Intermittent Rainstorms Cause Pulses of Nitrogen, Phosphorus, and Copper in Leachate from Compost in Bioretention Systems

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Abstract

Bioretention systems rely on vegetation and mixtures of soil, sand, and compost to filter stormwater runoff. However, bioretention systems can also leach metals and nutrients, and compost may be a major contributor to this leaching. To safely implement bioretention systems, it is crucial to determine the composition of compost leachate. We characterized and quantified the leachate composition of compost following intermittent, simulated storm events. Columns of municipal compost were irrigated to simulate 6-month, 24-hour rain storms in the Seattle-Tacoma region. Outflow was analyzed for

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pH, electrical conductivity (EC), particulate concentration, surface tension, dissolved organic carbon (DOC), nitrogen, phosphorus, and copper. Results indicate a decrease of chemical concentrations over the course of individual storms and following repeated storms, but each new storm released another peak of constituents. The decrease in phosphorus, copper, and DOC concentrations with repeated storms was slower than for nitrate and EC. Nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) showed that the DOC consisted mainly of aliphatic and aromatic components typical of fulvic and humic acids. Less than 3% of the original copper content from the compost leached out even after nine storm events. Nonetheless, copper concentrations in the leachate exceeded regulatory discharge standards. Our results show that compost can serve as a sustained source of leaching of nutrients and metals.

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

1. Introduction

Bioretention systems are designed to treat stormwater in a localized and more natural way than centralized stormwater facilities. Bioretention systems come in many different forms, such as raingardens, swales, or infiltration cells (Laurenson et al., 2013). These systems modulate peak flow through on-site retention of stormwater, and remove contaminants from stormwater through sorption, and biological uptake and degradation (Roy-Poirier et al., 2010). Compost is a valuable amendment to bioretention systems (Kim et al., 2003; Hinman, 2013; Palmer et al., 2013). Compost is beneficial for plant growth in bioretention systems as it provides nutrients, and improves water holding capacity and soil structure. Compost also has a high affinity to sorb contaminants, particularly metals (Morgan et al., 2011) and organics (Wu et al., 2013), and thereby helps to treat and clean stormwater.

However, compost also contains dissolved organic matter (DOM) which can leach out during rainstorms. Metals readily associate with DOM, and therefore its leaching out of compost may be of concern as metals may be mobilized and preferentially leached by facilitated transport (Kaschl et al., 2002; Bolea et al., 2006). In addition, nutrients present in compost, such as nitrogen and phosphorus, may leach during rainstorms (Palmer et al., 2013), and potentially contaminate environmentally sensitive waters or ecosystems (Washington State Department of Ecology, 2012). Therefore, it is important to consider leachates from compost when designing bioretention systems.

Several studies have shown that nutrients and contaminants can leach from mature compost. Christensen and coworkers (Christensen and Nielsen, 1982; Christensen, 1983; Christensen, 1984; Christensen and Tjell, 1984) conducted a 2.5-year study on the leachate composition from 17 lysimeters containing municipal compost of varying origin, age, and depth. Their analysis focused on organic matter, nitrogen species, inorganic ions, and heavy metals in the leachate. Their study revealed high initial concentrations of organic matter, nitrogen, and metals, followed by a pronounced tailing after 1.5 to 2 years. Leaching of metals from mature compost was also observed by others (Kaschl et al., 2002; Chen et al., 2010), who further demonstrated that the majority of the metals leaching was in the form of organometallic complexes.

Confesor et al. (2009) compared the leaching of total nitrogen, nitrate, ammonia, and ortho-phosphate from three compost feedstocks (yard, food, and farm wastes) at different stages of maturity. Their results showed decreasing leachate concentrations of total nitrogen and nitrate, and increasing concentrations of ortho-phosphate from all feedstocks as leaching progressed, with the magnitude of concentrations varying among feedstocks (Confesor et al.,

2009). The authors also noted elevated total nitrogen and nitrate concentrations in the leachate with increasing age of compost for all feedstocks, indicating that a mature compost has a greater nitrogen leaching potential than compost in the early stages of maturation. Unlike nitrogen, concentrations of ortho-phosphorus in the leachate were controlled more by the feedstock than the compost age (Confesor et al., 2009). Xia et al. (2007) evaluated the effect of compost proportion on leaching potential from mixtures with peat under intermittent irrigation. The authors found that dissolved salts, and nitrate, total and ortho-phosphorus, and copper concentrations increased with increasing proportion of compost.

