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SFEI Contribution #872

Suggested Citation:

Gilbreath A., L. McKee, I. Shimabuku, D. Lin, L. M. Werbowski, X. Zhu, J. Grbic, and C. Rochman. 2019. Multi-year water quality performance and mass accumulation of PCBs, mercury, methylmercury, copper and microplastics in a bioretention rain garden. SFEI Contribution #872. San Francisco Estuary Institute, Richmond, CA.

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## Abstract

A multi-year water quality performance study of a bioretention rain garden located along a major urban transit corridor was conducted to assess the efficacy of rain gardens to remove a variety of pollutants. Polychlorinated biphenyls and suspended sediment concentrations were reduced (>90%), whereas total mercury, methylmercury, and copper were only 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. 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.

## 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 receives no treatment prior to being discharged to the Bay. The local water quality control agency has adopted total maximum daily load (TMDL) clean-up plans for polychlorinated biphenyls (PCBs) and mercury (Hg) (Davis et al., 2007; Davis et al., 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). As municipalities strive to reach these stormwater wasteload allocations, green infrastructure such as 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, as well as the annual maintenance that is needed to sustain human health standards in these pollutant-accumulating structures.

Increasingly, studies from around the world 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., 2009; Hunt et al., 2006). These studies have primarily measured nutrients, trace metals and, to a lesser degree, trace organic contaminants. Studies to-date have indicated relatively good removal of Cu ranging between 40-100% capture efficiency, with effluent concentrations generally  $<10 \mu\text{g/L}$  (Davis et al. 2003; Davis 2007; Hunt et al. 2008; Hatt et al. 2009; Li and Davis 2009, David et al. 2015). In contrast, only one published study by David et al. (2015) measured 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 in Daly City (also located in the San Francisco Bay region). In that study, PCBs ranged from 180 - 1,300 (mean 730)  $\text{pg/L}$  pre-construction, and post-construction from 190 - 870 (mean 410)  $\text{pg/L}$ . Although post-construction concentrations decreased, the pre- and post-construction concentrations were two orders of magnitude lower than mean concentrations observed in other stormwater locations in the Bay Area (Gilbreath et al., 2015: 14,500  $\text{pg/L}$ ; McKee et al., 2017: 13,000  $\text{pg/L}$ ). David et al. (2015) also monitored for Hg and found post-construction concentrations were reduced by 18% down to concentrations of 18  $\text{ng/L}$ , but this is only marginally less than the mean observed in other untreated Bay Area urban drainage systems (29  $\text{ng/L}$ ; McKee et al., 2015). 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 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 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; Klosterhaus et al., 2014). 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. David et al. (2015) reported favorable performance for PCB reduction, but since the runoff came from a recently redeveloped parking lot, concentrations were low relative to concentrations more commonly measured in flows from the older urban areas in the region. It is in these areas where managers could focus green infrastructure efforts to make the greatest progress towards 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 performance so that Hg load reduction estimates can be generated with enough confidence for TMDL compliance. In the one study reporting on Hg performance, David et al. (2015) measured reduced concentrations after bioretention was implemented, but, complicating the performance results, the authors reported increased concentrations for total methylmercury (MeHg). The authors attributed the elevated MeHg to the anaerobic conditions caused by the incorrect installation of the subdrain, which led to an environment conducive to microbial methylation. Given that MeHg is the bioavailable form of Hg, the results from this single case study may contraindicate the use of bioretention for improving overall stormwater quality. Additional study is needed to understand the dynamics of Hg species generation or capture in bioretention and net performance.

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/km<sup>2</sup> in the first investigation of microplastics in San Francisco Bay, a result that appears greater than levels previously observed in other urban, North American water bodies (Eriksen et al. 2013; Yonkos et al. 2014). 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, the authors 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. In 2014, Yonkos et al. 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.

In addition to questions about the capability of bioretention 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 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). Verifying 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 multi-year water quality performance study on a bioretention rain garden for rarely studied PCBs, Hg species, and microplastics, in addition to copper, a more commonly studied pollutant.

