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Research article

Interactions of particulate- and dissolved-phase heavy metals in a mature stormwater bioretention cell

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ABSTRACT

Bioretention is an increasingly common stormwater control measure (SCM) for mitigation of stormwater quantity and quality. Studies from lab to field scale have shown successful removal of total metals from stormwater, especially Cu and Zn which are ubiquitous in the urban environment yet detrimental to aquatic ecosystems. While bioretention effectively removes particulate matter and particulate bound (PB) contaminants, removal performance of dissolved metals has been neglected in field studies. After approximately two decades of these systems being implemented, with a typical design-life of 20 years, performance of mature systems is unknown. This study examined the performance of a 16- to 18-year-old bioretention cell by characterizing Cu and Zn partitioning and removal. Flow-weighted composite samples of stormwater and bioretention effluent were collected and analyzed for total and dissolved metals. Size-fractioned road-deposited sediments (RDS) were collected and analyzed for metals and particle size distribution. The comparison of RDS and PB metals showed that PB-Zn was enriched in stormwater, indicating higher mobility of PB-Zn compared to PB-Cu. The mature bioretention system effectively removed particulates and PB-metals with average load reductions of 82% and 83%, respectively. While concentrations for dissolved metals were low (<40 μg/L), no significant difference between influent and effluent was observed. Effluent concentrations of total and dissolved Cu, total organic carbon, and particulates were not significantly different from those measured over 10 years ago at the site, while total Zn effluent concentration slightly increased. MINTEQ speciation modeling showed that Cu was approximately 100% bound with dissolved organic matter (DOM) in all bioretention effluent. While Zn was also mostly bound with DOM in effluent, some events showed free ionic Zn reaching concentrations in the same order of magnitude. Media amendments, maintenance, and monitoring of SCMs should be considered where further removal of dissolved metals is necessary for the protection of aquatic environments.

1. Introduction

Urban stormwater runoff is recognized as a major non-point source of pollution to receiving waters (US EPA, 2017). Metals, especially copper (Cu) and zinc (Zn), are ubiquitous in urban watersheds and threaten aquatic ecosystems with both acute and cumulative toxicity effects (Clements et al., 2013; Fu et al., 2016; Li and Davis, 2008; Pamuru et al., 2022; Sansalone and Buchberger, 1997; US EPA, 1983). Metals may be associated with particulates or dissolved as various organic or inorganic species in stormwater. This characterization determines metal fate, transport, and toxicity, but will also define appropriate removal processes necessary for the protection of the receiving environment.

Vehicle brake and tire wear have been reported as the major contributors of Cu and Zn, respectively, to road-deposited sediments (RDS), particulates that accumulate on roadways from various deposition processes (Banerjee et al., 2015; Loganathan et al., 2013; Zhang et al., 2019). Other notable sources of Cu and Zn in urban environments include gasoline exhaust, industry such as steel plants, petrochemical, non-ferrous metal industrial complexes, and building siding (Davis et al., 2001; Loganathan et al., 2013). Metals released from vehicular traffic can be a source of atmospheric particulates (Kreider et al., 2010; Scerri et al., 2022), and as such become an immediate health hazard. These metals can also be deposited onto roadways, and then washed off during the next storm event, creating potential risk to vulnerable aquatic organisms. This risk will depend on the loading of metals in stormwater, which will be determined by particle mobility, concentration, and speciation. Studies have observed the highest metals concentrations in

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finer particles, and highest mass contribution of metals in larger particles (Sansalone and Buchberger, 1997; Wang et al., 2018; Zafra et al., 2017; Zhang et al., 2019). Metal affiliation in RDS size fractions has been examined, but few studies have considered mobility of RDS in storm events (Kayhanian et al., 2012b; Zhao and Li, 2013). Understanding particle size and metal affiliations in stormwater particulates compared to RDS can help identify sources contributing to stormwater particulates, and is important for stormwater unit operations/design, and treatability (Cristina et al., 2002; Greb and Bannerman, 1997).

Stormwater control measures (SCM) such as bioretention have shown successful removal of particulates and total metals (Davis et al., 2003; Hatt et al., 2007; Søberg et al., 2017). Bioretention has been increasingly implemented in the last 20 years for management of stormwater quantity and quality. Bioretention consists of vegetated quick-infiltrating media that aims to reduce stormwater volume and delay peak flow, provide filtration and sedimentation of particulates, and potentially remove dissolved contaminants through chemical and biological processes. Removal of dissolved metals with bioretention has been evaluated in laboratory and field studies, but these studies have shown conflicting results, with highly variable removal rates and even leaching of metals (Davis et al., 2003; Hatt et al., 2007; Lange et al., 2020; Søberg et al., 2017). Few studies have examined dissolved metal removal in field studies, and none have evaluated performance in a functionally mature bioretention facility. This information will be especially important as many implemented bioretention systems near 10–20 years of age.

Metal speciation determines their toxicity in aquatic environments, with free ionic species being the most toxic (Magnuson et al., 1979). Bioretention can influence changes in stormwater chemistry that can have significant impacts on metal speciation like introduction of dissolved organic matter (DOM), pH changes, and salts. Cu is known to form strong complexes with DOM (Tipping, 2005; Zhu et al., 2022), and DOM has been reported to leach from bioretention (Chahal et al., 2016; Li and Davis, 2009). Additionally, a reduction in Cu toxicity in the presence of DOM has been observed in aquatic species (LaBarre et al., 2017; McIntyre et al., 2008). This discovery has led to updates in toxicity criteria in surface waters, including the last update in 2007 to the US EPA recommended ambient water quality criteria for Cu, now determined using the biotic ligand model, which incorporates the effect of DOM complexation on Cu toxicity (US EPA, 2007). The US EPA surface water toxicity criteria for Zn has not been updated since the hardness-based criteria established in 1995. Few studies have considered speciation and toxicity in bioretention effluent (Chahal et al., 2016; LaBarre et al., 2017; Lange et al., 2020), however this is an important criterion in evaluating performance of bioretention and ensuring continued protection of the environment.

This study aims to evaluate the performance of a 16- to 18-year-old bioretention system by discretely investigating particulate and dissolved phase metals in incoming and treated stormwater. The specific objectives include characterizing RDS and metal affiliations in size fractions, and comparing these with stormwater particulates to investigate particulate bound (PB) metals and the mobility of RDS. Second, the study aims to evaluate bioretention performance in removal of particulates, PB metals, and dissolved metals. The water quality performance characteristics of this mature bioretention cell are compared to those measured shortly after installation. Finally, bioretention effluent speciation was investigated using geochemical modeling and compared to US EPA surface water quality criteria to evaluate the effluent in meeting the criteria and make future recommendations for improvement of bioretention design.

2. Materials and methods

2.1. Bioretention field site and sample collection

The field bioretention cell is located on the University of Maryland College Park (UMD) campus on the south side of Regents Drive across from parking lot 9b (38.993574, −76.939161, Fig. 1). The bioretention cell was constructed in spring of 2004, treating a drainage area of 0.28 ha, with 90% impervious surface area comprised mostly of parking lots, streets, and sidewalks. The cell is a trapezoidal shape ranging from 2.4 to 4.8 m wide and 50 m long with a media depth sloping from 0.5 to 0.8 m deep. The stormwater volumetric storage of the cell is estimated as 37.2 m^3 (Davis et al., 2022), corresponding to 1.5 cm of rainfall over the impervious area. The 20 cm PVC perforated underdrain of the bioretention cell then conveys treated stormwater to Campus Creek, adjacent to the south of the bioretention cell. This bioretention cell has been part of several prior water quality research studies which describe its hydrologic and stormwater treatment performance (e.g., DiBlasi et al., 2009; Li et al., 2009; Li and Davis, 2014; Liu and Davis, 2014).

