Nutrient Leaching and Copper Speciation in Compost-Amended Bioretention Systems

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Abbreviations: DOC: Dissolved Organic Carbon; DOM: Dissolved Organic Matter; EC: Electrical Conductivity; TKN: Total Kjeldahl Nitrogen.

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2 **Abstract**

3 Bioretention systems are designed to remove contaminants from stormwater; however, studies have
4 shown that bioretention systems can export excess nitrogen, phosphorus, and copper when amended
5 with compost. The objectives of this study were (1) to quantify removal of nitrates, phosphorus,
6 copper, and dissolved organic matter (DOM) from compost-amended bioretention systems, and (2) to
7 investigate the role of DOM on the leaching of copper. Simulated bioretention systems were irrigated
8 with stormwater for seven storms in two-weeks intervals. Leachates were analyzed for nutrients,
9 copper, and DOM. Visual MINTEQ was used to determine the speciation of copper and to quantify
10 interactions of copper with DOM. Results showed that compost-amended bioretention systems were
11 a source of nitrates, phosphorus, and DOM. Nitrate and phosphorus amounts were elevated up to
12 three orders of magnitude in the leachate compared to the stormwater itself. Bioretention systems
13 were a source for copper during the first 3–5 storms, but during later storms, they were a sink for
14 copper. Copper speciation modeling indicated that the majority of dissolved copper was complexed
15 with DOM. Dissolved organic matter thus helps to mobilize copper from the compost, particularly
16 in the first few storms after compost application. However, since copper-DOM complexes are usually
17 much less toxic than free copper ions, we expect that compost amendments may reduce harmful effects
18 of copper on aquatic organisms.

19 *Keywords:* Bioretention Systems; Compost; Copper; Dissolved Organic Carbon; Leachate; Nutrients.

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21 **1. Introduction**

22 Urban stormwater runoff is a main cause of pollution for estuaries, lakes, and rivers (U.S.
23 EPA, 1998). In urban areas, the high proportion of impervious surfaces such as roads,

24 parking lots, and rooftops allows little infiltration of stormwater, and the resulting runoff is
25 collected in retention ponds or directly runs into surface waters. Stormwater runoff picks up
26 a variety of contaminants on its way to receiving waters. Road runoff contains metals such as
27 copper, cadmium, zinc, organic pollutants such as polycyclic aromatic hydrocarbons (PAH),
28 pesticides, and microbes (U.S. EPA, 1998).

29 Low Impact Development (LID) is an increasingly popular technique to manage stormwa-
30 ter (Coffman, 2002; Laurenson et al., 2013). Examples of LID techniques are bioretention
31 systems, which are designed to modulate or reduce stormwater flow and to remove contam-
32 inants from stormwater (Davis et al., 1998; Laurenson et al., 2013). Bioretention systems
33 allow stormwater to infiltrate through a porous medium, which usually consists of sand
34 amended with different materials to improve plant growth and contaminant retention (Hin-
35 man, 2009; Palmer et al., 2013). Compost is often a recommended amendment because it
36 provides nutrients to plants, improves infiltration capacity, and may retain metal and organic
37 pollutants (Prince George’s County, 2007; Hinman, 2009; Bicknell et al., 2012). However,
38 bioretention systems amended with compost can be a source of nutrients in the discharge
39 water (Davis et al., 2001; Mullane et al., 2015).

40 Of particular concern in bioretention systems are nitrogen and phosphorus because excess
41 amounts of these nutrients in stormwater cause eutrophication and groundwater contamina-
42 tion. Nitrogen in stormwater can be present in different inorganic (NH_4^+ , NO_3^- , NO_2^-) and
43 organic forms. Orthophosphate (PO_4^{3-}) is the most common and bioavailable form of phos-
44 phorus. Phosphorus reacts with iron, calcium, or aluminum, and therefore, can be retained
45 in bioretention systems by precipitation or adsorption to solid particles.

46 Experiments and monitoring studies have shown that nitrogen and phosphorus reten-

tion in bioretention systems is variable. For instance, in a column study where stormwater was passed through soil media, the Total Kjeldahl Nitrogen (TKN) was reduced to 65–75% and ammonium was reduced to 60–80%, but nitrate concentrations increased in the leachate (Davis et al., 2001). Export of phosphorus was reported from rain gardens, which was explained by decomposition of fresh plant materials during soil disturbance (Dietz and Clausen, 2005).

