Multiyear Water Quality Performance and Mass Accumulation of PCBs, Mercury, Methylmercury, Copper, and Microplastics in a Bioretention Rain Garden

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Abstract: A multiyear water quality performance study of a bioretention rain garden located along a major urban transit corridor east of San Francisco Bay was conducted to assess the efficacy of bioretention rain gardens to remove pollutants. Based on data collected in three years between 2012 and 2017, polychlorinated biphenyls (PCBs) and suspended sediment concentrations (SSCs) were reduced (>90%), whereas total mercury (Hg), methylmercury (MeHg), and copper (Cu) were moderately captured (37%, 49%, and 68% concentration reduction, respectively). Anthropogenic microparticles including microplastics were retained by the bioretention rain garden, decreasing in concentration from 1.6 particles/L to 0.16 particles/L. Based on subsampling at 50- and 150-mm intervals in soil cores from two areas of the unit, PCBs, Hg, and MeHg were all present at the highest concentrations in the upper 100 mm in the surface media layers. Based on residential screening concentrations, the surface media layer near the inlet would need to be removed and replaced annually, whereas the rest of the unit would need replacement every 8 years. The results of this study support the use of bioretention in the San Francisco Bay Area as one management option for meeting load reductions required by San Francisco Bay total maximum daily loads, and provide useful data for supporting decisions about media replacement and overall maintenance schedules. DOI: 10.1061/JSWBAY.0000883. © 2019 American Society of Civil Engineers.

Introduction

Surrounded by a dense urban area with approximately 7 million residents, the San Francisco Bay receives pollutants that are washed from the surrounding landscape during storm events into storm drains, streams, and rivers, most of which receive no treatment prior to being discharged to the Bay. The local water quality control agency has adopted total maximum daily load (TMDL) cleanup plans for polychlorinated biphenyls (PCBs) and mercury (Hg) (Davis et al. 2007, 2012) to reduce pollutant loads into the Bay. In addition, a site-specific objective has been written for copper (Cu) (Trowbridge et al. 2016), and microplastics are an emerging pollutant of concern in the estuary (Sutton et al. 2016). Because municipalities strive to reach these stormwater waste load allocations, green infrastructure such as bioretention rain gardens presents a promising solution for managing stormwater pollutants while achieving additional environmental and social benefits. However, numerous data gaps prevent local managers from accurately predicting the water quality benefits that would occur through application of green infrastructure (Wu et al. 2018), as well as the annual maintenance that is needed to sustain human health standards in these pollutant-accumulating structures.

Increasingly, studies from the United States and elsewhere have documented significant pollutant reduction in stormwater based on the use of bioretention rain gardens (Davis et al. 2003; Li and Davis 2009; Diblasi et al. 2009; Hatt et al. 2006). These studies have primarily measured suspended sediments, nutrients, trace metals, and, to a lesser degree, trace organic contaminants. Studies to date have indicated relatively good removal of Cu ranging from 40% to 100% capture efficiency, with effluent concentrations generally <10 μg/L. In contrast, only one published study by Davis et al. (2015) evaluated bioretention for the capture of PCBs and Hg. David et al. (2015) measured water quality prior to and after the construction of a bioretention swale next to a newly redeveloped parking lot in Daly City (also located in the San Francisco Bay region). In that study, the swale served to reduce PCB concentrations, but due to the location of the swale in a relatively clean landscape, the pre- and postconstruction concentrations were both two orders of magnitude lower than mean concentrations observed in other stormwater locations in the Bay Area (Gilbreath and McKee 2015): 14,500 pg/L; McKee et al. (2017): 13,000 pg/L, and therefore may not serve as a good representation of how effective bioretention may be in San Francisco Bay’s more polluted areas. David et al. (2015) also monitored for Hg and found that postconstruction concentrations were reduced by 18%, which had little effect, and concentrations were still similar to the mean.
observed in other untreated Bay Area urban drainage systems [McKee et al. (2015): 29 ng/L]. To the best of our knowledge, there have not been any published studies quantifying microplastics directly in urban stormwater runoff, let alone on the effectiveness of bioretention rain gardens in reducing the discharge of microplastics into water bodies. Given the dearth of existing case studies, stormwater managers remain uncertain about the overall capability of bioretention rain gardens to capture and reduce the transport of unique pollutants such as PCBs, Hg, and microplastics in stormwater.

PCBs were used as dielectric fluids in transformers and capacitors for power transmission, in heat-resistant plastics, hydraulic fluids and oils, and as a component of caulk (Erickson and Kaley 2011). Sources of PCBs in urban environments are mainly associated with residues from legacy uses in the older commercial and industrial areas that were developed prior to the ban of PCBs in the United States in 1979. It is therefore expected that the greatest reductions of PCBs using green infrastructure would be likely to occur in the older urban and industrial areas constructed or renovated before 1979. More study of bioretention rain gardens in areas such as these could help managers better understand where to focus green infrastructure efforts to make the greatest progress toward meeting PCB TMDL targets.