## **Materials and Methods**

### **Site design and drainage management area**

A bioretention cell located along a roadway with heavy car and foot traffic in El Cerrito, CA was monitored (Figure 1). The cell is rectangular (3.7 by 1.7 m) and planted with native drought-tolerant species. Bioretention media in the cell included a 0.46 m layer of engineered soil mix comprised of 70% sandy loam, 10% clay, and 20% composited organic matter (minimum infiltration rate 12.7 cm/hr) sitting directly atop the native soil. Native soil at the site is typed hydrologic soil group D with high clay content. This native soil type has an infiltration rate between 0 and 1.3 mm/hr, and therefore installation of an underdrain was required. An underdrain is embedded in 1.3 cm drain rock and installed directly below the engineered media. The depth of the space where ponding on the surface is enabled is 0.28 m. Some amount of stormwater volume is reduced by vegetation interception, evapotranspiration and infiltration, but predominantly the stormwater that enters the bioretention unit discharges to the main stormdrain conveyance system after filtration.



**Figure 1.** Map of the watershed area draining to the El Cerrito Rain Gardens. The upper watershed (green, 4080 m<sup>2</sup>) drains to the monitored cell. The lower watershed (blue) drains to the other rain garden cells, which also receive overflow and bypass from the monitored cell. The monitored cell and adjacent cell drain to a common subdrain.

Construction of the bioretention cell was completed in the fall of 2010. During installation, regular inspections were made by city engineers and the authors to verify 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.

The drainage management area consists of 4,080 m<sup>2</sup> (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 - 1965 (overlapping with the PCB and Hg peak usage periods), and the drainage area includes two older style electrical transformers attached to electrical poles that may contain PCB residues.

### **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 clean sampling protocols and peristaltic pumps fitted with trace-clean tubing (laboratory-cleaned Teflon 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 pre-cleaned, "SingleSample" Disposable Groundwater 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 standard methods were chosen to ensure high quality repeatable data could be delivered in relation to expected field conditions and needed detection limits (Table 1).

**Table 1.** Analyte and matrix, laboratory, and analytical methods for studied constituents in water and soil for water years 2012 and 2017. The method description provides further detail on sample processing.

Analysis	Analyzing Laboratory	Method	Analytical Method Description
Suspended Sediment Concentration (SSC): water	Graham Matthews and Associates, California	ASTM D3977	Samples were filtered through pre-weighed glass fiber filters. The sample containers were rinsed with deionized water to remove adsorbed particles and the filters were rinsed with 3 ml of water to remove entrapped dissolved solids. Filters were dried overnight at 103°C and re-weighed. This filtration and drying method was similar to Standard Methods 2540 D for total suspended solids (TSS), except that it avoids subsample variability by filtering the entire volume.
PCBs: water, soil	AXYS Analytical Services Ltd., British Columbia, Canada	EPA 1668 Rev A (40 congeners)	Samples were analyzed for 40 PCB congeners (PCB-8, PCB-18, PCB-28, PCB-31, PCB-33, PCB-44, PCB-49, PCB-52, PCB-56, PCB-60, PCB-66, PCB-70, PCB-74, PCB-87, PCB-95, PCB-97, PCB-99, PCB-101, PCB-105, PCB-110, PCB-118, PCB-128, PCB-132, PCB-138, PCB-141, PCB-149, PCB-151, PCB-153, PCB-156, PCB-158, PCB-170, PCB-174, PCB-177, PCB-180, PCB-183, PCB-187, PCB-194, PCB-195, PCB-201, PCB-203) using a high-resolution mass spectrometer coupled with a high-resolution gas chromatograph equipped with a SPB-Octyl chromatography column (30 m, 0.25 mm i.d., 0.25 µm film thickness). Soil samples followed the same procedure except the sample was first extracted in a Soxhlet/Dean-Stark extractor and then concentrated for cleanup.
Total Cu: water	Brooks Applied Labs LLC, Washington	EPA 1638	Prior to analysis, the samples were acidified to 1% (v/v) with ultra-pure nitric acid and heated with a closed-vessel digestion for a minimum of six hours in an oven at 85 °C. Analysis was performed by EPA Draft Method 1638 (modified) using inductively coupled plasma - mass spectrometry (ICP-MS). The MS/MSD set was prepared by adding known concentrations of metals to approximately 10-mL aliquot of sample. Instances where the MS/MSD sets were spiked at a concentration less than 25% of the