The Washington State Department of Ecology specifies that bioretention soil mixes should contain 60-65% mineral aggregate and 35-40% compost by volume (Washington State Department of Ecology, 2012). To determine if compost is a suitable component for bioretention media, and if used, how to safely apply it in bioretention systems, it is crucial to characterize the composition of compost leachate and its potential negative impacts on the environment. The literature indicates that compost can leach nutrients and metals. Little is known, however, about the exact chemical composition of leachates from mature compost and about the quantities of materials leached out of freshly applied mature compost, particularly as triggered by intermittent rainstorms.

The main goal of this study was to characterize and quantify how much material, i.e., organic matter, nitrogen, phosphorus, and copper, is leached out of mature compost during successive simulated rainstorms. Our specific objectives were (1) to characterize the chemical properties of compost leachate during a single rainstorm as a function of time, (2) to characterize the chemical properties of compost leachate during sequential rainstorms, and (3) to compare leachate from mature composts of two different ages. The compost was made of

yard and food waste, and aged 6 and 24 months. We hypothesized that substantial amounts of dissolved and particulate organic matter along with nitrogen, phosphorus, and copper are leached from compost during rainstorms, and that, while concentrations would decrease during the course of an individual storm, each sequential rainstorm would cause a renewed flush of constituents leached. We further hypothesized that leaching from the 24-month old compost will be less than from the 6-month old compost, because we expected the older compost to be more stable and contain less soluble organic carbon.

2. Materials and Methods

2.1. Compost Material and Characterization

Compost samples were obtained from a local composting facility in July 2013. The compost samples were 6- and 24-month old (to test the effect of compost age), and were made from a feedstock consisting of 80% yard waste and 20% food waste (by volume). This feedstock composition is typical for municipal compost in the U.S. Pacific Northwest. The composts as received was air-dried and stored until use in five-gallon plastic buckets (covered with a 5-mm mesh to allow air circulation) in a greenhouse (16 to 20°C). Triplicate samples of the composts were sent to Soiltest Farm Consultants, Inc (Moses Lake, WA) for characterization. Compost material was characterized for pH, electrical conductivity, various nutrients, heavy metals, and C/N ratio following the protocols of the Test Methods for the Examination of Composting and Compost (TMECC). A Solvita Compost Emissions Test (Woods End Laboratories, 2014) was performed on both the 6- and 24-month old composts to determine maturity.

The chemical structure of the composts prior to leaching was characterized with solid-

state ^{13}C -NMR spectroscopy and ATR-FTIR (Attenuated Total Reflectance-FTIR). Details on sample pre-treatment, preparation, instrumental settings, and data processing are given in the Supporting Information.

2.2. Experimental Setup

A total of six PVC columns (64 cm height, 10.2 cm diameter) were loosely packed with compost to a height of 25 cm. The packing consisted of filling in compost in 5- to 10-cm increments and gently shaking the column to let the compost settle. Prior to adding the compost, the interior of each column was roughened with sand paper to prevent preferential flow of water down the walls of the column. Each column was washed in a 10% HCl bath and then rinsed with deionized water. The bottom of the columns was made of a perforated end-cap, consisting of a plate with 150 3-mm diameter holes. This end-cap held the compost in place, but did not restrict outflow. Three columns were packed with 6-month old compost, and three were packed with 24-month old compost. These columns do not directly simulate bioretention systems where the compost is mixed with a mineral aggregate. However, by using compost alone, we are able to isolate the leachate contributions of the compost itself.

The columns were placed in wooden stands and set up in a greenhouse. A plastic funnel was used at the bottom to collect outflow into 1-L glass beakers. Each column was equipped with a custom-built sprinkler head, 5.7 cm in diameter, made of twelve 22-gauge syringe needles. The sprinkler heads were connected with Tygon tubing to Mariotte bottles made of 25-L Nalgene carboys. Deionized water, with a pH of around 6, was chosen as the irrigation solution as its low ionic strength represents a worst-case scenario for leaching. The flow rate was controlled by adjusting the height of the Mariotte bottles. Temperature in the greenhouse varied between 16 to 20°C.