Although there are legacy sources of Hg in older urban areas from uses in paint, batteries, thermostats, switches, and many other smaller uses, Hg is widely redistributed in the urban environment via atmospheric circulation and deposition (Davis et al. 2012). Wide distribution of green infrastructure may be a useful tool for reducing Hg loads. However, stormwater managers need more information about bioretention rain garden performance so that Hg load reduction estimates can be generated with enough confidence for TMDL compliance. In there is only one study reporting on Hg load reductions of PCBs using green infrastructure would be likely to occur in the older urban and industrial areas constructed or renovated before 1979. More study of bioretention rain gardens in areas such as these could help managers better understand where to focus green infrastructure efforts to make the greatest progress toward meeting PCB TMDL targets.

Anthropogenic microparticles, including microplastics, are plastic and other particles generally defined as smaller than 5 mm in size. Sutton et al. (2016) reported average levels of 700,000 particles/km² in the first investigation of microparticles in the San Francisco Bay (smallest size fraction measured was 0.355 mm), a result that appears greater than levels previously observed in studies of other urban North American water bodies using similar methods [Eriksen et al. (2013): smallest size fraction measured was 0.355 mm; Yonkos et al. (2014): smallest size fraction measured was 0.3 mm]. Sutton et al. (2016) also reported that the distribution of microparticle types (e.g., film, foam, fragment, pellet, or fiber) observed in Bay surface samples contrasted with the distribution of types found in effluent from Bay Area wastewater facilities. From this, Sutton et al. (2016) inferred that at least some other pathways such as urban stormwater may also contribute a significant load of microplastics to the Bay. There are numerous sources of microplastics to aquatic ecosystems including tire wear, road wear, and degradation of larger plastic litter items (Sutton et al. 2016), which are likely entrained in stormwater runoff during rain events. Yonkos et al. (2014) reported that concentrations of microplastics in four tributaries of the Chesapeake Bay were highest following rain events, suggesting a concentrated influx of particles to these tributaries from stormwater. Study is needed to understand the potential for bioretention rain gardens to filter out that influx of microparticles and microplastics from stormwater.

In addition to questions about the capability of bioretention rain gardens to capture and reduce transport of unique pollutants such as PCBs, Hg, and microplastics, stormwater managers also aim to understand where in the soil depth profile these pollutants accumulate and how performance changes over time. Other studies on bioretention rain gardens have shown that pollutants may disproportionately accumulate in the top layers of the soil profile, which has important implications for maintenance and life-cycle costs (Li and Davis 2008; Komlos and Traver 2012; Dechesne et al. 2005). Providing evidence as to whether this holds true for PCBs and Hg would help stormwater managers gain insight into what soil maintenance programs should include as well as the frequency of a maintenance schedule.

The purpose of this study was to fill some of these information gaps through a multiyear water quality performance study on a bioretention rain garden for rarely studied PCBs, Hg species, and microplastics, in addition to suspended sediments and copper, which are more commonly studied pollutants.

Materials and Methods

Site Design and Drainage Management Area

A bioretention rain garden cell (Fig. 1) located along a roadway with heavy car and foot traffic in El Cerrito, California, was monitored (Figs. S1 and S2 provide a drainage area map and picture of cell). The cell was rectangular (3.7 by 1.7 m) and planted with drought-tolerant species (Juncus patens, Festuca californica, Verbena lilacina “De la Mina”). Bioretention media in the cell included a 0.46-m layer of engineered soil mix selected to meet current guidelines for Bay Area bioretention, which was composed of 70% sandy loam, 10% clay, and 20% composted organic matter (minimum infiltration rate 127 mm/h). These media sat directly atop the native soil. Native soil at the site was typed as Hydrologic Soil Group D with high clay content. This native soil type has an infiltration rate between 0 and 1.3 mm/h, and therefore installation of an underdrain was required. An underdrain was embedded in 1.3-cm size drain rock, which was embedded in a small section of the native soil layer and installed directly below the engineered media. The depth of the space where ponding on the surface is enabled was 0.28 m. Some amount of stormwater volume was reduced by vegetation interception, evapotranspiration, and infiltration, but predominantly the stormwater that entered the bioretention rain garden.
cell discharged after filtration to the main storm drain conveyance system, which delivered it to the Bay with no further treatment.

