.4
140612	0.5	0.5	1.6	0.2	0.4	0.5	0.2	0.4	1.1	0.3
140704	1.6	0.4	0.5	0.4	0.4	0.6		0.6	1.4	1.3
140824			1.0	0.9	0.8	0.6	0.5	0.6	1.8	0.7
ISCO6 (avg.)				0.1		0.2				
Average	**1.0**	**0.8**	**0.6**	**0.5**	**0.5**	**0.6**	**0.5**	**0.6**	**0.9**	**1.6**
Total P					µg L^{-1}					
130508		26	16	28	88	39	14	24		
130808	18	30	31	16	26	83	21	24		999
140415	115	16	32	16	151	145	44	142	80	166
140824			29	22	97	68	32	23	289	20
Average	**66**	**24**	**29**	**21**	**90**	**84**	**28**	**53**	**185**	**395**

Table 2.6 - Regression analyses performed at the 95% confidence level for several variables. P-values are given for significant correlations. “pos.” is a positive correlation; “neg.” is a negative correlation. An “x” indicates no significant correlation. Blank spaces indicate correlations not measured. ADP is the antecedent dry period. RSI is rough storm intensity (mm/hr).

	p value	
	SCM influent total Cu	Planter box % attenuation
Averaged planter box total Cu	0.0284 pos.	
SCM influent total Cu		0.002 pos.
Time	x	x
ADP	x	
Total precipitation	0.00247 neg.	0.007 (PO-1) neg. 0.022 (PO-2) neg.
RSI	0.0068 neg.	x

Table 2.7 - Estimation of retention time by hydrograph analysis. High-resolution storm data from a 1 month period were used to estimate the retention time in PO-2 during 5 distinct events (storm set #1 had 4 periods of intensity, set #2 had 2 periods of intensity). Precipitation for these is given in mm. The minutes are in 3 groups of when 25, 50, and 75% of the influent passed through the planter box.

			minutes	
Storm set	mm	25%	50%	75%
1-A	5.5	10.8	7.2	45
1-B	5.5	14.4	13.8	15
1-C	5.5	18	20.4	21.6
1-D	5.5	7.2	18	28.2
2-A	3	7.2	10.8	15.6
2-B	10	4.2	6.6	10.2
3	2	92.4	163	90
4	43	28.8	34.2	24.6
5	4	18	23.4	40.8
avg.		**22.3**	**33.0**	**32.3**

Chapter 3

Stormwater Control Measures Decrease the Toxicity of Copper Roof Runoff

1. SUMMARY

In order to mitigate the potential impact of copper roof runoff on sensitive aquatic biota, stormwater control measures (SCMs) that incorporate low impact development (LID) designs were examined for influent and effluent water quality. Influent samples from a copper roof were compared to effluent samples from two types of SCMs – a bioretention planter box and a biofiltration swale. Each SCM type was examined in duplicate (i.e. two planter boxes and two swales) along with effluent from two reference structure roofs (an asphalt shingle roof and a Plexiglas roof). The biotic ligand model (BLM) was used as a means of evaluating stormwater toxicity and predicting stormwater *Daphnia magna* LC_{50}s. Due to the low ionic strength (LIS) of the stormwaters and the sensitivity of the BLM to pH, a LIS pH measurement technique was utilized for this study. To compare results from the BLM, five 48-hour toxicity tests were performed with LIS cultured *D. magna* using both influent and effluent waters. Forty-eight hour earthworm (*Eisenia fetida)* avoidance assays were performed one and two years after roof construction, in one soil media sample from each planter box, and two samples from each swale. The media was characterized for metal content and pH.

The SCMs decreased toxicity of copper roof runoff in both the BLM model results and the stormwater bioassays. Water exiting the SCMs was substantially higher in pH, ions, alkalinity and dissolved organic carbon (DOC) and substantially lower in total and dissolved free ionic Cu. As a result, the BLM predicted higher LC_{50}s for SCM

effluent waters compared to influent from the roof. None of the *D. magna* survived the 48 hour trials in SCM influent from the copper roof. For planter and swale effluent, survival averaged 86 and 95% respectively. The first year earthworm avoidance assay showed no significant avoidance behavior in the treatments except for one sample taken directly from the influent flow path in swale-2. The second year assay found significant avoidance only in swale-1 soil. Media Cu content increased in the planter boxes from year 1 to year 2 but swale Cu content decreased, possibly due to variations in sampling locations.

2. INTRODUCTION

It has been estimated that 13% of rivers, 18% of lakes, and 32% of estuaries in the US are impaired due to urban stormwater even though urban lands cover about 3% of the land surface (The National Academy of Sciences 2008). Stormwater control measures (SCMs) are intended to minimize stormwater pollution and/or reduce volume using flexible practices (Taylor & Fletcher 2007). Low impact development (LID) is a management approach to development (or re-development) that seeks to minimize stormwater as a waste product and incorporates various designs that preserve the natural setting or landscape and minimize the effects of impervious surfaces. Bioretention is a relatively new SCM that can have various designs but can be thought of as shallow areas for water storage, treatment or conveyance that contain a matrix of soils with mulch and drainage layers as well as plants. Organic matter can be incorporated into the matrix for its potential binding capabilities or other positive benefits. Ultimately, the performance of SCMs should be tied to receiving water health (Winston and Hunt 2007). A Relative Risk Model (RRM) has been implemented to evaluate the effectiveness of SCMs on a regional level in the Pacific Northwest (Hines & Landis 2014). The authors noted that areas with the highest amount of development (more urbanized) had the highest risks to prespawning mortality (PSM) in salmonids but that LID could decrease the overall risks if implemented on a large scale. The mechanism of treatment for dissolved metals is their sequestration in the bioretention soil media (BSM) and modification of chemical speciation in water exfiltrating from the structure.

Copper is a common element found throughout the biosphere. At low concentrations, it is an essential element for life. At high concentrations, it can be toxic to humans; at concentrations in the low μg L^{-1} range it can be detrimental to sensitive aquatic life affecting growth, reproduction and survivability (Boulanger & Nikolaidis 2003, Bertling et al. 2006). The most toxic form of copper is the free-metal ion (Cu^{2+}) or cupric form (Wallinder & Leygraf 1997). Copper enters the environment from many sources such as architectural materials, automobile brake pads and fluids, coinage, fertilizers, copper based pesticides, mining, municipal sewage plants, waste dumps, agricultural feedlot additives, sewage sludge applications, and other means (Berbee et al. 2014, Bertling, et al., 2006, Boulanger 2003). As of September 2014, the United States Environmental Protection Agency (US EPA) reports that 731 waterway segments of the United Sates are impaired with copper (US EPA, 2014).

Runoff from copper roofs may be responsible for as much as 4 to 20% of the copper in stormwater (Arnold 2005). In freshwater systems, naturally occurring copper can vary between 0.2 and 30 μg L^{-1} (Bowen 1985). New roofs have been demonstrated to have 1000 to 14,000 μg L^{-1} total Cu in runoff (Bertling, et al. 2006, and references therein) compared to some non-copper roof runoff concentrations such as 7.6 and 12.7 μg

L^{-1} for tar felt and asbestos cement, respectively (Quek & Forster 2000). Runoff rate or concentration from the roof itself does not give the whole picture, also important are the kinds of attenuation processes take place between the roof outlet and the receiving water (Hedberg et al. 2014).

States such as Washington and Oregon are seeking ways to mitigate potential harmful effects of diffuse and nonpoint sources of copper. Research in the Puget Sound Basin indicated that roofing materials of all types account for 11% of copper releases (Ecology & King County 2011). In 2010, Washington State passed a law restricting and phasing out the use of copper in brake pads as a way to decrease copper pollution to waterways (Washington Department of Ecology 2012a). The revised Western Washington Stormwater Manual, released in 2012, documents details related to various Stormwater Control Measures (SCMs). This research was designed with these SCMs in mind, and to conform to the water quality requirements for the State of Washington.

Salmonids are an important part of the economy, history and tradition of the Pacific Northwest but their numbers have been declining dramatically since the mid-19th Century and by 1933 they were estimated to be at about 1/5 of their previous levels (Lackey 2003). Thus regulators have paid particular attention to increased levels of copper in waterways where such sensitive species are of concern. Concern has arisen over the effects of low concentrations of Cu on the olfactory responses of fish and invertebrates. Concentrations of Cu in the single digit µg L^{-1} can cause them to avoid Cu-containing water when their olfactory system is not impaired, or when olfaction is impaired to lose important functions such as attraction to food and reproductive pheromones, and avoidance of predators (Hansen et al. 1999, McIntyre et al. 2012).

Geochemical metal speciation as an equilibrium process will determine the toxicity of metals in the environment. The presence or lack of ligands will ultimately be the most easily effective means of either immobilizing metals or making them less bioavailable to sensitive aquatic organisms (Rachou et al. 2007).

The effect of pH on metal toxicity can vary and appear inconsistent even though toxicity usually increases as pH decreases since metals begin to form complexes with CO_3^{2-}, HCO_3^-, and OH^- at higher pH. Cu toxicity is greatest at pH ~ 6 and decreases as pH increases in intermediate to high alkalinity waters, but toxicity only decreases above pH ~ 7 in low alkalinity waters (Meyer et al. 2007). Hardness cations (Ca^{2+} and Mg^{2+}) are both nutrients that can be outcompeted by metal ions preferentially attached to gill surfaces (Meyer et al. 2007). Alkalinity is usually dominated by HCO_3^-, CO_3^{2-}, and OH^- and usually covaries with pH. Though these ions usually do not interact directly with fish gills, changes in alkalinity will affect metal speciation and thus the free metal concentration. Dissolved organic carbon (DOC) used as a surrogate for dissolved organic matter (DOM) is usually plant-derived polydentate humic and fulvic acids that bind free metal ions and are protective against metal toxicity (Meyer et al. 2007). Up to 98% of Cu in circumneutral solutions has been reported to be complexed with DOM (Rachou et al. 2007). DOC has been found to be protective of Cu toxicity to *Daphnia magna* in a range of sources and concentrations from 0.9 – 22 mg L^{-1} (Kramer et al. 2004).

The biological receptor for metal toxicity is the biotic ligand. For aquatic organisms, biotic ligands are active ion uptake pathways (such as Na^+ and Ca^{2+} transporters). The biotic ligand model (BLM) is the basis for the EPA's national recommended water quality criteria (WQC) for copper (US EPA, 2007). It has been adopted by various states and is under consideration for adoption by Oregon and Washington for 2015/2016. The BLM is a quantitative model that takes chemical equilibrium, physiological and toxicological processes in to account (Paquin et al. 2002) and allows for the prediction of acute (criterion maximum concentration or CMC) (CMC = FAV/2) and chronic (criterion continuous concentration or CCC) water quality criteria, and LC_{50} values for several fish and invertebrates.

The goal of this study was to examine the effectiveness of SCMs in attenuating copper toxicity from copper roof runoff. Stormwaters from a copper roof picnic shelter were evaluated both before the water entered SCMs (as influent) and after it had passed through the SCMs (as effluent). There were two kinds of SCMs; one was a bioretention planter box; the other was a biofiltration swale. Each was examined in duplicate along with stormwaters from two reference structures, one made of Plexiglas (to account for atmospheric deposition) and another made of asphalt shingle (to compare a common roofing material).

The BLM was used with measured water chemistry parameters to model potential toxicity. Parameters for the BLM include pH, major ions, alkalinity, and DOC. This allows for an estimation of toxicity based on Cu bioavailability. Toxicity testing was also performed with stormwaters collected using *D. magna*. Additionally, soil toxicity was evaluated using earthworm avoidance assays. We hypothesized that the SCMs would raise the concentrations of copper complexing ligands and competing ions in a manner that decreases toxicity as stormwater passed through the structures.

3. MATERIALS AND METHODS

Influent stormwater from a copper roof and effluent stormwaters from two bioretention planter boxes and two biofiltration swales were sampled for 26 composite storm events, along with stormwater from two reference structures – Plexiglas and asphalt shingle roofing material. Additionally, seven discrete sampling events were analyzed for SCM influent and planter box effluent. [See Ch. 2 for a full site and sampling plan description].

3.1 Stormwater Sampling

3.1.1 pH Analysis

The use of conventional pH probes for measurement in LIS waters often produces non-reproducible results, substantial drift and high error (Wiesner et al. 2006, Koch et al. 1986, Davison et al. 1985). In order to more accurately measure pH in LIS waters, measurements were taken with an Orion 8102B Ross Ultra probe with Orion filling solution (810007) coupled with a Thermo Scientific Orion Star pH/ISE/Cond./DO bench-top meter. Calibrations were performed with LIS buffers 6.97 and 4.10 (Thermo Scientific 700702 and 700402 respectively; chemical composition listed as a trade secret). All buffers were certified at 25 ˚C.

Measurements for pH were made within 24 hours of sample collection with the addition of 120 µl of KCl Ionic-Strength Adjuster (ISA) (Orion Purewater pHISA 700003) to a 12 mL sample. Check standards were Standard Reference Material Traceable® pH 4.005 (Fisher Scientific, 06-664-259) and pH 10.012 (06-664-261) [both ± 0.010], and an in-house prepared solution of 3.387g KH_2PO_4 + 3.533g Na_2HPO_4 dissolved in 1L 18.2mΩ water (pH 6.863) (APHA 2005; Table 4500).

Through April 14, 2014, measurements were made using a calibrated Accumet 13-620-108 probe coupled to an Accumet AB 15 pH meter. However, these measurements appeared to be unreliable because of the low ionic strength of the stormwater samples. Therefore, all available archived samples were thawed, brought to room temperature, and remeasured using the Orion 8102B Ross Ultra probe.

Storm (140415) was analyzed to compare “standard” (Accumet) and LIS measurement techniques and evaluate any potential bias introduced by analyzing frozen archived samples. The storm contained ten sample locations; pH was measured for fresh samples with the standard probe and both fresh and frozen samples measured with the LIS probe.

Storm (140612) was used to measure the effects of sample aging in the refrigeration unit as well as the effects of the freezing process using the LIS probe. The storm contained all ten sample locations. Sub-samples were archived (frozen) the day of collection. The samples were measured for pH that same day using the LIS probe, then left in the refrigerator and remeasured subsequently for 20 days. The archived sub-sample was also thawed and remeasured after 20 days.

3.1.2 Ion analysis by Ion Chromatography (IC)

Within 48 hours of sample collection, samples were prepared for ion analysis by collecting the filtrate from a 3 mL syringe-driven Millex® PTFE membrane 0.45 µm disposable filter. Concentrations of the cations Na^+, K^+, Mg^{2+}, and Ca^{2+}, and the anions Cl^-, and SO_4^{2-} were analyzed using a Dionex ICS-5000 Ion Chromatograph. Check standards were prepared from SPEX CertiPrep standards. The limit of quantitation (LOQ) was 1 mg L^{-1}.

3.1.3 Alkalinity Analysis by Titration

Titrations were performed within 48 hours of sample collection using a commercial solution of 0.02 M trace metal grade H_2SO_4 according to Method 2320 B (APHA 2005). In addition to color change, pH was noted with a calibrated Accumet 13-620-108-A probe coupled to an Accumet AB 15 pH meter. When the sample was titrated to a value closest to pH 4.5, the volume of H_2SO_4 used was recorded. A 0.68 mM Na_2CO_3 solution (40 mg L^{-1} $CaCO_3$ alkalinity) was used as a check standard. The LOQ was 0.2 mg L^{-1} $CaCO_3$.

3.1.4 Dissolved Organic Carbon by NPOC

Using a vacuum flask, samples were passed through quartz filters or glass (0.45 µm) and filtrate was collected. Filtrates were then analyzed for DOC by measuring non-purgeable organic carbon (NPOC) using a Shimadzu TOC-VCPH Analyzer. A 20 mg L^{-1} carbon check standard was run with each batch of samples. The LOQ was 1 mg L^{-1}.

3.1.5 Free Ionic Copper by Ion Selective Electrode (CISE)

A Thermo Scientific Orion 9629 BNWP Ionplus Sure Flow Cupric probe with Orion Ionplus (900063) filling solution coupled to a Thermo Scientific Orion Star pH/ISE/Cond./DO bench-top meter was used to measure free ionic copper within 48 hours of sample collection. Calibration was performed using 0.02 M Ethylenediamine and 5 M $NaNO_3$ ionic strength adjuster (ISA) with subsequent additions of 0.1 N NaOH and 0.1 N HNO_3 to adjust pH. pH was measured using the calibrated Accumet 13-620-108 probe coupled to an Accumet AB 15 pH meter. These values were then modeled with the geochemical speciation program Visual MINTEQ in order to determine Cu^{2+} concentration corresponding to the pH of the sample. For sample analysis, 10 mL of sample and 200 µL of ISA were measured on a stir plate in polypropylene disposable cups.

3.2 Quality Control (QC)

Dilutions and rinsing of materials were done with 18.2 mΩ high-purity water. For all sample preparation and analysis, one method blank (18.2 mΩ water) and one or more duplicates were used. Acid washing with 1% HNO_3 (ACS certified 50-70% trace metal grade, diluted with 18.2 mΩ water) was performed on plastic and glassware reused for metal analysis. Samples were archived within 24 hours of collection.

During analysis of QC data, all data points below the LOQ were replaced with half the LOQ. Recovery for standards is reported as % recovery, and duplicates are reported as % relative standard deviations (% RSDs).

3.3 Statistical Analyses

For the water quality parameters of pH, alkalinity, DOC, and the six ions, a one way ANOVA was performed to see if SCM influent and SCM effluent values were the same by the Shapiro-Wilk normality test at the 95% confidence level. Then a Kruskal-Wallis One Way ANOVA on Ranks was performed to determine if the differences in median values among the treatment groups were greater than would be expected by chance. Last, to isolate groups that differ from others, a multiple comparison procedure (Dunn's Method) was performed at the 95% confidence level.

Three ANOVA regression analyses were performed at the 95% confidence level for data reported both in this chapter and from Chapter 2 for the following variables: correlations between SCM influent pH and planter box effluent total Cu; the correlation between planter box effluent pH and planter box effluent total Cu; the correlation between DOC and planter box % attenuation.

3.4 Modeling by the Biotic Ligand Model (BLM)

Influent and effluent waters from both composite and discrete storm events were modeled for *D. magna* LC_{50}, criterion maximum concentration (CMC), and criterion continuous concentration (CCC) water quality criteria using the BLM (Ver. 2.2.3; http://hydroqual.com/wr_blm.html). The default LA_{50} parameter was adjusted and a geometric mean LA_{50} value of 0.0532 nmol Cu g^{-1} wet wt. was entered into the BLM input for *D. magna* in toxicity mode (USEPA 2007, Appendix E) which is generally consistent with the value used by Fulton and Meyer (2014) to optimize BLM performance for the prediction of Cu toxicity to *D. magna.* Fulton and Meyer (2014) found that this LA_{50} value yielded a better fit between BLM-predicted and observed laboratory EC_{50} values. pH, DOC (as measured by NPOC), Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4, Cl^{-}, and alkalinity were entered as measured. A temperature of 20˚C and a value of 10% were used for temperature and humic acid, respectively. For cases where measured ions were below the detection limit, a value of half the LOQ was entered (0.5 mg L^{-1}). Measured dissolved Cu in SCM effluent was evaluated against the modeled FAV for composite storm events. CISE measurements were compared with the speciation mode BLM modeled free ionic Cu concentrations to evaluate the agreement of the BLM speciation to measure free Cu concentrations. The BLM speciation mode was used to predict Cu speciation in stormwater samples.

3.4.1 Sensitivity Analyses

Due to variability in pH measurement techniques a sensitivity analysis was performed for pH to evaluate the effect of pH measurement technique on the modeled FAV for storm 140522. The analysis was performed for selected samples by adding or subtracting half a pH unit and modeled with the BLM. Also, a sensitivity analyses for DOC was performed in a similar manner for storm 140522. DOC was varied ± 5 mg L^{-1} (close to the standard deviation of effluent waters).

3.5 Toxicity Testing

3.5.1 *Daphnia magna* Stormwater Bioassay

Toxicity tests were done with the cladoceran *Daphnia magna* through acute 48 hour static toxicity tests (US EPA, 2002). *D. magna* in early toxicity tests had poor survival in the C-2 stormwater (data not shown) which had an average hardness of 5.3 mg/L $CaCO_3$, which is below the limits of previous research that has tested this range for *D. magna* survival (Terra & Fieden 2003). In order to maximize survival in the low hardness conditions typical of stormwater, *D. magna* were cultured in and acclimated to intermediate hardness (48 – 80 mg L^{-1} $CaCO_3$) water and fed the algae *Raphidocelis subcapitata (Selenastrum capricornutum)*. Five *D. magna* (n = 5) neonates (<48 hours old) were placed into 50 mL polypropylene disposable cups that contained 25 mL of sample. Four replicates were used for each treatment and the culture water control. Tests were run for 48 hours in a light and temperature controlled aquatic laboratory (16 h light / 8 h dark; 20 ˚C). Organisms were not fed during the test period. Survival was checked visually at the end of the 48 hour period. Hardness was determined for the *D. magna* culture water by summing the Mg and Ca concentrations as determined by IC.

3.5.2 Earthworm Avoidance Assay for Soils

The International Organization for Standardization (ISO) method 17512-1:2008(E) was followed for testing avoidance behavior. The objective was to test the response of the earthworms (*Eisenia fetida)* in both the swale and planter box media one year and two years after treatment and compare them with a control soil. Native soil collected from the location of the picnic shelter, but outside of the construction zone served as control soil, and this was the same soil that was amended and used as a base soil for swale construction. Soils from each of the planter boxes were collected from around the containerized plants to a depth of approximately 20 cm. Each swale soil sample was taken from two positions in the respective swale – a site near the inlet pipe where the SCM influent exited the sampling box (labeled "uphill"), and a site at the lowest portion of the swale near the point farthest from the inlet pipe (labeled "downhill"). For year one soil sampling, an effort was made to collect soil directly from the flow path of the influent water in one swale (S-2 uphill). For year two soil sampling, both "uphill soils" were collected about 30 cm downstream from the SCM influent inlet pipe. In total there were six test soils (one from each planter box and two from each swale) and there were five replicates for each soil. Additionally, a positive control was used as recommended by adding 750 mg kg^{-1} boric acid to the native soil.

The soils were air dried for approximately 48 hours, then oven dried at 50 ˚C overnight. The following day, they were hand pulverized with a rubber mallet to break clods. Soils were then sieved through a #10 ASTM (2 mm) sieve on a soil shaker. For the tests, 1,500 mL cubical polypropylene containers were used; each had a Plexiglas divider to segregate the containers into two equal halves. The containers were filled to a depth of approximately 5 cm, with control soils on one side of the divider and treatment soils on the other. The soils were moistened to 60% of water holding capacity with 18 mΩ water.

The earthworms were acclimated in the native soil for 2 days at 20 ˚C and a 12 hr light / 12 hr dark period. Just after removal of the dividers, 10 worms were carefully inserted to the center of each container with gloved hands. The containers were then covered with ventilated lids and randomly placed on a shelf; the test ran for 48 hours. At the end of the test period the dividers were reinserted. Each side was carefully excavated and the worms on each side were counted. If a worm was found in both sides, it was counted as half a worm for each side. Worms not found were assumed dead and not counted. A t-test for paired two sample means was run for all samples that showed avoidance behavior.

3.6 Determination of the Acid Extractable Metal Content and pH of Soils

Metals analysis of planter box and swale media used in the earthworm assay was performed in October 2013 and 2014. Approximately 50 mg of media was put into a Teflon vial overnight with 7N HNO_3 at 120°C. Samples were evaporated to dryness and then reconstituted with 0.2 N HNO_3. An internal standard of Indium was added to the completed samples to obtain a final concentration of 1 ppb. The metals Fe, Cu, Zn, Cd, and Pb were measured using a Thermo (VG) PQ Excel ICP-MS and CETAC ASX-520HS auto-sampler. SRM (Standard Reference Materials) 2709 San Joaquin Soil (National Institute of Standards and Technology) was used as a check standard. The limit of quantitation (LOQ) was 1 µg L^{-1}.

Soil pH for each group was determined in October 2014 by combining a 1:1 (by weight) suspension of soil with 0.01 M $CaCl_2$ that was agitated and left overnight. Measurements were made directly in the solution vessel.

4. RESULTS

4.1 pH

Given the sensitivity of the BLM to pH, it was critical that accurate measurements be used. There was substantial variation between the results of the standard and LIS techniques.

All available archived samples were remeasured for pH using the LIS technique. After storm event 140415 (not inclusive) the pH of fresh samples was measured using the LIS technique. pH was elevated in SCM effluent compared to the copper roof SCM influent by about a full pH unit (Figure 3.1-a). Note that for storms 130131 swale outlet -2 (SO-2), 130227 (SO-2) and 140221 swale inlet -2 (SI-2), one sample was not available to be remeasured for each storm. No archives were available for either ISCO 2 or ISCO 3. Thus for missing archives, the values from the standard pH technique were used. Data for pH, as well as the concentrations of other stormwater analytes were not normally distributed and therefore the median is reported for analyte summary statistics.

Though both the Accumet (Standard) and Orion (LIS) pH probes were calibrated daily and gave similar results for pH buffers and our in-house standard, they behaved very differently in the stormwater samples, especially in the influent waters. The standard technique had been used up to storm 140415 to measure all samples. However, this probe and technique gave inconsistent results and a great deal of drift [% RSD of pH values for the standard technique ranged from 0.24 to 32.9% (avg. 7.43%)]. The Orion probe was used after that time on all samples, and consistency and repeatability improved substantially [% RSD of pH values for the new technique ranged from 0 to 4.11% (avg. 1.51%)]. The LIS technique not only used a low-resistance glass probe, but LIS buffers were used for calibration and an ISA was added to the samples. Several trials were done comparing samples with and without ISA (data not shown). The effect was minor (< 0.1 pH units averaged for 28 inlet, 28 outlet, and 2 reference structure samples).

The comparison of two probes from 140415 shows pH measurements increase greatly using the LIS technique (greater than 0.5 pH units averaged over all samples) (Figure 3.2). An ANOVA on ranks test at the 95% confidence level found that there was a statistically significant difference in median values between the three groups (LIS fresh, LIS frozen, standard technique) (P-value 0.046). A Student-Newman-Keuls multiple comparison procedure then was used to determine whether there were differences between each pair. There was not a significant difference between the LIS technique for fresh versus frozen samples, but there were significant differences between the LIS technique (either fresh or frozen) and the standard technique. The measurements repeatedly taken during the 20 day aging process and on frozen and thawed samples from 140612 (Figure 3.3) showed that there appears to be greater variation in the daily measurements than any consistent effect on pH either over time, or from freezing. Averages of fresh and frozen samples (averaged over the seven separate trials) differed by less than 0.1 pH unit and all differences from the frozen samples were less than the standard error of the fresh samples.

4.2 Water Chemistry Analysis

4.2.1 Quality Control Results

All SRM recoveries were within 90 - 110%. Most ion duplicate RSDs were within 10%, except Na^+ at 11.2%, and Cl^- at 13.8%. Though NPOC duplicate RSDs were within 10%, alkalinity and the CISE were 15.2 and 36.9%, respectively (Table 3.1).

4.2.2 Stormwater analytes

The analyses of major ions showed that many were below the LOQ of 1 mg L^{-1}, especially in SCM influent. Ca^{2+} and SO_4^{2-} were elevated in both SCMs but especially in the swale effluent. Mg^{2+} was below detection for more than 97% of influent samples, and averaged effluent values were in the low single digit mg L^{-1}. Also in the low mg L^{-1} range, Na^+ and Cl^- were elevated after stormwater passed through both SCMs but only slightly on average; values were highest in the swales. K^+ was near the LOQ for most inlet values, but was elevated by the SCMs to the low mg L^{-1} range (Figures 3.1-d). The SCMs elevated alkalinity considerably especially in the swales (Figure 3.1-b). DOC values were elevated in SCM effluent more than two-fold compared to inlet values (Figure 3.1-c).