123 2.3. Column Leaching Experiment

124 The irrigation rate for the compost columns was designed to simulate storm events passing
125 through a bioretention cell. For that purpose, the irrigation rate was based on a 6-month,
126 24-hour storm for the Seattle-Tacoma region of Washington State, which corresponds to a
127 rainfall of 33.5 mm/day (Washington State Department of Ecology, 2012). The drainage to
128 bioretention cell surface area was taken as 10:1, and we assumed that a fraction of 0.81 of the
129 runoff volume is collected by the bioretention system. Such drainage parameters are typical
130 for bioretention and raingarden designs in this region (Hinman, 2013). The resulting flow
131 rate was 9.7 mL/min, which was applied under steady-state flow for four hours. Leachate
132 was collected into 1-L beakers at the base of each column every hour during the storm event.
133 A storm was simulated every two weeks, so that the compost column could drain and air-dry
134 between storm events. In total, we simulated 18 individual, successive storms.

135 2.4. Leachate Characterization

136 The pH of each leachate sample was measured immediately following collection. The samples
137 were then transferred to a 1-L graduated cylinder to determine the volume, and stored in
138 Nalgene bottles in the dark at 4°C prior to analysis. Each sample was further analyzed for
139 electrical conductivity, particulate matter, UV-vis absorbance, dissolved organic carbon, and
140 surface tension.

141 Particulate concentrations were measured using sequential vacuum filtration through 11,
142 1, and 0.45 μm pore filters (Whatman 1, Millipore Glass Fibre without binders, Millipore
143 Mixed Cellulose Ester Membrane Filter, respectively; all filters from Fisher Scientific). Prior
144 to filtration, all filters were dried at 105°C for 24 hours, then cooled in a desiccator, and

weighed using an analytical balance. After filtration, the filters were transferred back to the oven to dry for 24 hours at 105°C, cooled in a desiccator, and measured gravimetrically. The particulate concentrations were then determined by dividing the mass difference by the volume of solution filtered.

Dissolved organic carbon (DOC) was measured via spectrophotometric absorbance at a wavelength of 465 nm (Zmora-Nahum et al., 2005). A calibration curve was developed by plotting absorbance at 465 nm against the total organic carbon (TOC) for a series of 0.45 μm -filtered dilutions from the column leachate for each compost treatment. These calibration standards were analyzed for TOC using a TOC analyzer (TOC-V_{CSH}, Shimadzu, Tokyo, Japan). Surface tension of the filtered leachate samples was measured using the Wilhelmy plate method at 20°C (Processor Tensiometer K100, Krüss, Hamburg, Germany). Nanopure water (electrical conductivity of $5.5 \times 10^{-5} \text{ dS m}^{-1}$) water was used to verify surface tension measurements.

Selected storms were analyzed for nitrogen, phosphorus, and copper. For each storm a total of six composite samples (one per column) were made. The composite samples were made by collecting 20% of the outflow volume in each hourly outflow-increment. These samples were collected in acid-washed amber glass bottles and placed on ice until analysis. The samples were analyzed for total Kjeldahl nitrogen (EPA 351.2), nitrate and nitrite (EPA 353.2), total and ortho-phosphorus (EPA 365.2), and total and dissolved copper (EPA 200.8). In EPA 200.8, total and dissolved concentrations are differentiated by filtration through a 0.45 μm filter.

Selected leachate samples were analyzed with liquid-state ^1H -NMR and ATR-FTIR. ^1H -NMR spectra were acquired with 0.1 N NaOD in D_2O at 399.764 MHz and 303 K (Varian

400 MR equipped with a Varian One-NMR multi-tunable probe) at the WSU NMR center. In addition to the compost leachate, a 100 mg/L humic acid standard (1S102H, International Humic Substances Society) was used for comparison. The NMR capillary contained 550 μ l sample with an insert treated with trimethylsilyl propanoic acid (TMSP, 2 mg/mL). The spectra were acquired using a spinning speed of 6 kHz, a saturation frequency of -191.6 Hz, a relaxation delay of 2.5s, and a saturation delay of 2.2s. The spectra were analyzed using Varian VnmrJ 3.2A software, and peak assignments and interpretations are based on Sparks (1999) and Genest et al. (2014). FTIR analysis for the leachate samples was performed as described in the Supporting Information.

2.5. Statistical Analysis

Statistical analysis was performed using the three replicates from both the 6- and 24-month old compost. Analysis of variance was carried out to determine significant differences in compost characteristics between the two treatments both before and after leaching ($p < 0.05$) (R Core Team, 2013).