Construction of the bioretention rain garden cell was completed in September 2010. During installation, regular inspections were made by city engineers and several of the authors to verify that all aspects of installation at this site were correct, helping to ensure the resulting water quality data could be linked to specific known and verified aspects of the design. By special request, the city installed a sampling hatch in the sidewalk to access the outflow from the subdrain before it comingle with the main storm drain.

The drainage management area consisted of 4,080 m² (1 acre) of mostly impervious cityscape, including 20% medium-density residential, 13% commercial offices, and 67% local roads. All buildings in the drainage area were constructed between 1940 and 1965 (overlapping with the PCB and Hg peak usage periods), and the drainage area included two older style electrical transformers attached to electrical poles that may contain PCB residues, as could the surrounding soils.

Stormwater Sampling and Analysis

Typical of a Mediterranean climate, the San Francisco Bay Area has predominantly wet and dry seasons, with approximately 95% of rainfall occurring between October 1 and April 30. During 11 storms in the rainy seasons of water years (WYs) 2012, 2014, 2015, and 2017, whole-water composited samples were collected at the inlet and outlet of the bioretention rain garden using trace-metal-clean sampling protocols and peristaltic pumps fitted with trace-metal-clean tubing (laboratory-cleaned polytetrafluoroethylene intake tubing was installed prior to each storm). The same sampling techniques were implemented during all WYs. Samples collected for dissolved-phase analytes were filtered immediately at the end of each storm event using a precleaned SingleSample (Voss Technologies, San Antonio, Texas) disposable filter capsule (0.45-μm pore size). Samples were stored at ≤4°C and shipped to the analytical laboratories within analyte-specific appropriate hold times. Laboratories and EPA standard methods were chosen to ensure that high-quality repeatable data could be delivered in relation to expected field conditions and needed detection limits. Table S1 provides information on the matrix, laboratory, and analytical methods for the studied constituents. A review of quality assurance sampling and results is also available in the “Supplemental Data” section.

Microplastics Sampling and Analysis

During three storm events monitored for water quality in WY 2017 (January 3, February 9, and March 24), samples for analysis of microplastics were collected at the inlet and outlet. Between each aliquot collected for water quality samples, 20–40 L of stormwater were pumped and filtered through two stacked sieves (355 and 125 μm). After the storm, the microplastics were flushed from the sieves with deionized water into glass containers and shipped to the laboratory (at the University of Toronto) for analysis. Two field blanks were also sampled to account for possible procedural contamination during sampling. Approximately 10 mL of isopropyl alcohol was added to each sample for storage until analysis.

The method used for microplastic extraction from stormwater included a density separation method modified from Stolte et al. (2015). Briefly, the particles were separated from the sediment in the samples via density separation using a calcium chloride solution with a density of 1.4 g/mL. The separated particles were then further separated into two size fractions using 500- and 106-μm sieves. The greater than 500-μm fraction was sorted visually under a dissection microscope. The smaller size fraction was density separated. Briefly, each size fraction was mixed with approximately 200 mL of CaCl₂ solution in a separatory funnel and left to sit until the material settled—generally overnight. The next day, the floating portion was filtered through a 20-μm polycarbonate filter and sealed into a Petri dish for visual sorting. Individual particles were enumerated and sorted according to color and morphology under a dissecting microscope. Each piece was labeled and lined up on double-sided tape. Next, the polymer type was identified for a subset using Raman spectroscopy (Horiba Xplora, France). All particles were also imaged and measured using ImageJ software. For quality assurance and quality control, one laboratory blank was run with every set of 10 samples. All glassware was cleaned with soap and water, followed by a triple rinse with reverse osmosis water. Laboratory practices to avoid procedural contamination included sealing all glassware from air as much as possible, working in a clean cabinet as much as possible, and wearing cotton lab coats during laboratory analysis. All laboratory and field blanks were analyzed using the same methods as described.

Soil Core Sampling and Analysis

Two composite soil core samples were collected from the bioretention cell in May 2017, at which time the cell had received stormwater runoff during seven wet seasons since installation. The composite sampling design aimed to represent two areas of the cell (Fig. S3). The first composite consisted of homogenized samples from four cores collected in front of the two street inlets to the bioretention rain garden cell, thus representing the component of the cell that is near field. A second composite consisted of homogenized samples from six far-field cores spaced throughout the remainder of the cell (hereafter referred to as the body of the bioretention rain garden cell).

Cores were collected using a stainless steel hand shovel that was cleaned prior to and between sample collection using an anionic free-rinsing detergent and deionized water rinse. The core composites were composed of homogenized subsamples collected at four depths: 0–50 mm, 50–100 mm, 100–150 mm, and 150–300 mm, all of which were located within the engineered bioretention soil mix. The soil segments at each depth were composited into a cleaned glass receptacle, mixed with a hand trowel for 3 min, subsampled into sterile glass jars, and shipped frozen to the analytical laboratories.