			native sample result, the recoveries were not reported (NR).
Total Hg (HgT): water, soil; Dissolved Hg (HgD): water	Brooks Applied Labs LLC, Washington	EPA 1631 Rev E	All samples were prepared and analyzed in accordance with EPA Method 1631E. Samples were oxidized with bromine monochloride (BrCl) and then analyzed with stannous chloride (SnCl <sub>2</sub> ) reduction, dual gold amalgamation, and cold vapor atomic fluorescence spectroscopy (CVAFS) detection using a Brooks Rand Instruments MERX-T CVAFS Mercury Automated-Analyzer. The MS/MSD sets were prepared by adding a known concentration of Hg to 25-mL of sample volume. The instrument was calibrated with 6 standards ranging from 10 pg to 10,000 pg (0.10 ng/L to 100 ng/L).
Methyl Hg (MeHg): water, soil	Brooks Applied Labs LLC, Washington	EPA 1630	Water samples were prepared by distillation. Distillates were analyzed by ethylation, Tenax trap collection, gas chromatography separation, isothermal decomposition, and cold vapor fluorescence spectroscopy (CVAFS) detection using a Brooks Rand Instruments MERX-M CVAFS Methylmercury Automated-Analyzer. The MS/MSD sets were prepared by adding a known concentration of MeHg to 50-mL of sample volume. The instrument was calibrated with 7 standards ranging from 0.5 pg to 1,000 pg (0.005 ng/L to 10 ng/L). A slight modification on this method was used for analysis of methylmercury in soils.

### Microplastics sampling and analysis

During three storm events monitored for water quality in WY 2017 (Jan. 3, Feb. 9, March 24), samples for analysis of microplastics were collected at the inlet and outlet. Between each aliquot collected for water quality samples, 20-40 liters of stormwater were pumped and filtered through two stacked sieves (355 µm and 125 µm). After the storm, the microplastics were flushed from the sieves with deionized water into glass containers and shipped to the laboratory (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 µm 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 CaCl<sub>2</sub> 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 using Raman spectroscopy (Horiba Xplora). All particles were also imaged and measured using ImageJ software. For QA/QC, 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 above.

### **Soil core sampling and analysis**

Two composite soil core samples were collected from the bioretention cell in late spring 2017, at which time the cell had received stormwater runoff from seven wet seasons since installation. The composite sampling design aimed to represent two areas of the cell (see diagram in Supplemental Materials). The first composite consisted of homogenized samples from four cores collected in front of the two street inlets to the bioretention 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 bioretention cell (hereafter referred to as the “body” of the bioretention 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 comprised of homogenized sub-samples 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 three minutes, subsampled into sterile glass jars and shipped frozen to the analytical laboratories.

## **Results and Discussion**

### **Storms sampled**

The 11 storms sampled represent a range of moderate sized events for the rain garden location in terms of total rainfall, peak hourly rainfall intensity, and antecedent dry days (Table 2). The total rainfall for each storm ranged from 17 - 50 mm (median = 23 mm). Peak 1-hour rainfall ranged from 3-15 mm. For context, the 1 hour, 1 year return precipitation for this location is about 11.2 mm, and the 1 hour, 2 year return precipitation is about 13.7 mm. Of the 11 storms, the antecedent dry period was 0 days for 4 storms (a day is counted as a rainfall day if 2.5 mm or more of rain had fallen), 1 day for 4 storms, and >1 day for 3 storms. Total rainfall in the previous seven days varied between 0 and 105 mm (median = 17 mm). This bioretention system was designed to drain completely within 6 hours 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 build-up, wash-off pollutants like suspended sediment concentration (SSC), Cu and Hg.