3. Results and Discussion

3.1. Compost Characteristics

The results of the compost characterization before (initial) and after leaching (final) are listed in Table 1. Comparison between the initial and final values within both treatments revealed statistically significant differences in pH, EC, potassium, sodium, and boron. Leaching resulted in a significant decrease in pH in the 6-month treatment, but a significant increase in the 24-month treatment. Both treatments experienced a noticeable reduction in EC, potassium,

sodium, and boron following the leaching experiment. These reductions were consistent with our expectations, as monovalent alkali metals potassium and sodium are readily exchanged with protons during leaching.

The results of the Solvita Compost Emissions Test revealed that both the 6- and 24-month composts were mature. Each compost scored a 5 and a 6 on the ammonia and the carbon dioxide emissions indices, respectively. These two numbers correspond to the mature stage of the composting process (Woods End Laboratories, 2014).

The NMR spectra for both composts showed the same peaks (Figure S1, Supporting Information), which are typical of municipal compost (Wilson et al., 1981; Chen and Inbar, 1993; Spaccini and Piccolo, 2008). The spectra indicate the presence of aliphatic and aromatic groups, and phenolic and carboxylic functional groups. The spectra reveal a predominance of ligno-cellulose and recalcitrant aliphatic compounds (Chen and Inbar, 1993; Spaccini and Piccolo, 2008; Genest et al., 2014). There were only small differences between the two composts. A more detailed analysis and interpretation of the NMR spectra is given in the Supporting Information.

The FTIR spectra of both composts were similar (Figure S2, Supporting Information). The most intense absorbance bands occurred at 1024 and 1028 cm^{-1} , which are associated with C-O stretching of polysaccharides (Chen and Inbar, 1993; Carballo et al., 2008; Smidt et al., 2011; Wang et al., 2013; Provenzano et al., 2014). A shallow band around 3280 cm^{-1} indicates O-H stretching of bonded and non-bonded hydroxyl groups (Smidt et al., 2011; Higashikawa et al., 2014; Provenzano et al., 2014). Phenol and carboxyl groups are indicated by the band at 1416 cm^{-1} (Smidt et al., 2011; Wang et al., 2013; Ouagoudi et al., 2014), while aliphatic groups are indicated by weak bands at 2924 and 2853 cm^{-1} (Chen and Inbar,

1993; Huang et al., 2006; Ouagoudi et al., 2014; Provenzano et al., 2014). Aromatic groups are indicated by absorbances at 1590, 1505, and 1265 cm^{-1} . More details on the FTIR spectra is given in the Supporting Information.

Similar to the observations by Chen and Inbar (1993), the FTIR spectra support the structural information obtained from the ^{13}C -NMR spectra. Both spectra indicate the presence of aliphatic, aromatic, and carboxylic functional groups, as well as lignin. Both the ^{13}C -NMR and FTIR spectra suggest that there is no significant difference between the chemical compositions of the organic matter of the 6- and 24-month composts.

3.2. Leachate Dynamics

Figure 1 shows a comparison of the leachate dynamics between the two compost treatments. The figure includes pH, electrical conductivity, DOC, and surface tension as a function of cumulative flux. Overall, the pH of the leachate from both treatments increased during the first few storms, but leveled off as the leaching continued (Figure 1a). The initial pH of the leachate samples of both treatments was 6.5. In the subsequent samples until 600 mm cumulative flux, the pH increased, and then plateaued at a pH between 7.5 and 7.8. This increase in pH is likely caused by the leaching of base cations and the buffering capacity of the compost (Table 1).

The electrical conductivity of leachates from both treatments followed a decreasing trend as leaching progressed (Figure 1b). The initial electrical conductivities were higher in the 24-month treatment than in 6-month treatment. Electrical conductivities were elevated for the first two to three storms, corresponding to about 500 mm cumulative flux, and then dropped below 1 dS/m. Each storm was characterized by a distinct peak in electrical conductivity followed by a continuous decrease in electrical conductivity as the storm progressed. The

peaks of successive storms decreased continuously; however, peak concentrations remained above 0.08 dS/m even after 18 storms.

The rapid decline in electrical conductivity of the leachate as a function of increased rainfall was also observed by Xia et al. (2007), who irrigated a compost composed of biosolids and yard waste with deionized water for a total of 330 mm of water flux. The electrical conductivities fell below 1 dS/m after 180 mm water flux (Xia et al., 2007).