Copper (Cu) is a primary concern in urban stormwater management (Pitt et al., 1995; Weiss et al., 2006). Toxic forms of copper to aquatic life are aqueous free Cu^{2+} and cationic copper hydroxide complexes, which contribute to the majority of the toxic effect, followed by neutral and anionic copper hydroxide complexes (Magnuson et al., 1979). While copper can be removed from stormwater by bioretention systems (Davis et al., 2003; Dietz and Clausen, 2006), some studies have also shown that copper was released from compost-amended bioretention systems (Li and Davis, 2008; Mullane et al., 2015). Copper strongly interacts with organic matter by complexation; thereby compost can act as an effective adsorbent for copper present in the stormwater. However, compost also contains copper, and dissolved organic matter (DOM) released from compost can mobilize that copper (Mullane et al., 2015). Copper readily forms soluble complexes with DOM (Römken and Dolfing, 1998; Hsu and Lo, 2000; Yin et al., 2002), and thus any release of DOM from a bioretention system may contribute to copper leaching. This dual role of organic matter in compost can make a compost-amended bioretention system either a sink or source for copper.

In previous experiments, we have studied leaching of dissolved organic carbon (DOC) and nutrients from compost columns under worst case scenarios, i.e., by leaching pure compost columns with deionized water (Mullane et al., 2015). We have also mixed compost with

biochar, but have not observed reduced leaching (Iqbal et al., 2015). In this study, we expand these experiments by using real stormwater and a bioretention mix consisting of sand and compost. We further use chemical speciation modeling to quantify complexation of copper with DOM, and assess the potential environmental impact of copper leached from compost.

The overall objective of our study was to quantify the leaching of nitrogen, phosphorus, copper, and DOC from compost-amended bioretention systems during stormwater infiltration. Specific objectives were (1) to quantify the leaching of nitrogen, phosphorus, copper, and DOC from compost-amended bioretention systems, and (2) to assess the interactions of copper with DOM in the leachates. We hypothesized that freshly-applied compost present in bioretention systems contributes to leaching of nutrients and copper in excess of what is present in stormwater. We further hypothesized that compost characteristics affect leachate composition and that sufficient DOM is released from the compost in the early stage of stormwater leaching, which may effectively complex free copper ions.

2. Materials and Methods

2.1. Overall Experimental Design

In Washington State, the recommended bioretention system medium is a mix of 40% compost and 60% sand by volume (Hinman, 2012; Washington State Department of Ecology, 2012). Similar media mixes with 30 to 40% compost are specified in other regions of the United States (Prince George’s County, 2007; Bicknell et al., 2012). To test its performance as bioretention medium, the 40:60 mix was packed into columns and then subjected to repeated storm events. Discharge from the bioretention systems was analyzed for basic constituents including pH, electrical conductivity (EC), dissolved organic carbon, nitrogen, phosphorus,

92 and copper. Contaminant removal efficiencies R were then computed as:

$$93 \quad R = \left[1 - \frac{\int_0^{t_{tot}} C_{out}(t) J_{out}(t) dt}{\int_0^{t_{tot}} C_{in}(t) J_{in}(t) dt} \right] \times 100\% \quad (1)$$

94 where C_{in} and C_{out} are the contaminant concentration in the inflow and outflow, respectively,
 95 J_{in} and J_{out} are the inflow and outflow water fluxes, respectively, and t_{tot} is the total time
 96 of a storm.

97 Organic matter in the compost and the discharge was further analyzed for chemical struc-
 98 ture and functional groups by spectroscopic methods. Finally, chemical speciation modeling
 99 was used to quantify the interactions between organic matter and copper.

100 2.2. Bioretention Soil Mix

101 A bioretention soil mix was prepared by mixing compost with sand at a 40:60 compost:sand
 102 ratio by volume. Prior to packing, the sand (average particle size 1–2 mm) was washed with
 103 deionized water two to three times to remove suspendable fine materials and water-soluble
 104 impurities. Two different types of composts were used, thus producing two different types of
 105 bioretention soil mixes for our study. The two composts selected represented typical municipal
 106 compost from two climatic regions in Washington State; the semi-arid eastern and the humid
 107 western region, and two composts are called Royal Classics and Silver Springs, respectively.
 108 Composts were analyzed for pH, EC, organic matter, C:N ratio, total N, ammonium-N,
 109 nitrate-N, phosphorus, potassium, calcium, copper, iron, magnesium, manganese, sodium,
 110 zinc, chloride, and sulfates (see supporting information for details on compost sources and
 111 analyses methods).