Two ISCO 6712 autosamplers were installed at the site, programmed to collect flow-weighted composite samples from storms ranging from 6 to 76 mm in precipitation depth for this subcatchment area. Both influent and effluent autosamplers are equipped with ISCO 730 bubbler flow modules to accurately measure depth/flow. The influent channel has a 20 cm cutthroat flume, and the effluent pipe has a 20 cm Thel-Mar V-notch weir. The site also has a ISCO 674 Tipping Bucket Rain Gauge with 0.0254 cm sensitivity and logs rainfall depth in 2-min increments. Flow-weighted composite samples were collected by the autosampler into acid-washed 19-L HDPE carboys.

2.2. Road deposited sediment site and collection

A RIDGID® cordless 9-gal wet/dry vacuum equipped with a HEPA certified filter was used to collect RDS. Sample collection took place in an asphalt parking lot located approximately 500 m south of the bioretention field site. The first sampling event took place on November 11, 2020, and the second on December 8, 2020. Both samples were collected before a storm event with more than two antecedent dry days to ensure a build-up of sediment. The sampling area was approximately 14 m^2.

2.3. Sample analysis

2.3.1. Metals

Stormwater samples were processed within 24 h of the end of the storm event; pH, and electrical conductivity were analyzed immediately. Samples were then separated for total and dissolved metals analysis by filtering through 0.22 μm filters. The particulate bound (PB) concentration was calculated by difference. Then samples were preserved with trace metal grade HNO_3 (Fisher Chemical) to pH < 2 as described in EPA Method 200.9 for total recoverable metals. Zn and Cu were analyzed using EPA Method 200.7 (ICP-OES, Shimadzu ICP9800) and using EPA Method 200.9 using a graphic furnace atomic absorption spectrophotometer (Shimadzu AA-7000, GFAA). A blank (deionized water), fortified blank (spiked with 1 ppb metals stock solution), and fortified matrix sample (sample spiked with 1 ppb of metals stock solution) were run as quality control to ensure recovery was within the acceptable range of 85–115% according to EPA Method 200.9 for GFAA. Detection limits for Cu and Zn on ICP-AES were 5 μg/L and detection limit for Cu measured on GFAA was 2.4 μg/L. Recovery for metals analysis ranged from 88 to 104.7%. Standards were prepared from a 10-ppm multi-element stock solution (Inorganic Ventures Labs, Inc.), ranged from 0.8 to 300 μg/L, and calibration gave an R^2 of 0.999 or greater. A standard check was performed every 9 samples with <5% error acceptance. Particulate matter concentration was measured gravimetrically using Standard Method 2540D, and using 0.22 μm filters when processing for metals, to calculate the PB metal concentrations from total recoverable metals concentrations.

Dry RDS samples underwent acid digestion using EPA Method 200.7. A blank, fortified blank (spiked with 50 μg/L metals stock solution), and fortified matrix sample (sample spiked with 50 μg/L of metals stock solution) were run as quality control. Acid digestion was done by adding

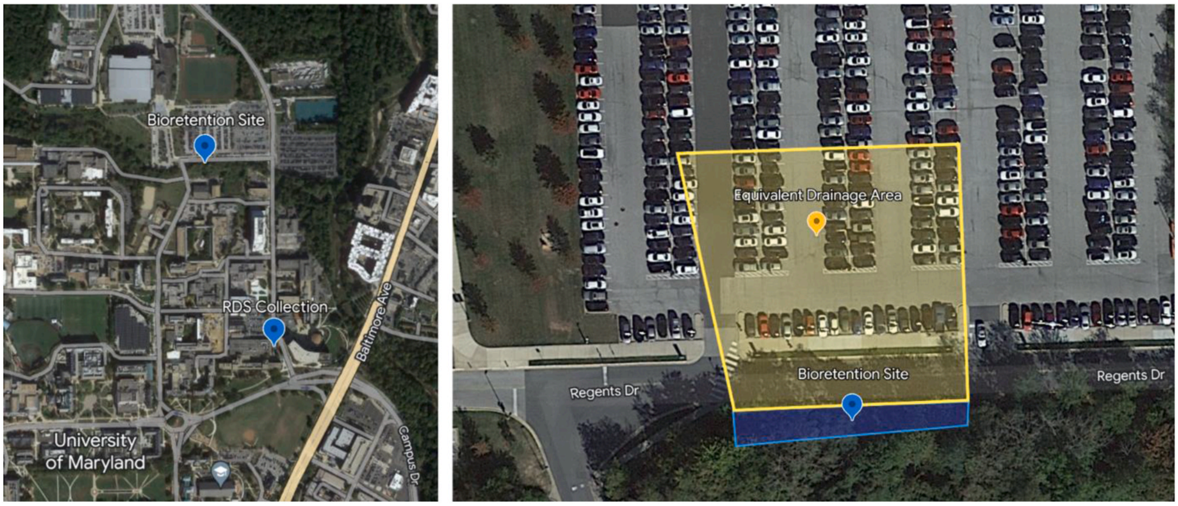

Fig. 1. Left: Location of bioretention field site and RDS collection on University of Maryland College Park campus. Right: Close up of bioretention drainage area and site with equivalent drainage area (yellow) and bioretention area (blue) shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

1 g (±0.01) of dry sediment to 50 mL polypropylene digestion vials, adding trace metal grade nitric acid and hydrochloric acid, and refluxing using a digestion block. After digestion, aliquots were analyzed on ICP-AES with an Ultrasonic Nebulizer to increase sensitivity, using a calibration curve that ranged from 1 ppb–1 ppm. The calibration curves accepted had an $R^2 > 0.999$. Acceptable recovery from fortified blank and sample is from 85% to 115%.

2.3.2. Particle size distribution and fractionation

RDS samples were dry sieved to separate into <75 μm, 75–250 μm, 250–1000 μm, and 1–4.75 mm fractions. Particle size distribution (PSD) of <1 mm RDS samples and stormwater samples were measured using a SALD-2300 particle size analyzer (Shimadzu, Japan). The total mass collected in each RDS sample event was 2007 g and 810 g respectively for events I and II.

2.3.3. Total organic carbon, pH, and electrical conductivity

TOC was analyzed using a TOC analyzer (TOC-L, Shimadzu, Japan). The calibration curve was made with glycine with a range of 1–100 mg/L, and the method quantification limit for TOC was 1 mg/L. Sample pH and electrical conductivity were measured using a VWR sympHony™ (B40PCID) benchtop meter with a Thermo Scientific pH probe and VWR conductivity electrode, respectively.

2.4. Annual metals loading

Annual metals loading was calculated for influent, effluent, and reductions for all storm events where influent and effluent were measured (Liu and Davis, 2014).

$$L = MP/AD \quad \text{(Eqn. 1)}$$

Where M is cumulative mass, determined as the flow-weighted concentration multiplied by total volume of stormwater, P is average annual rainfall (107 cm for College Park, MD), A is drainage area (0.28 ha for the UMD bioretention cell), and D is total depth of rainfall for measured storm events.