In both treatments, the dissolved organic carbon concentrations peaked between 400 and 600 mg/L during the first two storms (Figure 1c). At the initiation of the third storm, the DOC concentrations increased to greater than 1000 mg/L. After the spike of the third storm, the DOC concentrations decreased with each successive storm. Each storm was characterized by a distinct peak in DOC followed by a continuous decrease in DOC as the storm progressed. The peaks of successive storms decreased continuously, similar to, but more gradual than what was observed for the electrical conductivity.

Surface active compounds, i.e., DOM, decreased the surface tension of the leachate compared to that of the influent. We hypothesized that the dynamics of the surface tension would follow the same pattern as observed for the DOC. Over the course of the experiment, the surface tension of the leachate from both treatments varied between 60 and 72 mN/m (Figure 1d); however, there was no temporal trend. This indicates continued mobilization of surface active compounds, but no distinct temporal pattern, contrary to what was seen in case of EC and DOC. There was no correlation of surface tension within individual storms.

Similar to the pattern seen in the DOC dynamics, the particulate concentrations for each size fraction (11, 1, and 0.45 μm) reached a peak after the first few storms (Figure 2). After reaching this peak, the particulate concentration in both treatments decreased with

each successive storm. As observed for both the electrical conductivity and DOC, each storm was characterized by a distinct peak in particulate concentration followed by a continuous decrease as the storm progressed. The peaks of successive storms decreased continuously.

The particulate concentrations for each size fraction were less in the 24-month old compost than in the 6-month old compost. The majority of particulates in both treatments were retained on the 1 μm filter, indicating that the particulates of 1 to 11 μm in diameter were the dominant fraction leached (on a mass basis).

Figure 3 shows the ^1H -NMR spectra of the humic acid standard and the compost leachate for each hour of the first storm. The spectra from both composts correlated well with the humic acid standard; with all three spectra exhibiting the same resonance signals. The major peaks in the spectra occurred between 0.7 and 2.5 ppm. Signals in this region correspond to protons of aliphatic chains and protons adjacent to carbonyl groups such as those in fatty acids, and esters (Genest et al., 2014). The most intense peak at 1.9 ppm is associated with methyl and methylene protons α to aromatic rings as well as protons α to carboxylic acid groups (Sparks, 1999). The signals at 2.2 ppm correspond to protons α to carbonyl groups (Sparks, 1999; Genest et al., 2014). The signals at 0.9 and 1.07 ppm are associated with the protons of terminal methyl groups and methylene chains, respectively. Genest et al. (2014) identified similar signals at 0.9 and 1.05 ppm as protons from terminal and chain methyl groups of aliphatic compounds composing plant cuticles and microbial lipids. The signals at 1.07 and 1.3 ppm indicate protons of methylene chains within two carbons of a ring or polar group, and the signal at 1.55 ppm represent protons specific to alicyclic carbon structures (Sparks, 1999).

Overall, the leachate ^1H -NMR spectra do not indicate a change in the functional group

composition of the dissolved organic matter over the course of an individual storm. The decrease in peak intensity likely resulted from the decreasing concentrations of dissolved organic matter in the leachate as the storm progressed (Figure 1c).

The FTIR spectra of the leachates from both composts were similar, and there was little difference over the course of a storm (Figure 4). The main absorbance bands for both leachates occurred at 3300, 2360, 2330, 1635, 660, and 600 cm^{-1} . The broad FTIR peak at 3300 cm^{-1} is associated with O-H hydroxyl bonds of organics and water. Absorbance at this band was likely dominated by water. The leachates from both composts showed bands at 1635 cm^{-1} . Absorbance bands in this region are typically associated with vibrational C=C bonds in aromatic structures as well as vibrational C=O bonds in amides, ketones, esters, and carboxylic acids (Chen and Inbar, 1993; Smidt and Meissl, 2007; Carballo et al., 2008; Smidt et al., 2011; Wang et al., 2013; Ouagoudi et al., 2014; Higashikawa et al., 2014). There were no distinctive trends observed over the course of a storm for either compost.

The leachate FTIR confirmed the presence and mobility of the organic matter in the compost. The results of the leachate FTIR analysis also complemented the ^1H -NMR spectra as both revealed signals corresponding to aromatic and carbonyl groups.

3.3. Nitrogen, Phosphorus, and Copper Dynamics

Figure 5 shows the average concentrations per storm for nitrogen, phosphorus, and copper. The data represent concentrations in composite samples for selected storms. Due to the gradual decline of concentrations, we did not analyze each storm, but skipped several storms in the later part of the experiment.