The CISE showed a considerable decrease of free Cu^{2+} in SCM effluent compared to influent stormwater (Figure 3.4). Generally, the CISE showed SCM inlet values about an order of magnitude higher than BLM modeled free Cu^{2+} and showed SCM effluent values about two orders of magnitude higher. The CISE showed a decrease in free Cu of about two orders of magnitude from SCM influent to SCM effluent however the BLM modeled values showed a decrease of roughly four or five orders of magnitude.

Statistical analysis of water chemistry results showed that all of the dissolved constituents of the SCM effluent were significantly elevated when compared to SCM influent values, except Na^{+} in planter effluent (Table 3.2). Additionally, the analysis shows that alkalinity, Ca^{2+}, and SO_4^{2-} were significantly higher in the swale effluent compared to the planter effluent, and that Mg^{2+} was significantly higher in the planter effluent compared to the swale effluent.

The three ANOVA regression analyses showed no statistically significant correlations related to planter box pH, total Cu, or % attenuation. Nor were there significant correlations related to SCM influent pH or DOC.

4.3 BLM Modeling Outcomes

4.3.1 Composite Sampling

After chemical analysis, toxicity of each composite stormwater sample was modeled using the BLM for *D. magna*. The results indicate that toxicity decreased as stormwater passed through the SCMs (Figure 3.5). SCM effluent FAV values increased by about an order of magnitude compared to SCM influent FAV values.

BLM speciation predictions showed the majority of Cu in all cases was bound to DOC, including the copper SCM influent where ~63% was bound to DOC. For the SCM effluent and reference structures, DOC bound Cu was greater than 99%. Excluding DOC, the inorganic Cu speciation in SCM influent was dominated by the free metal ion (46.6% averaged for all storms) or bicarbonate species (47.3% averaged for all storms). The remainder of Cu was complexed with hydroxide (3.5%), carbonate (2.4%), sulfate (1.7%), and other ligands. By contrast, the averaged planter box effluent Cu was modeled as 6.9% free Cu, 62.9% complexed with bicarbonates, 25.8% complexed with carbonate, 3.7% to hydroxide, and the remainder to other ligands. The swales were similar to the planter boxes with only 3.2% free Cu, 68.8% complexed with bicarbonate, 25.9% complexed with carbonate, 1.7% to hydroxide, and the remainder to other ligands.

Measured planter outlet (PO)-1 effluent dissolved Cu was below the modeled FAV in 80% of composite samples while measured PO-2 effluent was below the FAV in 96% of samples. Measured effluent dissolved Cu values were below the FAV in 100% of stormwater samples from the swales.

4.3.2 Discrete Sampling

Many of the discrete events show higher FAV values in the earlier parts of the storms, both for SCM influent as well as SCM effluent. In four out of seven events (ISCO 2, 3, 6, and 7) the first sample from SCM influent was four to 35 times higher than the mean of the remaining samples (Figure 3.6). For ISCO 1 and 4, the SCM influent in the first 5 bottles was more than double the remainder of sample FAV averages while for ISCO 5 the first bottle was not quite double the remainder average.

For planter box effluent, FAVs were higher in first samples in eight out of eleven sampling events, possibly representing residual water that had a relatively long contact-time with the media. However, rather than approaching a steady-state as the storms progressed, FAVs of later samples often varied, and FAVs rose near the end of the storm for five out of eleven events.

Since pH tended to vary little during one storm in a given sample site (roof or SCM) the FAV trends in the discrete events tended to most closely reflect the patterns found in DOC as levels are both highest in the first sample bottles and well above mean concentration for nine out of eleven events.

4.3.3 Sensitivity Analysis

Alterations of pH for the 140522 storm produced changes of about an order of magnitude in all cases with a corresponding decrease in FAV with a decrease in pH (Figure 3.7 a). An alteration of DOC for the same storm raised and lowered the FAV considerably when 5 mg L^{-1} were added or subtracted respectively; the difference was about an order of magnitude between the highest and lowest values (Figure 3.7 b).

4.4 Laboratory Toxicity Testing

The intermediate hardness culture method was adopted because of poor survival in the initial C-2 toxicity tests with organisms that were cultured in moderately hard water. Culture water hardness was tested four times to compare actual hardness with the intended hardness value of 48 - 80 mg L^{-1} $CaCO_3$. The tests showed 91, 75, 21, and 62 mg L^{-1} $CaCO_3$ in four different batches of the water. Though this is greater variation than intended, there was improved survival in control and reference test waters.

4.4.1 D. magna

Toxicity to *D. magna* decreased in the stormwater after it passed through the SCMs. As of the time of this writing, toxicity testing has been performed for seven and one half of storm events (130131, 130607-B, 130808, 131007, 131223, 140329-A, 140612, and 140824) (To achieve a total of eight toxicity tests, additional testing will be performed for the incomplete test). None of the *D. magna* placed in the 27 trials of copper roof SCM influent water survived the 48 hour testing. However for planter outlets, survival averaged 84% over 14 trials. For swale outlets survival averaged 95% over 10 trials. For C-1 (asphalt shingle), survival averaged 37% for six trials. For C-2

(Plexiglas), survival averaged 78% over seven trials. All culture water trials had greater than 90% survival.

Toxic units (TUs) were calculated for each tested sample location by determining the ratio of measured dissolved Cu to the BLM modeled LC_{50}. In this way, a TU greater than 1 should result in greater than 50% mortality in *D. magna* and a TU less than 1 should result in less than 50% mortality. The TU value was then plotted against measured mortality from toxicity tests to determine how well the BLM based predictions performed against actual toxicity tests (Figure 3.8). The SCM and C-2 effluent were generally less than one TU while the SCM influent was always significantly greater than one TU. [It should be emphasized that this is not the same "TU" as given by the BLM, which is the ratio of modeled dissolved Cu/CMC]. This showed that there was strong agreement between BLM modeled toxicity for *D. magna* and laboratory toxicity tests.

4.4.2 Earthworm Avoidance Assay

The earthworm avoidance assay was performed two times (14 months and 26 months after roof construction) from six sample locations. The first assay showed no avoidance behavior in the test soils except for the S-2 uphill location which showed 54% avoidance behavior. Cu content was about two to four fold higher in the S-2 uphill location (101 mg kg^{-1}) compared to other locations. In fact, most of the tests showed a preference for the treatment soils (from the SCMs) but the test protocol states that positive preference should be reported as 0% avoidance. The boric acid positive control exhibited 46% avoidance behavior which is consistent with the 47% response reported in the ISO 17512-1:2008(E) method. Four worms were unaccounted for during the assay.

A t-test for paired two sample means showed a significant difference in avoidance behavior from the S-2 uphill site.

For the second assay, avoidance behavior was found in one out of the six sample locations (Table 3.3). Planter -2 (P-2) showed 22% avoidance; Swale -1 (S-1) uphill showed 100% avoidance; S-1 downhill showed 38% avoidance, and S-2 uphill showed 4% avoidance. There was again a positive preference for P-1 and S-2 downhill, but these are reported as 0% avoidance. Multiple t-tests for paired sample means showed that only the S-1 uphill site avoidance was statistically significant, however soil Cu for that location was relatively low (23 mg kg^{-1}) especially compared to the two planter box soils. Soil pH for S-1 uphill was the lowest of all sites and a stepwise multiple regression analysis showed that pH by itself predicted the avoidance behavior. The boric acid positive control exhibited 36% avoidance behavior which is also consistent with the 47% response reported in the ISO method since it was within one standard deviation.

4.5 Supplemental Information

Stormwater pH values for composite and averaged discrete events are presented in more detail in Appendix J. All detailed ion values for composite storm sampling events are presented in Appendix K. Details for alkalinity and DOC for composite storm events can be found in Appendices L and M. Details for CISE measurements for composite storm events can be found in Appendix N. Appendix O provides detail of the predicted LC_{50} (FAV) and summary information for composite storm events.

5. DISCUSSION

5.1 Stormwater Chemistry

The potential toxicity of stormwater influent from the copper roof was strongly attenuated by the SCMs. This is attested by a consilience of two primary lines of evidence: The increase in pH, ions, DOC, and alkalinity that provide protective water quality characteristics for aquatic organisms, and the results of direct toxicity testing that show increased survival in SCM effluent.

The pH of the waters was raised considerably in effluent compared to influent and this change improves water quality for sensitive aquatic organisms. Additionally, it is clear that the technique used for pH measurement in stormwater samples is critically important. Overall the measurements with the LIS technique raised the majority of pH values about 1 full pH unit (Figure 3.9). The difficulty of obtaining accurate pH measurements in LIS waters has been noted in previous research and recommendations have been made to ensure proper technique (Bunsenberg & Plummer 1987, Davison et al. 1985, Koch et al. 1986, Wiesner et al. 2006). Most researchers conclude that using a glass reference electrode with a KCl salt-bridge solution is the best choice for samples that are not sensitive to K^+ or Cl^-. Most importantly, daily calibrations should be done with LIS buffers. Due to the high variability and inconsistency with the Accumet probe and high ionic strength buffers, a decision was made to follow the recommended technique for LIS waters by Thermo Scientific (Thermo 2007). This is similar to the technique employed by the National Atmospheric Deposition Program (NADP) (SOP AN-0023. 13), though they do not add ISA (Weddle et al. 2011). Since the variability with using ISA was minimal, it was decided that this was an acceptable technique.

The SCMs elevated competing cations, organic and inorganic ligands in effluent waters. These increased values show that the SCMs enhanced effluent quality by providing essential ions, increasing buffering capacity, and providing ligands capable of binding Cu (Pennington & Webster-Brown 2008). Overall, ion concentrations were low in influent waters but substantially elevated in effluent waters. The planter effluent waters were dominated by Ca^{2+}, followed by K^{+}; Mg^{2+} was also notably raised in planter effluent. The swales were dominated by both Ca^{2+} and SO_4^{2-}, having increased more than 27 x on average from inlet averages. There appear to be few trends in ion data in the SCMs over time; however there are two exceptions, as both Na^{+} and K^{+} values were higher in the planter boxes in the earliest storms. It is possible that the BSM was leaching these ions until more steady-state levels were reached. Generally, the increase of these ions improves water quality for sensitive aquatic organisms (Meyer et al. 2007) (Fulton & Meyer 2014).

Alkalinity was increased over nine times in planter effluent and more than 21 times in swale effluent due to the limestone gravel in the SCM underlayers. This increase in alkalinity raised the buffering capacity of effluent waters making it less susceptible to pH fluctuations as well as formation of Cu carbonate complexes (Di Toro et al. 2001). Additionally, increased alkalinity can decrease the impairment of ionoregulation by Cu (Meyer et al. 2007). NPOC was increased almost three times in planter effluent and over four times in swale effluent which indicates that humic and fulvic acids were likely providing further Cu complexing sites.

The CISE also provided evidence for substantial decreases in SCM effluent free Cu compared to the influent. The clearest trend was a decrease by several orders of magnitude after waters had passed through the SCMs. Although some authors (Rachou et al. 2007, Di Toro et al. 2001) discuss the utility and accuracy of the CISE to very low Cu^{2+} concentrations (10^{-14} M), our results showed poor agreement between the CISE and BLM modeled free Cu in terms of concentration, when comparing similar waters (e.g. SCM influent waters by BLM to SCM influent waters by CISE) with some values differing by several orders of magnitude. Other studies have excluded or cautioned against the use of CISE data (Meyer et al. 2007) (Paquin et al. 2002) due to unreliability of the technique. Most CISE measurements were lower than ICP-MS measurements for SCM outlets, as may be expected since the CISE should only measure the free ionic concentration of Cu. Averaged values for SCMs were lower than the averaged values for C-2, which should only have captured atmospheric deposition. This would suggest the SCMs are effective at changing Cu speciation to a less bioavailable form. Since the CISE was interpolated on a log based curve, slight variations produced greatly different results. Results for the CISE are helpful but should be viewed with caution.

5.2 Regression Analyses

The lack of correlation between roof inlet pH and total Cu effluent from planter boxes may suggest that there was not enough variation in precipitation pH or that the planter boxes had sufficient buffering capacity and ability to bind Cu at ambient pH. This explanation is similar for the lack of correlation between planter box pH and planter box effluent Cu. Since there was not a statistically significant correlation between DOC and planter box % attenuation at the 95% confidence level, it may suggest that DOC levels remain steady as a function of storm intensity.

5.3 Modeling

In all cases the FAV values were substantially raised for effluent Cu concentrations when comparing the two pH measurement techniques (Figure 3.9). Had the standard technique values been used, toxicity predictions would have been higher (lower FAV) by almost an order of magnitude on average (Figure 3.10). Yet LIS BLM values showed good agreement with toxicity testing (below).

Modeled inlet FAV were similar among composite storm events, with no statistically significant differences among roof quadrants. There was also no significant difference in FAV values when comparing replicate SCMs, however averaged swale outlet FAV values exceeded the planter outlet values as could be expected given the overall volume of the soils and bioretention soil media (BSM) in the swales compared to the planter boxes. The volume of the BSM in one swale was about 0.85 m^3, while for the planter boxes it was 0.38 m^3.

The high levels of Cu complexation to DOC in SCM influent may seem counter intuitive but was consistent with the findings of Rachou et al., 2007. The DOC levels in the SCM influent were near the levels encountered in many surface waters (Bossuyt & Janssen 2003). While the gutters were covered with a commercially available mesh gutter cover, they often contained residual organic debris (primarily leaf litter and algae). Speciation analysis through the BLM showed that the majority of inorganic influent dissolved Cu complexed with carbonate, bicarbonate and other ligands.

Any exceedance of the FAV from the SCMs needs to be kept in context – namely that these are not standards for freshwater and in a realistic application of SCMs, most effluent enters the ground after leaving the system. Even if cases where effluent volumes or soil saturation preclude this possibility, further adsorption of free Cu could take place along building or ground surfaces. Though PO-1 and PO-2 would have exceeded the FAV in 20 and 4% of samples, respectively, by comparison, the asphalt shingle reference structure (C–1) would have exceeded the FAV in 36% of samples, and C-2 would have exceed the FAV in 13% of samples. Finally, the SCM influent would have exceeded the FAVs in all cases, usually by one to three orders of magnitude.

No attempts were made to characterize the organic components in terms of humic or fulvic acid composition. It is possible that there are differences in metal speciation in the media that were unaccounted for by the default 10% humic acid value given the source and age of the BSM (Mason et al. 1999). However, the data supported the idea that increased organic matter, ions, and alkalinity provide protection of aquatic biota and the model reflects these inputs (Niyogi & Wood 2004).

5.4 Discrete Sampling

For roof stormwater, the high initial FAV could be attributed to the dry deposition of carbon and other matter on the roof surface. While the higher FAVs of these earliest samples likely helped to ameliorate toxicity somewhat, dissolved Cu was still higher in earlier samples by orders of magnitude (see Chapter 2). For planter box effluent the initially high FAVs are likely a product of pre-event water being pushed out by the incoming event water. While there seems to be an initial first-flush, it is important to note that the FAV values remain relatively constant or may even improve through the storm. Thus the SCMs appear capable of greatly attenuating the high magnitude of Cu in first flush waters released from the roof.

5.5 Sensitivity Analyses

The results of the pH sensitivity analysis were somewhat predictable in most cases. The pH sensitivity analysis for the 140522 storm showed an expected trend with all structures showing an increase in modeled toxicity (lower FAV) with decreasing pH. This clear trend is more expected at circumneutral pH, which is the case for most surface waters. Because the variation in just 0.5 pH units can affect FAVs so dramatically, it is critical not to underestimate the importance of accurate and reproducible pH measurements. Results were similar for the DOC sensitivity analysis in that relatively minor variations in DOC can greatly affect modeled toxicity (Niyogi & Wood 2004). Both pH and DOC show consistent modeled behavior to what is known about these two criteria.

5.6 Toxicity

5.6.1 *D. magna* Toxicity Testing

The four analyses for ion concentrations in the intermediate culture water showed higher than expected variation for Ca^{2+} and Mg^{2+}, as dilution by hardness values should have been closer to 48 - 80 mg L^{-1} $CaCO_3$. EPA moderately hard water is 80 – 100 mg L^{-1} $CaCO_3$, and one of the measured values was higher than this. Two values were between moderately hard and soft water, and one value was below the range of soft water (40 – 48 mg L^{-1} $CaCO_3$).

The results of stormwater toxicity testing with *D. magna* show a trend similar to the BLM model – that there is decreased toxicity in the SCM outlets. Three out of four C-1 values show high mortality and their Cu concentrations were relatively high (17, 24 and 13 µg L^{-1}). One of those (130607-B) with a Cu concentration of 13 µg L^{-1} had a low

TU (0.23) yet still produced 95% mortality. One (C-2) sample had high mortality (84%) and the corresponding concentration was 13 µg L^{-1} (an order of magnitude higher than the other C-2 values).

While effluent water from the 140612 storm produced high mortality from PO-1, it is notable that PO-2 actually had a lower FAV (112 vs. 79.4 µg L^{-1} respectively). Corresponding dissolved Cu concentrations were much higher for PO-1 vs. PO-2 (154 and 76 µg L^{-1} respectively) for this storm event. Thus while the BLM was slightly over-predictive of toxicity in PO-2, the prediction was probably realistic for PO-1. Visual observations of Planter 1 showed that it contained prodigious numbers of ants. It is possible that their activity produced preferential flow paths in the media. This storm was among the highest intensities of all the sampled storm events.

Though toxicity testing for C-1 is based on limited trials, there appears to be appreciable toxicity of roof runoff from asphalt shingles containing copper algicides. It is possible however that the toxicity was not entirely due to Cu as some researchers have reported a greater-than-additive toxicity from PAH's (not quantified in this study) and metals (Gauthier et al. 2014 and references therin). The BLM predicted lower toxicity with increased pH, ions, alkalinity, and DOC. The results of the *D. magna* testing generally agreed with the model.

5.6.2 Earthworm Avoidance Assay

The year 1 earthworm avoidance assay for planter boxes did not show any avoidance behavior. Similarly, for three of the four swale locations, there was no avoidance behavior with the exception of one soil location that was purposefully excavated directly in the flow path of SCM influent; Corresponding media Cu levels for that location were more than double the next highest location.

The year-two assay found avoidance behavior in one out of the six sample locations. The Swale 1 uphill sampling site showed 100% avoidance behavior yet corresponding Cu values were only 23 mg kg^{-1} which is lower than 4 of the sampling locations that did not produce avoidance behavior in year 1. Only Planter Box 1 and the Swale 2 downhill location did not show avoidance behavior, yet Planter Box 1 actually had the highest Cu levels (72 mg kg^{-1}) of all of the test sites during the year 2 assay. Swale 2 uphill only showed 4% avoidance. The control soil had the lowest Cu values of all samples.

While the year-one assay avoidance levels seem to be explained by the corresponding Cu levels, the year-two assay does not seem to follow the expected trend. Thus it is difficult to draw many conclusions from the assays in terms of Cu soil levels. However for the swale 1 uphill location that did produce 100% avoidance behavior, the pH was comparatively low (4.8) and was statistically explained as correlated to the avoidance behavior.

6. CONCLUSIONS

Stormwater from the copper roof not only contained very high concentrations of Cu, but also lacked the ligands capable of complexing free copper and ions capable of competing with free copper for organismal binding sites. The SCMs functioned not only to sequester Cu, but also to augment stormwater effluent with these constituents which is the key to ameliorating impacts. The BLM predicts that increased pH, DOC, alkalinity, competing cations, and ligands will ameliorate the potential toxicity of Cu in stormwater, and the toxicity testing showed greatly improved survival in SCM effluent. The earthworm avoidance assay showed very little avoidance behavior that could be attributed to Cu accumulation in the soils unless soil samples were taken directly in the path of SCM influent water. Accurate pH measurements were critical to BLM predictions and the use of the LIS technique proved essential to this.

The SCMs were highly successful at reducing toxicity. If employed on a landscape-wide basis, they could be a tremendous benefit not only for decreasing metal levels in stormwater, but also in ameliorating the impacts of stormwater surges in freshwater bodies. Even with lower than specified organic matter in the BSM, the SCMs were able to ameliorate toxicity down to within an order of magnitude of the most conservative water quality standards. It must be emphasized that this has occurred without any additional attenuation between the downspout and the receiving water.

When considering the copper contributions of roofing materials to aquatic systems, more than downspout concentrations must be taken into consideration. Copper from roofs may adhere to the stormwater collection system as well as soils or other materials between the downspout and the receiving water. SCMs can not only attenuate copper, but can substantially improve water quality to so that ambient copper should be less toxic. Additionally, setting a single numerical Cu criteria will most likely fail to take site specific water quality into account. Copper is not equally bioavailable in all conditions and local criteria could be more accurately established using a tool such as the BLM.

Figures

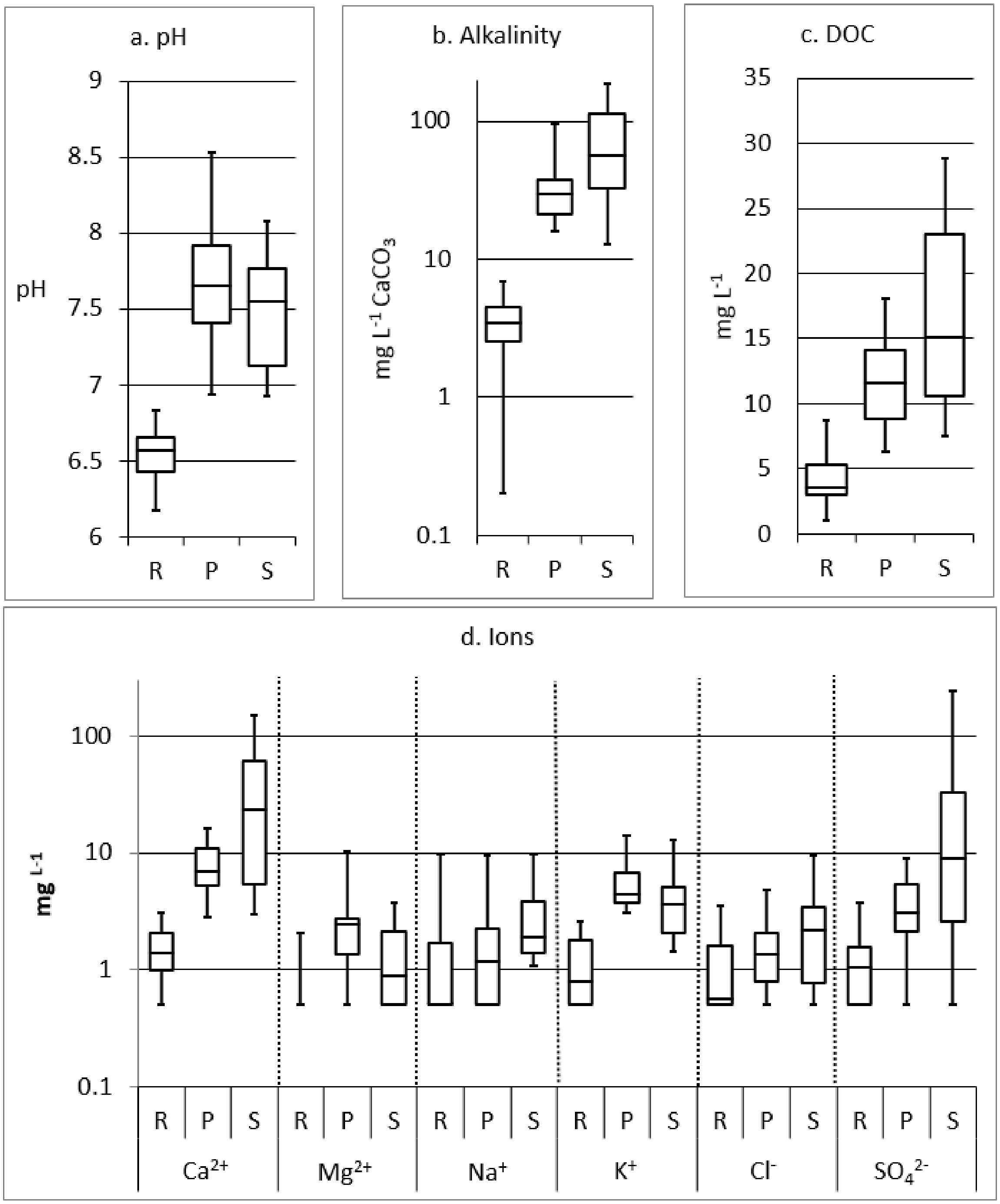


Figure 3.1 (a–d) – Summary of SCM influent and SCM Effluent BLM Parameters for composite storm events. R = Roof (n = 26), P = Planters (n = 26), S = Swales (n = 21). The middle bars are the median value; the boxes represent 25th and– 75th percentiles; bars represent the range of the data. For Mg^{2+} values from the roof, only 2 values were above the LOQ.

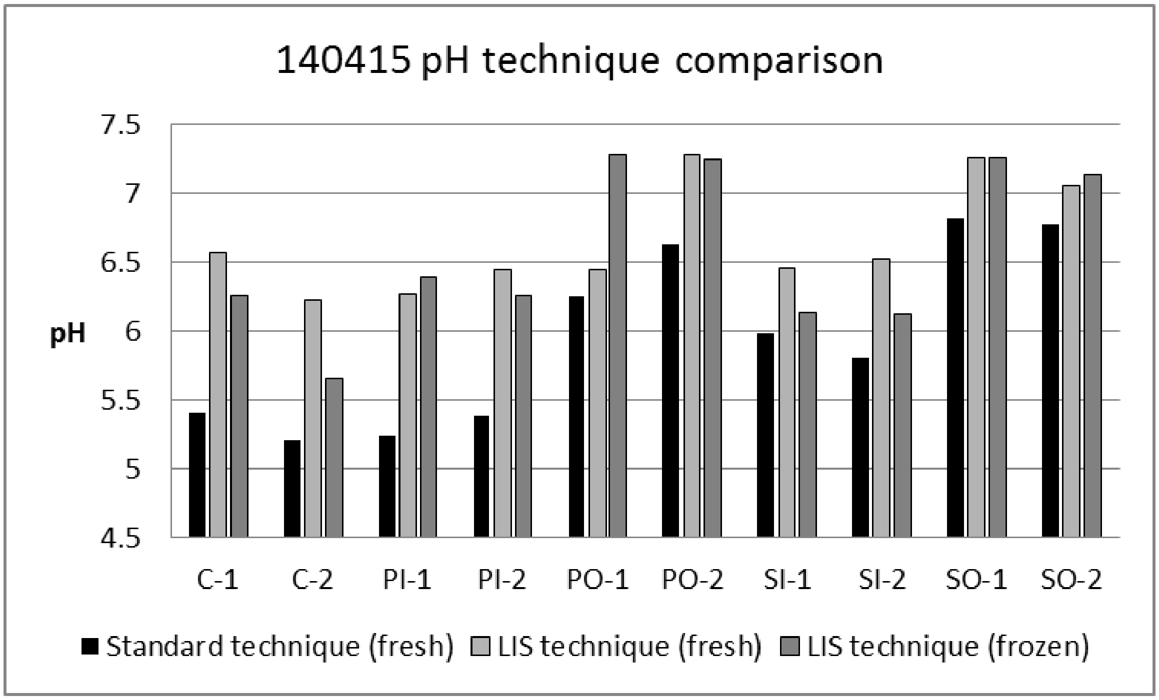


Figure 3.2 – pH comparison of one storm measured with two different probes. "Standard technique" used an Accumet 13-620-108. "LIS technique" used an Orion 8102B Ross Ultra probe with KCl as an ionic strength adjuster. The LIS technique using the LIS probe and buffers was used for both fresh and frozen samples.