**Table 2.** Total rainfall, peak intensity, and number of antecedent dry days for the water years in which water-quality samples were collected: 2012, 2014-2015, and 2017.

	Sampling Date	Storm Total Rainfall (mm)	Peak Rainfall Intensity (mm/hr)	# Antecedent Dry Days*
WY 2012	1/20/2012	43	13	0
	3/13/2012	37	4.8	11
	3/27/2012	33	15	1
	4/10/2012	20	4.6	9
WY 2014-15	2/26/2014	23	5.8	16
	3/31/2014	17	7.4	1
	12/2/2014	31	6.4	1
WY 2017	12/15/2016	50	11	0
	1/3/2017	20	3.3	0
	2/9/2017	21	5.1	0
	3/24/2017	17	4.6	1

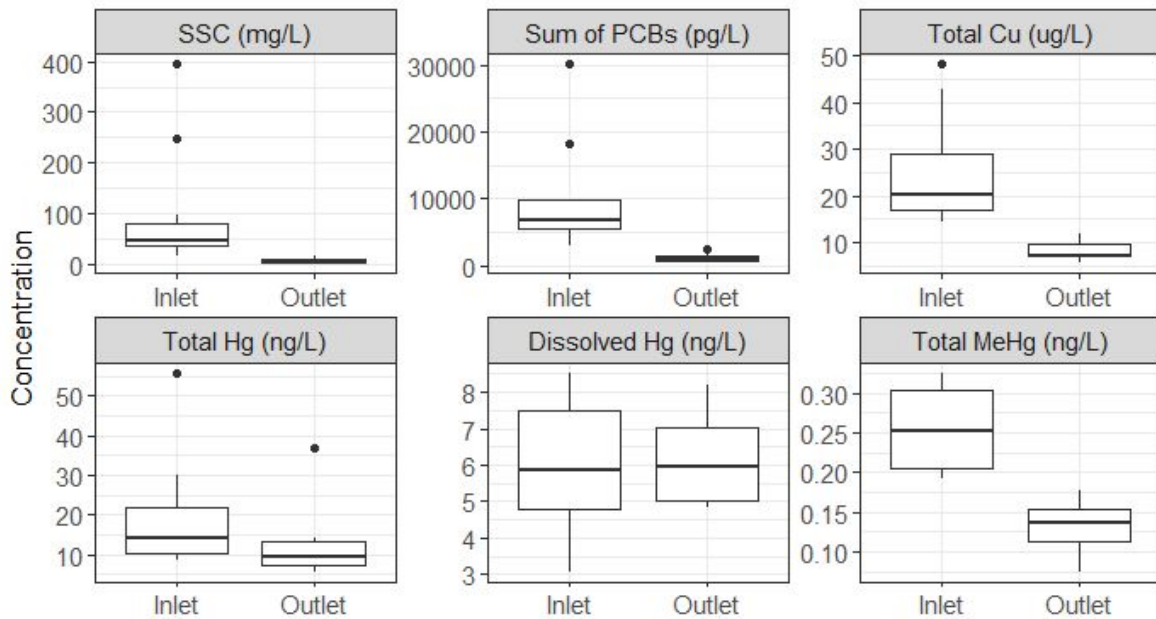
## Water Quality Results

### *Suspended Sediment Concentration (SSC)*

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 - 15.3 mg/L, with a median of 3.6 mg/L (Figure 3, Table 3). The nonparametric Wilcoxon matched-pairs signed-ranks test was used to determine if the differences between the inlet and outlet concentrations were statistically significant. 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 is in the higher end of typical performance. Other studies have reported lesser reductions (e.g., 29%: 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 rain garden

suggests that the garden design prevented most soil media export. A Wilcoxon rank-sum test was used to assess a temporal trend by first comparing inlet concentrations from WY 2012 samples to WY 2017 samples (no significant difference for SSC) and then the outlet concentrations from WY 2012 and WY 2017. The difference in the outlet concentrations between the two time periods was statistically significant (Wilcoxon  $p < 0.05$ ). On a storm by storm basis, the average reduction in SSC changed from 79% in WY 2012, to 86% in WYs 2014-15, to 97% in WY 2017. Despite the garden design preventing most soil media export in all storms measured, the increased removal in SSC over time may be the result of settling and compaction due to system maturation. Jia et al. (2015) also noted a similar trend. In that study, SSC actually increased at the outlet in the first few months after construction, but in the second year of sampling SSC was lower at the outlet relative to the inlet.