Statistical Analyses

To test whether the differences between the inlet and outlet concentrations were statistically significant, the nonparametric Wilcoxon matched-pairs signed-ranks test was applied. A Wilcoxon rank sum test was used to assess for a temporal trend by first comparing inlet concentrations from WY 2012 samples to WY 2017 samples and then the outlet concentrations from WY 2012 and WY 2017. Differences were considered significant at \( p < 0.05 \).

Storms Sampled

The 11 storms sampled represent a range of moderate-sized events for the bioretention rain garden location in terms of total rainfall, peak hourly rainfall intensity, and antecedent dry days (Table S3). The total rainfall for each storm ranged from 17 to 50 mm (median = 23 mm). Peak 1-h rainfall ranged from 3 to 15 mm. For context, the 1-h, 1-year return precipitation for this location is about 11.2 mm, and the 1-h, 2-year return precipitation is about 13.7 mm (return frequencies based on a partial-duration series). Of the 11 storms, the antecedent dry period was 0 days for four storms (a day is counted as a rainfall day if 2.5 mm or more of rain...
had fallen), 1 day for four storms, and >1 day for three storms. Total rainfall in the previous 7 days varied between 0 and 105 mm (median = 17 mm). This bioretention system was designed to drain completely within 6 h after rainfall cessation, so although treatment soil may have still been wet during some of the monitored storms as a result of antecedent conditions, the system was not completely saturated. Because many of the storms monitored had no or few antecedent dry days, the inlet concentrations may be biased low, particularly for traditional buildup, washoff pollutants like suspended sediment concentration (SSC), Cu, and Hg.

Results and Discussion

Water Quality Results

Suspended Sediment Concentration

Inlet concentrations of SSC ranged between 14.8 and 395 mg/L, with a median of 47.2 mg/L, while outlet concentrations ranged from 0.33 to 15.3 mg/L, with a median of 3.6 mg/L (Fig. 2, Table 1). At a 95% confidence level, there was a statistically significant difference in SSC inlet and outlet concentrations. The mean difference was 94%. This magnitude of reduction has been measured in other bioretention units (e.g., Hatt et al. 2009). The observed reduction in this unit was at the higher end of typical performance. Other studies have reported lesser reductions [e.g., 29% in David et al. (2015)], and in some cases net export of suspended sediment [e.g., 70% increase in effluent measured by Hunt et al. (2006)].

The variation in performance for SSC is generally attributed to whether or not the bioretention soil itself is contributing to the effluent. The high reduction in SSC at the El Cerrito bioretention rain garden suggests that the garden design prevented most soil media export. The observed reduction in this unit was at the higher end of typical performance. Other studies have reported lesser reductions [e.g., 29% in David et al. (2015)], and in some cases net export of suspended sediment [e.g., 70% increase in effluent measured by Hunt et al. (2006)].

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Polychlorinated Biphenyls

As is typical of urban stormwater during rain events (e.g., David et al. 2015; Gilbreath and McKee 2015), PCB concentrations at the

Fig. 2. Box and whisker plots showing the resulting data from water quality samples collected in storms during water years 2012, 2014, 2015, and 2017. The range, mean, quartiles, and data outliers for the six analytes are shown for both the inlet and outlet. One inlet PCB sample is not represented on the graph; it is 226,000 pg/L.

Table 1. Summary statistics for water quality samples collected during water years 2012, 2014, 2015, and 2017, including the percent reduction in contaminants from the inlet to the outlet

<table>
<thead>
<tr>
<th>Analyte</th>
<th>N</th>
<th>Inlet mean</th>
<th>Inlet median</th>
<th>Inlet minimum</th>
<th>Inlet maximum</th>
<th>Outlet mean</th>
<th>Outlet median</th>
<th>Outlet minimum</th>
<th>Outlet maximum</th>
<th>Percent reduction (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Wilcoxon p</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC (mg/L)</td>
<td>11</td>
<td>95.8</td>
<td>47.2</td>
<td>14.8</td>
<td>395</td>
<td>5.55</td>
<td>3.60</td>
<td>0.33</td>
<td>15.3</td>
<td>94</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Sum of PCBs (ng/L)</td>
<td>11</td>
<td>29.7</td>
<td>7.60</td>
<td>3.02</td>
<td>226</td>
<td>1.13</td>
<td>1.00</td>
<td>0.350</td>
<td>2.50</td>
<td>96</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Total Cu (μg/L)</td>
<td>8</td>
<td>25.5</td>
<td>20.3</td>
<td>14.5</td>
<td>48.2</td>
<td>8.11</td>
<td>7.03</td>
<td>5.64</td>
<td>11.7</td>
<td>68</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Total Hg (ng/L)</td>
<td>11</td>
<td>18.8</td>
<td>14.0</td>
<td>8.57</td>
<td>56.0</td>
<td>11.9</td>
<td>9.39</td>
<td>5.61</td>
<td>36.9</td>
<td>37</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Dissolved Hg (ng/L)</td>
<td>7</td>
<td>6.01</td>
<td>5.87</td>
<td>3.07</td>
<td>8.54</td>
<td>6.15</td>
<td>5.95</td>
<td>4.83</td>
<td>8.20</td>
<td>2</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Total MeHg (ng/L)</td>
<td>8</td>
<td>0.256</td>
<td>0.252</td>
<td>0.193</td>
<td>0.325</td>
<td>0.132</td>
<td>0.137</td>
<td>0.0750</td>
<td>0.178</td>
<td>49</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