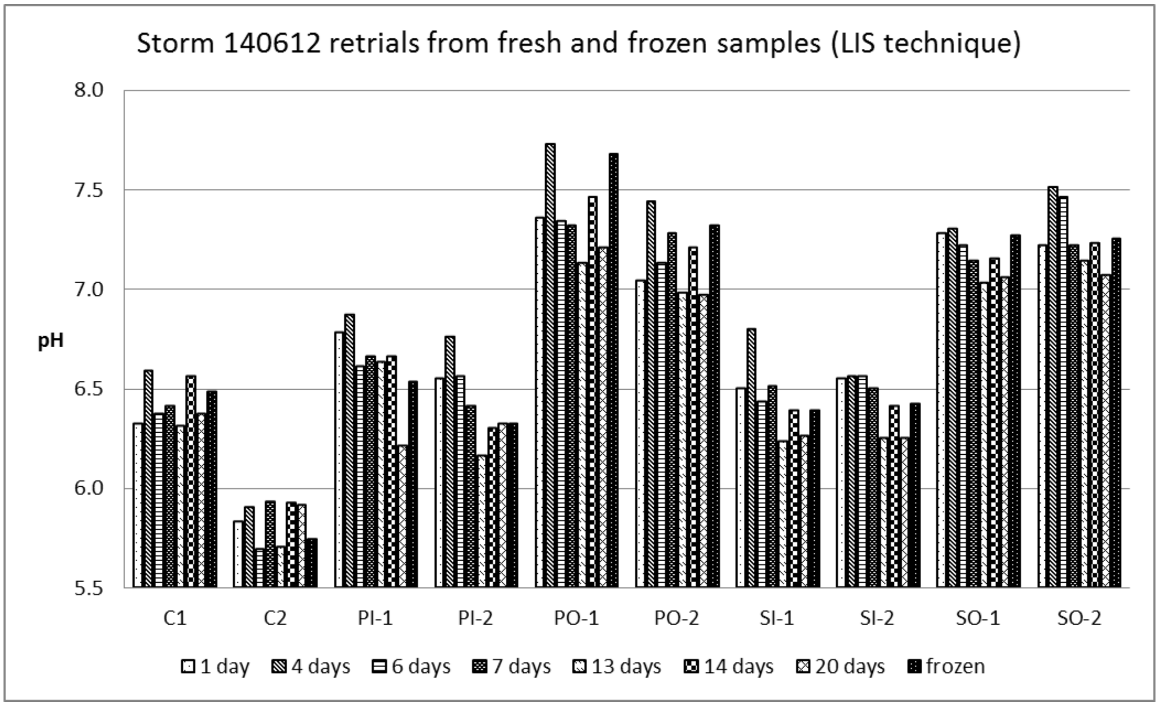


Figure 3.3 - One storm (140612) measured with the same technique, using the LIS probe (Orion 8102B Ross Ultra). The first 7 points labeled with elapsed days were from fresh samples (stored refrigerated at 0-1°C, measured at room temperature ~ 20°C). The last points (dark bars) were measured after samples had been frozen, then brought back to room temperature. For this trial, the frozen samples were archived (frozen) on June 13th and thawed on July 8th.

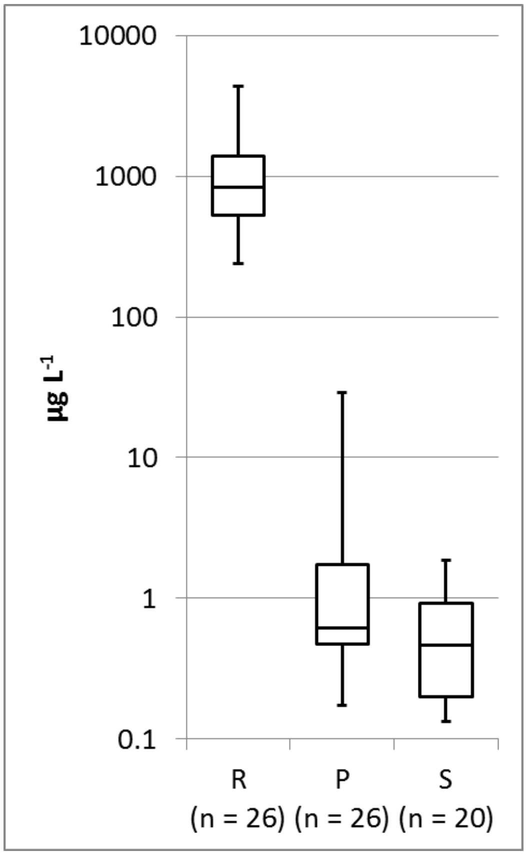


Figure 3.4 - Influent and effluent free Cu by CISE. R = Copper Roof; P = Planter boxes; S = Swales. The middle bars are the median value; the boxes represent 25th and– 75th percentiles; bars represent the range of the data.

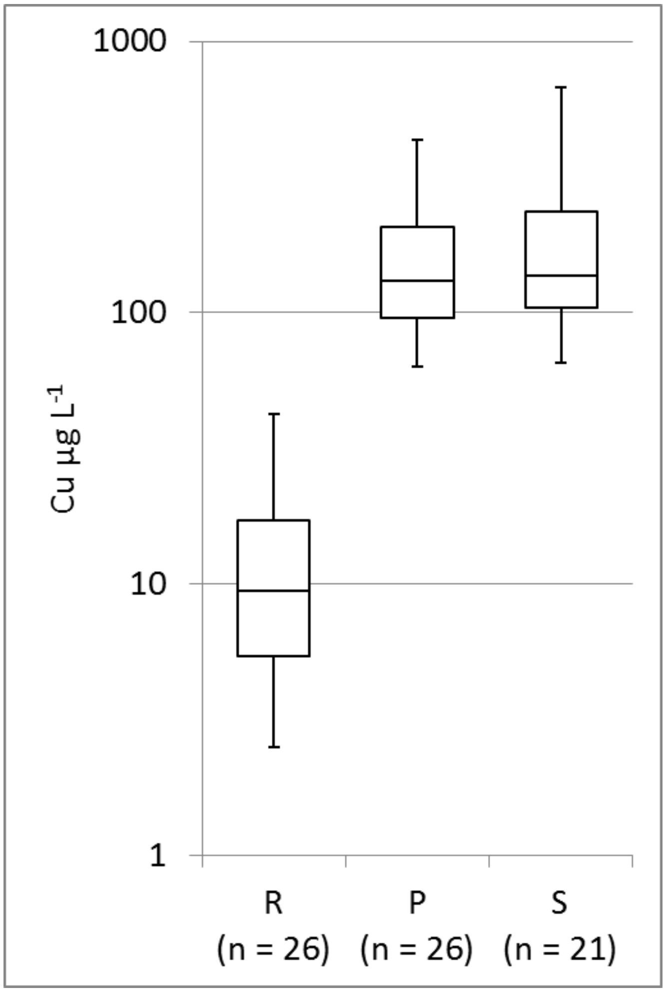


Figure 3.5 - Modeled Influent and Effluent D. magna LC_{50} for composite storm events. Data are presented as averages of all storms. R = Copper Roof; P = Planter boxes; S = Swales. The middle bars are the median value; the boxes represent 25th and– 75th percentiles; bars represent the range of the data.

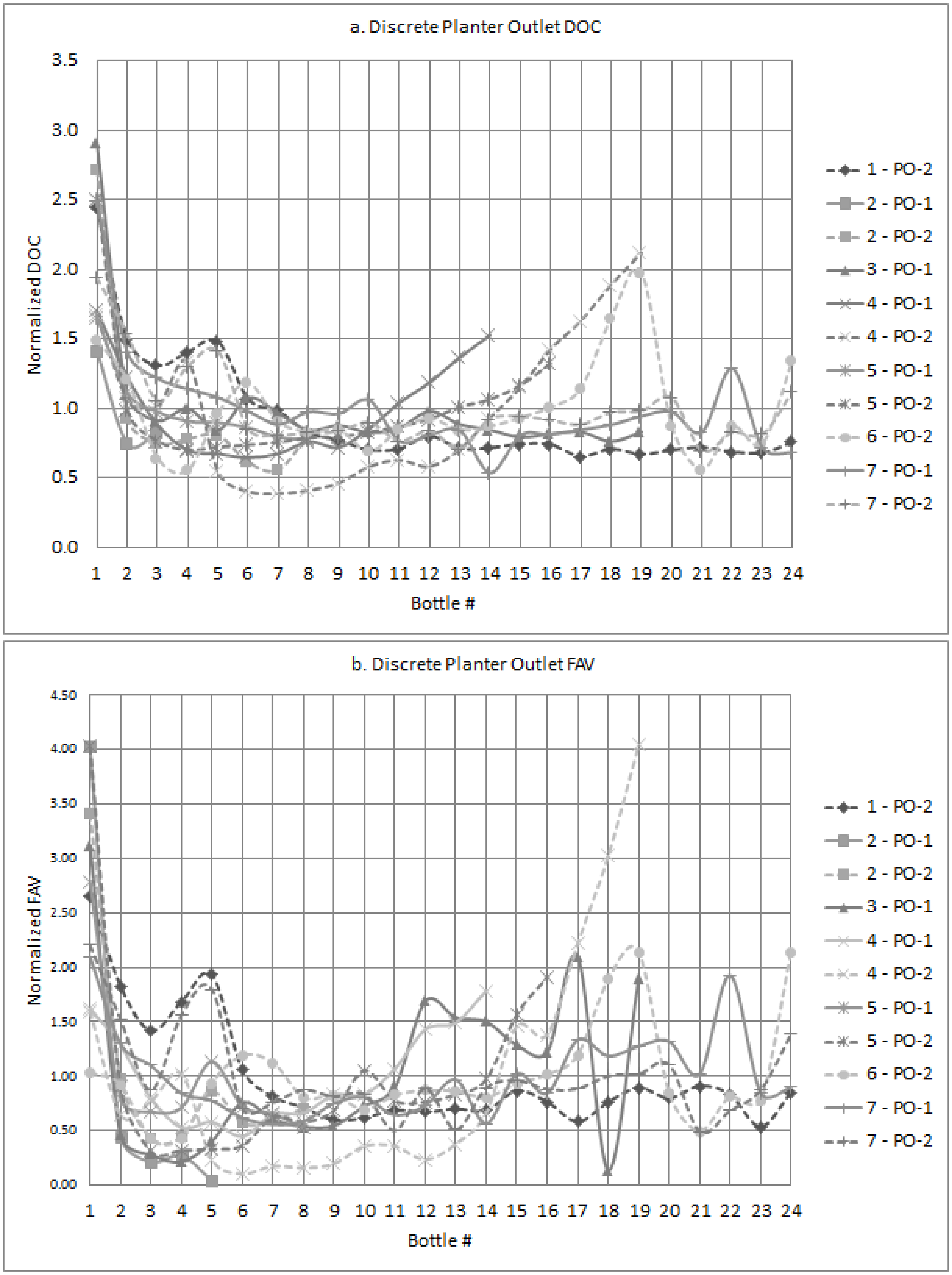
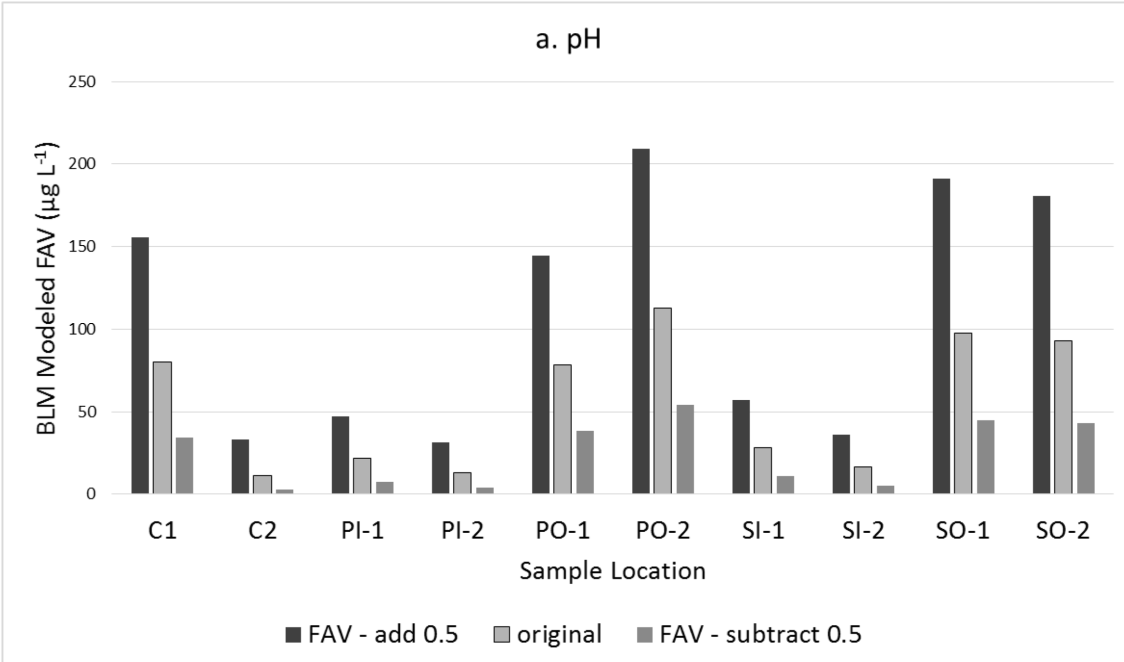


Figure 3.6 (a-b) –Normalized DOC and FAV for Planter Outlet Discrete Events. Values were divided by the mean value to normalize the mean at 1.



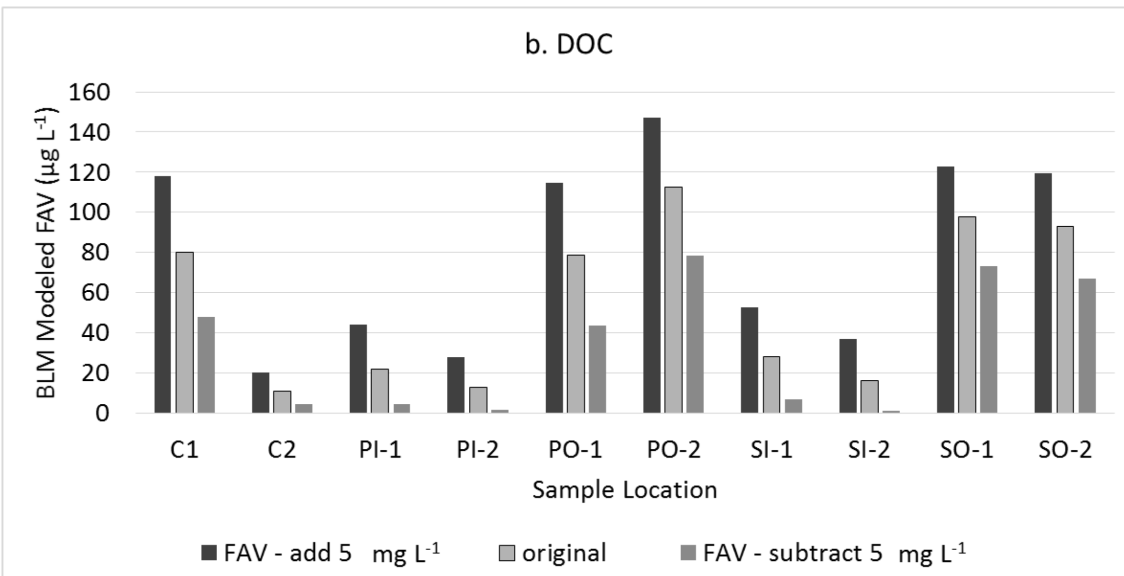


Figure 3.7 (a-b) - pH and DOC sensitivity analysis for storm 140522 for modeled Cu FAV. BLM modeled Cu FAV values are shown when entering the original measured pH value (by LIS technique) and entering those same pH measurements ± 0.5 pH units (a). Measured DOC values were entered into the BLM as the original value and are compared to those DOC levels with 5 mg L^{-1} added or subtracted (b).

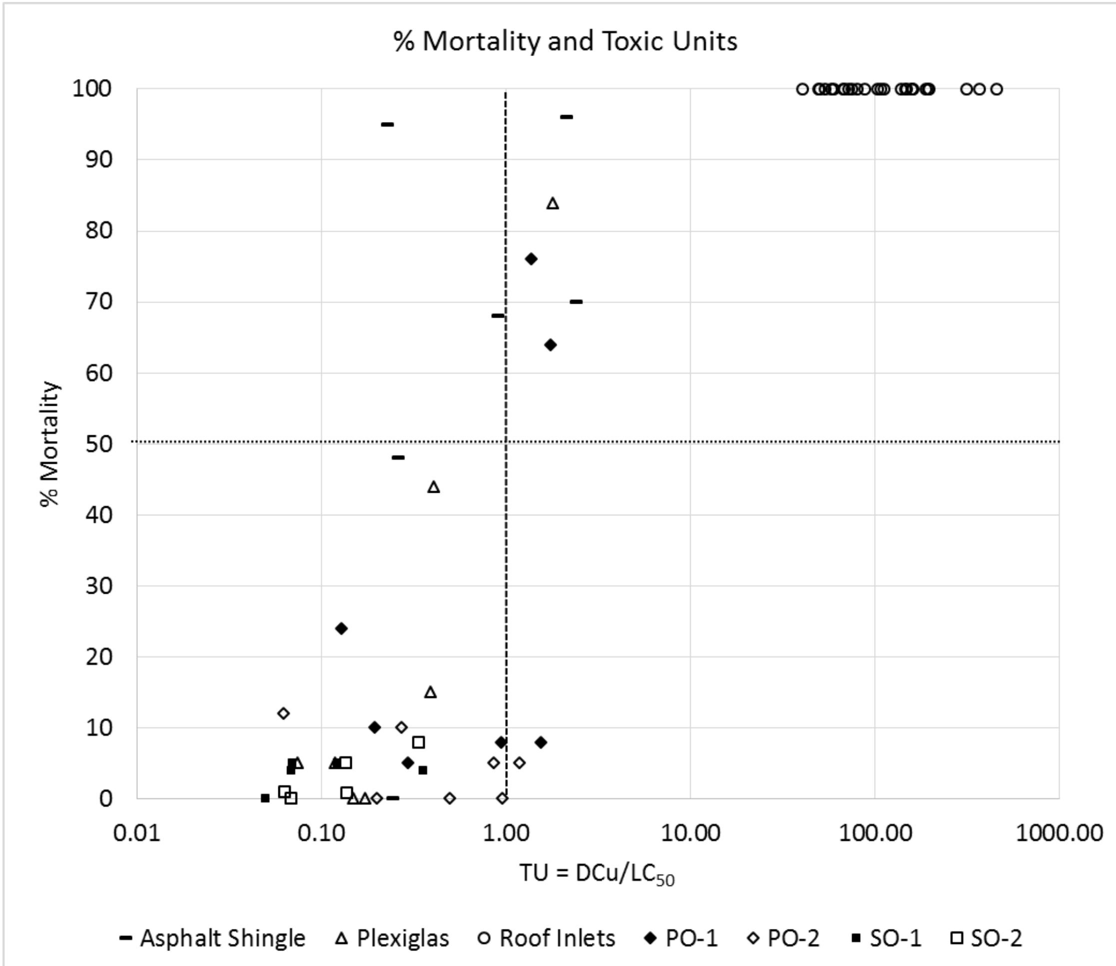


Figure 3.8 - Comparison of bioassay measured toxicity and BLM modeled toxicity. "D Cu" is the Dissolved Cu in µg L^{-1}. LC_{50} is the BLM predicted value; this ratio gives a Toxic unit (TU). % Mortality is based upon laboratory toxicity results. The dotted horizontal line shows the 50% expected mortality level.

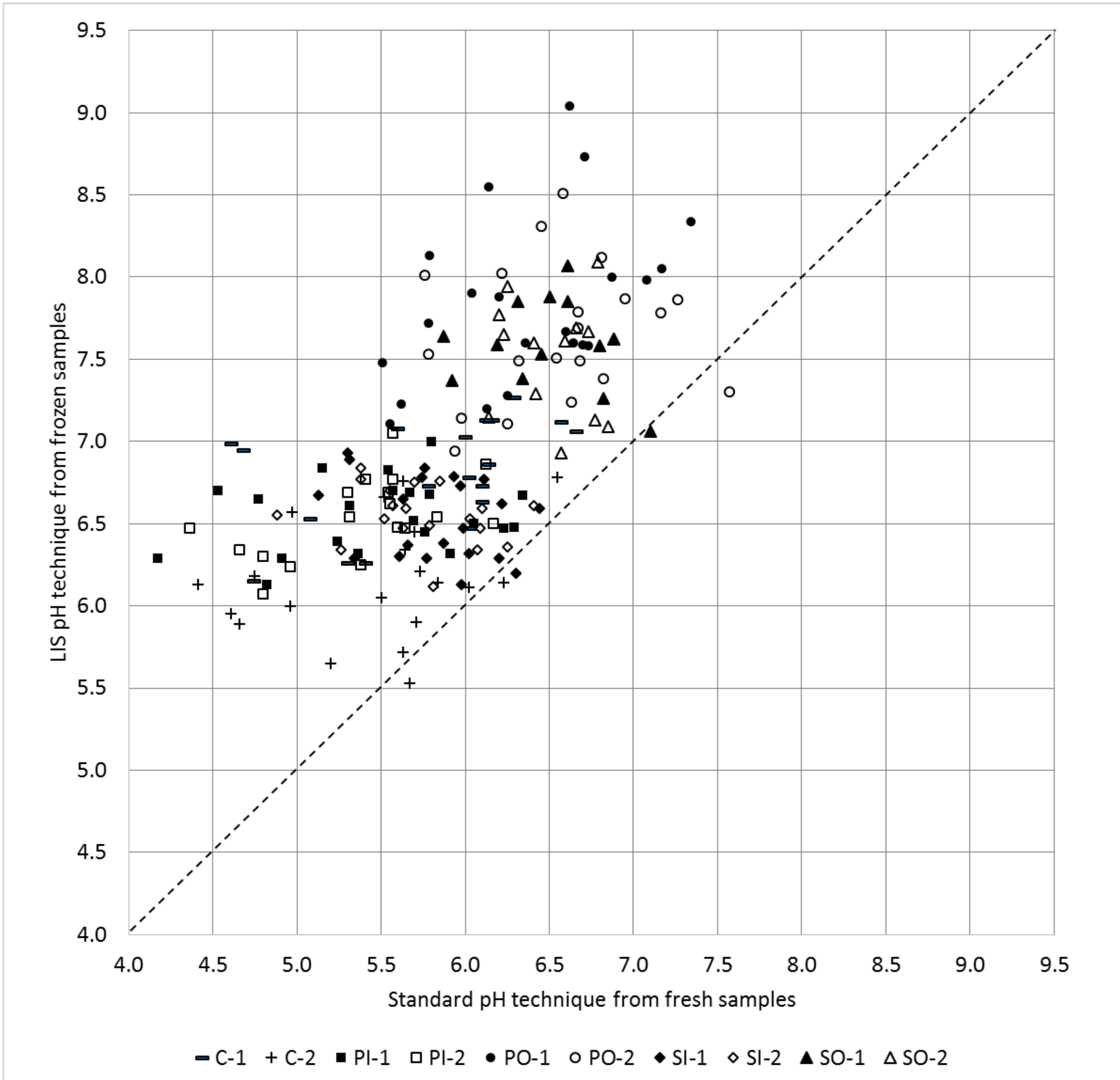


Figure 3.9 - Comparison of pH measurements for the two different probes. Standard pH measurements made with an Accumet probe along X axis; LIS technique with a Ross Ultra probe on Y-axis using archived storm samples 130111 – 140415. The dashed diagonal line shows where measurements would have fallen had both probes obtained the same result.

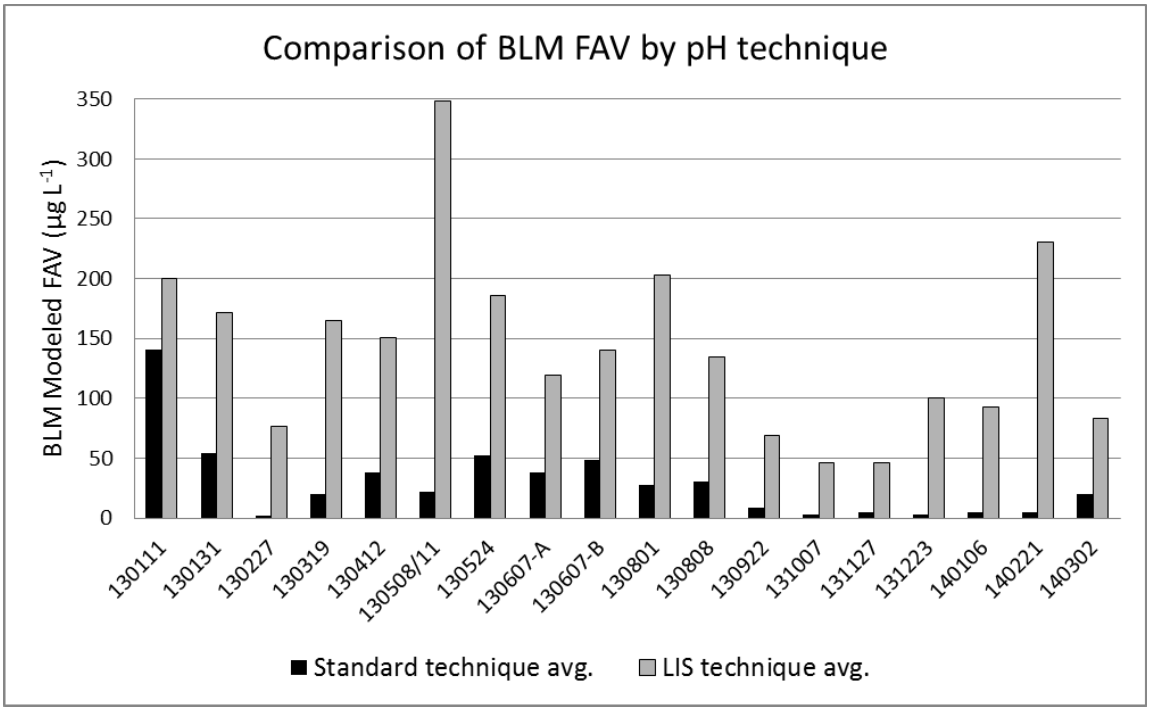


Figure 3.10 - A comparison of BLM modeled FAV Cu values for the same storm sets with different pH values. The standard pH measurement technique was used in the BLM and compared to measurements made with the LIS technique for 18 storms for averaged planter box values. The standard technique predicted much higher toxicity (lower FAV).

Tables

Table 3.1 - Quality Control for analytes.

	% recovery of check standards	n	% RSD Duplicate	n
Ions				
Na^{+}	98.6	23	11.2	31
K^{+}	97.5	23	7.6	37
Mg^{2+}	93.2	23	3.9	24
Ca^{2+}	106.0	23	4.4	41
Cl^{-}	101.9	23	13.8	26
SO^{4-}	107.7	23	4.3	37
pH	99.1	22	4.1	71
Conductivity	98.9	44	5.5	44
Alkalinity	108.0	29	15.2	48
CISE			36.9	50
NPOC	99.0	17	7.5	44

Table 3.2 – One way ANOVA for water chemistry. Comparisons were made between sample inlets (I), planter outlets (PO), and swale outlets (SO). Parameters represented are for values where there was a statistically significant difference.