Effluent volume data was collected from the weir and depth measurements at the site, however influent volumes were overestimated at the site due to ponding of water at the inlet. Thus, runoff volume was estimated in order to calculate annual loadings. The Natural Resources Conservation Service (NRCS) curve number method, using drainage area, hydrologic soil group, land cover type, and precipitation depth, was used to estimate direct runoff or excess precipitation (P_e) flowing into the bioretention cell (USDA, 2004). The site consists of 90% impervious surface and 10% grass from medians, so a CN of 98 was used. P_e is calculated for each storm event, and using the area, converted to a stormwater volume.

Rainfall data for 6 out of 14 storms was collected from the site. For the remaining storms, rainfall data was obtained from the surrounding NOAA weather stations, located between 1.32 and 4.02 km away from the site. The daily summary precipitation depths were retrieved from each station and an average was used to calculate runoff volume.

2.5. Statistics

Water quality data were tested for normality using the Shapiro-Wilk test. Data for dissolved and effluent Cu concentrations were not normally distributed, thus non-parametric tests including Mann-Whitney and Wilcoxon-Rank Sum were used for comparing concentrations and mass loadings in stormwater and bioretention effluent at 95% confidence. Data for all other constituents were found to be normally distributed and comparisons were made using paired and independent sample t-tests at 95% confidence. Exceedance probability plots were used to evaluate performance of the bioretention cell, created by first ranking event mean concentrations (EMCs) of stormwater and bioretention effluent from largest to smallest and plotting on a logarithmic scale. Values below detection limit were assumed to be half the detection limit in calculating summary statistics.

2.6. MINTEQ modeling

Visual MINTEQ (version 3.1) was used for geochemical equilibrium modeling of stormwater and bioretention effluent. Values of pH, EC, TOC, dissolved Cu and Zn, from stormwater and bioretention effluent EMCs were used to model chemical speciation of Cu and Zn. The complexation of metals with DOM is of particular interest due to its role in reducing toxicity in aquatic ecosystems and its common release from bioretention media. The advanced non-ideal competitive adsorption (NICA)-Donnan model was used in MINTEQ for modeling metal-DOM complexation. This allows for carboxylic-, and phenolic-site, and electrostatic interactions with the metals of interest and with competing cations. Ionic strength is used in MINTEQ to compute activity coefficients; this was indirectly measured through electrical conductivity and using an empirical conversion (Snoeyink and Jenkins, 1980). A sensitivity analysis was conducted in MINTEQ to determine the impact of varying common competing cations (Ca^{2+}, Mg^{2+}, Na^{+}) and common anions (Cl^{-}, alkalinity). The ranges for these were chosen to be conservative (i.e., to observe the largest impact to speciation) but within range of realistic stormwater values. The minimum and maximum values reported in the *International Stormwater Best Management Practices database* (https://bmpdatabase.org/) were used for these constituents, and the median or geometric mean (calculated in Pamuru et al., 2022) were used as constants when testing each parameter.

3. Results and discussion

3.1. Storm event Hydrology

Storm events were sampled from February 2020 to April 2022 (interrupted by COVID shutdowns and restrictions) and ranged from a total rainfall depth of 0.13 cm (0.05 inch) to 7.8 cm (3.1 inches); the mean and median rainfall depths of storms sampled were 2.4 cm (0.95 in) and 1.61 cm (0.63 in), respectively. A total of 17 storm events were sampled. Fourteen flow-weighted composite samples were collected for metals analysis using autosamplers. Of those events, 11 included paired effluent composite samples (due to autosampler error or insufficient effluent flow through bioretention cell). The majority (~30%) of rain events in this region have been found to be less than 0.254 cm (0.1 inch) in precipitation depth (Forgione et al., 2024; Kreeb, 2003) Forgione et al., (2024) found that storms of this size produced no measurable runoff flow or volume at a highway median site. The current study was able to measure and collect one storm with 0.13 cm (0.05 inch) of precipitation, due to the much larger catchment area compared to the Forgione et al., (2024) study. As with most SCM studies, in order to obtain SCM discharge, the storms analyzed in the current study skewed towards larger storms, compared to typical precipitation depth frequency in the area. Kreeb, (2003) found that storms less than 2.54 cm (<1 inch) accounted for approximately 86% of rainfall events in this region. In the current study, storms <2.54 cm precipitation depth consisted of 65% of collected storms, with the remaining 35% being storms greater than 2.54 cm precipitation.

Discrete grab samples for influent and effluent were collected for three events, on October 16, 2019, October 22, 2019, and December 13, 2019. The discrete grab samples only represent a snapshot of the hydrograph for that storm event, whereas the flow-weighted composite samples represent the EMC. Five other grab samples were collected for another study at this site (Cao et al., 2023), and some water quality parameters including pH, EC, and TOC were included in this study. The total volume of stormwater received at the bioretention cell ranged from approximately 45 L to 202,000 L.

3.2. Stormwater characterization

Sample pH, TOC, particulate concentration, electrical conductivity and total and dissolved metals measured during this study are listed in Table 1. These values are compared to values from the International BMP Database and the National Stormwater Quality Database as analyzed by Pamuru et al. (2022). The range of values for constituents in this study tightly brackets the geometric mean in Pamuru et al. (2022) (see Table 2).

Many studies have correlated total stormwater Cu and Zn concentrations with traffic counts, as vehicles provide a significant source of these metals to the urban watershed (Kayhanian et al., 2007; Thomson et al., 1997). It should be noted that three storms collected in this study occurred during campus-wide shut down due to the COVID-19 pandemic, therefore significantly fewer vehicles were on campus or in the study catchment area. These three storms had EMCs below detection limit (<5 μg/L) for total Cu and the mean of EMCs for total Zn pre-pandemic was 3.4 times higher than the mean of those during shut down.

Table 1
Summary of stormwater quality measured at bioretention site and compared to values obtained from stormwater database.

Constituent	*From this study (n = 17)*				*Database Comparison*[a]
	Min.	Max.	Geometric Mean	Standard Deviation	Geometric Mean
pH	7.3	8.7	7.9	0.4	7.1
Particulates (mg/L)	30.1	145	72.9	37.3	44
Conductivity (μS/cm)	68.5	1790	191	429	97
TOC (mg/L)	3.4	30.9	11.0	7.5	12.2
Total Cu (μg/L)	<5.0	56.7	15.6	14.9	13
Total Zn (μg/L)	29.9	286.5	109	70.4	71
Dissolved Cu (μg/L)	3.4	26.0	6.6	6.5	7.5
Dissolved Zn (μg/L)	<5.0	36.3	12.4	11.6	30.3

[a] Values from (Pamuru et al., 2022).

Table 2
Comparison of mean Cu and Zn concentrations and median particle diameter (d_{50}) in RDS samples to concentration in stormwater particles collected at UMD field site.

Sample		Cu (mg/kg)		Zn (mg/kg)		D_{50} (mm)
	Fraction	*Range*	*Mean*	*Range*	*Mean*	*Range*
RDS (n = 2)	< 25 μm	242–553	397	578–711	644	782–801
	25 – 75 μm	136–245	190	384–580	482	
	75 – 250 μm	123–319	221	220–373	296	
	250 μm – 1 mm	162–441	301	80–255	167	
	1 – 4.75 mm	85–113	99	4.7–39	68	
	Bulk	160–239	199	146–223	185	
Stormwater Particles (n = 14)		76–546	211	740–2268	1587	67–1043[a]

[a] Particle size distribution in stormwater measured at the site in a previous study (Cao et al., 2023). Stormwater Particles exclude three events captured during campus-wide shutdown due to COVID-19 pandemic. See section 3.4 for more details.