<sup>a</sup>Based on the mean of all inlet samples versus the mean of all outlet samples.
inlet varied by three orders of magnitude, and in this study averaged 30,800 pg/L (Table 1). The average is four times greater than the median due to a single high concentration of 226,000 pg/L measured in the first storm event sampled in WY 2012. Episodic high concentrations of PCBs are not uncommon in urban stormwater runoff (Gilbreath et al. 2016). The bioretention rain garden significantly reduced the concentration of PCBs in all storms, averaging a 96% reduction (89% if the first storm of WY 2012 is excluded).

The inlet concentrations of PCBs at El Cerrito were high relative to the one other PCB performance study to date (David et al. 2015). David et al. (2015) measured PCBs prior to the construction of a bioretention swale in Daly City (also located in the San Francisco Bay region), which ranged from 180 to 1,300 (mean 730) pg/L. The postconstruction concentrations at Daly City were 190–870 (mean 410) pg/L. Although the outlet concentrations at El Cerrito were slightly higher than the postconstruction concentrations at Daly City, the influent concentrations at El Cerrito were so much greater that the reduction was also much greater. This percentage reduction calculation in the two studies corroborates previous findings in which bioretention units with greater influent concentrations also tend to yield the greatest percent reduction, as opposed to units with less polluted influent (e.g., Strecker et al. 2001; McNett et al. 2011).

Total Copper
Total Cu reduction from the bioretention unit was significant and on average 68% over the eight storms sampled for Cu (Fig. 2, Table 1). A previous local study (David et al. 2015) showed comparable total Cu reduction (83%). Based on a review by Liu et al. (2014), four studies reported ranges in Cu removal performance between 65% and 98%. The results of 14 studies with Cu data reported in the International Stormwater Best Management Practices (IBMP) Database combine for an average decrease from influent to effluent of 38% (Geosyntec Consultants and Wright Water Engineers 2017), which is a relatively lower performance reduction than the current study. A common factor between this study, the David et al. (2015) study, and the IBMP Database compilation is that the average effluent concentrations reported are all in a very narrow range (8.1, 7.7, and 5.7 μg/L, respectively). This suggests that the 5–8 μg/L effluent concentrations may represent a lower limit of treatment based on the current range of specifications of bioretention systems being installed and the speciation characteristics of Cu in the influent (percent dissolved phase, and grain size and carbon content of particulates).

Mercury Species
Outlet total mercury (HgT) concentrations were significantly lower than inlet concentrations with a mean difference of 37%. On a storm by storm basis, performance varied widely between –164% (indicating an increase at the outlet relative to the inlet) up to an 85% reduction; however, there was no apparent trend in performance over time. With the exception of dissolved mercury (HgD), all other analytes measured in this study had greater reductions than that observed for HgT.

The range of HgT concentrations at the El Cerrito inlet (8.57–56 ng/L) was similar to the range measured by David et al. (2015) (3.5–47 ng/L), as were the concentration reductions [18% for concentration and 59% for load (David et al. 2015)]. The current study was consistent with David et al. in that reductions were greater for Cu than for Hg species.

Dissolved Hg was the only analyte that did not change significantly between inlet and outlet. These results deviate from the other study of Hg in bioretention in which the outlet concentrations were reduced by 50% (David et al. 2015). In the David et al. study, inlet concentrations of HgD were much higher (2.4–33 ng/L) than measured at El Cerrito (3.1–8.5 ng/L), which may account for the differing performance results from the two studies: typically bioretention shows a greater percentage reduction when the influent is more polluted. Major mechanisms for dissolved metal removal in bioretention include ion exchange, plant uptake, and adsorption, and these mechanisms are influenced by pH, ionic strength, competing cations, and plant species. It can be challenging in case studies such as these to hypothesize why one bioretention unit may perform better than others in dissolved metal reductions.