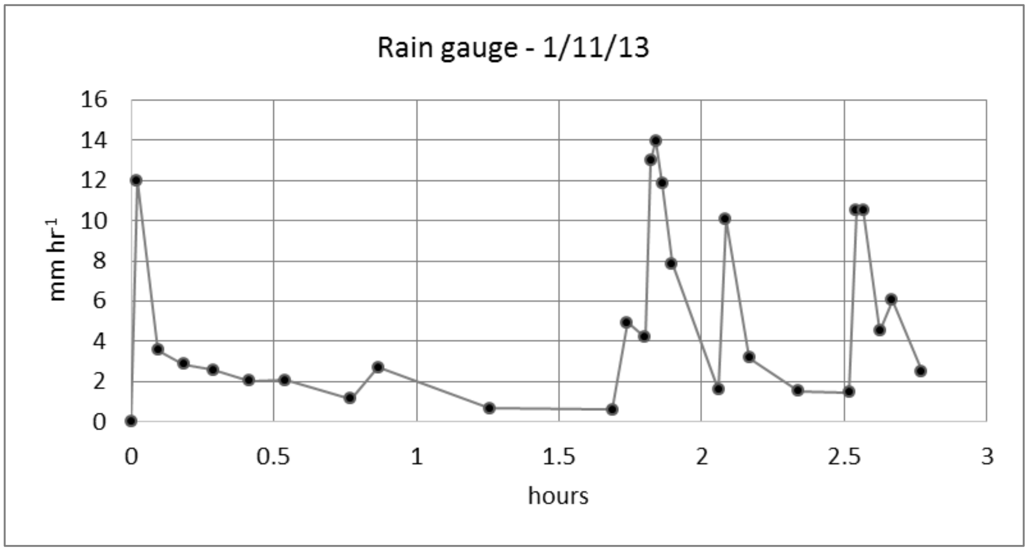
Parameter	Shapiro-Wiki p value	Kruskal-Wallis p value	Comparison	Dunn's Method p value
pH	< 0.05	<0.001	SO > I	< 0.05
			PO > I	< 0.05
Alkalinity	< 0.05	<0.001	SO > I	< 0.05
			SO > PO	< 0.05
			PO > I	< 0.05
DOC	< 0.05	<0.001	SO > I	< 0.05
			PO > I	< 0.05
Ca	< 0.05	<0.001	SO > I	< 0.05
			SO > PO	< 0.05
			PO > I	< 0.05
Mg	< 0.05	<0.001	SO > I	< 0.05
			SO < PO	< 0.05
			PO > I	< 0.05
Na	< 0.05	<0.001	SO > I	< 0.05
			SO > PO	< 0.05
K	< 0.05	<0.001	SO > I	< 0.05
			PO > I	< 0.05
Cl	< 0.05	<0.001	SO > I	< 0.05
			PO > I	< 0.05
SO4	< 0.05	<0.001	SO > I	< 0.05
			SO > PO	< 0.05
			PO > I	< 0.05

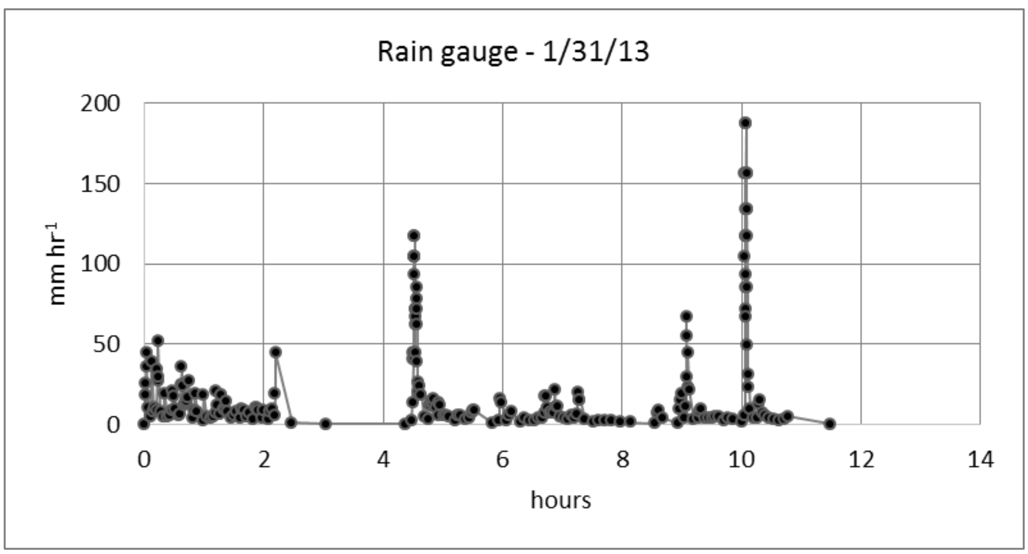
Table 3.3 – Earthworm Avoidance Assay Results. Data in bold represent a statistically significant response. Boric acid controls were used to elicit a positive response.

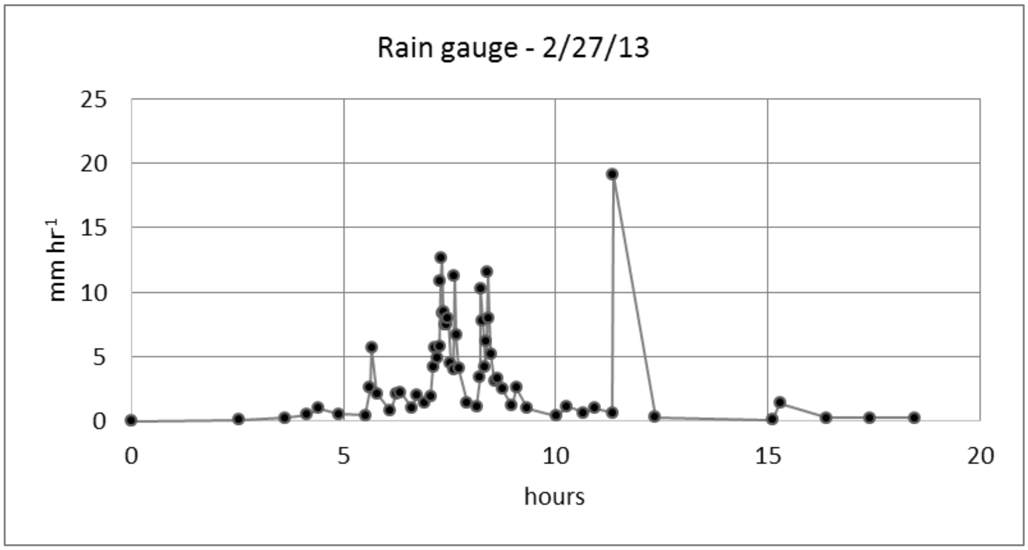
	Year 1		Year 2		
	Avoidance %	soil Cu mg kg^{-1}	Avoidance %	soil Cu mg kg^{-1}	soil pH
P-1	0	31	0	72	6.3
P-2	0	24	22	50	6.4
S-1 uphill	0	39	**100**	23	4.8
S-1 downhill	0	18	38	16	5.1
S-2 uphill	**54**	101	4	32	6.5
S-2 downhill	0	26	0	18	5.6
Boric acid control	46	26	36	16	5.9

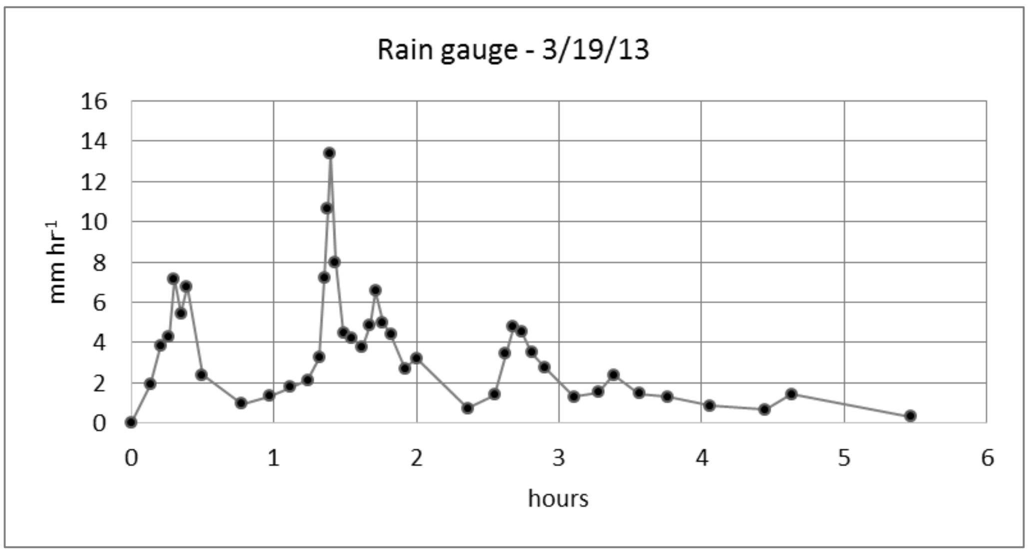
Appendices

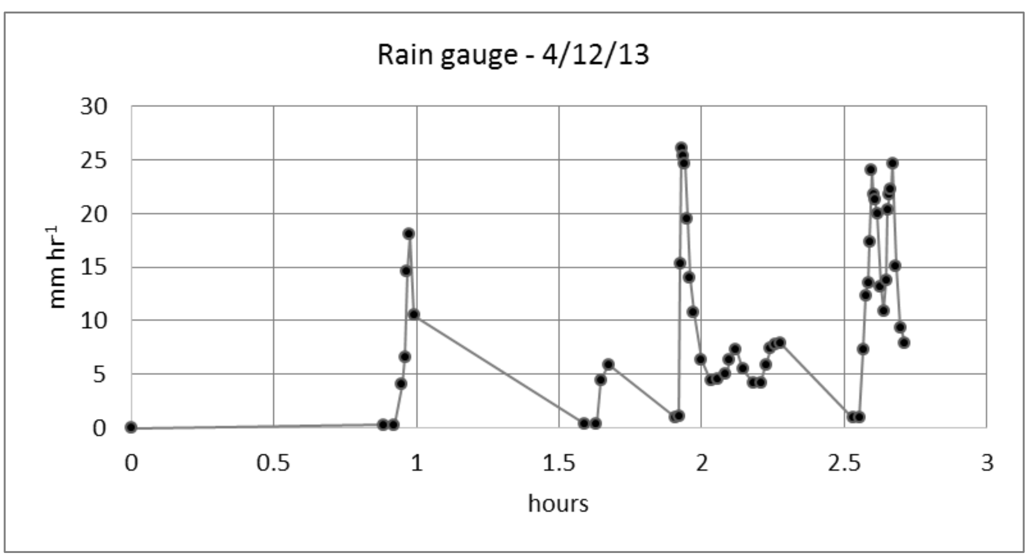
Appendix A - Hyetographs. Hyetographs were constructed from the ISCO grain gauge data for all available storms. Dates are included at the top of each graph.

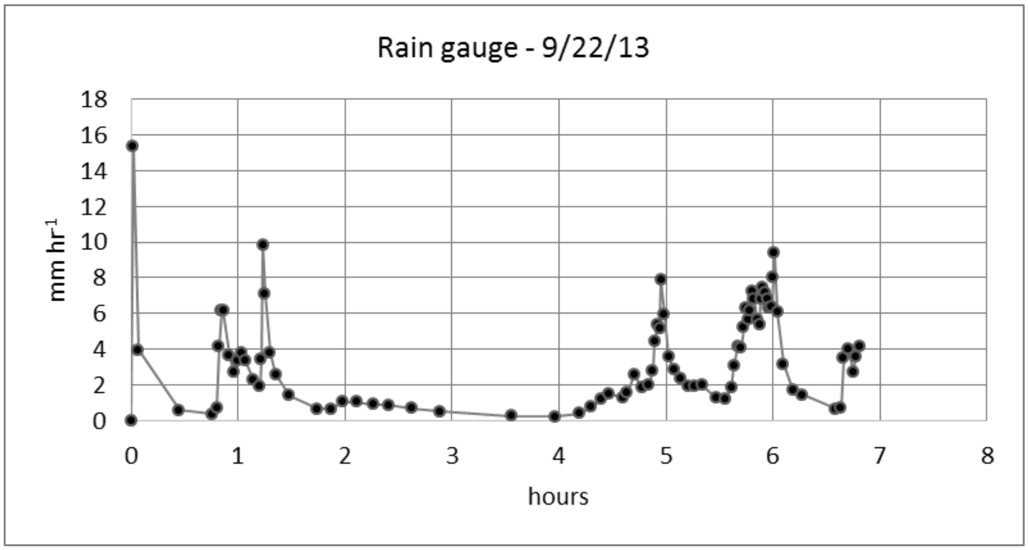


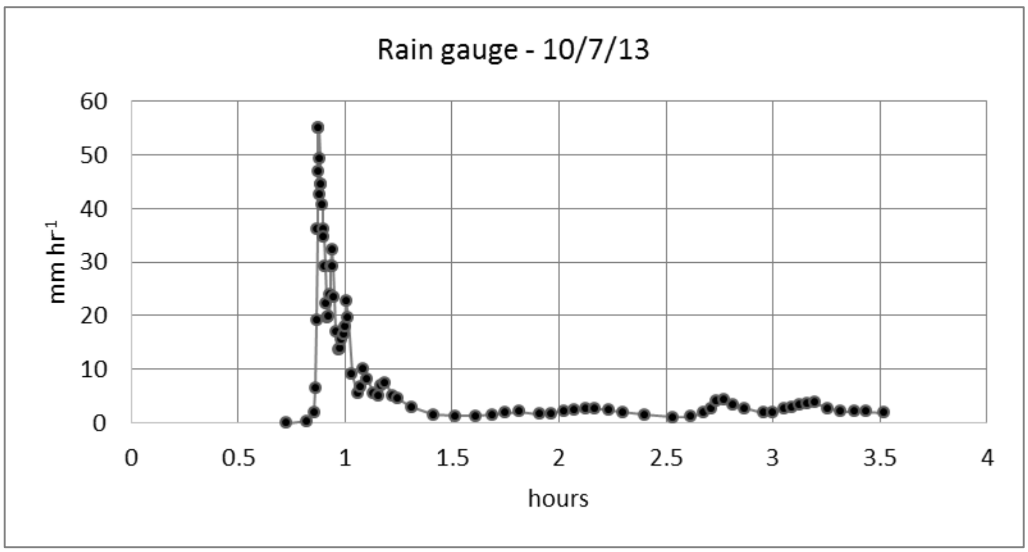


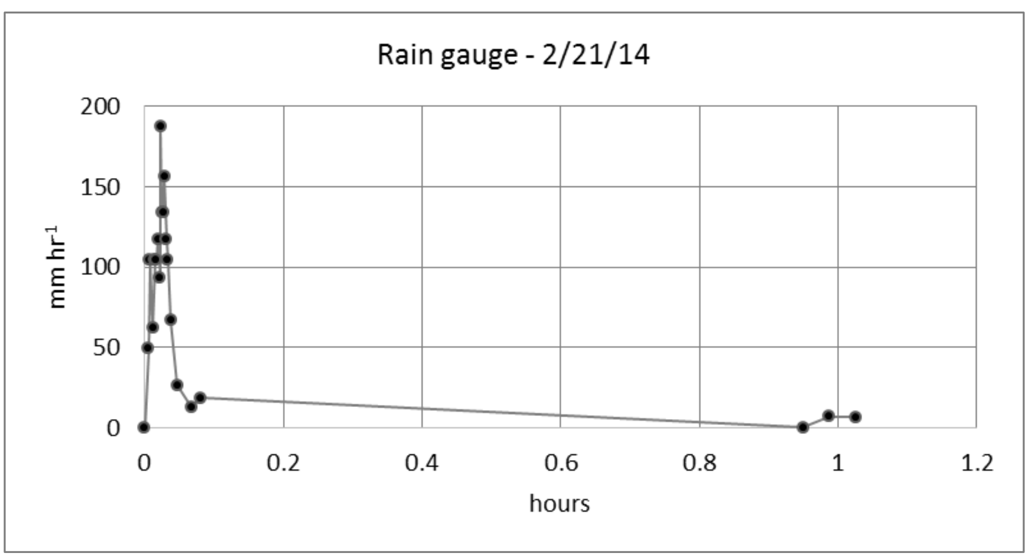

Rain gauge - 2/27/13
25
20
15
10
5
0
mm hr-1
0
5
10
15
20
hours

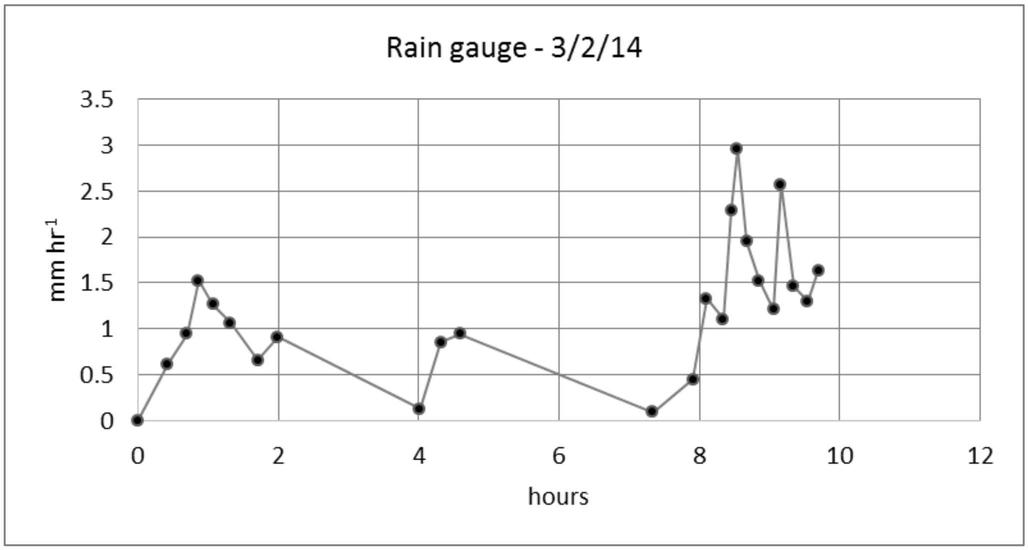

Rain gauge - 3/19/13
16
14
12
10
8
6
4
2
0
mm hr-1
0
1
2
3
4
5
6
hours

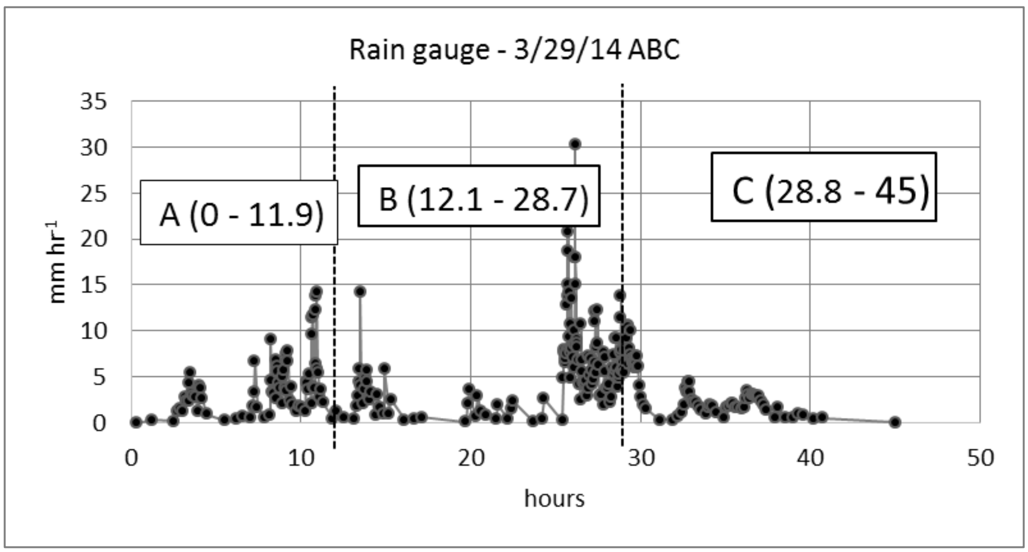

Rain gauge - 4/12/13
30
25
20
15
10
5
0
mm hr-1
0
0.5
1
1.5
2
2.5
3
hours

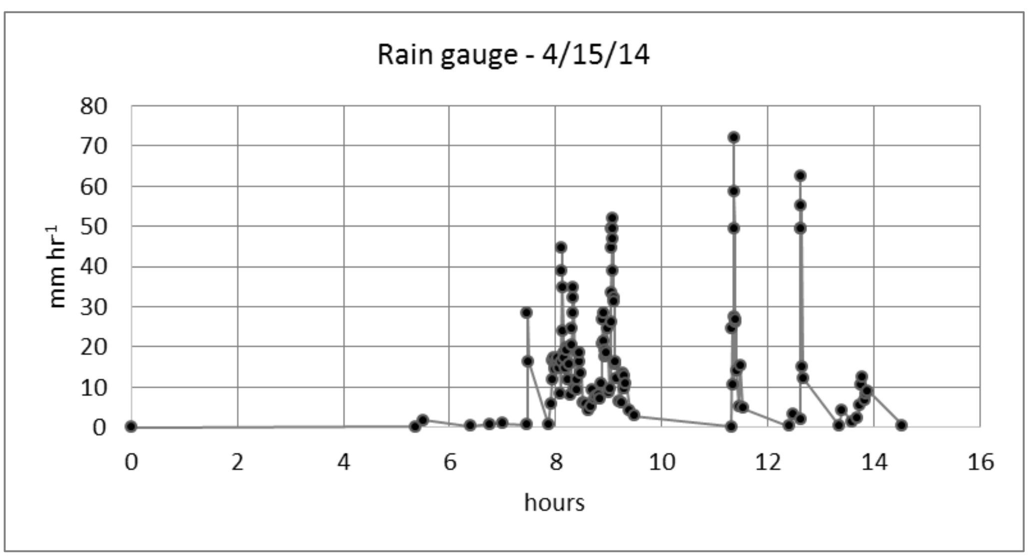

Rain gauge - 9/22/13
mm hr-1
hours
0 2 4 6 8 10 12 14 16 18
0 1 2 3 4 5 6 7 8

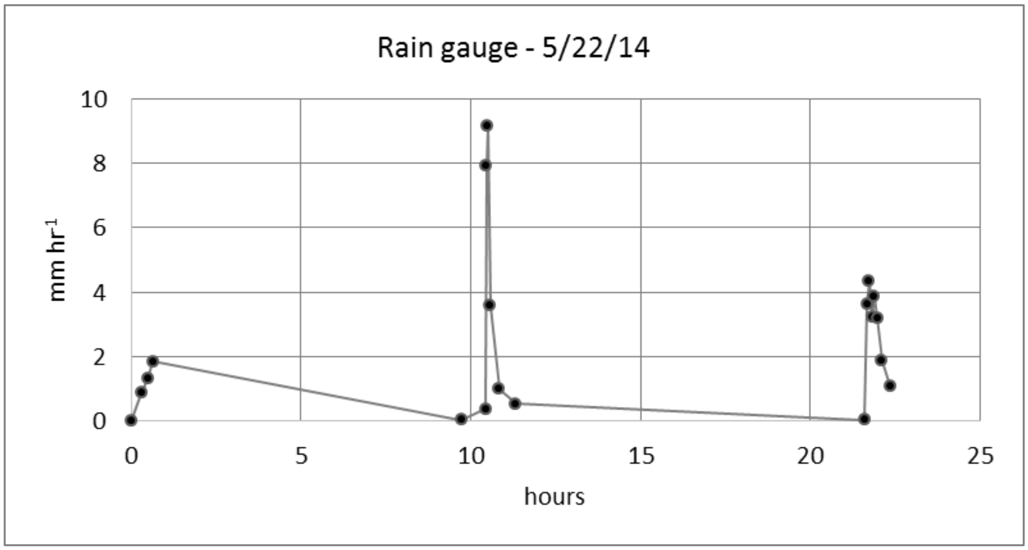

Rain gauge - 10/7/13
mm hr-1
hours
0 10 20 30 40 50 60
0 0.5 1 1.5 2 2.5 3 3.5 4

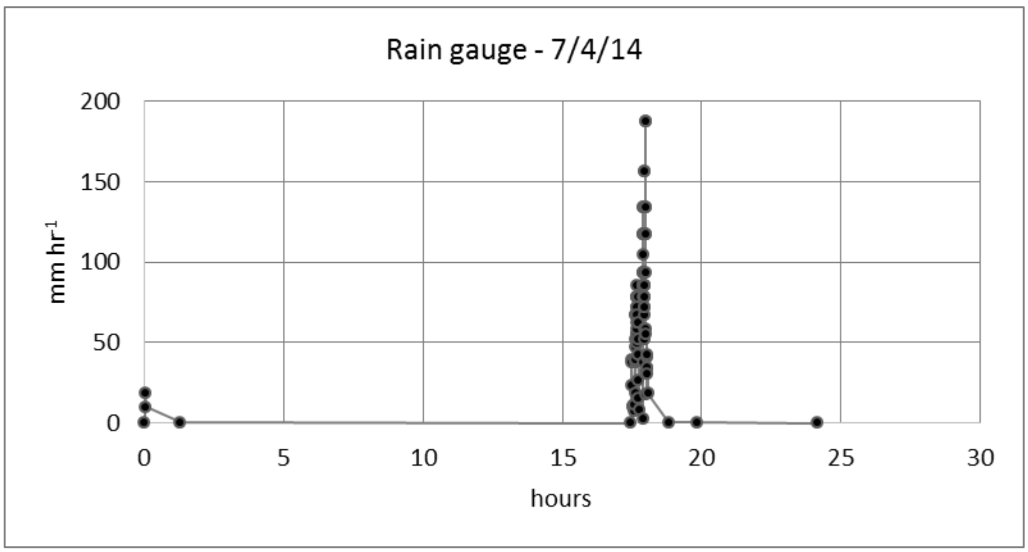

Rain gauge - 2/21/14
mm hr-1
hours
0 50 100 150 200
0 0.2 0.4 0.6 0.8 1 1.2

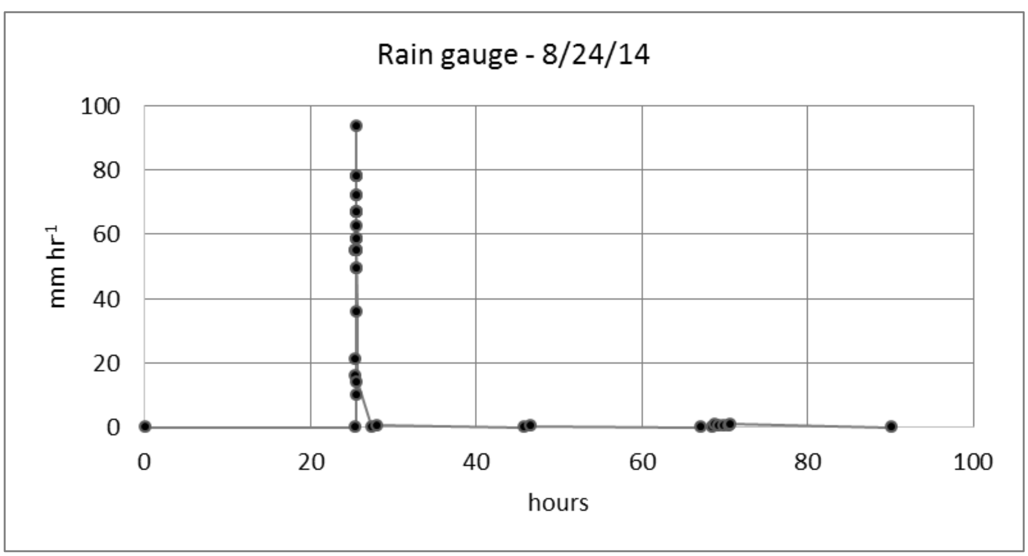

Rain gauge - 3/2/14
mm hr-1
hours

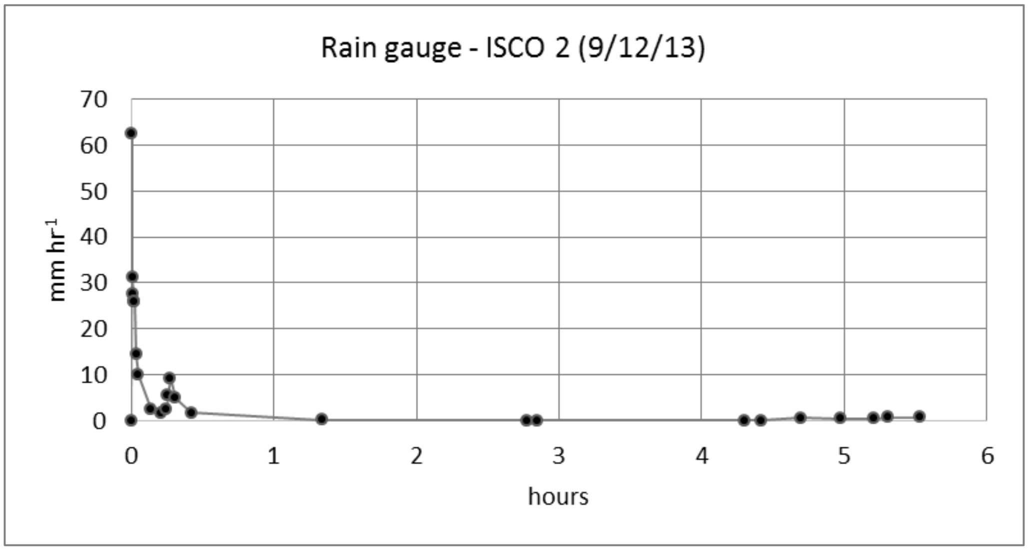

Rain gauge - 3/29/14 ABC
A (0 - 11.9)
B (12.1 - 28.7)
C (28.8 - 45)
mm hr-1
hours