112 The chemical structure of the two composts was analyzed by solid state ^{13}C -NMR (Neu-
 113 tron Magnetic Resonance) and ATR-FTIR (Attenuated Total Reflectance-Fourier Trans-

formed Infra Red) spectroscopy. The details about sample preparation and instruments for NMR and FTIR analysis are described in Mullane et al. (2015). Briefly, for NMR analysis, samples were pre-treated to remove iron, then ground, and analyzed with ^{13}C cross-polarization/magic angle spin (CP/MAS)-NMR (Bruker Avance 400 spectrometer) at a frequency of 100.63 MHz at Washington State University's NMR Center. For ATR-FTIR, samples were ground and analyzed with a Shimadzu IR-Prestige 21 (Columbia, MD) complemented with an ATR unit (PIKE Technologies, Madison, WI). Interpretation of the spectra are based on numerous NMR (Schnitzer et al., 1991; Amir et al., 2004; Spaccini and Piccolo, 2008; Gao et al., 2015; Pane et al., 2015) and FTIR studies (Chen and Inbar, 1993; Jouraiphy et al., 2005; Grube et al., 2006; Carballo et al., 2008; Smidt et al., 2011; Wang et al., 2013a). The NMR spectra were divided into multiple resonance regions (Spaccini and Piccolo, 2008), and normalized areas calculated by trapezoidal integration under each resonance region were used to calculate the following indices (Spaccini et al., 2012).

$$\text{Hydrophobic index (HB)} = \frac{(A_{0-45\text{ppm}} + A_{45-60\text{ppm}} + A_{110-160\text{ppm}})}{(A_{45-60\text{ppm}} + A_{60-110\text{ppm}} + A_{160-200\text{ppm}})} \quad (2)$$

$$\text{Lignin ratio (LR)} = \frac{A_{45-60\text{ppm}}}{A_{145-160\text{ppm}}} \quad (3)$$

where A is the normalized area under the NMR spectra for the range indicated in the subscripts.

2.3. Bioretention Column Packing

Six PVC columns (i.d. 5.1 cm, length 25 cm, acid-washed with 10% HCl) were packed with the two compost-amended bioretention mixes in 5-cm increments to a total depth of 15 cm. During packing, columns were tapped four to five times after each increment to avoid voids and inconsistencies in packings. To verify consistent blends in each bioretention column, the

137 mass of the packed columns was measured (395 ± 11 grams, coefficient of variation = 3%).
 138 The columns had a porosity of $0.39 \text{ m}^3/\text{m}^3$ and a pore volume of 118 mL (see supporting
 139 information). The bottom of the columns was made of two layers of 1-mm fiberglass mesh to
 140 hold the bioretention mix in place. Three columns were packed for each compost-amended
 141 bioretention soil mix.

142 2.4. Stormwater Runoff

143 Stormwater was collected as runoff from a building rooftop at the Washington State Uni-
 144 versity Research and Extension Center, Puyallup, WA. During rain events, runoff from the
 145 rooftop was collected and stored in an outdoor cistern, which was used as the stormwater
 146 supply in our experiment. Because the concentration of copper in the stormwater was low
 147 ($2\text{--}3 \text{ }\mu\text{g/L}$), we added copper by using laboratory-grade CuCl_2 (Lot No. 7447-39-4, Fisher
 148 Scientific, Pittsburgh, PA, USA) to give a final copper concentration of $17\text{--}70 \text{ }\mu\text{g/L}$. These
 149 concentrations are comparable with total copper concentrations in roof runoff reported in
 150 Good (1993). The contaminated stormwater was then stored at $4 \text{ }^\circ\text{C}$ in a cold room until use
 151 in the experiments. Concentrations of constituents of the stormwater are shown in Table 1.

152 To simulate stormwater infiltration into bioretention columns, storm events were applied
 153 using custom-built sprinkler heads (diameter 5.7 cm). Twelve 22-gauge syringe needles were
 154 embedded in each sprinkler head. The assembly of needles in the sprinkler head released the
 155 stormwater uniformly onto the column surface area. A peristaltic pump (IPC 4, Ismatec,
 156 Glattbrugg-Zürich, Switzerland) connected to Tygon tubes (i.d. 3 mm) was used to pump
 157 stormwater from a reservoir to the sprinkler heads.

158 Stormwater was applied as a 6-month 24-hour storm. This is the strongest storm that
 159 occurs on average every 6 months in a 24 h period. In the Seattle-Tacoma region, such a

storm has an intensity of 33.5 mm/day (Washington State Department of Ecology, 2012). We considered that the bioretention system collects stormwater from an area 10 times larger than the bioretention system itself and that 15% of the runoff is lost before it reaches the bioretention system. These parameters resulted in stormwater application of 0.58 liters (about 5 pore volumes) for a 6-month 24-hour storm for each of our columns. To account for highest rainfall intensities during these storms, we applied the storm over a four-hour time period with the application rate of 2.42 mL/min. The average retention time of stormwater was about 34 minutes.