Methylmercury (MeHg) decreased at the outlet to the El Cerrito bioretention rain garden by 50% on average relative to the influent, differing greatly from the results reported by David et al. (2015) for a bioretention swale. David et al. (2015) found that concentrations increased from an inlet range of 0.19–1.6 ng/L to an outlet range of 0.15–3.4 ng/L, and on average concentrations increased 52%. Construction implementation may be the key difference that explains the different results: the El Cerrito bioretention rain garden had a subdrain, whereas the subdrain was left out of the unit in the David et al. (2015) study. As noted by David et al., the subdrain being unintentionally left out of the construction may have fostered anaerobic conditions in the unit, which favored bacterial methylation. The subdrain in the El Cerrito bioretention rain garden drained water from the system more quickly, which most likely resulted in adequate aeration and reduced the chances for any variable anaerobic conditions required for Hg methylation (Colombo et al. 2013).

The overall good performance of the El Cerrito system for HgT and MeHg is an encouraging finding for stormwater managers who have Hg waste load allocations and are using bioretention rain gardens as a management practice.

Consistent with the findings from other studies (e.g.,Gatt et al. 2009) and with the other analytes in this current study, influent concentrations of all Hg species were more variable than effluent (Fig. 2 and Table 1). Variability in the influent due to varying storm characteristics (e.g., precipitation intensity, antecedent dry days) and landscape activities was muted by filtration through the bioretention rain garden, leading to more consistent effluent concentrations between storm events. For HgD, the variation decreased even though the median between influent and effluent was similar.

Multiple hypotheses could be tested to understand why HgT does not perform as well as SSC, PCBs, and Cu. First, on average, 32% of the total Hg was in the dissolved form, which more easily passes through the bioretention system. This may be a greater proportion than the dissolved portion of Cu or PCBs. Second, the particulate Hg may be on very small grain sizes, which facilitates these particles passing through the system without being filtered out. Similarly, Hg on very fine particles may not adsorb to particles within the bioretention units as readily as other analytes. Data collected as part of the WY 2014 and 2015 study at the El Cerrito site lend support to this hypothesis. In one storm event, both the total Hg fraction and the Hg fraction on particles smaller than 10 μm (including dissolved-phase Hg) were measured, and the concentration on particles larger than 10 μm was estimated by the difference. In the one sample measured, only 27% of the influent HgT mass was on particles larger than 10 μm, as opposed to 66% of PCB mass (Geosyntec Consultants and EOA Inc. 2017). Therefore, based on size alone and concerning physical filtration, a greater proportion of PCBs are more likely to filter out than HgT, assuming that there is a capture rate difference for particles less than 10 μm. This hypothesis appears consistent with a study of influent and effluent in three detention basins where Kayhanian et al. (2012) found that effluent samples contained much higher proportions of the finest size fractions. Thus, it seems plausible if not likely that both the proportion of dissolved phase and particle size may be playing a role in reduced capture of Hg relative to PCBs.

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More study on Hg dynamics in bioretention rain garden units would be helpful to further understand how to best design bioretention rain gardens as a management option for meeting stormwater Hg TMDL allocations.

**Microplastics**

Anthropogenic microparticles include microplastics and also other materials such as glass beads and asphalt fragments. As such, we refer to anthropogenic microparticles, which include microplastics, in the following discussion. Inlet concentrations for anthropogenic microparticles from three storms in 2017 were highly variable, ranging from 0.4 to 3.2 particles/L, with an average of 1.6 particles/L. Combining results from the three inlet samples, the particles were composed of 58% fibers from textiles, 15% fragments, 21% glass microbeads, 4% rubber fragments (e.g., tire dust), and 2% paint particles (Fig. 3). The microfibers included synthetic textiles (i.e., microplastics, 13%), natural-based fibers made from cotton or wool (11%), and microfibers where the material could not be identified due to the interference of anthropogenic dyes (76%). All but one of the 112 enumerated glass particles were spherical microbeads, which are hypothesized to come from reflective road paint, and most of the glass microbeads (95%) came from the March 24, 2017, storm event.

Stormwater likely plays an important role in microparticle contributions to the Bay. The average concentration measured in these stormwater influent samples (1.6 particles/L) is an order of magnitude higher than the average particle concentrations previously measured in wastewater effluent discharged to the Bay [Sutton et al. (2016), whose study used similar methods to this study and with size fractions down to 125 μm], which measured an average of 0.08 particles/L (n = 8). The composition of the stormwater samples was similar to the wastewater samples in that the majority were microfibers. This distribution of particle types measured in influent at this site is therefore not representative of the particle distribution found in the Bay. The microparticles found in Bay water were majority fragments (55%), whereas roughly 20% of the particles in stormwater at El Cerrito and the wastewater treatment effluent were fragments. While this study presents stormwater data from one demonstration pilot study involving a 4,080-m² (1-acre) catchment, another study is currently underway (Sutton et al. 2017) that involves sampling stormwater from a variety of large catchments with diverse land uses. It is hoped that this diversity of catchments will help to illuminate the variety, type, and concentrations of microplastics in urban runoff.