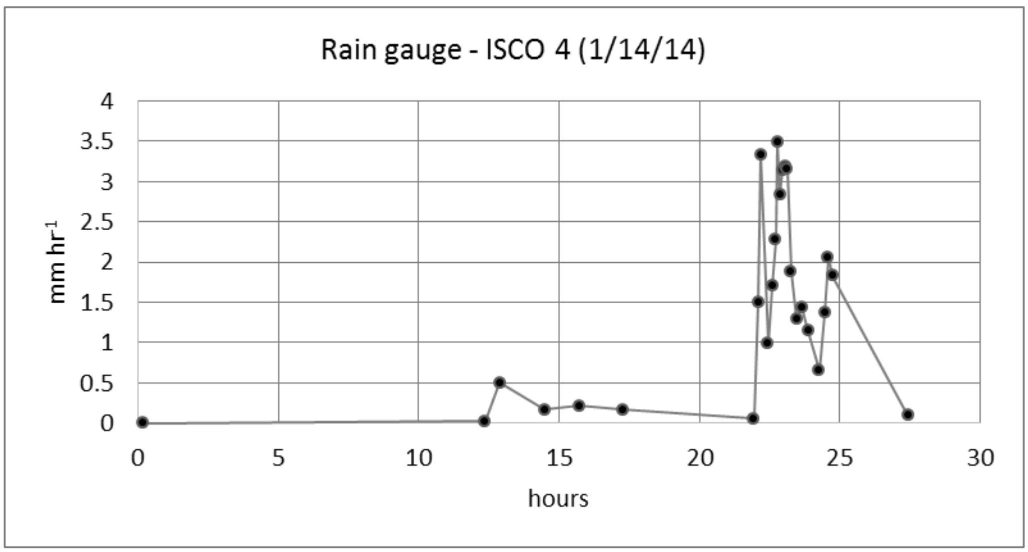

Rain gauge - 4/15/14
mm hr-1
hours

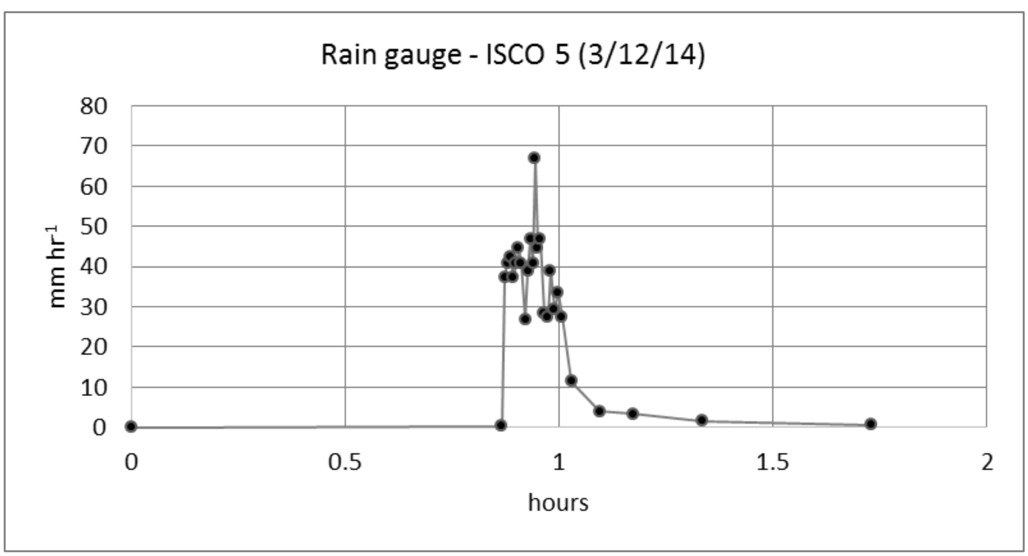

Rain gauge - 5/22/14
mm hr-1
hours
0
2
4
6
8
10
0
5
10
15
20
25

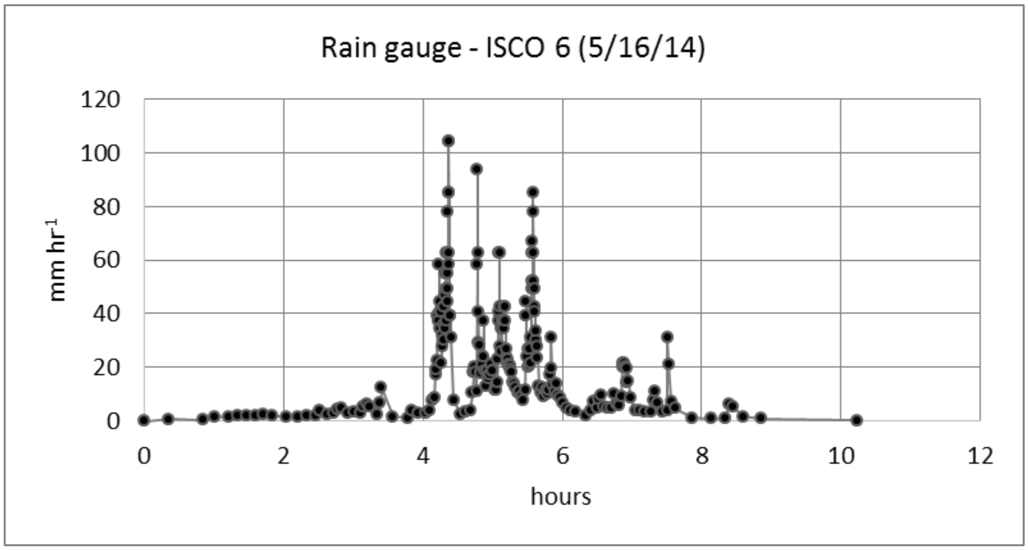

Rain gauge - 7/4/14
mm hr-1
hours
0
50
100
150
200
0
5
10
15
20
25
30

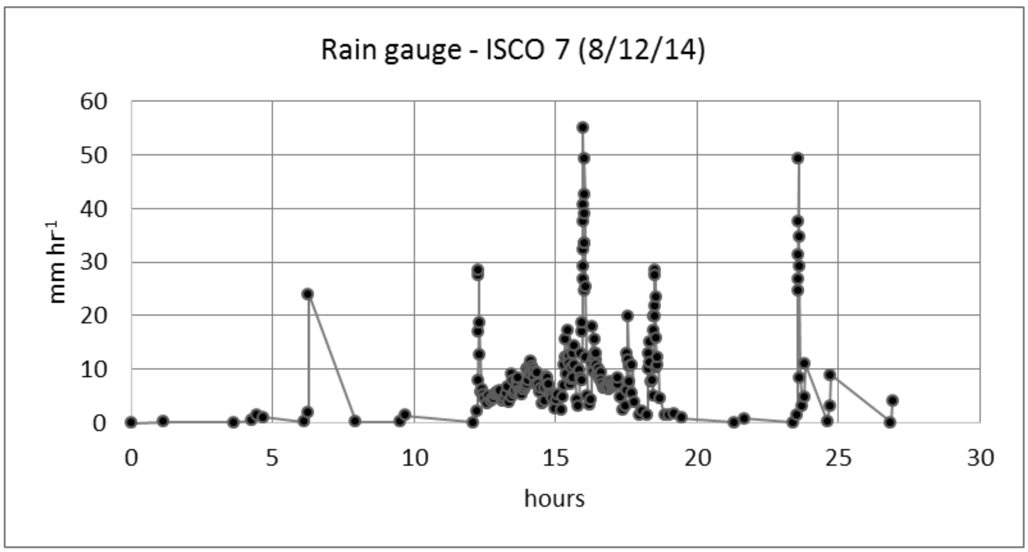

Rain gauge - 8/24/14
mm hr-1
hours
0
20
40
60
80
100
0
20
40
60
80
100


Rain gauge - ISCO 2 (9/12/13)
mm hr⁻¹
hours
0
10
20
30
40
50
60
70
0
1
2
3
4
5
6


Rain gauge - ISCO 4 (1/14/14)
mm hr⁻¹
hours
0
0.5
1
1.5
2
2.5
3
3.5
4
0
5
10
15
20
25
30


Rain gauge - ISCO 5 (3/12/14)
mm hr⁻¹
hours
0
10
20
30
40
50
60
70
80
0
0.5
1
1.5
2

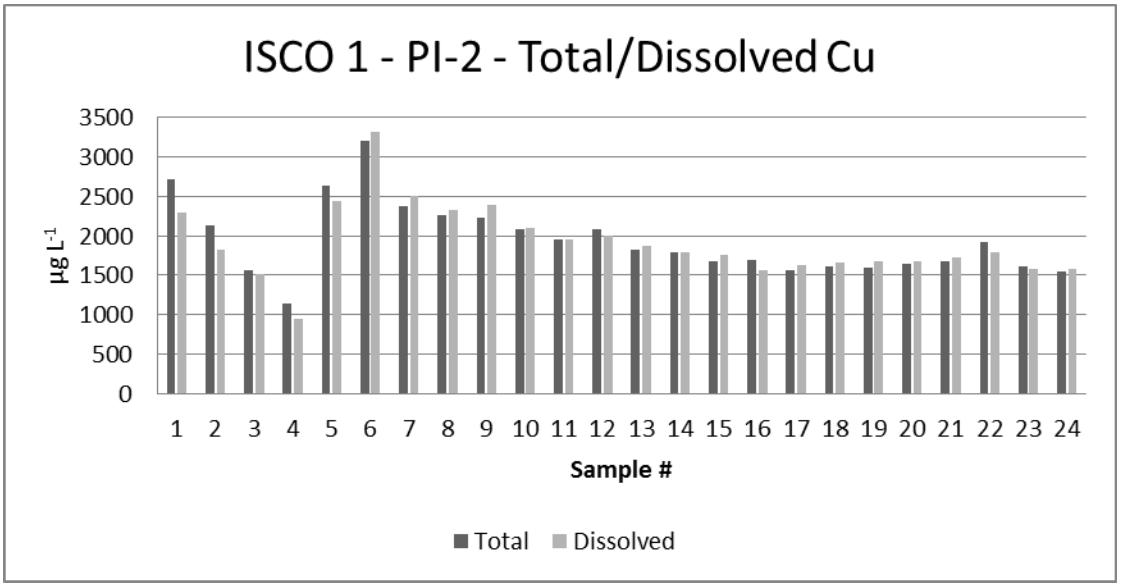

Rain gauge - ISCO 6 (5/16/14)
120
100
80
60
40
20
0
mm hr-1
0
2
4
6
8
10
12
hours

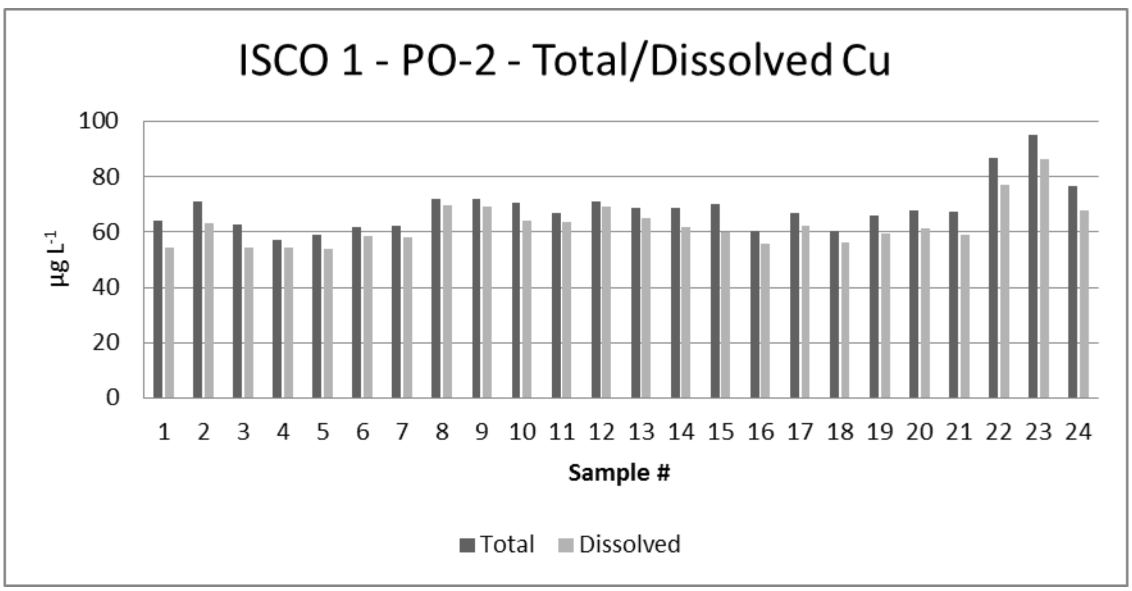

Rain gauge - ISCO 7 (8/12/14)
60
50
40
30
20
10
0
mm hr-1
0
5
10
15
20
25
30
hours

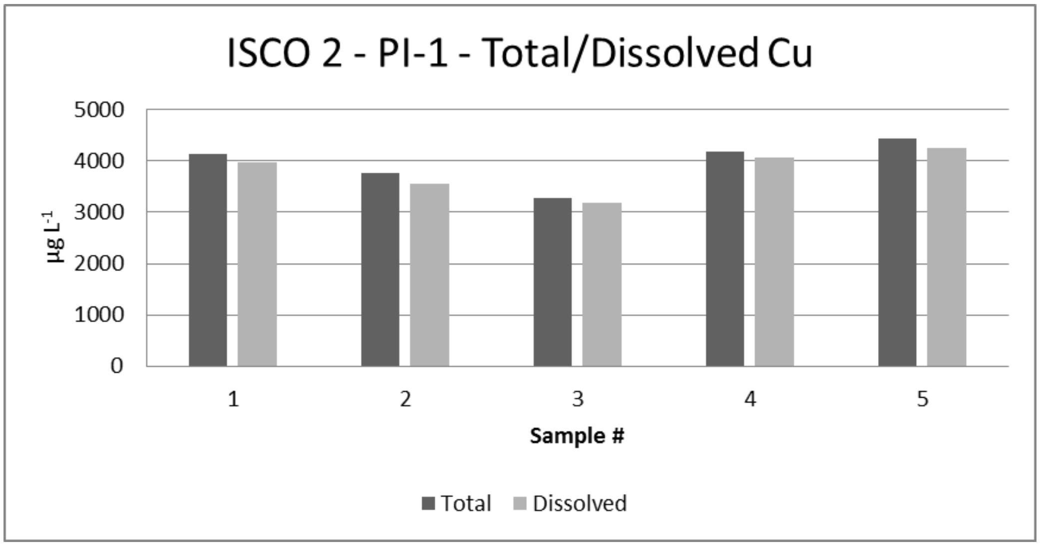
Appendix B - Total Cu (µg L^{-1}) for composite storm events. Values of 0.5 were below the LOQ.

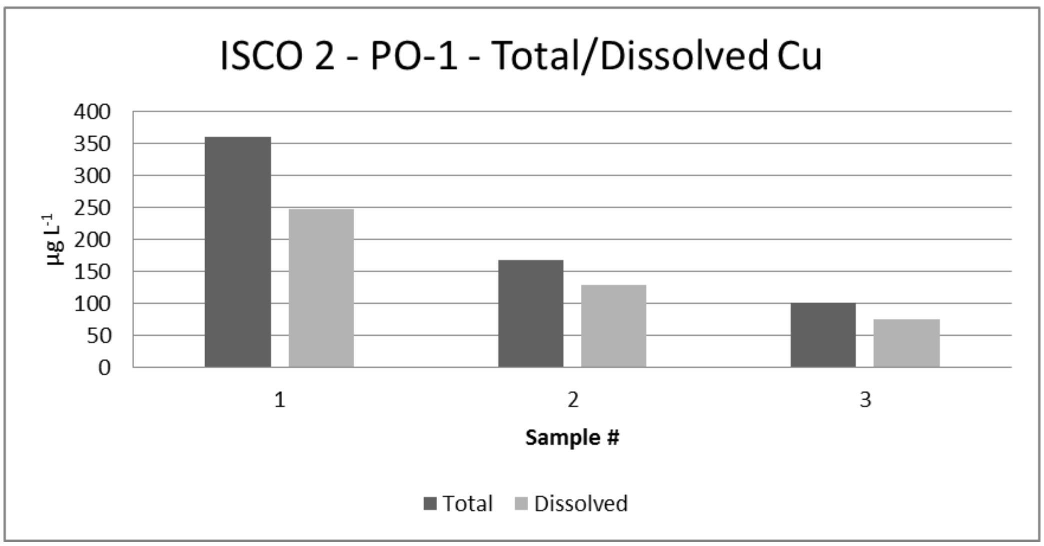
Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					µg L^{-1}					
130111	59	14	662		41	77	707	634		
130131	18	15	271	357	31	26	302	295		20
130227	22	2	1215		41		1447	1394	17	23
130319	52	6	1584	1284	51	36	1696	1422		
130412	377	3	1022	1109	92	63	999	992		
130508/11	243	3	1114	1420	84	110	1508	1472		19
130524	147	0.5	1849	1297	149	84	1513	1502		
130607-A	40	3	948	962	85	45	1450	908		7
130607-B	19	0.5	1051	992	82	35	1011	1033	20	
130801	69	0.5	1340	1369	114	93	1453	1335		
130808	30	0.5	1891	1943	156	107	1919	1771		20
130922	73	0.5			120	84	1280	1389	29	38
131007	171	1	769	813	122	92	920		34	31
131127	16	2	623	552		64			30	36
131223	16	2	728		63	53	876	904	35	37
140106			1608	854	78	65	1094	874	26	27
140221	236	4	2416	1567	90		2314	3192	27	26
140302			2804	3041	33	26	2720	2887	23	19
140329-A	23	1	679	686	40	30	686	723	37	36
140329-B	10	5	753	716	37	29	775	748	32	38
140329-C		7	933	801	38	25	854	900	25	32
140415	113	1	608	634	61	48	762	860	32	42
140522	128	9	1156	1704	71	65	2178	1766	28	27
140612	30	0.5	1090	760	190	92	998	990	59	43
140704	178	0.5	2133	2130	170	72		2154	33	28
140824			2351	2639	191	75	1914	2581	26	23
					Summary					
Average	**94**	**3.6**	**1264**	**1256**	**89**	**62**	**1307**	**1364**	**30**	**29**
Median	**55**	**1.9**	**1090**	**1050**	**82**	**64**	**1187**	**1184**	**29**	**27**
Lowest	10.2	0.5	271	357	30.7	25.0	302	295	17.0	6.9
Highest	377	14.8	2804	3041	191	110	2720	3192	59	43
Std. Dev.	96	4.2	655	689	50.2	27.0	590	726	9.2	9.3
n	22	23	25	22	25	24	24	24	17	20
Std. Error	20.6	0.9	131	147	10.0	5.5	120	148	2.2	2.1

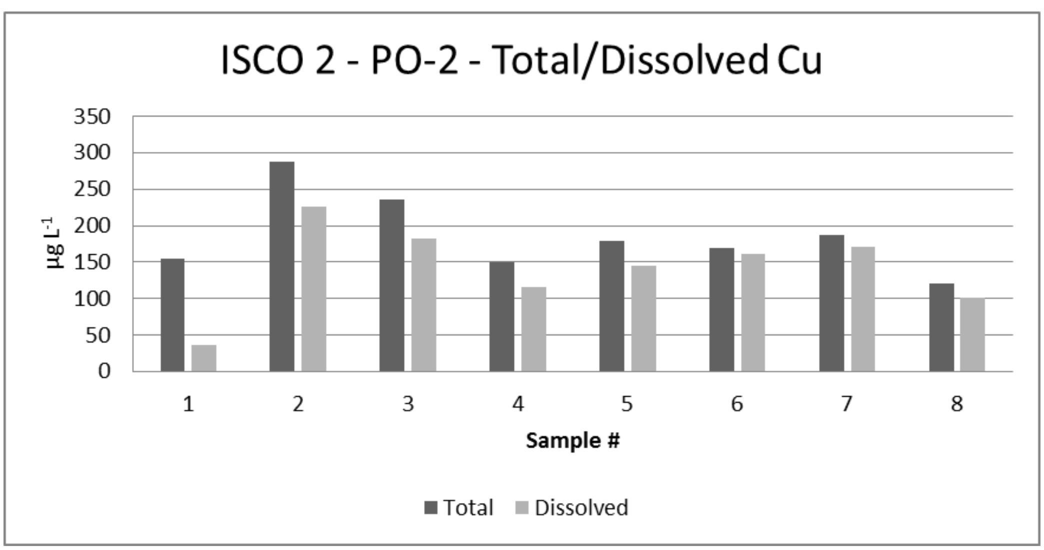
Appendix C – Total and dissolved Cu for seven discrete sampling events. Sample # is the collection bottle in the ISCO sampler. The noticeable drop through the 4th bottle for ISCO 1, PI-2 closely reflects a rise in pH (see Chapter 3) for that sample. Low pH in the first samples for inlets was seen in ISCO events 1, 3, 4, 5, and 6. However ISCO 7 had a relatively high pH in the first sample.

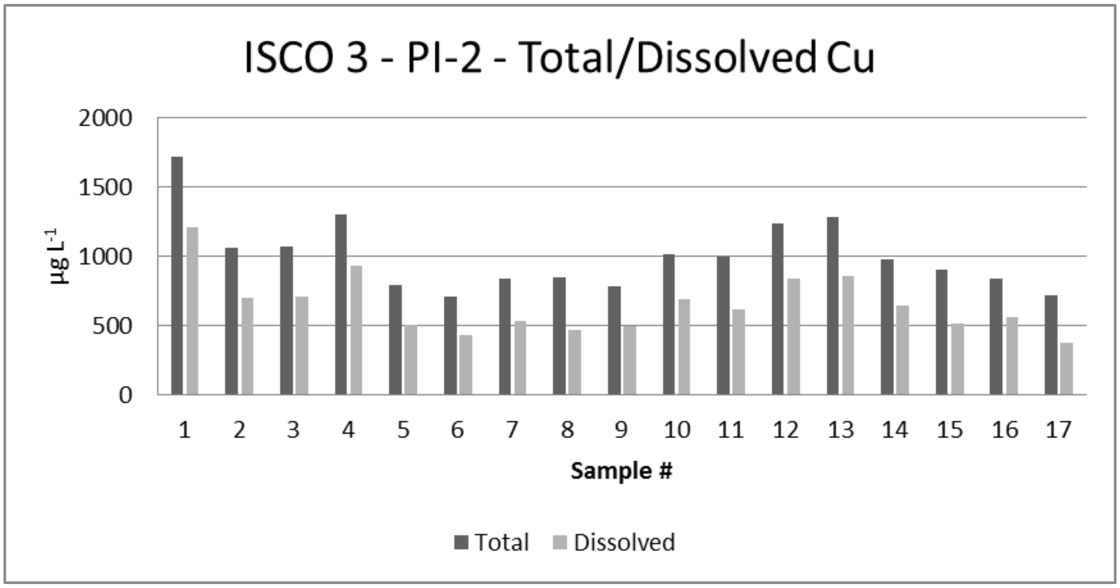


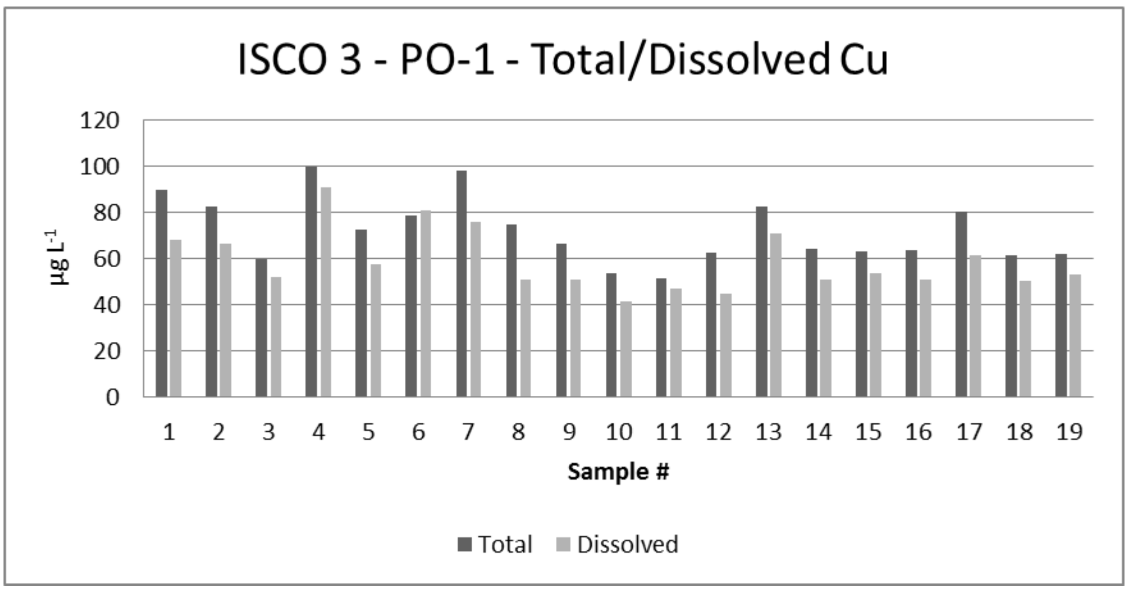


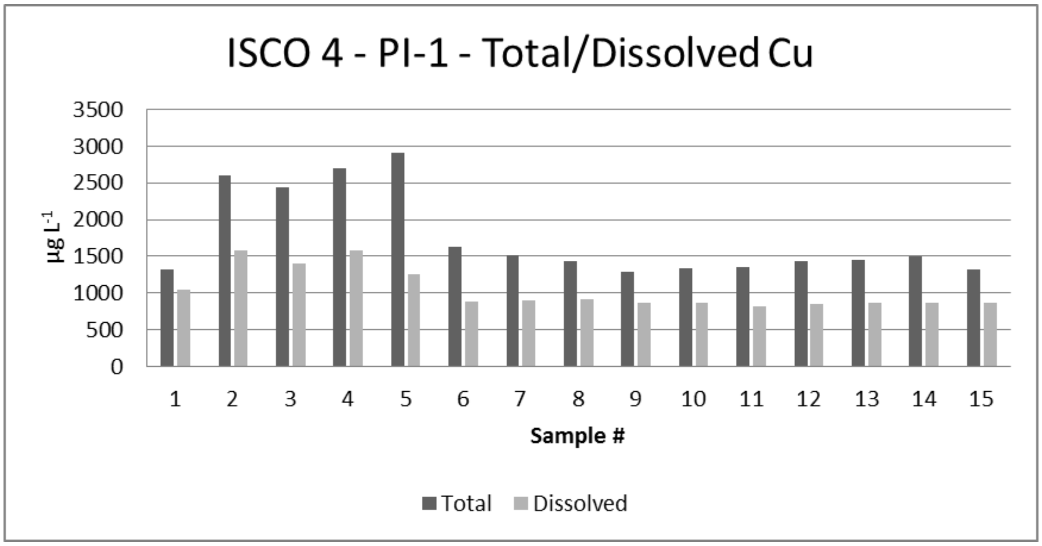

ISCO 2 - PI-1 - Total/Dissolved Cu
5000
4000
3000
2000
1000
0
µg L-1
1
2
3
4
5
Sample #
Total
Dissolved