We applied seven sequential storms to the bioretention columns, with one storm applied every two weeks. During each storm event, outflow was collected in 500-mL glass beakers in hourly sampling intervals. This produced five hourly samples for each column and storm; in the fifth hour, the columns drained by gravity, and this drainage was also collected. Between storm events, the columns were allowed to dry. This drying was quantified by measuring the water content of the columns after and before storm events (see supporting information).

2.5. Outflow Characterization and Analysis

For each hourly outflow sample, we determined the leachate volume, the pH, the electrical conductivity (EC), and the concentration of DOC. For EC and DOC, samples were transferred into 20-mL glass vial and stored at 4 °C. These samples were then filtered through a 0.45 μ m filter and EC and UV/Vis absorption (at 465 nm) was measured. The UV/Vis absorbance was then converted to DOC concentrations by developing a calibration curve from a series of diluted samples where both UV/Vis and DOC had been measured. Dissolved organic carbon for calibration standards was measured with a TOC analyzer after acid purging of samples (TOC-V_{CSH}, Shimadzu, Tokyo, Japan). In addition, for each storm a composite

sample was collected by merging 80% of each hourly outflow sample in a 500-mL Nalgene bottle. This composite sample was analyzed for nitrate/nitrite (Systea Easy, 1-Reagent), total Kjeldahl Nitrogen (SM 4500-N-C), total and ortho-phosphorus (SM 4500-P-E), and total and dissolved copper (EPA 200-7). Composite samples for each storm were analyzed by ATR-FTIR as described in the supporting information.

2.6. Chemical Speciation Modeling

Visual MINTEQ, version 3.1 (Gustafsson, 2013), was used to determine the chemical speciation of copper and complexation reactions of copper with DOM in leachate solutions. Measured and estimated ionic compositions of the outflow samples were used as inputs for the Visual MINTEQ modeling. Measured input parameters were pH, NO_3^- , PO_4^{3-} , Cu, DOC, and EC. The concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- , which were the most prevalent ions in the stormwater, were estimated so that the overall EC of the simulated solution matched the measured EC and charge balance was maintained. The partial pressure of carbon dioxide was fixed at $2 \times 0.038\% \text{ atm} = 0.076\% \text{ atm}$ to account for the elevated carbon dioxide in the soil mix due to microbial activity. We used the Stockholm Humic Model (SHM) (Gustafsson, 2001) to model copper complexation with DOM.

We calculated the copper speciation as a function of DOC concentrations and pH. The pH was varied from pH 5.0 to 8.5 and DOC concentrations were varied from 0.01 to 1500 mg/L. The input parameters for the modeling are listed in Table S2 (supporting information). Model outputs were the activities of different copper species.

203 2.7. Statistical Analysis

204 Descriptive statistical parameters (mean, standard deviation, range) were calculated from the
 205 three replicates using R (Version 3.1.3) (R Core Team, 2015). One-way ANOVA at $p < 0.05$
 206 was used to determine statistical differences between treatments and samples.

207 3. Results and Discussion

208 3.1. Compost Variability

209 The two composts differed in pH, forms of nitrogen, and sulfate, chloride, and sodium contents
 210 (Table S1, supporting information). The most pronounced difference was the form of nitrogen:
 211 the Royal Classics compost contained inorganic nitrogen in form of nitrate, whereas the Silver
 212 Springs compost contained mostly ammonium.

213 The ^{13}C -NMR spectra of the two composts were similar (Figure 1A). The NMR spectra
 214 were divided into multiple resonance regions: alkyl carbon (C) (0–50 ppm), O-substituted
 215 alkyl C (60–110 ppm), lignin aromatic C (110–160 ppm), and carboxyl- and carbonyl-C (160–
 216 200 ppm) (Spaccini and Piccolo, 2008). Both composts were dominated by alkyl C, which
 217 occupied 72% (Royal Classics) and 69% (Silver Springs) of the entire areas. Similar results
 218 were reported by others (Amir et al., 2004; Mullane et al., 2015; Pane et al., 2015), where
 219 53–71% of the integrated area was dominated by aliphatic groups. This region represents
 220 proteins, lipids, and aliphatic branched and short-chained molecules. Aromatic carbons (110–
 221 160 ppm) contributed 22–23% to the entire spectrum. The carboxyl and carbonyl region
 222 (160–200 ppm) contributed 6–9% to the total area. The peak at 180.8 ppm can be assigned
 223 to carboxyl groups, specifically to methoxy groups in syringyl units of lignin (Gao et al.,
 224 2015).