**Figure 3.** 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. Note: One inlet PCB sample is not represented on the graph; it is 226,000 pg/L.

**Table 3.** 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.

	N	Inlet				Outlet				Percent Reduction (%) <sup>a</sup>	Wilcoxon <i>p</i>
		Mean	Median	Min	Max	Mean	Median	Min	Max		
SSC (mg/L)	11	95.8	47.2	14.8	395	5.55	3.60	0.330	15.3	94%	<0.05
Sum of PCBs (ng/L)	11	29.7	7.60	3.02	226	1.13	1.00	0.350	2.50	96%	<0.05
Total Cu (ug/L)	8	25.5	20.3	14.5	48.2	8.11	7.03	5.46	11.7	68%	<0.05
Total Hg (ng/L)	11	18.8	14.0	8.57	56.0	11.9	9.39	5.61	36.9	37%	<0.05
Dissolved Hg (ng/L)	7	6.01	5.87	3.07	8.54	6.15	5.95	4.83	8.20	-2%	0.94
Total MeHg (ng/L)	8	0.256	0.252	0.193	0.325	0.132	0.137	0.0750	0.178	49%	<0.05

<sup>a</sup>Based on the mean of all inlet samples versus the mean of all outlet samples.

### *Polychlorinated Biphenyls (PCBs)*

As is typical of urban stormwater during rain events (e.g. David et al., 2015; Gilbreath and McKee, 2015), PCB concentrations at the inlet varied by three orders of magnitude, and in this study, averaged 30,800 pg/L (Table 3). 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).

Indicator congeners in the inlet water samples suggest that the 1254 and 1260 PCB commercial mixture Aroclors dominate the influent stormwater. Aroclor 1254, as indicated by the proportion of PCBs 87, 95, 99, 101, 110 and 118, relative to the other 34 congeners quantified (Frame et al., 1996), was the dominant source signal in the highest inlet concentration sampled in January 2012 (226,000 pg/L). A second PCB source signal for Aroclor 1260 as indicated by the proportion of PCBs 149, 170, 180 and 187 (Frame et al., 1996), dominates the next two highest concentration inlet samples (~30,000 pg/L each). It is interesting that such a small catchment includes two distinct source signals of PCBs, each of which can produce high concentrations in stormwater runoff. The variability in PCB concentrations from storm to storm, and the fact that two sources exist in such a small drainage, provides some insight into the complexity that stormwater managers face when trying to identify and manage sources of PCBs or treat stormwater.

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 - 1,300 (mean 730) pg/L. The post-construction concentrations at Daly City were 190 - 870 (mean 410) pg/L. Although the outlet concentrations at El Cerrito were slightly higher than the post-construction 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 (Figure 3, Table 3). A previous local study (David et al., 2015) showed comparable total Cu reduction (83%). The current study was consistent with David et al. in that reductions were greater for Cu than for Hg species. 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 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 (% 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 that we measured in this study had greater reductions than was 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).

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 greater percentage reduction when the influent is more polluted.

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 which explains the different results; El Cerrito rain garden had a correctly installed subdrain whereas the subdrain was left out of the unit in the David et al. (2014) 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 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 wasteload allocations and are using bioretention as a management practice.

Consistent with the findings from other studies (e.g. Hatt et al. 2009), and with the other analytes in this current study, influent concentrations of all Hg species were more variable than effluent (Figure 3, Table 3). Variability in the influent due to varying storm characteristics (e.g. precipitation intensity, antecedent dry days, etc.) 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 is in the dissolved form. A greater proportion of HgT (than Cu or PCBs) may be in the dissolved form which more easily passes through the bioretention system. Secondly, 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 2014-2015 study at the El Cerrito site lends support to this hypothesis. In one storm event, both the total Hg fraction and the Hg fraction on particles smaller than 10  $\mu\text{m}$  (including dissolved phase Hg) were measured, and the concentration on particles larger than 10  $\mu\text{m}$  was estimated by difference. In the one sample measured, only 27% of the influent HgT mass was on particles larger than 10  $\mu\text{m}$ , as opposed to 66% of PCB mass (Geosyntec Consultants, 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  $\mu\text{m}$ .