3.3. Metals partitioning in stormwater

Fig. 2 shows the partitioning between PB and dissolved fractions for Cu and Zn in stormwater samples across 17 storm events as a percent of the total metal concentration. Two storm events (11/11/2020 and 11/30/2020) had total and dissolved Cu below the detection limit (during campus shutdown), thus partitioning for these two events cannot be quantified. The mean and standard deviation for percent PB Cu and Zn was 56.4% ± 22.7 and 85.6% ± 8.0, respectively. Overall, a large fraction of the total metal is PB, especially for Zn with seven events having >90% PB Zn, thirteen having >80% PB Zn, and the lowest fraction being 65%. Cu showed more variability in partitioning, but still had >60% PB Cu for 8 out of 15 storm events. However, PB Cu was below 50% for 6 storm events, with a minimum of 20%.

Using data from the BMP database, Pamuru et al. (2022) calculated partitioning of Cu and Zn was 42.7% and 57.2% respectively. Partitioning in stormwater has been examined in several highway studies and one study in an urban watershed (Kayhanian et al., 2012a; Nason et al., 2012; Sansalone et al., 2010; Zgheib et al., 2011). These studies show wide variability in partitioning behavior of metals in stormwater, with PB-Cu fractions ranging from 30.9% to ~100% and PB-Zn fractions observed as low as 17.9% and as high as 98%. While Cu partitioning in this study follows the wide variability found within and across these other studies, Zn partitioning showed less variability in this study compared to the other studies. It should be noted that many of the studies conducted on partitioning of metals in stormwater have been on

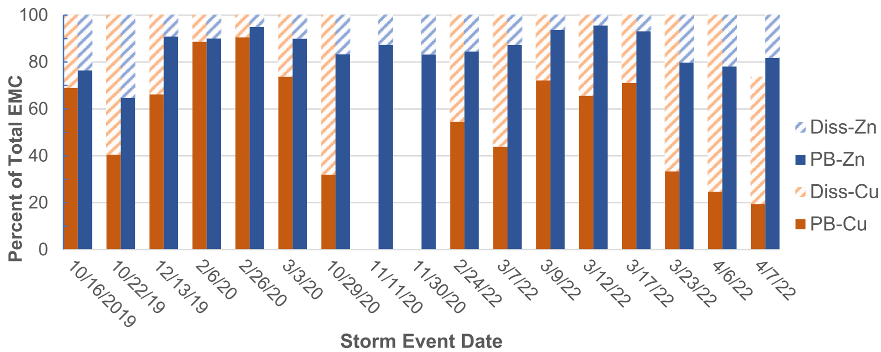

Fig. 2. Partitioning of Cu and Zn in stormwater from 17 storm events. *Storm events on 11/11/20 and 11/30/20 measured Cu below detection limits.

highway sites, where the conditions may be different compared to the site in this study – on a university campus road. Overall, metal partitioning varies widely across studies, storm events, and even throughout the duration of a storm event.

3.4. Stormwater vis-à-vis road deposited sediments

RDS can serve as both a source and a sink for metals in stormwater. During storm events, fractions of RDS will wash off, and between storm events RDS can build up from various sources like vehicular wear and exhaust, erosion, and atmospheric deposition. Both the concentration and mass distribution of Cu and Zn in RDS size fractions (<25 μm–4.75 mm) are show in Fig. 3. Concentrations of Cu ranged from 85 mg/kg to 553 mg/kg from the largest (1–4.75 mm) RDS fraction and the smallest (<25 μm) fraction, respectively. Similarly, Zn concentrations ranged from 4.7 mg/kg in the largest fraction to 711 mg/kg in the smallest. This trend of increasing concentration with decreasing particle size is in agreement with the other studies (Zafra et al., 2017; Zhang et al., 2019). While these high concentrations are a concern, their total mass contribution to RDS depends on the particle size distribution.

Typically, the finer, "unsettleable" (<75 μm) particulates contribute the least to the overall mass of available RDS. This is reflected in metal mass contributions in RDS size fractions, where the 250 μm–1 mm fraction contributed 70% of Cu mass, and >75 μm fraction contributes 76% of Zn mass. Zafra et al. (2017) also conducted a study examining metal loads from RDS and found that Cu and Zn in the <250 μm fraction accounted for 57–58% and 65–72% of metal load in RDS, respectively, from two sites. The <63 μm load of Cu and Zn only accounted for 13–16% and 20–26% of the total, respectively (Zafra et al., 2017). Larger particulates (>75 μm) have lower mobility and greater settleability than finer particulates, thus the larger load contribution of Cu and Zn in the larger fractions can lead to better treatability. However, metal accumulation in the finer fractions may be cause for concern due to the difficulty in targeting these finer particles.

Stormwater particulates were analyzed for metal concentrations for 17 samples. Three events were collected during the COVID-19 shutdown and as such exhibited significantly lower influent concentrations for both total Cu ($p = 0.008$) and total Zn ($p = 0.004$). The observed lower concentrations of Cu and Zn are attributed to the greatly reduced traffic density around campus during the shutdown. PB-Cu concentration in

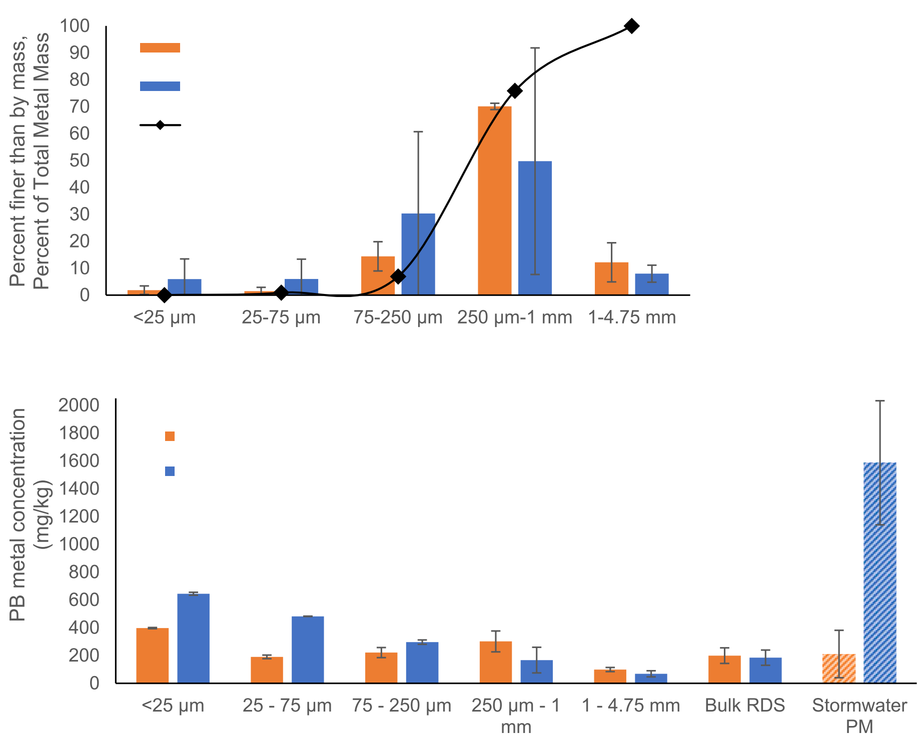

Fig. 3. Top: Cumulative particle size distribution by mass, as percent finer than, and Cu and Zn loads in size fractions as percent of total metal mass. Bottom: RDS Cu and Zn concentrations in five size fractions compared to PB Cu and Zn concentrations in stormwater samples.

stormwater excluding shutdown events was 76–546 mg/kg; PB-Zn concentrations excluding shutdown storm events ranged from 740 to 2268 mg/kg. The median PB-Cu and PB-Zn concentrations were 146 and 1739 mg/kg, respectively, excluding events during shutdown. Stormwater particulate concentrations of Cu and Zn in this study are generally in agreement with the literature. Concentrations for PB-Cu ranged from 2 to 6600 mg/kg, and PB-Zn concentrations ranged from 6 to 4670 mg/kg in studies that measured metals in urban stormwater particulates at a stormwater outfall, in sediment traps, and a roadside catchment (Jartun et al., 2008; Wang et al., 2018; Zgheib et al., 2011).