225 The hydrophobic index (HB) for both compost materials was low ($HB = 0.7$), which
 226 suggests that hydrophilic carbons predominate. The lignin ratio was relatively high ($LR =$
 227 $1-1.1$). Total aromaticity was calculated by dividing the peak areas of aromatic C ($110-160$
 228 ppm) as percentage of peak areas of aliphatic-C ($0-110$ ppm) plus aromatic carbon (Schnitzer
 229 et al., 1991). Results showed that both compost materials had 75–77% aliphatic and 23–25%
 230 aromatic characteristics, with no difference between the two composts.

231 The infrared spectra of the two compost materials (Figure 1B) were also similar. The
 232 band at 3289 cm^{-1} can be assigned to O–H vibrations of phenolic hydroxyls, water molecules
 233 or N–H bonds (Chen and Inbar, 1993). Bands at 2924 and 2853 cm^{-1} can be assigned to
 234 C–H vibrations of aliphatic groups (Jouraiphy et al., 2005; Carballo et al., 2008; Wang et al.,
 235 2013a) and to fats and lipids (Grube et al., 2006). The band at 1614 cm^{-1} corresponds to
 236 stretching of aromatic C=C and asymmetric COO^- (Chen and Inbar, 1993), and the one at
 237 1418 cm^{-1} to stretching of COO^- groups (Smidt et al., 2011; Wang et al., 2013b). Overall,
 238 consistent with the NMR results, the FTIR spectra confirm the aliphatic and aromatic nature
 239 of the compost as shown by the NMR data.

240 3.2. Leaching Dynamics of pH, Dissolved Organic Carbon, and Electrical Conductivity

241 Figure 2 shows the dynamics of pH, DOC, and EC in the column outflow. Leachate pH
 242 increased gradually and leveled off after about three storms. Mean leachate pH of all storms
 243 ($n = 35$) was significantly higher for Silver Springs than Royal Classics compost and influent
 244 stormwater with LSD of 0.14. The difference in pH between the two treatments can be
 245 explained based on the pH values of both solid composts, with the Silver Springs compost
 246 having a higher pH than Royal Classics compost (Table S1).

247 The increase in pH for the first few storms is likely due to leaching of base cations (Ca,

248 Mg, Na) from the compost mix. Figure 2B shows the decreasing trend of DOC within each
 249 individual storm for all storms. Each new storm caused a new peak of DOC in the outflow.
 250 This renewed release of DOC at the onset of each new storm was also observed by Mullane
 251 et al. (2015). Maximum DOC concentrations at each new storm gradually decreased, but
 252 DOC concentrations remained high. The seventh storm still released about 230 mg/L DOC in
 253 the first outflow sample. The concentrations of DOC in the leachates were one to three orders
 254 of magnitude higher than the DOC concentration of the influent stormwater (0.4 mg/L).

255 More DOC was released from the Royal Classic compost compared to the Silver Springs
 256 compost. This is at odds with the spectroscopic characterizations, which did not show sig-
 257 nificant difference between hydrophilic and hydrophobic groups between the two composts.

258 The dynamics of the EC followed a similar pattern as of DOC, where a decreasing trend
 259 was monitored in each storm with a peak for the first hour (Figure 2C). About 80–84%
 260 of the total salts leached (19–24 mS/cm) were eluted in first three storms (77 cm leachate
 261 flux). After three storms, leachate EC approached the stormwater influent EC. Similar trends
 262 were observed for leachate EC from composts of different ages and feedstocks (Xia et al.,
 263 2007; Mullane et al., 2015), where EC values decreased below 1 mS/cm after 180 mm and
 264 500 mm leachate flux, respectively.

265 3.3. *Spectroscopic Characterization of Leachate*

266 The FTIR spectra of composited leachate samples did not change over successive storms for
 267 both composts (Figure S2, supporting information). The spectra indicate the presence of
 268 different functional groups, mainly -OH containing groups such as water molecules, phenols,
 269 alcohols, and carboxylic acids, alkenes and S–O or alkyne groups. This correlates well with
 270 the groups identified in the compost NMR and FTIR described above. And, as was the

case for the compost characterization, no difference in chemical structure of the leachate was detected between the two composts. More details on interpretation of the FTIR spectra are given in the supporting information.

3.4. *Nutrient and Trace Metal Leaching*

The leaching of nitrogen, phosphorus, and copper over successive storms is shown in Figure 3, and storm-based removal efficiencies are summarized in Table 2. The amounts of nitrates and total Kjeldahl nitrogen (TKN) in the leachate decreased over successive storms; most of the nitrates (80–100%) and TKN (66–74%) were eluted in the first three storms. This is also evidenced by the drastic change in removal efficiency (up to three orders of magnitude) in Table 2; where negative removal efficiencies indicate that bioretention columns export nitrates and TKN from the system. Because of large amounts of nitrates in the Royal Classics compost, this bioretention system released more nitrates than the Silver Springs compost, and at a faster removal rate in the first two storms. The Silver Springs bioretention system released nitrates more gradually than Royal Classics (at storms 3–6); suggesting that nitrification occurred during the experiment.