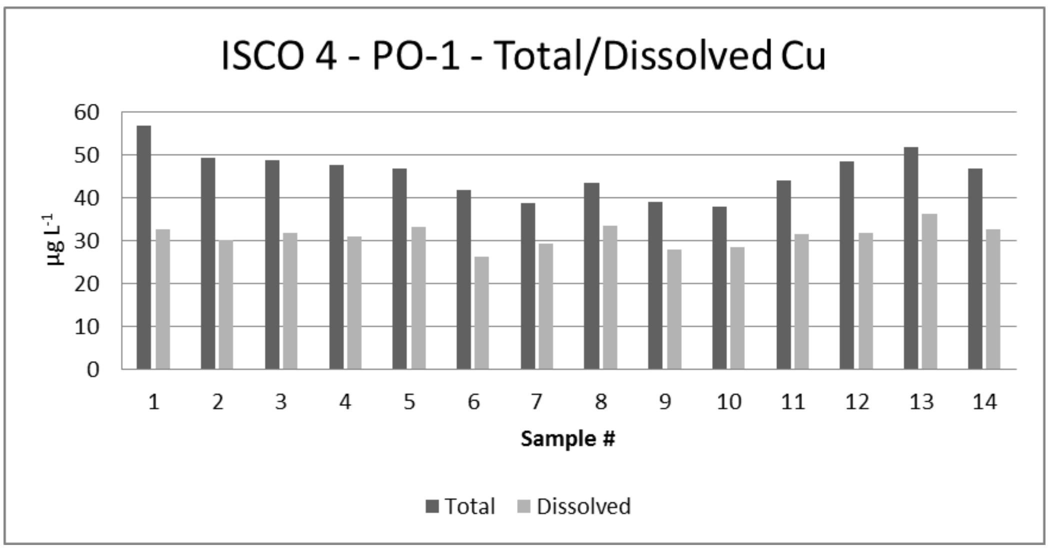

ISCO 2 - PO-1 - Total/Dissolved Cu
400
350
300
250
200
150
100
50
0
µg L-1
1
2
3
Sample #
Total
Dissolved

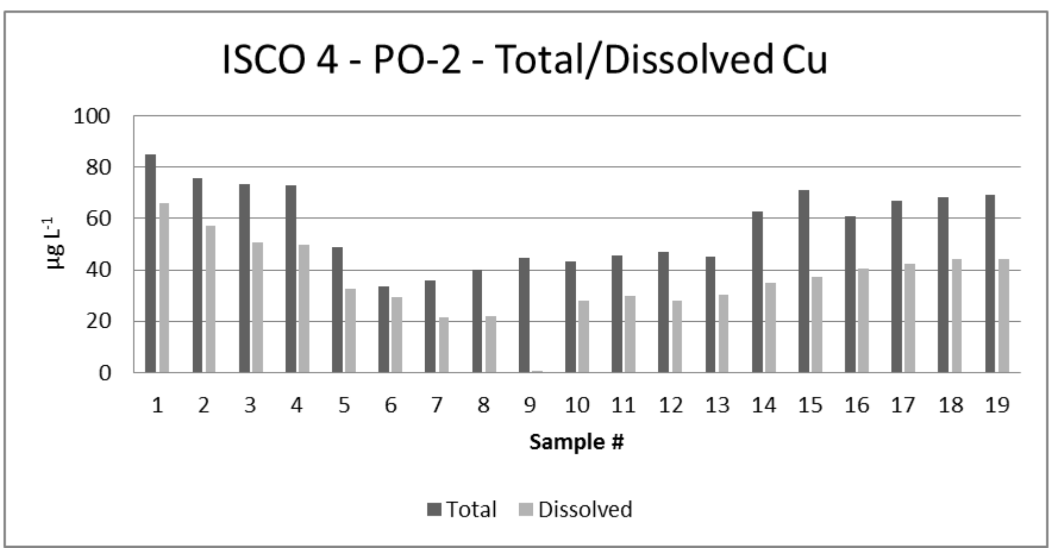

ISCO 2 - PO-2 - Total/Dissolved Cu
350
300
250
200
150
100
50
0
µg L-1
1
2
3
4
5
6
7
8
Sample #
Total
Dissolved

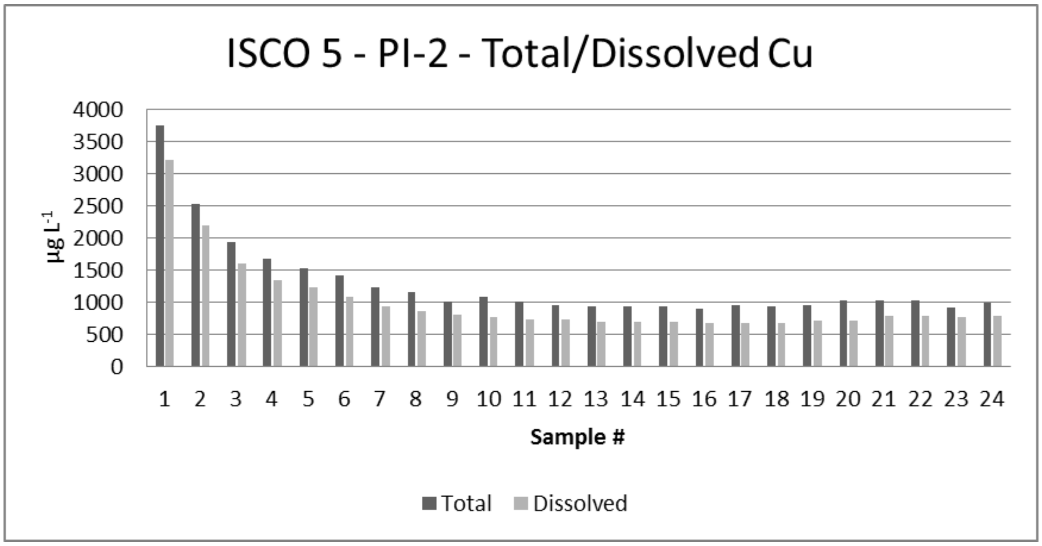

ISCO 3 - PI-2 - Total/Dissolved Cu
2000
1500
1000
500
0
µg L-1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
Sample #
Total
Dissolved

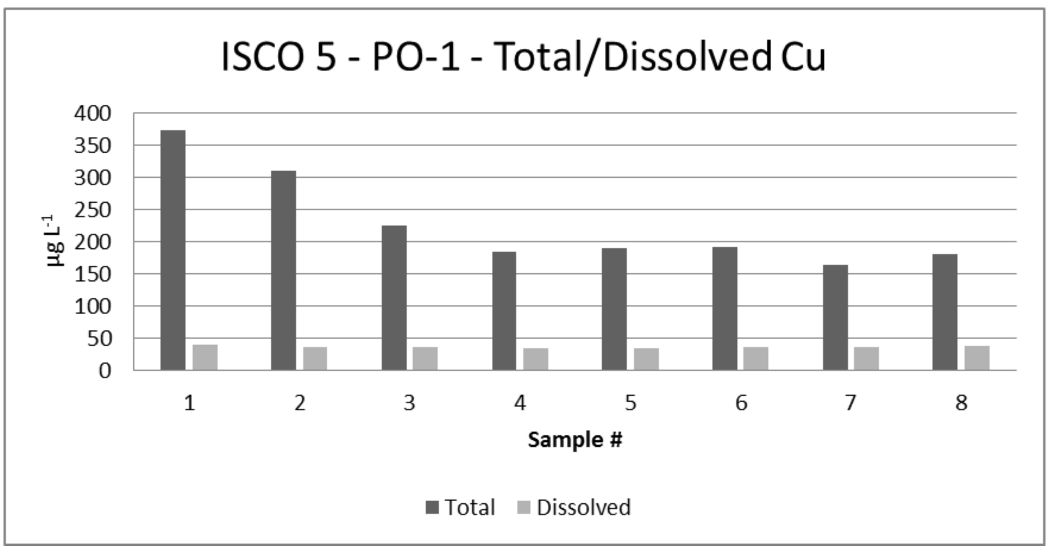

ISCO 3 - PO-1 - Total/Dissolved Cu
120
100
80
60
40
20
0
µg L-1
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Sample #
Total
Dissolved

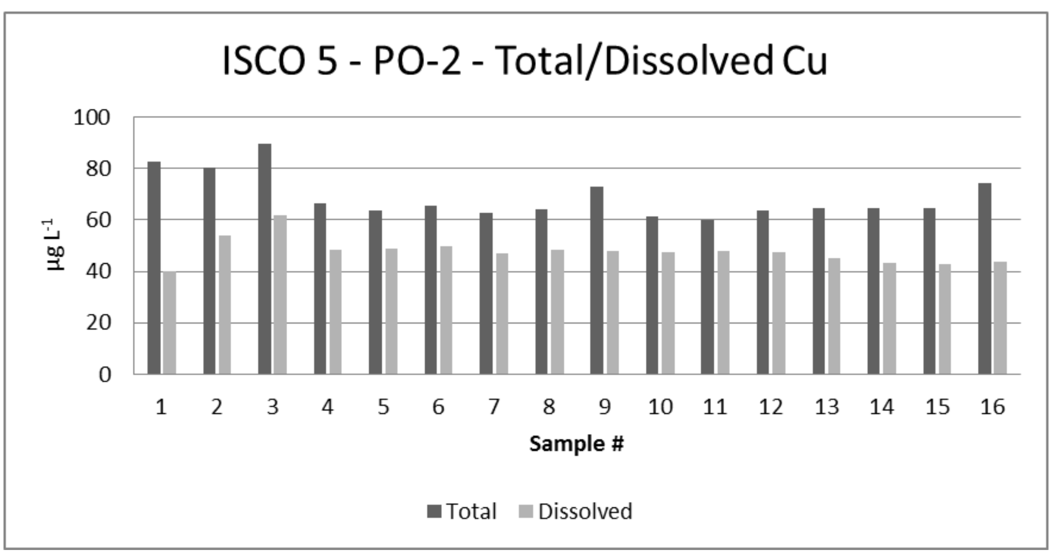

ISCO 4 - PI-1 - Total/Dissolved Cu
µg L-1
3500
3000
2500
2000
1500
1000
500
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Sample #
Total
Dissolved

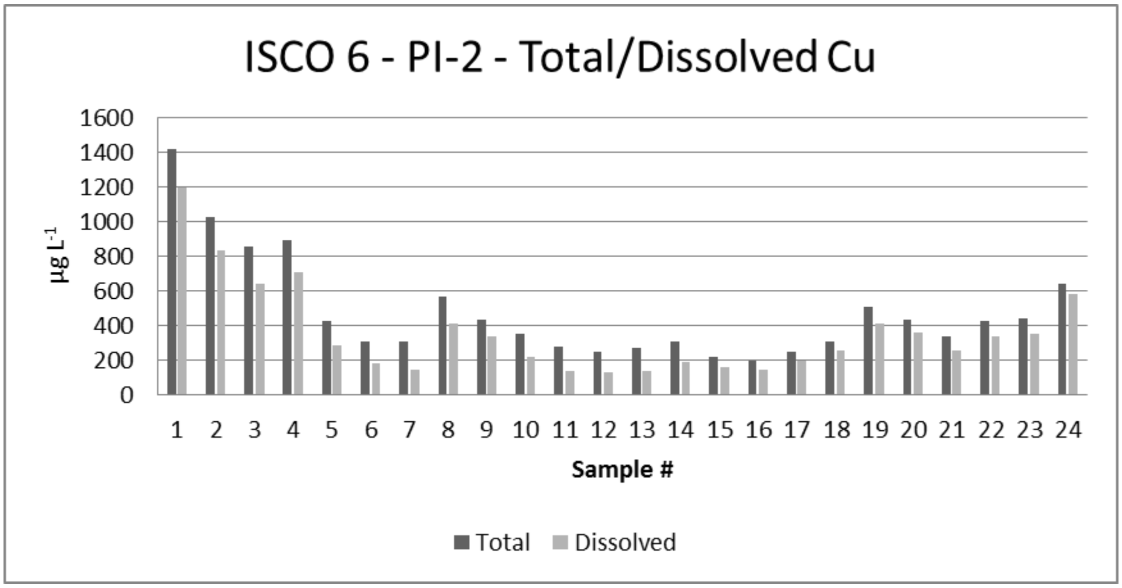

ISCO 4 - PO-1 - Total/Dissolved Cu
µg L-1
60
50
40
30
20
10
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Sample #
Total
Dissolved


ISCO 4 - PO-2 - Total/Dissolved Cu
µg L-1
100
80
60
40
20
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
Sample #
Total
Dissolved

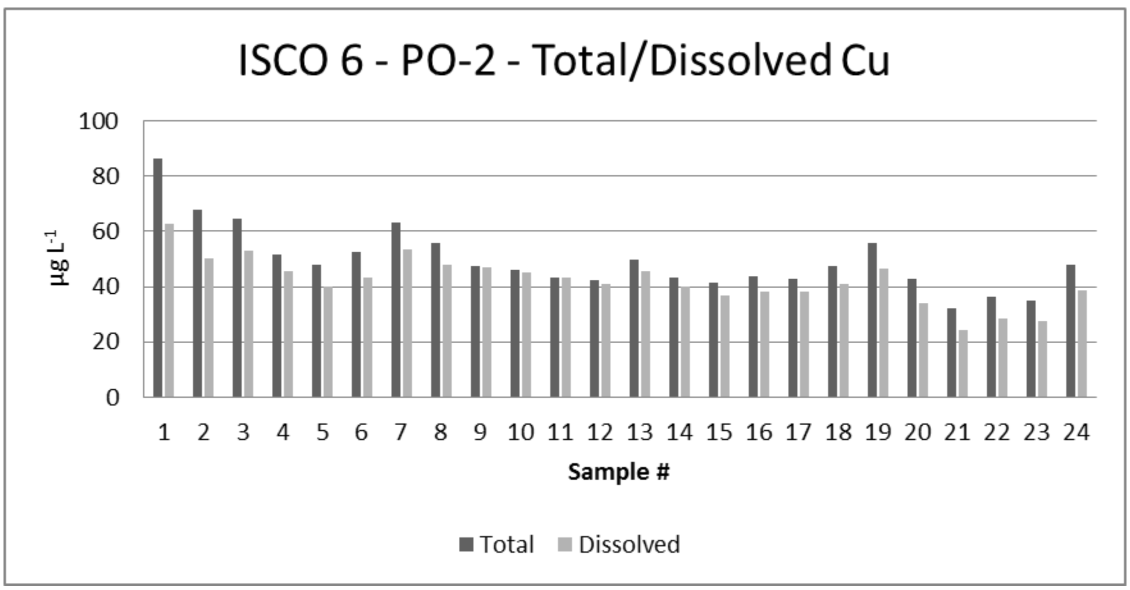

ISCO 5 - PI-2 - Total/Dissolved Cu
4000
3500
3000
2500
2000
1500
1000
500
0
µg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved


ISCO 5 - PO-1 - Total/Dissolved Cu
400
350
300
250
200
150
100
50
0
µg L-1
1 2 3 4 5 6 7 8
Sample #
Total
Dissolved

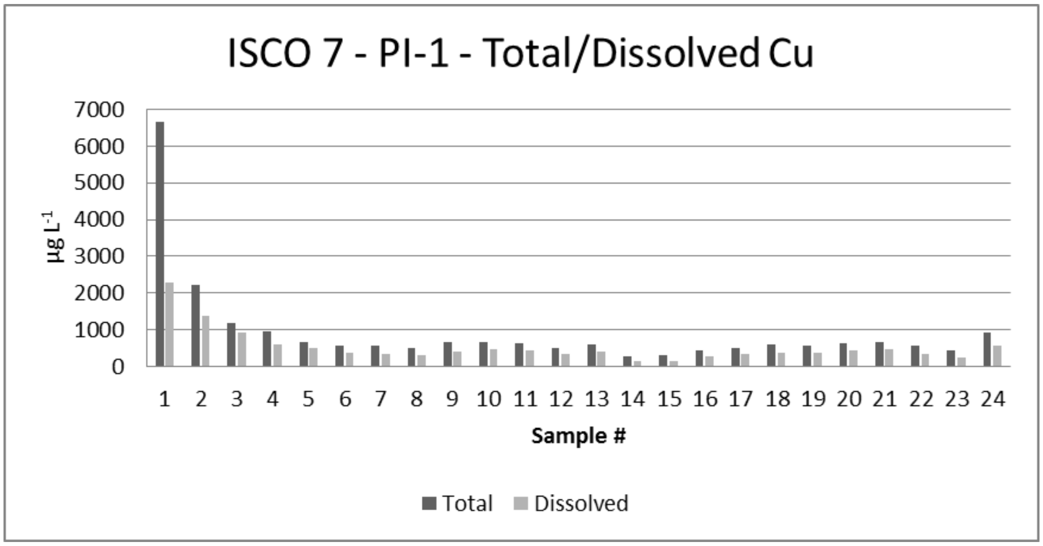

ISCO 5 - PO-2 - Total/Dissolved Cu
100
80
60
40
20
0
µg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Sample #
Total
Dissolved

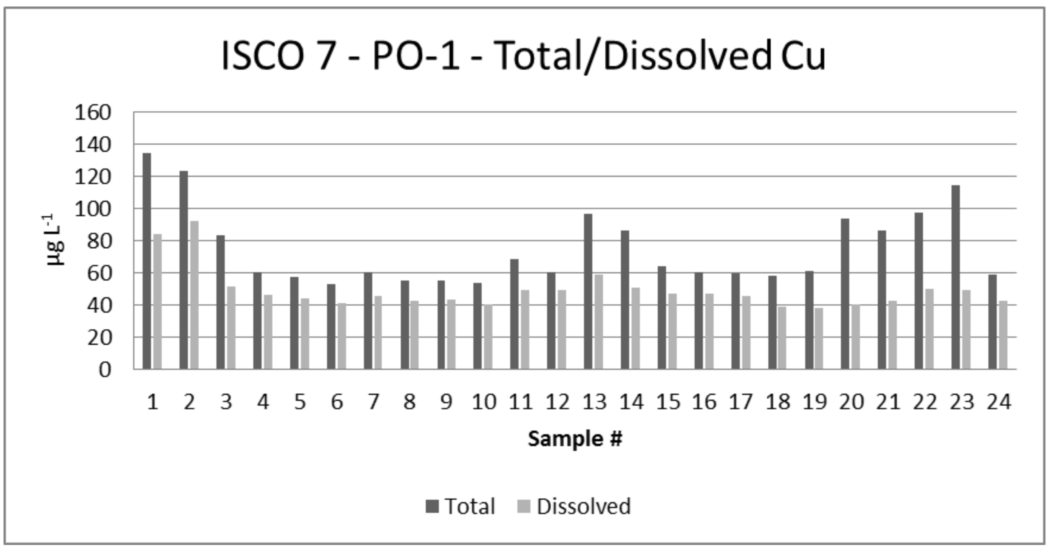


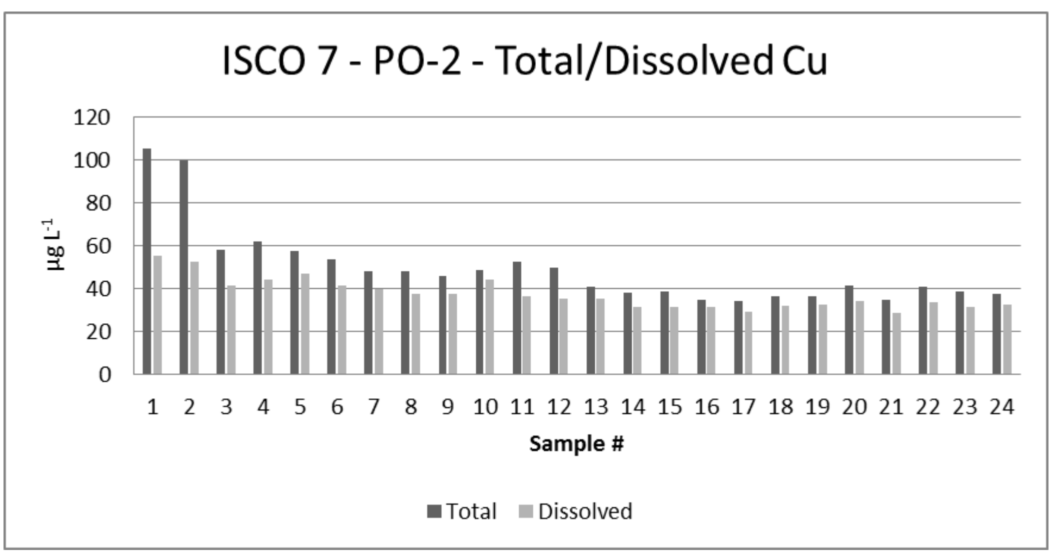
ISCO 6 - PI-2 - Total/Dissolved Cu
1600
1400
1200
1000
800
600
400
200
0
μg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved



ISCO 6 - PO-2 - Total/Dissolved Cu
100
80
60
40
20
0
μg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved


ISCO 7 - PI-1 - Total/Dissolved Cu
7000
6000
5000
4000
3000
2000
1000
0
μg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved


ISCO 7 - PO-1 - Total/Dissolved Cu
160
140
120
100
80
60
40
20
0
μg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved


ISCO 7 - PO-2 - Total/Dissolved Cu
120
100
80
60
40
20
0
μg L-1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Sample #
Total
Dissolved

Appendix D - Dissolved Cu (μg L^{-1}) for composite storm events. Values of 0.5 were below the LOQ.

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					μg L^{-1}					
130111	45	14	710		40	34	726	660		
130131	23	13	203	272	22	18	220	223		13
130227	20	1	1098		29		1366	1134	15	18
130319	51	6	1569	832	40	25	1619	1380		
130412	381	3	827	970	70	40	922	923		
130508/11	247	3	953	1266	79	91	1330	1302		4
130524	134	0.5	1649	1098	131	68	1318	1322		
130607-A	38	1	826	847	75	40	1221	759		4
130607-B	13	0.5	886	815	68	24	782	780	6	
130801	71	0.5	1177	1248	109	89	1326	1255		
130808	27	0.5	1799	1798	147	100	1728	1569		15
130922	68	0.5			111	75	931	1148	26	34
131007	154	1	651	688	106	79	746		31	27
131127	16	3	467	394		50			27	35
131223	15	0.5	582		54	45	562	590	28	30
140106			728	682	45	53	881	655	23	24
140221	26	3	1173	1171	34		987	1087	20	22
140302			2167	2505	23	22	2192	2455	20	16
140329-A	16	1	469	399	26	25	479	496	29	26
140329-B	7	4	542	501	26	24	561	556	24	26
140329-C		6	655	687	23	19	669	646	18	20
140415	81	1	435	462	39	37	552	576	26	29
140522	29	8	1222	1310	55	57	1725	1384	19	22
140612	24	0.5	720	488	154	75	634	655	48	24
140704	170	0.5	1731	1837	139	62		1753	29	24
140824			2044	2329	186	67	1679	2298	22	22
					Summary					
Average	**75**	**3.1**	**1011**	**1027**	**73**	**51**	**1048**	**1067**	**24**	**22**
Median	**34**	**1.3**	**827**	**840**	**55**	**47**	**927**	**1005**	**24**	**23**
Lowest	7.5	0.5	203	272	21.8	17.8	220	223	6.3	3.7
Highest	381	14	2167	2505	186	100	2192	2455	48	35
Std. Dev.	92	3.9	538	620	48.7	25.2	497	559	8.6	8.5
n	22	23	25	22	25	24	24	24	17	20
Std. Error	19.7	0.8	108	132	9.7	5.1	101	114	2.1	1.9

Appendix E - % Particulate Cu for composite storm events. In cases where the total Cu concentration exceeded the dissolved Cu concentration, the particulate component was estimated at 0%.

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					%					
130111	24.0	0.4	0.0		2.8	56.0	0.0	0.0		
130131	0.0	12.2	25.2	23.7	29.0	31.0	27.2	24.3		35.7
130227	5.3	26.7	9.6		28.0		5.6	18.7	11.1	21.4
130319	1.9	1.9	0.9	35.2	21.0	31.2	4.5	3.0		
130412	0.0	7.4	19.1	12.6	24.3	35.4	7.7	7.0		
130508/11	0.0	3.7	14.5	10.8	6.1	17.4	11.8	11.5		80.1
130524	8.9	0.0	10.8	15.3	11.9	19.0	12.9	12.0		
130607-A	5.2	82.1	12.9	12.0	11.5	11.2	15.8	16.4		43.5
130607-B	30.3	0.0	15.7	17.8	16.5	29.8	22.7	24.5	68.5	
130801	0.0	0.0	12.2	8.8	4.6	4.9	8.7	6.0		
130808	11.9	0.0	4.9	7.5	5.6	7.0	10.0	11.4		28.6
130922	6.7	0.0			7.6	10.9	27.3	17.4	8.2	10.3
131007	9.7	18.5	15.4	15.4	13.4	14.1	18.9		11.4	14.5
131127	4.1	0.0	25.0	28.6		22.3			8.2	0.4
131223	7.9	68.8	20.0		15.3	15.8	35.9	34.8	19.4	18.8
140106			54.8	20.2	42.7	17.7	19.5	25.0	10.7	12.5
140221	88.8	32.3	51.4	25.3	62.2		57.3	65.9	23.6	14.9
140302			22.7	17.6	31.6	14.8	19.4	15.0	14.1	13.7
140329-A	28.0	2.7	30.9	41.8	33.3	15.1	30.2	31.4	23.3	27.8
140329-B	26.2	16.3	28.1	30.0	31.5	16.1	27.6	25.6	25.8	30.9
140329-C		11.4	29.7	14.2	38.9	22.4	21.7	28.2	27.4	36.8
140415	28.3	40.4	28.5	27.1	35.7	23.0	27.5	33.0	19.0	29.5
140522	77.0	15.1	0.0	23.1	21.8	12.2	20.8	21.6	31.7	19.2
140612	20.4	0.0	33.9	35.8	18.8	18.1	36.5	33.9	18.5	43.6
140704	4.4	0.0	18.8	13.8	18.1	13.5		18.6	11.0	12.5
140824			13.1	11.7	2.7	10.0	12.3	11.0	16.8	1.0
Average	**17.7**	**14.8**	**19.9**	**20.4**	**21.4**	**19.5**	**20.1**	**20.7**	**20.5**	**24.8**
Median	**8.4**	**3.7**	**19.0**	**17.8**	**19.9**	**17.4**	**19.5**	**18.7**	**18.8**	**21.4**

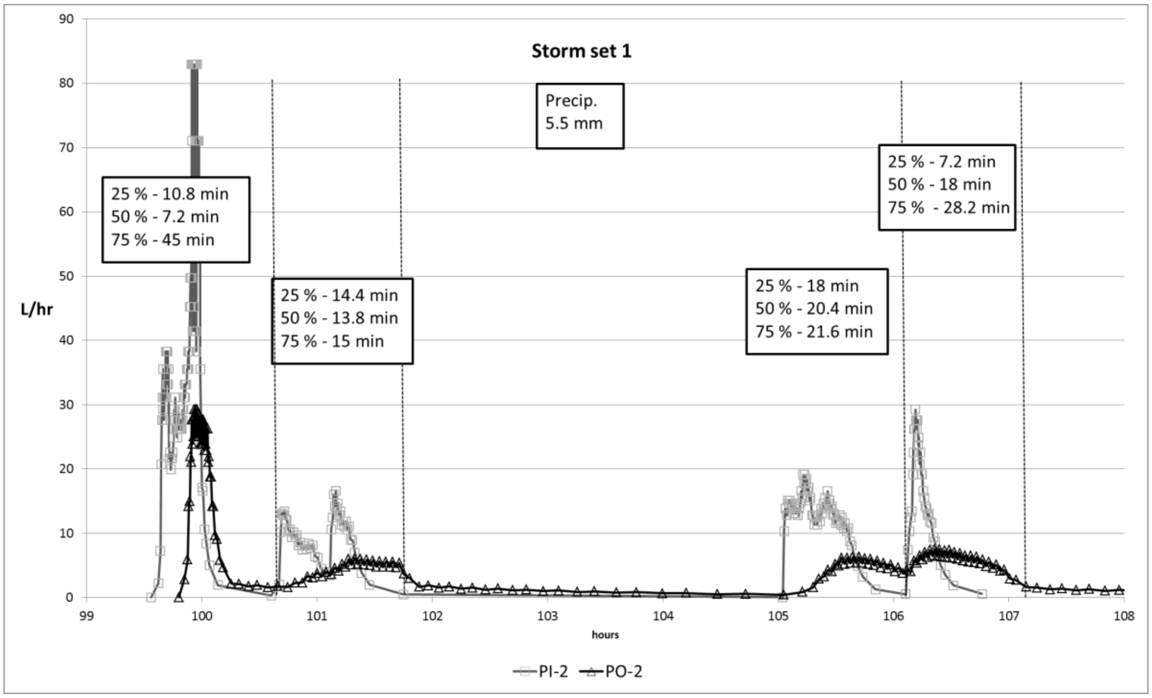
Appendix F - Total Suspended Solids for composite storm events. Missing values represent no data or amounts below the LOQ.