The variability of metals concentration in stormwater particulates is larger than the variability of metal concentration in RDS; this difference in variability can also be observed in particle size distributions resulting from RDS versus stormwater particulates. A larger variability in particle size distributions in stormwater particulates compared to RDS has been found in many studies (Kayhanian et al., 2012b; Kim and Sansalone, 2008 and references therein). Regardless of study site (e.g., parking lot, highway, urban roads), the particle size distributions from collected RDS were similar with a range of median diameter (d_{50}) of 200–1000 μm compared to d_{50} in stormwater particulates which ranged from 20 to 700 μm across 15 studies (Kim and Sansalone, 2008). In the current study, the d_{50} measured in RDS ranged from 782 to 801 μm and the d_{50} measured in stormwater particulates at this site in a previous study (Cao et al., 2023) ranged from 67 μm–1043 μm. Kayhanian et al. (2012b) found fine particulates (<38 μm) in stormwater contributed 65–80% of total particle mass compared to <5% in RDS samples, demonstrating the substantial mobility of fine particles in stormwater. While the amount of sediment build up on urban impervious surfaces will depend on many factors including characteristics relating to traffic, land use, and surface roughness (Wijesiri et al., 2015; Zhao et al., 2018), it has little effect on the particle size distribution of RDS on these impervious surfaces. However, stormwater sediment particle size distributions have wider variability depending on site, surface, and hydrologic characteristics, and tend to be made up mostly of finer particles compared to RDS.

Because fine particles tend to accumulate metals and have increased mobility, it is important to evaluate how this impacts the mobility of PB metals. The mean PB-Cu in stormwater samples was 211 ± 171 mg/kg, while Cu concentration in the finest RDS fraction (<25 μm) was 397 ± 220 mg/kg, and 199 ± 56 mg/kg in bulk RDS. The mean of PB-Zn in stormwater samples was 1587 ± 446 mg/kg, while Zn concentration in finest RDS fraction was 644 ± 95 mg/kg and 185 ± 55 mg/kg in bulk RDS. This shows that Zn was significantly enriched in stormwater particulates compared to RDS, with elevated concentration in stormwater particulates by a factor of 2.5 compared to fine RDS fraction and by a factor of 9 compared to bulk RDS. Several studies have compared RDS and stormwater particulates and have found that stormwater particulates tend to have elevated PB-Cu and PB-Zn concentrations compared to even the finest fractions of RDS (Furumai et al., 2002; Kayhanian et al., 2012b; Wang et al., 2018; Zhao and Li, 2013). The elevated concentration of PB-Zn in stormwater compared to finer RDS fractions shows that PB-Zn has greater mobility than PB-Cu, in which RDS and stormwater particulates are similar. Other studies examining temporal variability in RDS also conclude that Cu has low mobility compared to other traffic-derived metal contaminants (Fe, Mn, Pb, and Zn) in RDS (Robertson and Taylor, 2007).

The greater mobility of PB-Zn in stormwater compared to PB-Cu is likely due to the different sources of these metals in the urban environment. Tire wear particulates are considered as the major contributor of Zn to RDS (Banerjee et al., 2015; Loganathan et al., 2013; Zhang et al., 2019). Klöckner et al. (2019) found that particles >1.9 g/cm^3 were attributed to tire wear. However, Kayhanian et al. (2012b) found that the density of particles in the finest RDS fraction were 1.80–1.73 g/cm^3, which is lighter than tire wear particulates according to Klöckner et al. (2019). Moreover, Kayhanian et al. (2012b) found that stormwater particulates in the finest fraction (<38 μm) was the least dense (1.55 g/cm^3). Thus, the mobility of tire wear particulates may not explain why PB-Zn is enriched in stormwater. Non-exhaust emissions contribute to metals in coarser particles, while metals in finer fractions have been attributed to exhaust emissions (Ewen et al., 2009; Lin et al., 2008).

Zn in vehicle exhaust particles has been found at relevant concentrations for RDS (e.g., 3225 μg/g, (Kadıoğlu et al., 2010). Additionally, while non-exhaust emissions from vehicles (brake, tire, and road wear) have been found to contribute ~87% to airborne traffic PM_{10} (particulate matter <10 μm), vehicle exhaust still contributes the remainder (Scerri et al., 2022). This study also found that approximately 46% and 59% of Zn and Cu in PM_{10} resulted from brake and tire wear, but also that approximately 20% of Zn was contributed by exhaust (Scerri et al., 2022). Thus, tire wear particulates should not be the only source considered for PB-Zn in stormwater since the mobility of tire wear particulates is not yet well understood, and it is likely that vehicle exhaust emissions are an important contributor of fine and light stormwater particulates that are most easily mobilized in smaller more frequent storm events.

3.5. Bioretention Hydrology

The ratio of effluent to influent stormwater volume ($f_v = V_{effluent}/V_{influent}$) was used to examine the bioretention cell hydrologic performance. A wide range of f_v were observed at the site (13.77–0.58), The maximum f_v of 13.77 was observed after snow fall and increase in temperature after days of freezing temperatures, and the high volume is attributed to snow melt and thawing of soil. Eliminating this value gives a median and mean of 1.4 and 2.5, respectively. These high f_v values were observed in previous studies at this field site (DiBlasi et al., 2009; Li et al., 2009) where it was suggested that larger storm events may cause the nearby creek to fill to a level that infiltrates the bioretention media and increases observed effluent volume. Similarly, DiBlasi et al. (2009) found f_v at the UMD site to range from 2.61 to 0.61, although the storms they collected were much smaller than those collected in this study (0.28 cm–0.83 cm compared to 7.81 cm–0.13 cm in this study), which may explain some of the higher f_v values.

While the increase in effluent volume suggested groundwater infiltration in the effluent, the impact was determined to be inconsequential to the results of this study. Effluent concentrations of all constituents showed no significant differences when compared to samples collected during smaller and larger storms. Nor was there a trend between precipitation depth and effluent concentration.

3.6. Particulate matter, particulate-bound metals, and TOC removal

The particulate concentrations in stormwater at the bioretention site had a median of 71 mg/L (range: 30–145 mg/L) and was reduced through bioretention treatment to a median of 8 mg/L (range: <5–48 mg/L). A paired *t*-test showed that particulates per storm event for concentration and mass loading were significantly reduced ($p < 0.001$) with mean reductions of 71 mg/L and 4120 g, respectively. The annual mass load reduction of particulates at the site was reduced from 549 to

Table 3
Annual mass loadings calculated for pollutants in influent and effluent samples at bioretention site. Influent volume is predicted based on curve number method and effluent volume is actual volume obtained at field site.