About 73–90% of total phosphorus in the bioretention outflow was present as bioavailable ortho-phosphate (PO_4^{3-}). Like nitrates, total and ortho-phosphate decline gradually over successive storms, with the Silver Springs bioretention system releasing more phosphorus than Royal Classics (Figure 3), and with significantly higher concentrations in the first storm. By the end of the seventh storm, about 5–6 mg/L of total phosphorus was still being leached. The bioretention systems were the sole source of phosphorus in the leachate; the influent stormwater had phosphorus concentrations below detection limits (<0.01 mg/L). Phosphorus export was also reported by Mullane et al. (2015), who studied composts of different ages,

294 and Hunt et al. (2006), who used bioretention systems with soils saturated with phosphorus.

295 Most of the copper (70–96%) in the bioretention outflow was in dissolved form. Total and
 296 dissolved copper concentrations showed a decreasing trend over successive storms (Figure 3).
 297 Statistical differences between the two treatments were detected during storm 3, 4, 5, and
 298 6, with the Royal Classic bioretention system leaching more copper than the Silver Springs
 299 system. Elevated copper leaching was observed for the third storm. The bioretention systems
 300 showed net release of copper for the first few storms, but retention of copper in the last two
 301 storms (Table 2). Copper concentrations monitored in the outflow for all seven storms were
 302 greater than 20 $\mu\text{g/L}$, which exceeds the benchmark for industrial stormwater discharge in
 303 the State of Washington of 14 $\mu\text{g/L}$ total copper (Washington State Department of Ecology,
 304 2009).

305 In a monitoring study from a bioretention system in the city of Redmond, WA (Herrera
 306 Environmental Consultants, 2012), where similar bioretention system specifications (40%
 307 compost) were used as in our study, mean concentrations ($n = 8$) of nitrate/nitrite in the
 308 leachate were 67 mg/L (7,900% net export), TKN was 17 mg/L (1,516% net export), total
 309 phosphorus was 4.4 mg/L (3,300% net export), total copper was 47 $\mu\text{g/L}$ (300% net export),
 310 and dissolved copper was 20 $\mu\text{g/L}$ (600% net export). Our data show lower nitrate/nitrite
 311 concentrations in the leachate (4–34 mg/L), but the percentage of export was higher (up
 312 to 216,000%) because our stormwater itself had low nitrate/nitrite concentrations. More
 313 TKN (29–33 mg/L), total phosphorus (10–16 mg/L), and dissolved copper (38–44 $\mu\text{g/L}$)
 314 were released in our study with comparable removal efficiencies. Palmer et al. (2013) found
 315 that bioretention systems, similar to ours but with 15% compost only, retained nitrates (33%
 316 retention was reported in unsaturated bioretention systems, and 71% retention was reported

when a saturated zone was present) and ortho-phosphate (80% in unsaturated bioretention systems and 67% when a saturated zone was present), but organic phosphorus was exported. Our study suggests that export of nitrogen, phosphorus, and copper in bioretention systems (with 40% compost) can be prevalent.

3.5. Copper Speciation Modeling

Copper in the aqueous environment forms various organic and inorganic complexes. Some of these complexes are toxic to aquatic organisms. The most toxic form of copper is the free copper ion (Cu^{2+}), followed by copper hydroxide complexes (Magnuson et al., 1979; Eisler, 2011). Copper also forms dissolved complexes with inorganic ions (CuCl^+ , CuCO_3 (aq)) and DOM. These complexes are generally less toxic than free copper or hydroxide complexes (Seligman and Zirino, 1998; Linbo et al., 2009). Particularly, complexation of copper with DOM significantly reduces toxicity to fish (Niyogi and Wood, 2004; McIntyre et al., 2008; Linbo et al., 2009).

Based on the chemical speciation modeling with Visual MINTEQ, the major aqueous copper species in our system were organic Cu species and the inorganic species Cu^{2+} , CuOH^+ , $\text{Cu}(\text{OH})_2$ (aq), $\text{Cu}_2(\text{OH})_2^{2+}$, CuCO_3 (aq), CuCl^+ , and CuHCO_3^+ . The first five of the inorganic copper species are the most toxic to aquatic organisms (Magnuson et al., 1979; Niyogi and Wood, 2004). In the presence of DOM (i.e., fulvic acid, FA), copper formed various organic complexes, mainly bidentate and monodentate complexes.