Corroborating these findings, a study by Kayhanian et al. (2012) compared 27 samples for particle size distribution between influent and effluent of three different detention basins, and found that the effluent samples contained much higher proportions of the finest size fractions; the larger particles were disproportionately filtered out. The size distribution of particles from highway runoff (a close surrogate for runoff from urban roadways) are disproportionately very fine: particles smaller than 50  $\mu\text{m}$  in diameter account for >70% (by weight) of the TSS in runoff (Vignoles and Herremans, 1995; Roger et al., 1998; Andral et al., 1999; Kayhanian et al., 2008a) and one study reported that particles smaller than 20  $\mu\text{m}$  account for more than 50% of the particulate mass in samples that have TSS concentrations below 100 mg/L. These very fine particles have higher organic content (Kayhanian et al., 2008a, 2015; Lee et al., 2005), higher metal concentrations (Sansalone and Buchberger, 1997; Roger et al., 1998; Morquecho and Pitt, 2003; McKenzie et al., 2008; Kayhanian and Givens, 2011, Kayhanian et al., 2015), and higher surface potential, which creates strong particle-particle repulsion and prevents particles from aggregating into larger particles that would be more effectively filtered out. Consistent with these statements, several studies have reported that particles <10  $\mu\text{m}$  are not well captured in BMPs (Pettersson, 1998; Backstrom, 2002; Han et al., 2005; Li et al., 2006; Backstrom, 2002; Han et al., 2005).

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

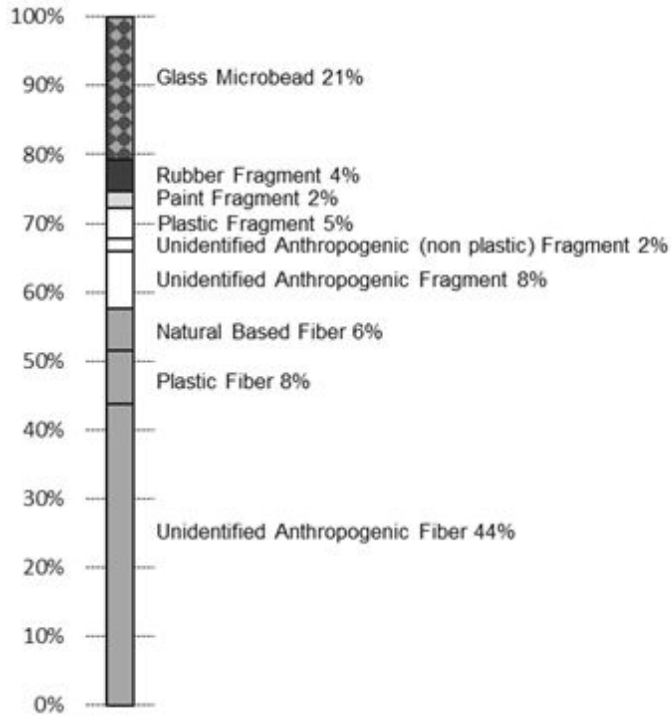
### *Microplastics*

Anthropogenic microparticles included microplastics and also other materials such as glass beads and asphalt fragments. As such, we refer to anthropogenic microparticles, which include microplastics, below. 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 all three inlet samples, the particles comprised 58% fibers from textiles, 15% fragments, 21% glass microbeads, 4% rubber fragments (e.g., tire dust), and 2% paint particles (Figure 4). The microfibers include 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 storm event.