Pollutant	Mass Load In (kg/ha-yr)	Mass Load Out (kg/ha-yr)	Load Reduction (%)
Particulates	549	99	81.9
TOT Cu	0.12	0.094	23.5
PB-Cu	0.079	0.013	83.1
Diss Cu	0.058	0.081	−38.5
TOT Zn	0.708	0.2	71.7
PB-Zn	0.725	0.126	82.6
Diss Zn	0.113	0.074	34.1
TOC	71.8	152	−112

99 kg/ha-yr corresponding to an 82% reduction (Table 3). Li and Davis (2009) conducted water quality study at the same site just two years after construction and found particulates loading in and out to be 1190 and 37 kg/ha-yr, respectively corresponding to a 97% reduction.

Fig. 4 shows an exceedance probability plot of particulates concentrations in stormwater and bioretention effluent at the site from this study and a 2009 study (Li and Davis, 2009). The 2009 study had slightly lower particulates effluent concentrations, however the difference is not statistically significant ($p = 0.06$). Results from the current study indicate that this bioretention facility reduced stormwater particulates concentration to <1 mg/L in approximately 35% of storms and to <20 mg/L in approximately 80% of storms. This is unsurprising as bioretention uses filtration and sedimentation to effectively remove particles from stormwater (Davis et al., 2022).

Total Cu and Zn concentrations in stormwater at the bioretention site were reduced from a median of 20.5 to 6 μg/L and 112 to 25 μg/L, respectively. The annual load reductions for PB Cu and PB Zn were 83% for both, while the annual load reductions for total Cu and Zn were 24% and 72%, respectively (Table 3). This difference reflects the difference in partitioning for Cu and Zn observed at the site, where Zn was mostly PB, and Cu had more storm-to-storm variation between dissolved and PB.

Figs. 5 and 6 shows exceedance probability plots for total Cu and Zn from this study and that of Li and Davis (2009). No significant difference in influent concentrations were found between the previous study and this study for both total Cu and total Zn ($p > 0.05$). However, effluent EMCs for total Zn increased from the 2009 study to the present study ($p < 0.01$). Since the previous study did not measure dissolved Zn, it is unknown if the increase in effluent Zn concentration is a result of dissolved (possibly from saturated adsorption sites) or PB-Zn (release from the media). The effluent particulates concentration increased from the previous to the present study, however not significantly ($p = 0.06$). Total Cu in effluent was unchanged from the 2009 study to the present one ($p = 0.06$).

These data were compared to the EPA aquatic freshwater criteria. Total Zn in bioretention effluent exceeded this criterion at low hardness (<60 mg/L as $CaCO_3$) for 70% of storms observed in this study. For moderate and hard hardness levels, there is <5% probability that the criterion for total Zn will be exceeded. Total Cu exceeded these criteria for 55% to >95% of storms for low to high hardness levels in bioretention effluent for this study. Cu forms strong complexes with DOM (Craven et al., 2012; Marzouk et al., 2022; Nierop et al., 2002; Tipping, 2005), and the recommended criteria are determined using the biotic ligand model (US EPA, 2007). It is unsurprising that Fig. 5 shows total Cu and dissolved Cu as exceeding these hardness-based criteria, since these criteria have been found to be overprotective considering the important relationship between Cu and DOM (McIntyre et al., 2008; Niyogi and Wood, 2004). This relationship is further explored through MINTEQ modeling analysis.

3.7. Removal of dissolved metals

No significant difference ($p > 0.05$) in concentration or loading of dissolved Cu, Zn, and TOC through bioretention treatment was found (Table S1, Figs. 4–6). The concentration of dissolved Cu in stormwater and the effluent discharge from the bioretention had a median of 5 μg/L (input range: <5–26 μg/L, effluent range: <5–19 μg/L). The median concentration for dissolved Zn in stormwater was 13 μg/L (range: <5–36 μg/L) and that for the effluent was 6 μg/L (range: <5–21 μg/L).

Effluent dissolved Cu concentrations, in agreement with total Cu, were unchanged from the 2009 study ($p = 0.12$). This is likely due to the influence of DOM in the bioretention media, and its ability to dissolve and transport Cu as Cu-DOM complexes. Additionally, while an increase in influent TOC was found comparing the previous study to the current one ($p = 0.01$), the effluent TOC remained relatively constant ($p = 0.11$), which further implicates the role of Cu-DOM in Cu mobility in bioretention.

Linear regression analysis was used to examine correlation among all measured constituents to observe if some constituents affected removal of the other. Zn did not demonstrate any significant correlations in effluent with other constituents. However, one event with high electrical conductivity seemed to influence dissolved Zn concentration in the effluent, and not total Zn. This event was after snow fall, and the high electrical conductivity results from application of deicing salts applied to the roads. This event resulted in the highest observed dissolved Zn concentration (20 μg/L) in the effluent, likely due to ion exchange, assuming that Zn is mostly being bound to exchangeable fractions of media in bioretention (Zhang et al., 2019). Note this was only observed by a single data point in this study, however other studies have observed elevated dissolved Zn concentrations as a result of increased salts (Acosta et al., 2011; Esfandiar and McKenzie, 2022).

Effluent total Cu concentration has a positive correlation with pH and TOC concentration (Figs. S1 and S2), ($R^2 = 0.75$, $p < 0.0001$ and $R^2 = 0.41$, $p = 0.013$ for total Cu, respectively). These relationships can be explained by the strong affiliation Cu has with DOM, and DOM has been shown to mobilize with increasing pH, i.e., desorption of DOM from mineral surfaces occurs with increasing pH (e.g. Niitsu et al., 1997; Righetto et al., 1991; Schulthess and Hunag, 1991). Another study similarly found Cu to mobilize through bioretention with increasing DOC and pH, and also indicated this Cu is essentially 100% bound with DOM (Chahal et al., 2016).

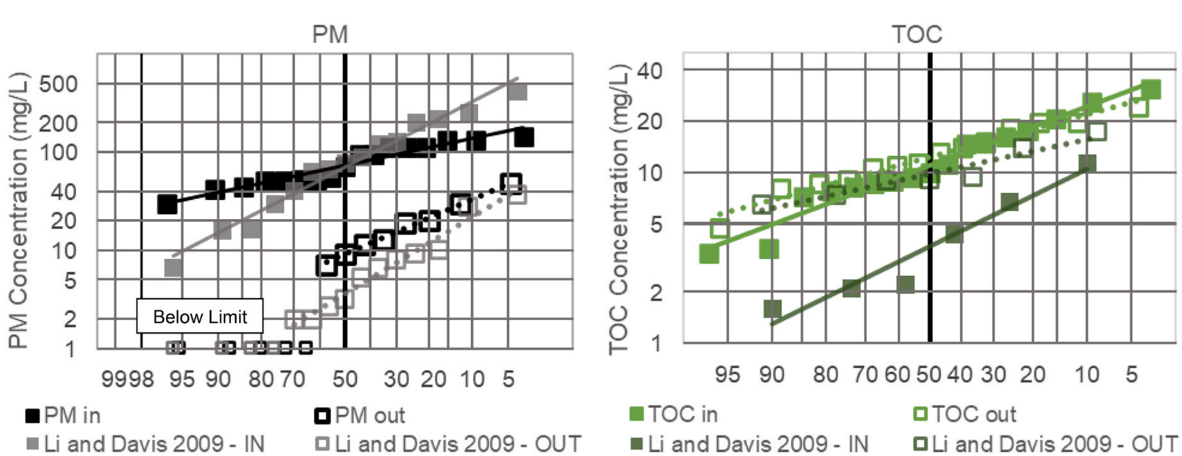

Fig. 4. Exceedance probability plots of EMCs of stormwater (IN) and bioretention effluent (OUT) for particulate matter (PM) and TOC from this study and a previous 2009 study at the same site (Li and Davis, 2009).