According to the modeling, the dominant inorganic Cu species in our system was free Cu^{2+} and the dominant organic Cu species was the bidentate complex. We discuss the distribution of these species as a function of pH and $[\text{DOC}]/[\text{Cu}]$ ratio, which are controlling variables for copper speciation (Figure 4). Figure 4A shows that the activities of free Cu^{2+}

340 decrease by several orders of magnitude as the pH and $[\text{DOC}]/[\text{Cu}]$ ratio increase. This
341 decrease in free Cu^{2+} activity is because of formation of organic Cu-DOM complexes and
342 copper-carbonate complexes (at high pH). Figure 4B shows the strong effect of DOC on
343 copper complexation. When the ratio of DOC to copper exceeds about 1 g DOC/mmol Cu,
344 copper is predominantly found as organic Cu-DOM complex.

345 Also shown in Figure 4 are the ranges of pH and $[\text{DOC}]/[\text{Cu}]$ for our stormwater and
346 bioretention effluent. The bioretention effluent reduced free Cu^{2+} activities by orders of
347 magnitude by formation of Cu-DOM complexes. Almost all of the copper was organically
348 complexed at the observed total copper concentrations in the leachate samples, indicating
349 that DOM released from the compost effectively complexed aqueous copper.

350 These modeling results are supported by experimental studies that have shown that
351 copper in presence of DOM readily forms copper-DOM complexes (Römkens and Dolfing,
352 1998; Hsu and Lo, 2000; Yin et al., 2002) and that DOM can enhance the mobility of copper
353 (Temminghoff et al., 1997). The presence of carboxyl groups identified by the spectroscopic
354 characterization of the leachate further supports the formation of Cu-DOM complexes iden-
355 tified in the modeling.

356 Copper toxicity to aquatic organisms varies depending on the specific target. For in-
357 stance, gills and chemosensory neurons respond differently, where Cu-bicarbonate complexes
358 show reduced toxicity to gills, but still are toxic to chemosensory neurons (McIntyre et al.,
359 2008). However, DOM generally reduces copper toxicity, and DOM in natural waters is
360 therefore beneficial to reduce harmful effects of copper. At concentrations of 3.8 and 6 mg
361 DOC/L, copper neurotoxicity to juvenile Coho salmon (at a dissolved Cu concentration of
362 20 $\mu\text{g/L}$) was reduced by 50% and 100%, respectively (McIntyre et al., 2008). These DOC

363 concentrations are higher than what was present in our stormwater (0.4 mg DOC/L), but
364 lower than in our bioretention systems leachates (30–1370 mg DOC/L). Consequently, any
365 copper leaching from the bioretention systems should be much less toxic to aquatic organisms
366 than inorganic copper ions.

367 3.6. *Limitations*

368 The leaching studied in our experiments constitutes a short-term scenario only: the seven
369 simulated rainstorms amount in total to 243 mm of cumulative rainfall, which corresponds
370 to one fourth of the annual rainfall in the Seattle–Tacoma region (960–1000 mm). If we were
371 to continue to leach our columns, concentrations of DOC in the leachate would decrease,
372 but we expect that DOC concentrations will remain sufficiently high for an extended period
373 of time to complex most copper leaching from the columns. For example, in experiments
374 where we had leached compost with 18 storms (corresponding to 570 mm rainfall), DOC
375 concentrations in the leachate still remained at about 50% of that after 7 storms (Mullane
376 et al., 2015). Long-term monitoring is needed to determine after what duration the DOC
377 concentrations reduce to a level where copper complexation would become ineffective.

378 3.7. *Conclusions and Implications*

379 Although bioretention systems are designed to reduce the loads of contaminants from stormwa-
380 ter for their safe discharge into surface and groundwater, compost-amended bioretention sys-
381 tems in our study acted as a source of DOM, nitrate/nitrite, phosphorus, and copper in the
382 leachate. Excess leaching of these constituents occurred for several storms after installation,
383 but concentrations in the leachate decreased with each storm. During an individual storm,
384 the first leachate contained the highest concentrations of organic matter, and nutrients, and

385 as the storm progressed, concentrations in the leachate decreased, but increased again at the
386 onset of a new storm.

387   The bioretention systems were initially a source of copper. Chemical speciation modeling
388 indicated that DOM in the bioretention leachate complexed the majority of the copper in
389 solution, due to the strong binding ability of DOM to complex copper. As complexation
390 with DOM has been shown to reduce copper toxicity to aquatic organisms, the risk that
391 toxic copper species (free Cu and Cu hydroxide complexes) are being released from compost-
392 amended bioretention systems tends to be minimal, at least as long as the DOM remains
393 stable. Dissolved organic carbon plays a dual role in copper leaching: it helps to mobilize
394 copper through the formation of dissolved complexes, but at the same time makes the copper
395 less bioavailable and less toxic to aquatic organisms.