The majority of nitrate/nitrite was leached within the first three storms (Figure 5a). The 24-month old compost leached a significantly higher concentration of nitrate/nitrite than the

6-month old compost (334 mg N/L vs. 72 mg N/L) during the first storm. There was a pronounced decrease in nitrate/nitrite concentration between storm 1 and storm 2 in the 24-month old compost. Although the nitrate/nitrite concentration decreased considerably after four storms, there was a sustained leaching of nitrate/nitrite on the order of 1 to 10 mg N/L.

The nitrate concentrations in the initial leachate were substantially lower than those reported by Xia et al. (2007), who found nitrate concentrations up to 2,000 mg N/L in compost leachate. This difference may be due to the presence of biosolids feedstock, low C/N ratio of the compost, and therefore greater degree of mineralization in Xia's study as compared to our compost. Our initial nitrate/nitrite concentrations were similar to the concentrations reported by Confesor et al. (2009), who found up to 344 mg N/L for food waste and up to 157 mg N/L for yard waste compost.

The difference in nitrate/nitrite leaching between 6- and 24-month old compost observed in our experiment may be attributed to greater amount of nitrification in the 24-month old compost. This is corroborated by Christensen (1983), who observed greater initial nitrate leaching from a 12-month old compared to a 3-month old compost. Confesor et al. (2009) also noted that nitrate concentrations in the leachate increased with increasing compost maturity.

Total Kjeldahl nitrogen represents the organically-bound nitrogen and ammonia in the leachate. During each storm the 6-month old compost leached a higher concentration of Kjeldahl nitrogen than the 24-month old compost (Figure 5b). Within the first three storms, the concentrations of Kjeldahl nitrogen in the leachate from both composts were significantly lower than the concentrations of nitrate/nitrite. Similar to nitrate/nitrite, there was a sustained leaching of organic nitrogen on the order of 5 to 9 mg N/L.

In the later part of the experiment, significantly more nitrogen (both nitrate/nitrite

and Kjeldahl nitrogen) was leached from the 6-month compost compared with the 24-month compost. This is consistent with more nitrogen-mineralization occurring in the younger compost during the course of the experiment. Confesor et al. (2009) also speculated that the observed increase in ammonia-N concentrations in the leachate resulted from increased mineralization with the continued addition of irrigation water.

Most of the phosphorus leached was in the form of ortho-phosphorus (Figure 5c,d). During the first two storms, significantly more phosphorus leached from the 24-month compared to the 6-month old compost. After storm 2, there was a steady decrease in phosphorus concentrations; however, sustained leaching of phosphorus was observed at concentrations of several milligrams of phosphorus per liter. Similar to the case of nitrogen, more phosphorus was leached from the 6-month compost compared to the 24-month compost in the later part of the experiment, supporting more mineralization occurring in the younger compost.

The leaching pattern of total and ortho-phosphorus differed from that observed by Xia et al. (2007), where phosphorus concentrations in the leachate increased after the second leaching event, and never declined below 10 mg/L. The higher leachate concentrations of phosphorus observed by Xia et al. (2007) are likely due to the different feedstock (biosolids and yard waste mix) and the higher initial phosphorus content of the compost.

The majority of copper leached was in the dissolved phase (Figure 5e,f). The largest portion of copper leached within the first five to six storms. This was likely the labile fraction of copper leaching out. After the sixth storm, the copper concentrations decreased, but remained on the order of 10-30 μg Cu/L. Although Xia et al. (2007) observed higher initial leachate concentrations (148.1 μg /L) than those in our experiment, they observed a similar pattern for the leaching of copper where the concentrations did not decline until after

several leaching events.

Despite the decline of copper concentrations in our experiment, the final leachate concentrations from both composts exceeded the allowable discharge level of 14 $\mu\text{g Cu/L}$ for Western Washington (Washington State Department of Ecology, 2014). The observed total copper concentrations were far below the National Recommended Water Quality Criteria (NRWQC) for human health (1,300 $\mu\text{g Cu/L}$), but exceeded the saltwater NRWQC for aquatic life (4.8 and 3.1 $\mu\text{g Cu/L}$ for acute and chronic exposure, respectively) (USEPA, 2014). However, the copper concentrations observed in our experiment may not be toxic due to the presence of elevated DOC, as it is known that DOC readily forms complexes with dissolved copper (McBride, 1994), thereby reducing its toxicity to aquatic organisms (Linbo et al., 2009; USEPA, 2014). To highlight the complexation, we plotted copper vs. DOC concentrations (Figure S3). This plot revealed a significant linear correlation between dissolved copper and DOC in the leachate from both composts ($p < 0.05$). It is likely that most of the dissolved copper was complexed with DOC.