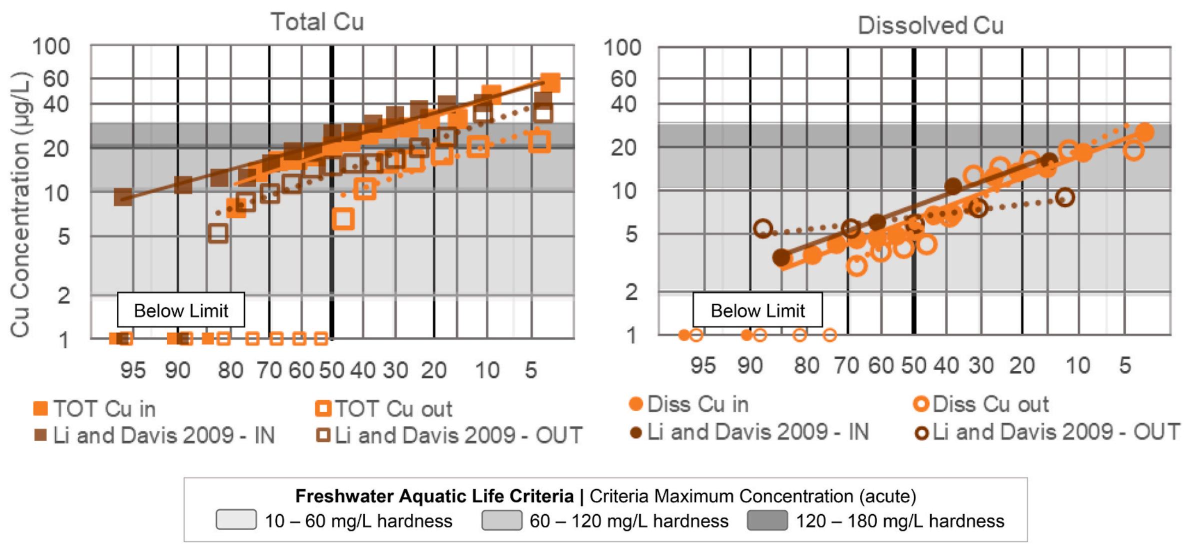

Fig. 5. Exceedance probability plots of EMCs of stormwater (IN) and bioretention effluent (OUT) for total and dissolved Cu from this study and a previous 2009 study at the same site (Li and Davis, 2009). Freshwater aquatic life criteria at range of hardness levels depicted by shaded regions for metals.

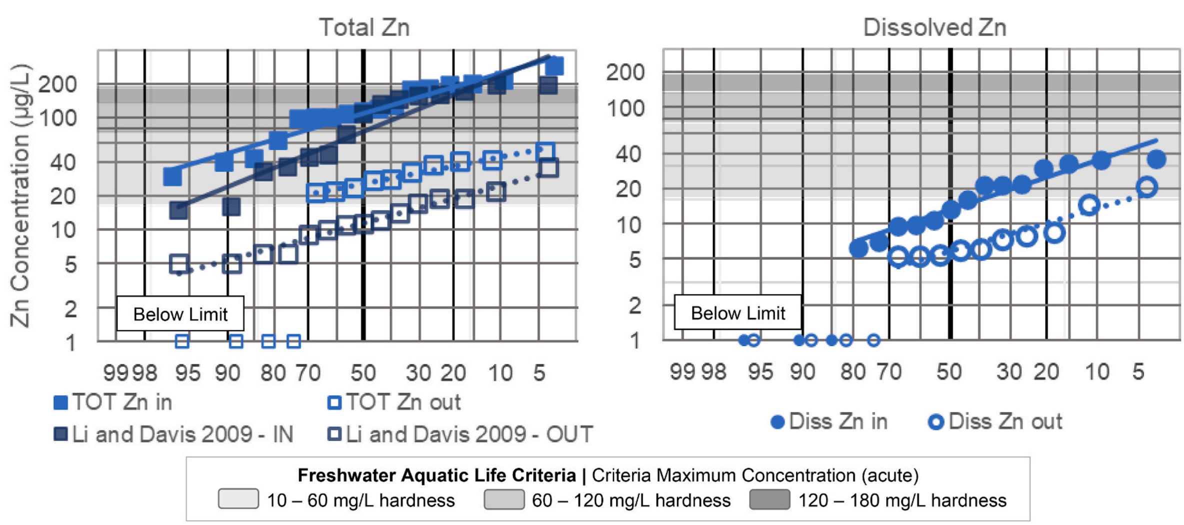

Fig. 6. Exceedance probability plots of EMCs of stormwater (IN) and bioretention effluent (OUT) for total and dissolved Zn from this study and a 2009 study at the same site (Li and Davis, 2009). Freshwater aquatic life criteria at range of hardness levels depicted by shaded regions for metals.

3.8. Metals speciation

Speciation modeling can aid in understanding what dominant species are likely present in the stormwater, which is important when considering treatability and toxicity. Table S2 shows input values for the modeling. Fig. 7 shows results of MINTEQ modeling for stormwater and bioretention effluent. The affiliation of Cu and Zn with DOM is a key difference between these two metals. Cu, unsurprisingly, is >99.99% bound with DOM, and is predicted to form inner-sphere complexes with carboxylic and phenolic sites. Zn is predominately bound with DOM; however free aqueous Zn (Zn^{2+}) and several other inorganic species are present at concentrations >0.1%. Free aqueous Cu (Cu^{2+}) is shown in Fig. 7 to be several orders of magnitude below the inner-sphere DOM complexed Cu species. Cu complexed with DOM has been shown to reduce Cu toxicity in aquatic organisms (LaBarre et al., 2017; McIntyre et al., 2008; Niyogi and Wood, 2004). However, Cu also causes chemosensory deprivation in fish, which results in impaired avoidance of excess Cu concentrations and predators (McIntyre et al., 2008; Sommers et al., 2016); complexation of Cu with DOM has shown to have minimal effect on Cu influence on olfactory senses in juvenile coho salmon (McIntyre et al., 2008). Thus, in regions with sensitive organisms, further reduction of Cu may be necessary, despite Cu-DOM being the dominant species. Zn is predicted to have not only free aqueous Zn in relevant concentrations, but also inorganic species that also contribute to aquatic toxicity. Similar to Cu, in regions with aquatic organisms sensitive to Zn toxicity, further reductions of dissolved Zn in stormwater may be necessary to protect aquatic life.