396   In situ leaching from bioretention system is of particular concern if there is a shallow
397 groundwater table or if the systems contain an underdrain which will route drainage water
398 directly to surface or groundwater. In the presence of a deep unsaturated soil zone beneath
399 the bioretention systems, there is a better chance that contaminants and dissolved organic
400 matter will be sorbed before drainage reaches surface and groundwater.

401 **Supporting Information**

402 Supporting information includes details on composts, stormwater composition, water contents
403 of bioretention systems, and FTIR spectra of leachate samples.

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411 **Disclaimer**

412 The contents of this paper does not necessarily reflect the official views or policies of the
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Table 1. Chemical constituents in the stormwater used in the experiment.

Constituent	Concentration/Value [†]
pH	6.8 ± 0.05
Electrical conductivity (mS/cm)	0.02 ± 0.003
Dissolved organic carbon (mg/L)	0.4 ± 0.5
Total Kjeldahl N (mg/L)	2.2 ± 1.3
Nitrate + Nitrite (mg/L)	0.10 ± 0.02
Total phosphorus (mg/L)	$< 0.01^{\ddagger}$
Ortho-phosphorus (mg/L)	< 0.01
Total copper (mg/L)	0.04 ± 0.02
Dissolved copper (mg/L)	0.03 ± 0.01
Total calcium (mg/L)	2.2 ± 0.4
Total magnesium (mg/L)	0.14 ± 0.03
Total zinc (mg/L)	0.18 ± 0.09

[†]Values represent mean $\pm$ standard deviation ($n = 14$)

[‡]Below detection limits of 0.01 mg/L

Table 2. Storm-based pollutant removal efficiencies of simulated bioretention systems with Royal Classics- and Silver Springs-amended bioretention mix, where removal efficiency percentages were calculated using Equation 1. Negative values indicate net export of pollutants, positive values indicate retention of pollutants in bioretention systems.

Storm no.	Royal Classics	Silver Springs	Royal Classics	Silver Springs	Royal Classics	Silver Springs	Royal Classics	Silver Springs
	____ Nitrate/Nitrite (%) ____		____ TKN (%) ____		____ Total Cu (%) ____		____ Dissolved Cu (%) ____	
1	-216,000 [†]	-1,100	NA [‡]	NA	-150	-250	-200	-260
2	-43,900	-540	-1,400	1,300	-86	-169	-87	-104
3	-7,700	-16,100	-1,200	-1,100	-178	-84	-163	-76
4	-940	-5,400	NA	NA	-47	8	-93	-33
5	-37	-830	-1,600	-1,100	-23	23	-43	14
6	-72	-410	NA	NA	42	60	33	58
7	-53	-510	-1,600	-1,100	40	52	27	49

[†]Values represent pollutant removal efficiencies calculated from mean concentration of leachates ($n = 3$) and influent stormwater ($n = 2$).

[‡]NA: Data not available because concentrations in stormwater were below-detection limit, and removal efficiencies cannot be calculated. Similarly, for phosphorus, removal efficiencies cannot be calculated, because of the below detection concentrations of phosphorus.

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Fig. 1. (A) ^{13}C -NMR spectra and (B) ATR-FTIR spectra of Royal Classics and Silver Springs composts used in the study. Spectra are offset along the Y-axis.

Fig. 2. Chemical characteristics of bioretention outflow for successive storms. (A) pH, (B) dissolved organic carbon, and (C) electrical conductivity. Symbols are means of three replicates and vertical lines indicate $\pm$ one standard deviation. Inflow values are indicated by dashed lines. Alternate grey/white areas indicate different storms.

Fig. 3. Nutrient and trace metal concentrations in composite samples for successive storms. Horizontal black lines indicate nitrogen and copper concentrations in influent stormwater; no lines are drawn for phosphorus because no phosphorus was detected in the influent. Asterisks at specific storms indicate significant difference between the two composts at $p < 0.05$.

Fig. 4. Copper speciation as calculated from Visual MINTEQ as a function of pH and [DOC]/[Cu] ratio. (A) Activity of free Cu^{2+} ($\text{pCu} = -\log_{10} \{\text{Cu}\}$, where $\{\text{Cu}\}$ is the activity of Cu^{2+}). (B) Percentage of copper complexed with dissolved organic matter (DOM). The black bar depicts the range of pH and [DOC]/[Cu] for the stormwater in our experiments, and the shaded area depicts the range for the bioretention effluent.

(Note: this is a color figure).