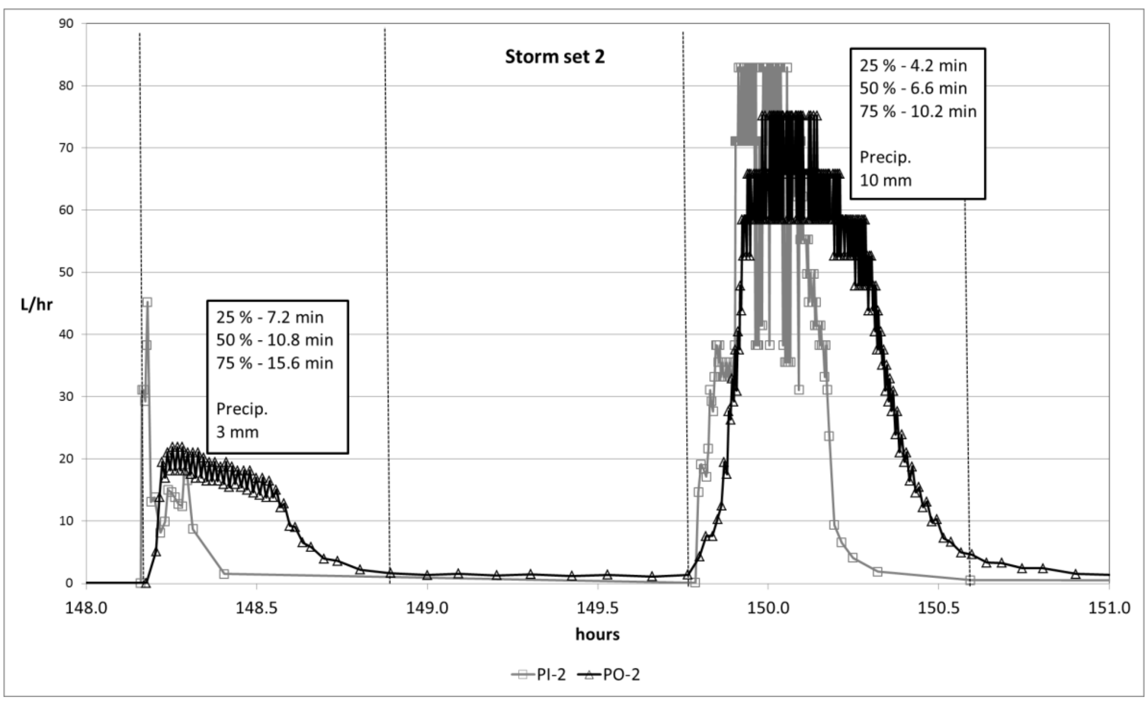
Storm Code	C-1	C-2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					mg L^{-1}					
130111	1.3				14.3	464		1.7		
130131	3.9	2.9	4.5	10.0	75.0	93.1	4.3	5.2		126
130227			5.6		15.6		3.9	12.5	37.9	185
130319	5.6				7.8	34.8		12.7		
130412	4.2	5.6	4.0	1.4	34.9	67.0	1.8	2.6		
130508/11	7.6	0.5	1.5	4.2	7.7	27.8		5.3		1854
130524	53.9	4.7	9.3	6.0	12.8	68.2		8.5		
130607-A	6.6				14.7	16.0				56.0
130607-B					6.9	8.4			259.0	
130801			2.4		6.0	8.6				
130808		2.9			10.1	8.2		2.5		
130922	4.8	2.9						2.8	5.4	10.9
131007	11.7				12.6	14.7			14.6	21.9
131127										
131223						18.7		10.9	11.3	30.3
140106			19.1	2.4	23.8	11.3	6.0	4.3	8.2	19.4
140221	110	9.6	40.8	13.0	160		31.2	191	32.0	10.6
140302			14.1	5.9	11.6		3.6	5.6	12.0	4.0
140329-A	3.2		4.0		7.9	9.1		2.3	14.9	31.3
140329-B	2.2		1.2		23.1	12.0			22.4	24.8
140329-C			2.7		27.9	7.9	2.5	2.5	16.6	34.3
140415	14.8				19.1	23.3	4.6	3.0	25.9	31.5
140522	2.0		3.6	2.2	6.1	4.9	3.2	2.2	16.1	22.3
140612	2.4		6.0		10.6	11.1	4.7	3.1	14.2	42.0
140704	9.6	3.9	4.1	3.1	8.5	18.2		4.1	8.5	30.8
140824						4.0	2.2		26.4	
					Summary					
Average	**15.2**	**4.1**	**8.2**	**5.4**	**23.5**	**44.3**	**6.2**	**14.9**	**32.8**	**149**
Median	**5.2**	**3.4**	**4.1**	**4.2**	**12.7**	**14.7**	**3.9**	**4.1**	**15.5**	**30.8**
Lowest	1.3	0.5	1.2	1.4	6.0	4.0	1.8	1.7	5.4	4.0
Highest	110	9.6	40.8	13.0	160	464	31.2	191	259	1854
Std. Dev.	28	2.7	10.3	3.9	33.9	99	8.4	43	61	442
n	16	8	15	9	22	21	11	19	16	17
Std. Error	7.0	0.9	2.6	1.3	7.2	21.6	2.5	9.8	15.2	107

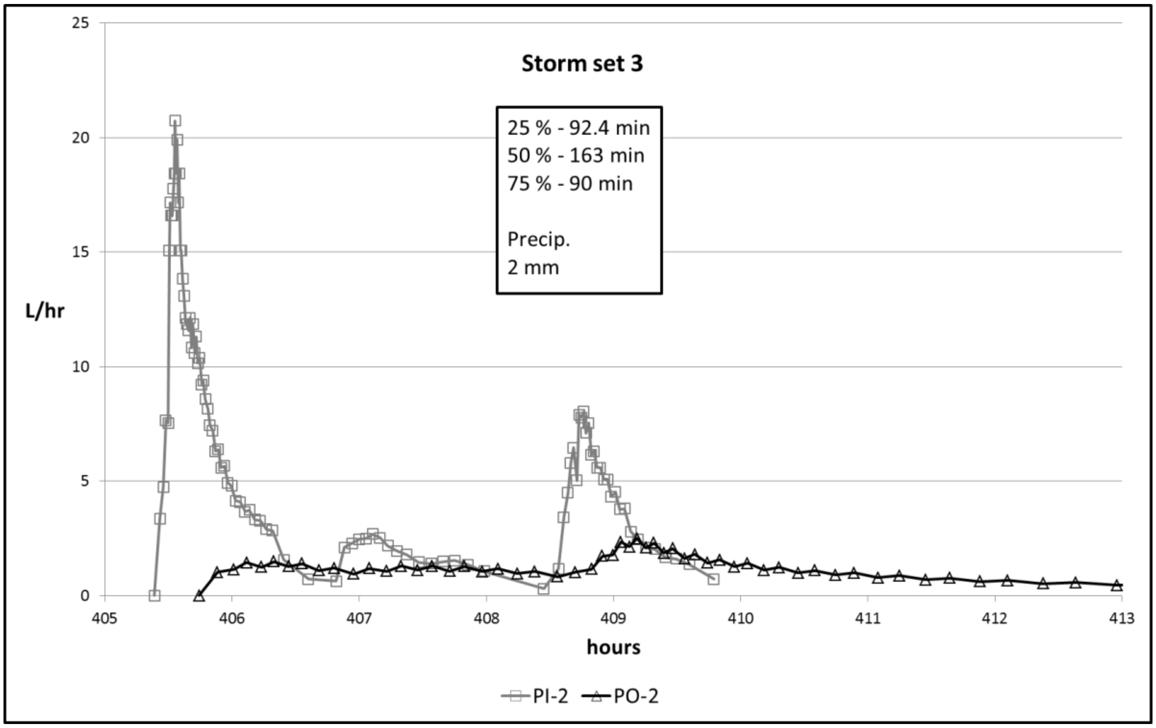
Appendix G – Cu loading estimates for composite storm events. Blank spaces represent no sample. "na" represents no flow data available to estimate loading.

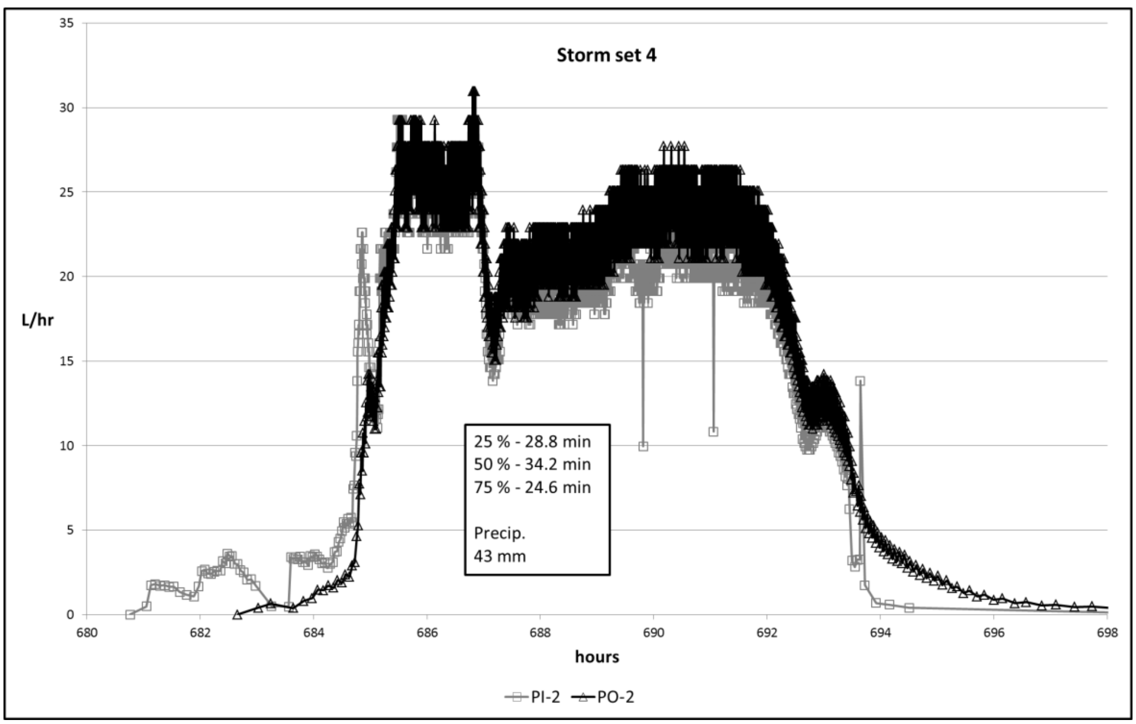
Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					mg					
130111	0.75	na	na		na	3.6	32	na		
130131	0.46	0.90	83	26	11	4.3	101	88		na
130227	0.54	0.02	138		5.0		178	170	0.07	0.10
130319	0.87	0.08	126	92	3.9	na	133	95		
130412	3.7	0.06	78	93	6.9	6.2	57	68		
130508/11	3.1	0.02	72	110	6.8	10	59	114		0.03
130524	1.6	0.01	220	161	18	13	42	175		
130607-A	0.67	0.13	213	180	17	10	32	199		0.02
130607-B	0.13	0.00	162	160	13	7.0	158	170	0.34	
130801	0.87	0.00	120	119	8.7	7.1	128	116		
130808	0.34	0.00	229	218	23	16	242	199		0.12
130922	1.0	0.00			18	16	213	114	0.41	1.0
131007	1.4	0.04	84	102	13	15	108		2.3	1.2
131127	0.27	0.05	155	134		20			0.34	0.40
131223	0.21	0.05	117		11	10	147	173	3.0	3.4
140106			96	50	5.4	3.4	69	40	0.22	na
140221	0.79	0.02	68	35	4.4		26	53	1.5	4.1
140302			107	114	1.3	1.1	46	120	na	na
140329-A	0.67	0.03	95	85	4.8	3.9	86	99	2.9	na
140329-B	0.11	0.20	211	157	9.0	7.2	204	205	3.6	na
140329-C		0.18	95	120	6.9	4.9	97	101	6.7	na
140415	1.7	0.04	na	95	10	9.0	127	153	5.0	7.6
140522	0.90	0.07	33	na	3.1	3.0	61	68	na	na
140612	0.38	0.00	107	135	25	21	152	163	5.8	4.8
140704	1.3	0.00	120	175	11	5.2		89	na	na
140824			130	142	8.5	3.3	112	139	na	0.67
					Summary					
Average	**1.0**	**0.09**	**124**	**119**	**10.2**	**8.7**	**109**	**127**	**2.5**	**1.9**
Median	**0.8**	**0.03**	**117**	**119**	**8.8**	**7.1**	**105**	**116**	**2.3**	**0.8**
Lowest	0.11	0.00	33	26	1.3	1.1	26	40	0.07	0.02
Highest	3.7	0.90	229	218	25	21	242	205	6.7	7.6
Std. Dev.	0.9	0.19	53	48	6.3	5.6	61	49	2.3	2.5
n	22	22	23	21	24	23	24	23	13	12
Std. Error	0.19	0.04	11.0	10.5	1.3	1.2	12.5	10.2	0.63	0.7

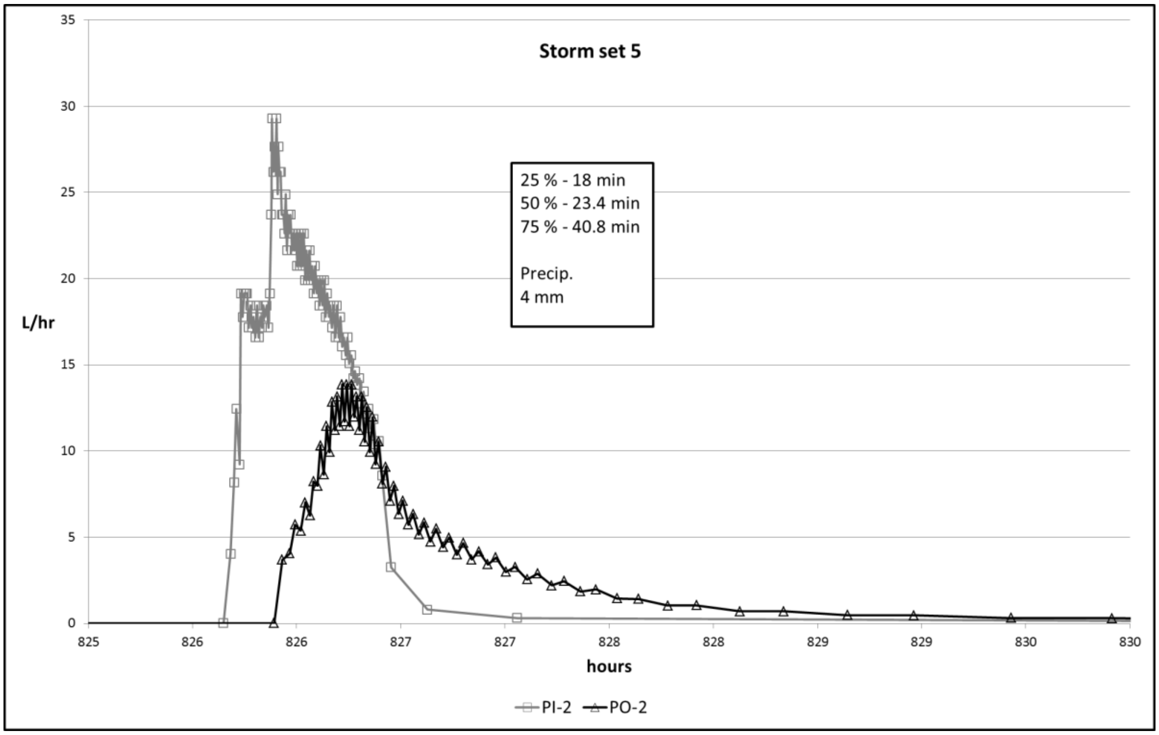
Appendix H – High-resolution hydrographs. 5 Storm sets used to estimate retention times in PO-2. Total precipitation is given in mm; percentages and minutes are the points at which 25%, 50% and 75% of the volume passed through the outlet flow gauge.



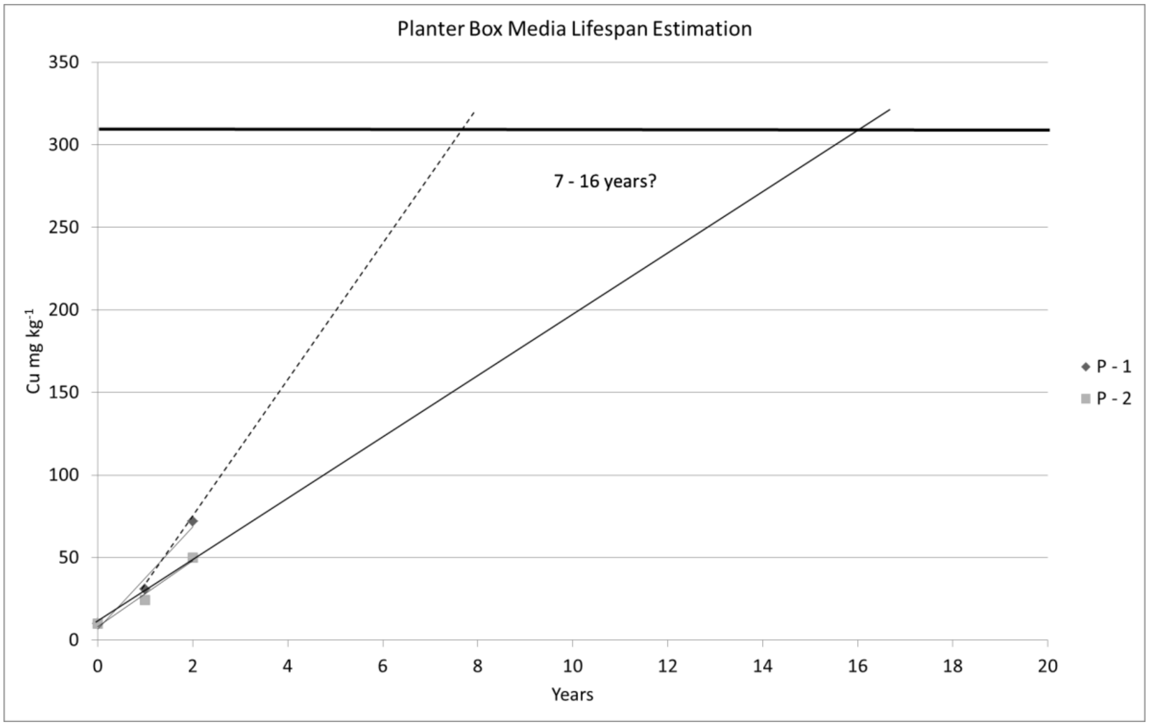



Storm set 3
25 % - 92.4 min
50 % - 163 min
75 % - 90 min
Precip.
2 mm
L/hr
hours
PI-2
PO-2


Storm set 4
25 % - 28.8 min
50 % - 34.2 min
75 % - 24.6 min
Precip.
43 mm
L/hr
hours
PI-2
PO-2


Storm set 5
25 % - 18 min
50 % - 23.4 min
75 % - 40.8 min
Precip.
4 mm
L/hr
hours
PI-2
PO-2
35
30
25
20
15
10
5
0
825
826
826
827
827
828
828
829
829
830
830

Appendix I - Media lifespan estimations for planter boxes. Graphical estimates made using the most conservative points. The state of Maryland's Cu limits of 310 mg kg^{-1} for residential soil were used to bound the acceptable limits of soil Cu.



Appendix J - pH for all storm samples. Note the key at the bottom and consult Table 2.3 for additional information. Some samples were not measured with the LIS pH technique. Averages are given for composite storm events to compare the effects of structures or SCMs. pH for discrete events are the average of all bottles collected.

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Composite Storm Events - pH										
130111	7.1	6.8	6.5		8.3	7.3	6.4	6.5		
130131	7.0	6.3	6.7	7.1	7.9	7.9	6.4	6.6		7.2 st
130227	6.9	6.2	6.7		7.7		6.7	6.5	7.6	6.9
130319	6.8	6.1	6.5	6.5	8.7	8.1	6.8	6.8		
130412	7.1	6.6	6.8	6.8	8.0	7.9	6.9	6.8		
130508/11	7.1	6.8	6.7	6.8	9.0	8.0	6.8	6.8		7.2
130524	7.3	6.5	7.0	6.7	8.0	7.7	6.8	6.6		
130607-A	6.7	5.9	6.5	6.9	7.6	7.4	6.7	6.5		7.1
130607-B	7.1	6.1	6.5	6.5	8.1	7.8	6.6	6.6	7.1	
130801	6.6	6.1	6.3	6.5	7.6	8.5	6.3	6.4		
130808	6.7	5.5	6.3	6.5	7.6	7.8	6.3	6.5		6.9
130922	7.1	6.7			7.2	7.1	6.8	6.5	8.1	8.1
131007	7.0	6.2	6.7	6.3	7.1	7.1	6.3		7.9	7.7
131127	6.5	6.0	6.3	6.2		6.9			7.5	7.6
131223	7.0	6.1	6.7		7.5	7.5	6.7	6.3	7.6	7.8
140106			6.3	6.5	7.2	8.0	6.9	6.6	7.6	7.9
140221	6.3	6.0	6.1	6.1	8.1		6.3	5.0 st	7.4	7.7
140302			6.8	6.7	7.7	7.5	6.5	6.7	7.9	7.6
140329-A	6.2	5.9	6.7	6.6	7.9	7.5	6.3	6.6	7.9	7.7
140329-B	6.5	6.1	6.5	6.5	8.6	8.3	6.2	6.8	7.4	7.6
140329-C		5.7	6.6	6.3	7.6	7.5	6.6	6.3	7.6	7.3
140415	6.3	5.7	6.4	6.3	7.3	7.2	6.1	6.1	7.3	7.1
140522	7.1	6.3	6.8	6.6	7.4	7.4	7.0	6.8	7.1	7.2
140612	6.3	5.8	6.8	6.6	7.4	7.0	6.5	6.6	7.3	7.2
140704	6.5	5.3	6.7	6.3	7.2	7.3		6.3	7.1	7.1
140824			6.7	6.5	7.5	7.3	6.7	6.7	7.8	7.8
average	**6.8**	**6.1**	**6.6**	**6.5**	**7.8**	**7.6**	**6.6**	**6.5**	**7.5**	**7.4**
Discrete Storm Events - pH										
ISCO 1				7.1		8.4				
ISCO 2			5.9 st		6.2 st	6.6 st				
ISCO 3				5.1 st	6.1 st					
ISCO 4			6.6		8.7	7.6				
ISCO 5				6.8		7.6				
ISCO 6				6.4		7.1				
ISCO 7			6.4		7.4	7.5				
Key	blank = no sample				st = standard pH technique (not LIS)					

Appendix K – Ions (Ca^{+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}) for composite storm events. Values of 0.5 were below the LOQ.