A sensitivity analysis was conducted in Visual MINTEQ to test the impact of 1) including competing ions and 2) concentration of these ions on metal speciation, especially with DOM. The constituents tested included Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, and alkalinity. A wide concentration range was tested for each constituent, using the minimum and maximum values from the BMP Database (Table S2), reported in Pamuru et al. (2022). Unsurprisingly, the competitive nature and higher concentrations of these species resulted in an observed impact on metal speciation. The results showed that including these constituents had a major impact on metal species, e.g., without these ions Zn was essentially 100% bound with DOM, but including these ions predicted free aqueous Zn^{2+} to be up to 15% of the Zn speciation. However, the predicted dominant species were still the DOM-metal complexes. Therefore, for speciation analysis

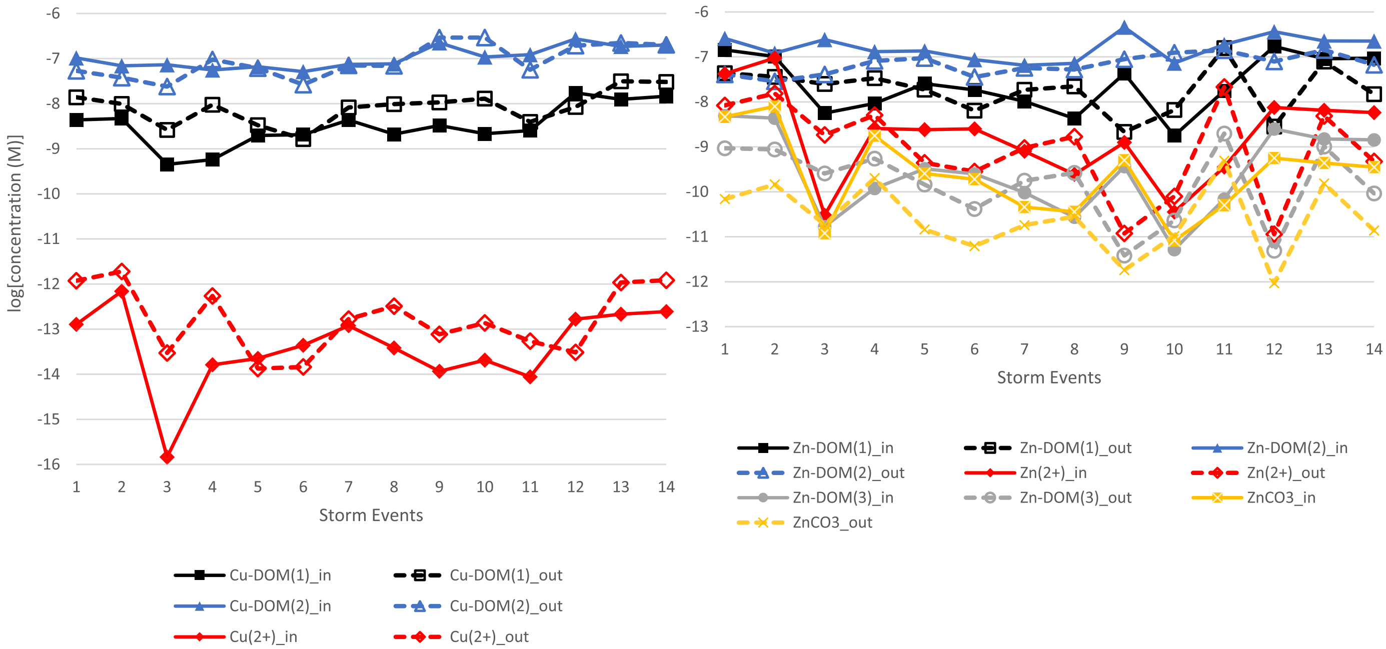

Fig. 7. Speciation modeling results for influent and effluent storm events for dissolved Cu and Zn species. DOM(1) indicates Cu or Zn bound with DOM carboxylic sites, DOM(2) indicates bonding with phenolic sites, and DOM(3) indicates electrostatically bound with DOM, i.e., weak outer sphere complex. See Table S2 for input values.

of field data, a constant value (geometric mean, calculated in Pamuru et al., 2022, Table S2) was used for competing cations and common anions in the MINTEQ modeling.

4. Conclusions

This study examined the behavior of Cu and Zn in stormwater, RDS, and through 16- to 18-year-old bioretention treatment. Cu and Zn in stormwater was found to be mostly PB, however this varied depending on watershed and hydrologic characteristics. While metal concentration generally increased with decreasing size fraction in RDS, the mass contribution was typically dominated by the 250 μm–1 mm size fraction. The comparison between Cu and Zn in RDS size fractions and PB in stormwater revealed differences in behavior between them. PB-Zn was enriched in stormwater particulates compared to fine RDS fractions, indicating higher mobility compared to PB-Cu. This is likely related to differences in metal sources, which determines affiliation with particle size and particle densities. Moreover, while tire wear particulates are likely a major source of Zn in RDS, this is likely not the most mobile source of PB-Zn in stormwater; other sources of Zn may significantly contribute to PB-Zn loading.

The bioretention cell showed effective removal of particulates and PB Cu and Zn, which had average load reductions of 82% and 83% for both Cu and Zn. Dissolved metals showed no significant difference in EMC or load reductions for each storm event, indicating no major interactions between dissolved metals and media. This may be due to the age of the bioretention cell/media, where most of the available sorption sites for metals have been filled. Increases in pH were correlated with increase in dissolved Cu in effluent, likely due to increase in TOC with increase in pH. Effluent Zn did not show any significant correlations with measured water quality parameters, except for one single point with high electrical conductivity from road application of deicing salts, which has been shown to cause leaching of Zn in bioretention.

Although Zn did not have a significant decrease in dissolved concentration through bioretention, the toxicity criterion by the EPA is higher for Zn, and there is a low probability (<5%) of Zn exceeding this limit. However, these limits are based on empirical relationships with water hardness, and do not take into account complexation with DOM. Speciation modeling predicts that greater than 10% of Zn may be present as Zn^{2+} and inorganic Zn complexes. This is important to consider as these species contribute the most to toxicity (Magnuson et al., 1979). Alternatively, Cu had a higher probability of exceeding the EPA aquatic criteria overall, however the speciation modeling showed essentially 100% of Cu formed inner-sphere complexes with DOM sites, thus significantly reducing toxicity. Regions where aquatic organisms are sensitive to Cu and Zn toxicity should consider further reductions of dissolved metals.

Depending on treatment goals and water quality criteria, additional targeted treatment of stormwater may be necessary for Cu and Zn removal. Comparing bioretention effluent quality from over a decade ago, total and dissolved Cu and TOC remain unchanged, while total Zn effluent concentration has increased. Dissolved Cu and Zn in the present study were unchanged through bioretention treatment, while particulates and PB-metals were reduced. This shows that bioretention can be employed and provide a reliable degree of metals removal, especially PB, in many urban settings. For further removal and reduction of dissolved constituents, more frequent maintenance or a specified adsorptive media as a polishing treatment should be considered.

Monitoring of bioretention systems, old and new, should be emphasized as there are still many variables that are not yet understood in how they may influence performance and downstream water quality. Evaluating performance of mature bioretention systems can help indicate what types of maintenance will improve water quality and quantity performance in order to extend the life of these systems and ensure continued protection of the environment.

CRediT authorship contribution statement

Kristen Croft: Data curation, Investigation, Methodology, Writing – original draft. **Birthe V. Kjellerup:** Funding acquisition, Project administration, Supervision, Writing – review & editing. **Allen P. Davis:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Birthe V. Kjellerup reports financial support was provided by Strategic Environmental Research and Development Program. Kristen Croft reports financial support was provided by National Science Foundation (Amy Sapkota, PI).

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.120014.

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