There are very limited urban runoff studies to which particle concentrations can be compared, but the concentrations measured in this study are higher than estimates from other heavily urbanized areas. A Swedish study estimated stormwater microplastic particle counts to be 0.07 particles/L based on surface water concentrations in an urban harbor (Magnusson et al. 2016). Another study of 29 Great Lakes tributaries that were sampled during low-flow and storm-driven high-flow events found a range of concentration from 0.00005 to 0.032 particles/L and a mean of 0.001 particles/L (Baldwin et al. 2016). Data collected by Baldwin et al. (2016) used a mesh size of 333 μm, which may not capture some of the smaller particles that were captured in the inlets of our El Cerrito bioretention rain garden, where a 125-μm sieve was used. Concentrations were also likely lower because they were sampled from the streams, which are more dilute than the direct samples of stormwater runoff in this study.

Particle concentrations between influent and effluent from the bioretention rain garden decreased by 83% and 95% (mean 91%) during the three storms (Fig. 4), indicating that the bioretention system was effective at reducing particles from stormwater runoff. Removal efficiency by particle size was 100% for particles >500 μm, 81% for particles between 355 and 500 μm, and 55% for particles between 125 and 355 μm. Although the size ranges are quite different, the general trend of microplastic capture is consistent with the observations for PCBs and Hg described previously; larger particles are captured more easily.

**Soil Profile Results**

The soil profile results show a similar pattern for PCBs, Hg, and MeHg. Concentrations for each of the pollutants decreased with soil depth, with a few exceptions (Figs. 5–7). Horizontally within the unit, each of the pollutants measured were found in higher

![Fig. 3. Microparticle composition of inlet samples (n = 3 storms).](image)

![Fig. 4. Anthropogenic microparticle reductions during three separate storm events in 2017.](image)
concentrations nearest the inlets [except at the 50–100 mm depth for PCBs, where the concentrations are equivalent (Figs. 5–7)]. In particular, PCBs accumulated heavily in the top 50-mm layer near the inlets, with concentrations more than 10 times greater than in the top layer of the rest of the unit (the body), as well as the deeper media layers. Mercury and MeHg had slightly higher concentrations near the inlets, but the difference was less pronounced. This suggests that Hg and MeHg are not settling out as quickly once they enter the bioretention rain garden unit, and are therefore distributing more evenly across the surface.

The vertical distribution of pollutant capture across a small number of other field studies has a similar trend to that seen for the El Cerrito bioretention rain garden. For example, Komlos and Traver (2012) found that orthophosphate concentrations were highest on the surface layer, decreased with depth from 0- to 100 mm, and then were relatively constant from a depth of 100–300 mm. Dechesne et al. (2005) found that in four infiltration systems ranging between 10 and 21 years old, heavy-metal accumulation was greatest at the surface and decreased rapidly from the surface down to a depth of 300–400 mm. Li and Davis (2008) collected 900-mm cores and analyzed them for Cu, Pb, and Zn 3.5 and 4.5 years after construction of a bioretention unit, and also found high surface accumulations in the top 200 mm. Thus, based on published work to date and the El Cerrito study, pollutant capture is dominant in the top layers of the soil profile and decreases rapidly with increasing depth.

Using the composite concentration data from this study and the soil mass in the unit, total pollutant mass in each depth interval of the soil profile was estimated (Fig. 8). A greater proportion of the overall Hg and MeHg mass is present in the lower soil depths than for PCBs (Fig. 8). In light of the PCB and Hg fractionation data collected by Geosyntec Consultants and EOA Inc. (described in the “Mercury Species” section), these findings are all consistent with the conceptual model that PCBs in stormwater influent are attached to larger particles in greater proportions than are the Hg species, and therefore deposit more immediately nearer the inlets and are more likely to be filtered on the surface with less downward mobility than Hg and MeHg. The findings also suggest that filtration at the surface is likely one of the most important pollutant capture mechanisms for PCBs. Filtration also likely plays a role for Hg capture, but sorption in the lower layers may also be important.

### Management Implications

Several implications for stormwater management can be drawn from these results. This study shows that a bioretention rain garden can effectively capture PCBs and microplastics and is somewhat less effective in capturing both Cu and Hg species. The lesser performance for Cu and Hg species is likely due to a greater proportion in the dissolved phase and on particles smaller than 10 μm.