3.4. Mass Balance of C, N, P, and Cu

Table 2 shows the percentage of carbon, nitrogen, phosphorus, and copper that leached from the two composts. The mass balance of carbon was calculated from the entire 18-storm experiment, while the mass balances of nitrogen, phosphorus, and copper were calculated from the nine selected storms mentioned previously. In general, the 6-month compost leached a greater percentage of these constituents than did the 24-month, although the difference was not always significant.

The 6-month compost leached a significantly greater percentage of both dissolved and particulate carbon than the 24-month compost. For both composts, the dissolved organic

carbon leached was an order of magnitude greater than the particulate carbon. These results are consistent with the observed leaching of DOC (Figure 1c) and particulate concentrations (Figure 2). This also supports our hypothesis that the 24-month compost would be more stable and therefore contribute less to leaching.

There was no significant difference in the percentage of nitrogen and phosphorus leached from the two composts. This result is consistent with the leachate concentrations of nitrogen and phosphorus (Figure 5), where also no consistent differences were observed between the two composts.

The 6-month compost leached a significantly greater percentage of total copper than the 24-month compost ($p = 0.035$). However, there was no significant difference in the leaching of dissolved copper ($p = 0.072$). About 90% of the leached copper was in the dissolved form. The 6-month compost leached just under 3% of the original total copper content, while the 24-month compost leached just above 1%. This low percentage of copper leached is supported by the findings of Christensen and Tjell (1984), who noted that only 0.1 to 1.9% of original heavy metal content leached from their compost lysimeters. The mass balance of copper in our study shows that the majority of the original copper content remained in the compost. This, combined with the relatively stable leachate concentrations of copper in later storms (Figure 5e,f), shows that compost can be a source for continuous copper export. As mentioned earlier, the copper in the leachate is most likely complexed with DOC (Kaschl et al., 2002; Chen et al., 2010), which mitigates its toxicity to aquatic organisms (Smith et al., 2006; Smith et al., 2015).

4. Conclusions

Our results suggest that, in general, leachate concentrations from mature compost decrease over the course of individual rainstorms as well as following successive storms. However, we observed that this overall decline was not smooth, as the initiation of each storm mobilized a new peak of constituent concentrations in the leachate. The pattern of decline also depends on the constituent, and can be rapid as in the case of EC and nitrate/nitrite, or slow and less pronounced as in the case of DOC, total Kjeldahl nitrogen, and copper. The elevated leachate concentrations from both composts at the beginning of the experiment and the beginning of each new rainstorm suggest that leaching from mature compost is less a function of age and more a function of leaching history.

Bioretention systems that rely on a mixture of compost and mineral aggregate to filter stormwater have been found to export nutrients and trace elements. In this study, we focused solely on the compost fraction of the bioretention mix in order to identify the leachate contributions from compost. We observed that freshly-applied, mature compost may leach substantial concentrations of organic carbon, nitrogen, phosphorus, and copper. This leaching can potentially lead to contamination of surface and groundwater, and should therefore be considered when mature compost is included as a component of bioretention systems designed for stormwater management. Our results represent a “worst case” scenario for leaching from freshly-applied compost, and indicate that the effluent from the first several storms pose the greatest threat to water quality. This suggests that it may be beneficial to prevent bioretention system outflow from discharging to surface or groundwater for the first several storms following installation.

Supporting Information

Supporting information includes details on NMR and FTIR methods and interpretations, NMR and FTIR spectra, and a figure showing the correlation between copper concentrations and dissolved organic matter.

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Disclaimer

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TABLES

Table 1. Chemical characteristics of the 6- and 24-month old compost at the beginning and the end of the leaching experiments.