Ca^{+}	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Storm Code					mg L^{-1}					
130111	4.1	3.0	3.2		13.8	15.6	3.0	2.9		
130131	2.8	0.5	0.5	2.7	10.8	11.5	0.5	0.5		5.3
130227	1.3	1.9	1.3		5.0		1.3	1.5	3.0	3.0
130319	1.7	1.1	1.5	1.1	6.4	5.0	1.5	1.4		
130412	4.6	2.3	2.1	2.2	6.2	6.9	2.2	2.2		
130508/11	4.1	2.1	2.0	2.0	11.6	8.3	2.3	2.0		4.3
130524	3.9	1.6	2.0	0.5	8.2	8.7	2.0	1.7		
130607-A	2.3	1.3	1.4	1.5	6.1	6.8	1.6	1.4		4.6
130607-B	2.0	1.3	1.4	1.3	0.5	6.3	1.3	1.4	5.4	
130801	3.2	2.0	2.1	2.2	9.6	10.1	0.5	0.5		
130808	3.4	2.0	0.5	2.2	11.6	10.0	2.1	2.1		17.7
130922	3.3	2.3			7.3	0.5	2.1	2.2	137.9	89.9
131007	5.4	2.2	2.2	2.2	6.9	6.7	2.5		139.0	161
131127	3.2	0.5	0.5	2.9		5.2			29.0	35.2
131223	3.1	0.5	0.5		6.9	7.1	0.5	2.8	30.3	24.2
140106			2.7	2.9	5.4	5.9	2.8	2.9	17.8	15.0
140221	0.5	0.5	0.5	0.5	16.4		0.5	0.5	15.6	16.3
140302			0.5	0.5	16.8	14.2	0.5	0.5	30.8	27.0
140329-A	1.1	0.5	1.2	1.1	0.5	5.1	1.2	1.2	25.0	22.4
140329-B	0.5	0.5	0.5	0.5	4.9	4.8	1.0	0.5	12.9	15.4
140329-C		0.5	0.5	0.5	4.3	3.8	0.5	0.5	13.3	10.8
140415	2.8	0.5	0.5	1.0	6.1	6.1	1.2	1.1	28.1	22.5
140522	3.7	1.9	1.9	1.9	14.2	14.9	2.7	1.9	69.4	61.9
140612	1.4	0.5	1.1	0.5	11.0	11.5	0.5	0.5	29.6	26.4
140704	3.6	1.0	1.3	1.1	9.0	9.2		1.4	61.7	61.3
140824			1.2	1.1	10.7	12.8	1.4	1.7	95.5	93.0
					Summary					
Average	**2.8**	**1.3**	**1.3**	**1.5**	**8.4**	**8.2**	**1.5**	**1.5**	**43.8**	**35.9**
Median	**3.2**	**1.3**	**1.3**	**1.2**	**7.3**	**7.0**	**1.4**	**1.4**	**29.0**	**22.5**
Lowest	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	3.0	3.0
Highest	5.4	3.0	3.2	2.9	16.8	15.6	3.0	2.9	139.0	161.4
Std. Dev.	1.3	0.8	0.8	0.8	4.3	3.8	0.8	0.8	42.9	39.8
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.28	0.16	0.16	0.18	0.85	0.77	0.17	0.16	10.40	8.90

Mg^{2+}	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Storm Code					mg L^{-1}					
130111	1.8	0.5	1.8		5.2	5.2	0.5	0.5		
130131	0.5	0.5	0.5	0.5	4.3	4.0	0.5	0.5		2.1
130227	0.5	0.5	0.5		2.7		0.5	2.1	2.1	2.1
130319	0.5	0.5	0.5	0.5	2.9	2.4	0.5	0.5		
130412	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		
130508/11	0.5	0.5	0.5	0.5	4.3	2.6	0.5	0.5		0.9
130524	0.5	0.5	0.5	0.5	2.7	2.6	0.5	0.5		
130607-A	0.5	0.5	0.5	0.5	1.9	2.2	0.5	0.5		1.0
130607-B	0.5	0.5	0.5	0.5	1.5	2.0	0.5	0.5	0.5	
130801	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		
130808	0.5	0.5	0.5	0.5	2.7	2.5	0.5	0.5		2.1
130922	0.5	0.5			2.2	0.5	0.5	0.5	3.2	3.2
131007	0.5	0.5	0.5	0.5	2.3	2.2	0.5		3.0	4.3
131127	0.5	0.5	0.5	0.5		0.5			0.5	0.3
131223	0.5	0.5	0.5		0.5	0.5	0.5	0.5	0.5	0.5
140106			0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
140221	0.5	0.5	0.5	0.5	10.4		0.5	0.5	0.5	0.5
140302			0.5	0.5	16.5	0.5	0.5	0.5	0.5	0.5
140329-A	0.5	0.5	0.5	0.5	2.0	1.4	0.5	0.5	0.5	1.3
140329-B	0.5	0.5	0.5	0.5	1.4	1.3	0.5	0.5	0.5	1.0
140329-C		0.5	0.5	0.5	1.2	1.1	0.5	0.5	0.5	0.5
140415	0.5	0.5	0.5	0.5	1.7	1.7	0.5	0.5	1.0	1.3
140522	0.5	0.5	0.5	0.5	1.8	2.0	0.5	0.5	0.5	0.5
140612	0.5	0.5	0.5	0.5	2.7	2.8	0.5	0.5	0.5	1.0
140704	0.5	0.5	0.5	0.5	2.7	2.5		0.5	2.0	2.5
140824			0.5	0.5	2.8	3.0	0.5	0.5	2.8	3.4
					Summary					
Average	**0.6**	**0.5**	**0.6**	**0.5**	**3.1**	**1.9**	**0.5**	**0.6**	**1.2**	**1.5**
Median	**0.5**	**0.5**	**0.5**	**0.5**	**2.3**	**2.0**	**0.5**	**0.5**	**0.5**	**1.0**
Lowest	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.3
Highest	1.8	0.5	1.8	0.5	16.5	5.2	0.5	2.1	3.2	4.3
Std. Dev.	0.3	0.0	0.3	0.0	3.4	1.2	0.0	0.3	1.0	1.2
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.06	0.00	0.05	0.00	0.69	0.25	0.00	0.07	0.25	0.26

Na^+	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Storm Code					mg L^{-1}					
130111	3.7	3.2	3.2		4.2	5.9	3.0	3.0		
130131	3.0	2.9	2.7	2.8	3.6	4.2	2.7	2.7		3.0
130227	0.5	0.5	0.5		1.0		0.5	0.5	1.1	1.2
130319	1.9	1.4	2.0	1.4	2.2	2.2	1.8	1.5		
130412	3.8	2.2	2.2	2.2	2.6	3.1	2.2	2.2		
130508/11	3.3	2.3	1.8	2.0	2.7	2.3	2.2	2.1		1.7
130524	2.8	1.4	1.5	1.4	2.2	2.1	1.4	1.4		
130607-A	2.0	1.8	1.7	1.8	2.0	2.1	1.7	1.7		1.8
130607-B	1.6	1.6	1.6	1.6	1.8	0.5	1.6	1.6	1.7	
130801	1.1	0.5	0.5	0.5	1.2	1.2	0.5	0.5		
130808	1.0	0.5	0.5	0.5	1.0	1.3	0.5	0.5		1.4
130922	1.1	0.5			1.1	1.0	0.5	0.5	9.3	6.4
131007	1.8	0.5	0.5	0.5	1.3	1.2	0.5		7.6	10.4
131127	0.5	0.5	0.3	0.5		0.5			2.8	2.3
131223	0.5	0.5	0.5		1.1	1.7	0.5	1.6	2.3	2.0
140106			0.5	0.5	0.5	0.8	0.5	0.5	1.1	1.1
140221	7.3	7.3	7.4	7.5	7.6		7.3	7.5	7.5	7.7
140302			9.8	10.2	9.6	9.6	9.9	9.5	9.7	9.9
140329-A	0.5	0.5	0.5	0.5	1.2	1.4	0.5	0.5	1.9	1.9
140329-B	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.4	1.5
140329-C		0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.3	1.2
140415	1.7	0.5	0.5	0.5	0.5	1.1	0.5	0.5	1.7	1.7
140522	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.9	2.2
140612	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.4	1.4
140704	1.3	0.5	0.5	0.5	0.5	0.5		0.5	3.1	2.6
140824			1.1	0.5	0.5	0.5	0.5	0.5	3.7	4.1
					Summary					
Average	**1.9**	**1.4**	**1.7**	**1.7**	**2.0**	**1.9**	**1.7**	**1.7**	**3.5**	**3.3**
Median	**1.4**	**0.5**	**0.5**	**0.5**	**1.2**	**1.2**	**0.5**	**0.5**	**1.9**	**1.9**
Lowest	0.5	0.5	0.3	0.5	0.5	0.5	0.5	0.5	1.1	1.1
Highest	7.3	7.3	9.8	10.2	9.6	9.6	9.9	9.5	9.7	10.4
Std. Dev.	1.6	1.6	2.3	2.5	2.2	2.1	2.3	2.2	3.0	2.9
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.34	0.33	0.45	0.52	0.45	0.43	0.47	0.46	0.73	0.65

K^+ Storm Code	C1	C2	PI-1	PI-2	PO-1 mg L^{-1}	PO-2	SI-1	SI-2	SO-1	SO-2
130111	2.8	2.7	2.6		10.7	15.6	2.6	2.6		
130131	2.6	2.6	0.5	0.5	9.9	13.2	0.5	0.5		3.7
130227	0.5	0.5	0.5		4.2		0.5	0.5	1.7	1.2
130319	1.2	0.5	1.2	0.5	4.9	5.0	1.2	1.2		
130412	2.7	2.5	2.5	2.5	6.1	7.6	2.5	2.5		
130508/11	2.9	2.1	2.1	2.5	7.5	7.3	2.8	2.6		5.1
130524	2.2	1.8	2.3	1.8	6.4	6.8	2.0	1.9		
130607-A	1.9	1.7	1.8	1.9	4.5	5.6	1.8	1.7		4.8
130607-B	1.8	1.7	1.7	1.7	4.2	5.0	1.7	1.7	4.7	
130801	1.7	1.3	1.3	1.5	3.7	4.3	0.5	0.5		
130808	1.3	1.1	0.5	1.2	3.4	4.3	1.2	1.2		11.1
130922	2.2	1.5			2.7	4.4	1.2	1.5	6.4	4.9
131007	2.8	1.5	1.4	1.4	3.3	4.3	1.6		4.8	5.0
131127	2.9	2.4	2.4	2.5		4.0			3.0	4.2
131223	2.2	0.5	0.5		3.7	4.5	0.5	2.3	3.4	3.8
140106			0.5	0.5	3.4	4.1	0.5	0.5	2.9	3.1
140221	0.5	0.5	0.5	0.5	14.0		0.5	0.5	11.0	11.2
140302			0.5	0.5	14.3	13.6	0.5	0.5	13.0	13.2
140329-A	0.5	0.5	0.5	0.5	4.2	3.6	0.5	0.5	1.8	1.9
140329-B	0.5	0.5	0.5	0.5	3.5	3.8	0.5	0.5	1.7	1.9
140329-C		0.5	0.5	0.5	3.0	3.3	0.5	0.5	1.3	1.8
140415	0.5	0.5	0.5	0.5	3.7	4.4	0.5	0.5	2.0	2.1
140522	0.5	0.5	0.5	0.5	3.9	4.7	1.0	0.5	1.8	2.8
140612	0.5	0.5	0.5	0.5	3.0	4.8	0.5	0.5	2.4	2.9
140704	1.0	0.5	0.5	0.5	3.1	4.4		0.5	3.1	4.2
140824			0.5	0.5	3.3	4.5	0.5	0.5	5.0	4.7
					Summary					
Average	**1.6**	**1.2**	**1.1**	**1.1**	**5.4**	**6.0**	**1.1**	**1.1**	**4.1**	**4.7**
Median	**1.7**	**1.1**	**0.5**	**0.5**	**3.9**	**4.5**	**0.5**	**0.5**	**3.0**	**4.0**
Lowest	0.5	0.5	0.5	0.5	2.7	3.3	0.5	0.5	1.3	1.2
Highest	2.9	2.7	2.6	2.5	14.3	15.6	2.8	2.6	13.0	13.2
Std. Dev.	0.9	0.8	0.8	0.8	3.3	3.3	0.8	0.8	3.3	3.3
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.20	0.17	0.16	0.16	0.67	0.68	0.16	0.16	0.80	0.74

$SO4^{2-}$	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Storm Code						mg L^{-1}				
130111	3.3	2.1	4.1		4.2	14.0	3.3	3.2		
130131	1.1	0.5	0.5	1.2	2.1	10.2	0.5	1.0		2.6
130227	0.5	0.5	0.5		1.2		0.5	0.5	1.8	1.3
130319	1.2	0.5	1.8	0.5	1.8	2.5	1.9	1.1		
130412	4.2	1.9	2.0	2.2	2.9	4.0	2.2	2.0		
130508/11	1.7	1.2	1.0	1.2	3.7	2.9	1.4	1.3		2.9
130524	2.7	0.5	2.0	1.2	3.4	2.2	1.6	1.4		
130607-A	0.5	0.5	0.5	0.5	1.3	1.0	0.5	0.5		1.3
130607-B	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
130801	0.5	0.5	0.5	0.5	2.6	3.0	0.5	0.5		
130808	1.5	0.5	1.4	1.6	2.2	3.7	1.4	1.3		3.5
130922	1.4	0.5			5.6	4.3	0.5	0.5	202	120
131007	4.5	0.5	0.5	0.5	6.8	4.6	1.1		209	280
131127	1.6	1.3	1.1	1.2		3.5			43.0	22.6
131223	1.1	0.5	1.1		2.6	3.7	1.3	1.2	12.1	6.6
140106			0.5	1.0	2.4	3.5	1.2	0.5	11.3	5.7
140221	2.8	2.5	2.6	2.7	5.6		2.5	2.6	6.1	4.0
140302			3.8	4.5	5.5	5.3	3.5	3.3	10.8	9.6
140329-A	0.5	0.5	0.5	0.5	3.0	2.5	0.5	0.5	11.4	7.2
140329-B	0.5	0.5	0.5	0.5	1.7	2.0	0.5	0.5	5.4	3.3
140329-C		0.5	0.5	0.5	1.3	1.2	0.5	0.5	3.0	1.9
140415	2.5	0.5	0.5	1.0	2.1	2.7	1.1	1.2	12.7	9.0
140522	2.7	2.0	1.9	2.0	4.9	4.8	2.4	1.8	21.1	26.7
140612	0.5	0.5	0.5	0.5	1.9	1.9	0.5	0.5	10.6	7.3
140704	1.9	0.5	1.5	1.3	7.8	3.8		1.5	52.0	39.8
140824			2.6	1.8	7.2	7.5	2.6	2.5	75.4	88.7
					Summary					
Average	**1.7**	**0.8**	**1.3**	**1.2**	**3.4**	**4.0**	**1.3**	**1.3**	**40.5**	**32.2**
Median	**1.5**	**0.5**	**1.0**	**1.1**	**2.6**	**3.5**	**1.2**	**1.1**	**11.4**	**6.9**
Lowest	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.3
Highest	4.5	2.5	4.1	4.5	7.8	14.0	3.5	3.3	209	280
Std. Dev.	1.2	0.6	1.1	1.0	2.0	3.0	0.9	0.9	65	66
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.26	0.13	0.21	0.21	0.41	0.61	0.19	0.18	15.8	14.8

Cl^-	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
Storm Code					mg L^{-1}					
130111	2.2	1.9	1.7		2.4	7.4	1.5	1.5		
130131	1.6	1.5	1.4	1.6	2.4	3.4	1.4	1.5		1.9
130227	0.5	0.5	0.5		1.1		0.5	0.5	2.1	2.5
130319	1.9	1.7	2.1	1.7	2.1	2.1	2.1	1.8		
130412	2.7	2.0	1.9	1.9	2.2	2.3	1.9	1.9		
130508/11	4.0	3.8	3.2	3.6	4.0	4.2	3.9	3.6		3.4
130524	0.5	0.5	0.5	0.5	1.7	1.2	0.5	0.5		
130607-A	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		0.5
130607-B	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
130801	0.5	0.5	0.5	0.5	1.3	1.1	0.5	0.5		
130808	0.5	0.5	0.5	0.5	1.0	1.6	0.5	0.5		2.7
130922	1.0	1.0			1.1	0.5	0.5	0.5	11.2	7.7
131007	2.6	1.1	0.5	1.1	1.4	1.5	1.4		7.5	8.3
131127	0.5	0.5	0.5	0.5		0.5			4.0	7.5
131223	0.5	0.5	0.5		2.1	0.5	3.1	1.7	2.1	5.8
140106			0.5	0.5	1.4	1.5	0.5	0.5	1.8	2.2
140221	2.2	2.2	2.2	2.4	2.5		2.1	2.2	2.6	2.5
140302			3.0	3.6	3.1	3.2	2.8	2.3	2.5	2.8
140329-A	1.1	0.5	1.0	0.5	1.3	1.3	0.5	0.5	2.4	2.0
140329-B	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.2	1.3
140329-C		0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	0.5
140415	2.3	1.1	0.5	1.0	1.1	2.5	1.2	1.0	1.5	1.2
140522	1.0	0.5	0.5	0.5	1.4	1.9	0.5	0.5	0.5	0.5
140612	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
140704	1.5	0.5	0.5	1.9	2.0	1.6		1.0	2.7	2.1
140824			1.1	1.6	1.3	1.1	1.1	1.3	1.2	1.5
					Summary					
Average	**1.3**	**1.0**	**1.0**	**1.2**	**1.6**	**1.8**	**1.2**	**1.1**	**2.7**	**2.9**
Median	**1.0**	**0.5**	**0.5**	**0.5**	**1.4**	**1.4**	**0.5**	**0.5**	**2.1**	**2.2**
Lowest	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Highest	4.0	3.8	3.2	3.6	4.0	7.4	3.9	3.6	11.2	8.3
Std. Dev.	1.0	0.8	0.8	1.0	0.9	1.6	1.0	0.8	2.8	2.5
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.21	0.17	0.17	0.21	0.18	0.32	0.20	0.17	0.67	0.55

Appendix L - Alkalinity for composite storm events. Values of 0.2 were below the LOQ.

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					mg L^{-1} $CaCO_3$					
130111	4.0	6.0	4.4		63.6	59.6	3.6	4.8		
130131	8.4	5.2	5.2	4.0	102	87.6	6.0	7.2		28.8
130227	6.8	2.8	1.2		26.4		5.2	1.2	184	187
130319	1.2	2.0	2.4	4.4	28.0	23.2	3.6	4.4		
130412	5.2	0.8	1.6	2.0	27.6	32.8	2.0	5.2		
130508/11	8.0	4.8	5.6	3.2	48.4	10.0	4.4	4.4		20.0
130524	6.4	0.8	4.0	3.2	39.2	36.0	4.8	5.2		
130607-A	6.4	3.2	4.8	6.8	4.0	32.0	4.0	3.6		13.2
130607-B	0.8	4.0	7.2	4.0	32.0	30.8	3.2	5.2	12.8	
130801	0.4	1.6	2.4	4.4	39.2	40.4	4.0	3.6		
130808	5.2	2.8	4.0	4.0	36.4	36.8	4.4	3.2		55.2
130922	2.4	2.8			20.0	16.4	4.4	2.0	117	62.0
131007	3.6	0.2	0.2	0.2	22.4	20.4	0.2		141	87.6
131127	0.2	0.2	0.2	2.0		16.0			50.0	70.0
131223	0.2	0.2	2.0		25.6	26.0	2.0	2.0	76.0	64.0
140106			4.0	4.0	16.0	20.0	1.2	4.0	45.2	46.8
140221	0.2	0.2	4.0	2.0	64.0		5.2	6.8	38.0	46.4
140302			2.0	2.0	40.0	22.0	2.0	0.2	68.0	62.0
140329-A	2.0	0.2	4.0	2.0	26.0	20.0	2.0	2.0	56.0	52.0
140329-B	4.0	2.0	2.0	4.0	20.0	20.0	2.0	4.0	30.0	42.0
140329-C		2.0	4.0	2.0	20.0	16.0	2.0	4.0	36.0	30.0
140415	6.0	4.0	2.0	2.0	24.0	24.0	2.0	2.0	60.0	54.0
140522	6.0	20.0	6.0	4.0	42.0	46.0	12.0	4.0	160	138
140612	0.2	0.2	4.0	0.2	36.0	38.0	4.0	2.0	62.0	64.0
140704	7.2	2.8	6.0	4.0	26.0	34.0		4.0	108	126
140824			6.0	8.0	34.0	42.0	6.8	7.2	180	168
					Summary					
Average	**3.9**	**3.0**	**3.6**	**3.3**	**34.5**	**31.3**	**3.8**	**3.8**	**83.8**	**70.9**
Median	**4.0**	**2.0**	**4.0**	**3.6**	**28.0**	**28.4**	**3.8**	**4.0**	**62.0**	**58.6**
Lowest	0.2	0.2	0.2	0.2	4.0	10.0	0.2	0.2	12.8	13.2
Highest	8.4	20.0	7.2	8.0	102	87.6	12.0	7.2	184	187
Std. Dev.	2.9	4.1	1.9	1.8	19.6	16.6	2.4	1.8	54.3	47.7
n	22	23	25	22	25	24	24	24	17	20
Std. Error	0.61	0.86	0.38	0.39	3.92	3.40	0.49	0.37	13.2	10.7

Appendix M – DOC for composite storm events (mg L^{-1}) **–** Dissolved Organic Carbon by NPOC. Blank spaces represent no data. Note that 3 values are slightly below the LOQ of 1 mg L^{-1}.

NPOC Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					mg L^{-1}					
130111	9.6	12.5	4.7		13.4	22.9	2.7	2.9		
130131	8.8	3.8	0.8	2.4	10.9	18.3	1.3	1.4		9.4
130227	5.5	15.3	1.5		7.7		4.7	3.7	21.3	26.1
130319	11.8	11.3	2.8	1.0	8.0	7.9	2.8	12.0		
130412	25.5	9.2	6.4	2.9	10.4	12.4	8.0	7.5		
130508/11	26.9	22.9	7.7	6.4	16.4	12.8	9.3	6.1		28.3
130524	43.2	12.1	13.3	4.6	17.8	13.0	9.1	5.1		
130607-A	34.5	10.3	5.0	3.7	17.7	11.2	6.5	3.3		13.5
130607-B	7.5	4.1	1.1	1.8	10.8	8.8	1.6	1.8	14.5	
130801	35.4	14.9	3.6	5.3	16.0	12.3	6.3	6.2		
130808	21.2	5.7	3.3	3.8	13.7	14.1	2.7	4.3		21.5
130922	12.9	5.4			11.3	11.3	4.1	13.2	30.3	27.3
131007	27.3	6.7	3.1	3.2	10.1	10.5	4.4		23.0	26.3
131127	14.6	10.4	3.2	3.1		12.5			10.8	17.4
131223	10.1	5.6	2.4		9.2	15.1	3.8	4.3	18.5	17.7
140106			1.8	1.8	6.3	10.7	2.3	1.9	9.1	10.6
140221	7.6	8.5	4.8	4.2	13.6		4.7	4.1	9.6	8.8
140302			3.1	3.5	9.7	7.9	3.2	3.7	12.6	9.0
140329-A	6.0	5.4	3.3	2.5	8.5	8.9	3.0	3.1	15.3	14.9
140329-B	2.9	2.2	1.4	1.3	6.3	8.5	1.4	1.3	10.3	10.8
140329-C		2.1	1.0	0.9	5.3	7.2	1.2	1.1	6.9	8.0
140415	13.4	6.0	2.7	3.1	8.7	12.9	3.3	3.8	22.6	16.2
140522	14.3	9.3	6.5	5.9	11.6	17.4	6.9	5.4	19.9	17.9
140612	6.3	5.4	3.3	2.3	13.3	14.5	2.9	2.9	17.2	10.2
140704	16.8	10.1	6.9	6.6	10.7	12.9		7.7	19.9	17.7
140824			3.7	4.7	12.2	9.8	4.8	4.9	26.6	19.5
					Summary					
Average	**16.5**	**8.7**	**3.9**	**3.4**	**11.2**	**12.2**	**4.2**	**4.6**	**17.0**	**16.6**
Median	**13.2**	**8.5**	**3.3**	**3.2**	**10.8**	**12.3**	**3.5**	**3.9**	**17.2**	**16.8**
Lowest	2.9	2.1	0.8	0.9	5.3	7.2	1.2	1.1	6.9	8.0
Highest	43	23	13	6.6	17.8	22.9	9.3	13.2	30.3	28
Std. Dev.	11	4.8	2.7	1.7	3.4	3.7	2.4	3.1	6.6	6.7
n	22	23	25	22	25	24	24	24	17	20
Std. Error	2.4	1.0	0.5	0.4	0.7	0.7	0.5	0.6	1.6	1.5

Appendix N - Free ionic Cu as measured by the CISE for composite storm events.

CISE Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					μg L^{-1}					
130111	27.7	21.8	966		0.47		748	742		
130131		14.7	182		0.26	0.21	247	294		
130227	6.88	37.1	655		0.58		1157	526	1.54	2.17
130319	13.2	18.1	656	392	1.06	0.23	507	354		
130412	15.6	5.12	916	1372	1.34	0.71	676	656		
130508/11	5.33	4.21	1106	1074	0.47	3.00	1122	1383		0.92
130524	3.82	7.26	722	580	1.27	1.16	504	466		
130607-A	1.16	2.51	167	276	0.49	0.27	406	244		0.13
130607-B	4.22	3.63	372	422	0.28	0.22	457	296	0.41	
130801	86.6	86.0	1451	1396	16.1	41.7	1894	1319		
130808	0.74	8.46	1440	1473	0.47	0.25	1377	1484		0.22
130922	2.85	1.44			1.44	1.87	497	552	2.24	0.89
131007	4.74	6.28	367	295	7.49	4.94	312		0.94	1.77
131127	5.51	21.2	519	575		1.95			0.58	0.96
131223	1.12	3.23	473		0.97	0.20	548	527	0.27	0.13
140106			350	406	0.95	0.34	729	734	0.21	0.13
140221	4.43	3.10	737	899	0.17		703	1029	0.48	0.15
140302			925	983	0.28	0.29	1062	1147	0.21	0.16
140329-A	5.42	5.99	1103	1236	0.68	0.38	1625	1588	0.59	0.24
140329-B	2.34	7.63	1062	1128	0.97	0.29	1255	1208	0.30	0.30
140329-C		10.5	1054	1070	0.79	0.40	1070	1095	0.75	0.45
140415	9.14	4.69	669	679	0.93	0.16	872	1087	0.19	0.18
140522	7.22	1.68	1342	1691	0.66	0.47	1113	1501	1.56	0.94
140612	2.73	7.35	1451	1076	3.95	0.71	2018	1957	0.61	0.43
140704	26.8	19.0	3017	3113	7.76	2.08		3041	0.93	0.58
140824			3472	4842	5.26	1.45	3929	5232	0.57	0.49
					Summary					
Average	**11**	**13.1**	**1007**	**1190**	**2.2**	**2.8**	**1034**	**1186**	**0.7**	**0.6**
Median	**5.3**	**7.3**	**916**	**1070**	**0.9**	**0.4**	**810**	**1058**	**0.6**	**0.4**
Lowest	0.74	1.44	167	276	0.17	0.16	247	244	0.19	0.13
Highest	87	86	3472	4842	16	42	3929	5232	2.24	2.17
Std. Dev.	19	18.1	778	1051	3.6	8.6	781	1073	0.57	0.57
n	21	23	25	21	25	23	24	24	17	19
Std. Error	4.1	3.8	156	229	0.72	1.8	159	219	0.14	0.13

Appendix O - BLM modeled *D. magna* FAV (LC_{50}) Cu for composite storm events ($\mu g\ L^{-1}$).

Storm Code	C1	C2	PI-1	PI-2	PO-1	PO-2	SI-1	SI-2	SO-1	SO-2
					$\mu g\ L^{-1}$					
130111	58.7	55.5	10.5		330	190	4.52	6.05		
130131	55.7	7.26	2.97	14.2	169	284	2.50	4.15		65.6
130227	28.0	26.6	5.26		101		16.4	8.07	255	133
130319	58.8	12.0	5.95	2.55	254	159	11.5	60.6		
130412	209	27.7	29.6	11.2	191	199	41.7	35.2		
130508/11	242	179	27.5	26.1	630	233	44.3	24.8		244
130524	783	33.0	92.7	18.7	317	168	41.8	15.7		
130607-A	435	6.57	12.1	17.6	219	98.9	26.5	8.47		88.8
130607-B	56.8	4.21	2.40	4.15	233	123	4.88	5.18	91.1	
130801	393	20.0	5.44	11.8	186	335	12.0	13.9		
130808	104	1.24	5.71	9.52	156	202	3.76	10.7		109
130922	91.1	18.0			77.9	105	16.3	36.5	726	626
131007	169	7.72	9.65	4.61	60.9	66.4	6.62		453	428
131127	41.7	10.8	5.09	3.70		63.1			112	205
131223	61.4	6.71	9.70		94.2	172	14.9	7.14	219	254
140106			2.41	3.56	45.0	197	11.3	4.49	106	172
140221	14.1	7.06	5.76	4.26	296		8.82	0.63	84.9	110
140302			17.0	15.1	139	83.3	8.83	16.3	206	111
140329-A	6.87	3.45	11.5	8.02	136	91.8	4.41	9.75	236	194
140329-B	7.33	2.18	3.59	3.06	173	200	1.65	5.33	88.1	123
140329-C		0.76	3.09	1.59	60.9	76.9	3.56	1.86	75.0	60.4
140415	20.9	2.23	5.66	4.51	66.1	95.6	3.19	3.69	172	102
140522	109	16.8	31.0	18.6	107	153	39.3	22.7	138	131
140612	11.1	2.91	14.4	6.77	112	79.4	7.84	8.74	135	71.7
140704	43.8	3.14	25.5	11.3	72.5	98.5		14.5	133	121
140824			12.6	12.1	121	78.5	16.1	16.6	438	327
					Summary					
Average	**136**	**19.8**	**14.3**	**9.68**	**174**	**148**	**14.7**	**14.2**	**216**	**184**
Median	**58.8**	**7.26**	**9.65**	**8.77**	**139**	**138**	**10.1**	**9.24**	**138**	**127**
Lowest	6.87	0.76	2.40	1.59	45.0	63.1	1.65	0.63	75.0	60.4
Highest	783	179	93	26	630	335	44.3	60.6	726	626
Std. Dev.	187	37.1	18.5	6.6	126	72.3	13.7	13.7	173	140
n	22	23	25	22	25	24	24	24	17	20
Std. Error	39.8	7.7	3.7	1.4	25.2	14.8	2.8	2.8	42.0	31.3

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