With respect to long-term maintenance, the pollutant accumulation in green infrastructure units may need to be addressed. Several studies have reported the challenge with surface clogging leading to the decline in infiltration rate (e.g., Hatt et al. 2008). In addition to clogging, there are two primary triggers for soil-replacement maintenance due to pollutant accumulation: (1) pollutant saturation in the soil, leading to the unit becoming a source of export to the downstream environment; and (2) pollutant accumulation in the surface layer that exceeds regulatory limits for health and safety. After seven wet seasons, the surface accumulation of Hg and MeHg was low relative to EPA screening concentrations (EPA 2017) that could trigger the need for replacement, but PCBs had exceeded the screening concentration for residential and industrial soils near the inlets (Table 2).

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Surface concentrations of PCBs in the main body of the bioretention unit were only slightly less than the screening concentration for residential soils, but more than four times lower than the industrial screening concentration. It is unclear whether the standards for residential or industrial soils would apply; this unit is located in a commercial area on a high-traffic road with moderate pedestrian traffic. Assuming that the pollutants accumulate at a constant rate, which may not be the case, if the unit were held to the residential screening concentrations, it appears that buildup in the inlet surface areas may exceed such concentrations in just 1 year and the surface of the entire unit would reach an average residential screening level concentration in about 8 years. In contrast, if the unit were to be held to the industrial screening concentrations, the inlet surface areas would be expected to reach concentrations of concern in about 2 years, and the surface of the entire unit would reach an average industrial screening concentration in about 31 years.

In this unit alone, replacing the top 50 mm of soil equates to a soil volume of 0.3 m³, which is inconsequential for the single unit. However, in the case of the San Francisco Bay region, stormwater managers are charged with meeting a TMDL calling for a 90% decrease in PCB loads to the Bay and are planning that, by 2040, green infrastructure will capture 3 kg of PCBs annually (CRWQCB, San Francisco Bay Region 2015). Assuming soil replacement is triggered at PCB surface soil concentrations of 1 mg/kg (the screening concentration for industrial soils) and 45% of PCB loads captured reside in the surface soils, then for every kilogram of PCBs captured, 450 t of soil would need replacement annually (or 1,350 t annually of soil when capturing 3 kg annually).

This estimate assumes the same soil profile distribution and rate of accumulation as occurred in the El Cerrito bioretention unit over the 7 years leading up to this study and does not take into account potential degradation or volatilization of the surface layer PCBs. The total of 1,350 t of soil is neither trivial nor insurmountable, but it is something to plan for. However, the residential and industrial screening levels are well below the Department of Toxic Substance Control’s (DTSC’s) (the relevant state agency) classification of hazardous waste for PCBs (≥50 mg/kg, DTSC Title 22 CCR 66261.24); therefore, no special disposal would be required. In addition, however, DTSC’s classification for Hg hazardous waste is 20 mg/kg, which is below the industrial soil screening level, and this should be considered when developing maintenance schedules. Other options besides soil replacement may include adding fresh soil on top of the exposed surface layer, soil wet sieving, or bioremediation. These questions and management options should be explored in further studies as the San Francisco Bay Area gears up to implement bioretention as a major management tool for meeting TMDL targets.

The findings in this study support the use of bioretention as a management option for meeting load reductions required by water quality regulation. PCBs and SSC were well captured (≥90%) by the bioretention rain garden, whereas Cu and Hg were moderately well captured (37%–68%), likely because they were present in greater proportions in the dissolved phase or on finer particles, although additional study should be done to test that hypothesis. Methylmercury reduction performance was moderate, likely due to proper drainage design and implementation, an encouraging finding for stormwater managers. Anthropogenic microparticles, including microplastics, were also well captured by the bioretention rain garden (91% reduction on average), decreasing the concentrations from 1.6 particles/L to 0.16 particles/L.

Similar to other soil profile studies, PCBs, Hg, and MeHg were all present at the highest concentrations in the top 100 mm in the surface media layers. PCBs deposited nearest the inlet to the unit, whereas Hg was dispersed further from the inlet, indicating a slower settling rate consistent with its presence on finer particles. These findings are important for managers to understand how frequently soil maintenance is required, especially since green infrastructure is intended for PCB capture, and in this unit the trigger for industrial soils had already been met for the surface layer near the inlet. This study highlights the importance of the surface layer for capturing PCBs and Hg species and provides useful data for supporting decisions about media replacement and overall maintenance schedules.

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Supplemental Data

Figs. S1–S3 and Tables S1–S3 are available online in the ASCE Library (www.ascelibrary.org).

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