Parameter	Units	Compost Age			
		6-Month Old Compost		24-Month Old Compost	
		Initial	Final	Initial	Final
pH		6.7±0 ^{a,A}	6.6±0.1 ^B	6.4±0.1 ^{b,A}	6.8±0.1 ^B
Electrical Conductivity	dS/m	2.75±0.26 ^A	0.26±0.06 ^B	2.8±0.73 ^A	0.26±0.05 ^B
Organic Matter	g/kg	406±54	381±20	400±17	405±30
Organic Carbon (C)	g/kg	205±38	191±27	206±10	213±21
Total Nitrogen (N)	g/kg	14±2	13±1	15.6±0.3	15±1
Total Iron (Fe)	g/kg	16±1.7	15.6 ±1.1	17±1.1	18± 1.7
Total Phosphorus (P)	g/kg	2.9±0.6	2.5±0.3	2.7±0.1	2.7±0.4
Total Potassium (K)	g/kg	7.3±0.9 ^A	1.4±0.2 ^B	6.9±0.1 ^A	1.5±0.2 ^B
Total Calcium (Ca)	g/kg	20±0 ^a	20±1.4	19±0.6 ^b	20.1±2.6
Total Magnesium (Mg)	g/kg	5.8±0.8	5.2±0.1	5.8±0.3	6.1±0.3
Total Sodium (Na)	g/kg	1.5±0.2 ^{a,A}	0.3±0.1 ^B	0.9±0.6 ^{b,A}	0.3±0.6 ^B
Total Sulfur (S)	g/kg	1.8±0.2	1.7±0.1	2.1±0.6	2±0.3
Total Boron (B)	mg/kg	10.3±2.7 ^A	5.2±0.7 ^B	11.4±0.6 ^A	4.2±0.6 ^B
Total Zinc (Zn)	mg/kg	183±12	194 ±10	193±5	213 ±30
Total Manganese (Mn)	mg/kg	464±34	504±22	476±11	533±51
Total Copper (Cu)	mg/kg	45±4	64±21	50±2	122±65
C/N Ratio	—	14.3±0.7	14.3±0.5	13.1±0.4 ^A	14.3±0.3 ^B

Superscripts indicate a significant difference, while the absence of

a superscript indicates no difference.

^{a,b} denotes significant difference between initial 6- and 24-month old compost.

^{A,B} denotes significant difference before and after the leaching experiments within the 6- and 24-month old compost.

Table 2. Mass balance of C, N, P, and Cu from the 6- and 24-month old compost. Data represent percentages of material leached compared with initial content. The percentages listed for each compost represent an average and standard deviation of three replicates.

Parameter	Compost Age	
	6-month old	24-month old
	% Leached	% Leached
Dissolved organic carbon	5.39 ± 0.05^a	3.98 ± 0.37^b
Particulate organic carbon	0.53 ± 0.12^a	0.31 ± 0.04^b
Total nitrogen	8.07 ± 0.19	7.63 ± 1.46
Total phosphorus	8.87 ± 0.44	7.37 ± 1.39
Total copper	2.82 ± 0.88^a	1.21 ± 0.14^b
Dissolved copper	2.36 ± 0.84	1.13 ± 0.25

^{a,b} denotes significant difference between 6- and 24-month old compost.

Fig. 1. Dynamics of leachate from 6-month (left column) and 24-month old compost (right column). (a) pH, (b) electrical conductivity (EC), (c) dissolved organic carbon (DOC), (d) surface tension. Distinct peaks visible in EC and DOC coincide with the initiation of a new storm. (This is a color figure.)

Fig. 2. Dynamics of particulate leaching from 6-month (left column) and 24-month (right column) old compost. (a) particulate fraction $> 11 \mu\text{m}$, (b) particulate fraction $1 - 11 \mu\text{m}$, (c) particulate fraction $0.45 - 1 \mu\text{m}$. Distinct peaks coincide with the initiation of a new storm. (This is a color figure.)

Fig. 3. ^1H -NMR spectra from 6-months (left) and 24-months (right) old compost for hourly intervals during the initial storm. Spectra are offset for clarity. (This is a color figure.)

Fig. 4. FTIR transmittance spectra from 6-month and 24-month old compost. Spectra are offset for clarity. (This is a color figure.)

Fig. 5. Concentrations of nitrogen, phosphorus, and copper in the leachate from 6-month and 24-month old compost for successive storms. In the later part of the experiment, not all storms were analyzed, as indicated by the gaps in the storm number sequence. Significant differences between 6-month and 24-month old compost are denoted by an asterisk ($p = 0.05$). Error bars represent $\pm$ one standard deviation.

*Graphical Abstract

Bioretention System with Compost