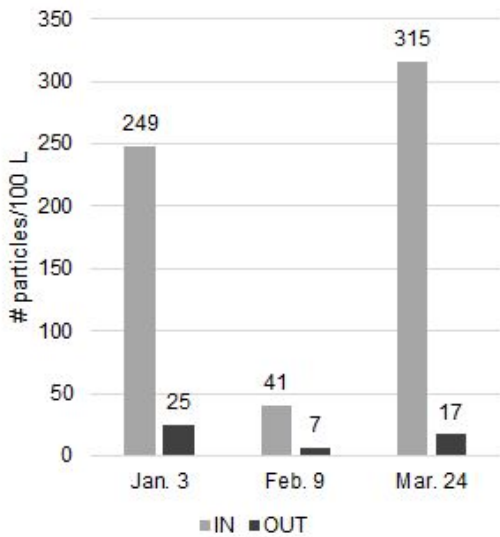
In terms of microparticle contributions to the Bay, stormwater likely plays an important role. The average concentration measured in these stormwater influent samples (1.6 particles/L) is an order of magnitude higher than the average particle concentrations previously measured in wastewater effluent discharged to the Bay (Sutton et al., 2016), 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 4080 m<sup>2</sup> (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 compare particle concentrations to, 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 - 0.032 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 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 rain garden decreased by 83-95% (mean 91%) during the three storms (Figure 5), 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 355-500 μm, and 55% for particles between 125-355 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.



**Figure 4.** Microparticle composition of inlet samples (n=3 storms).



**Figure 5.** Anthropogenic microparticle reductions during three separate storm events in 2017.

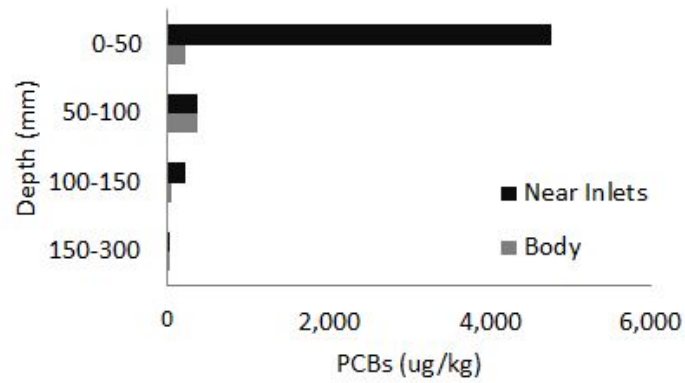
### Soil Profile Results

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 (Figures 4-6). Horizontally

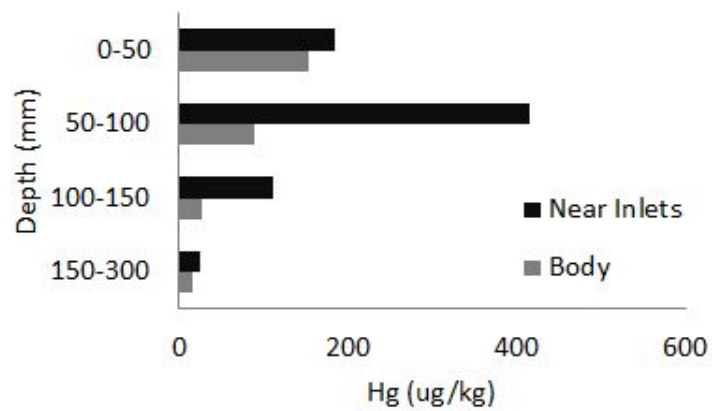
within the unit, each of the pollutants measured are found in higher concentrations nearest the inlets (except at the 50-100 mm depth for PCBs, where the concentrations are equivalent; Figures 6-8). In particular, PCBs accumulated heavily in the top 50 mm layer near the inlets, with concentrations more 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 entering the bioretention 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 as 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 0-100 mm, and then were relatively constant from 100-300 mm deep. 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 in the first 300-400 mm. Li and Davis (2008) collected cores down to a depth of 900 mm and analyzed 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. Consistent across all of these studies, including the El Cerrito bioretention unit study, is that pollutant capture is dominant in the top layers of the soil profile and decreases rapidly with increasing depth.

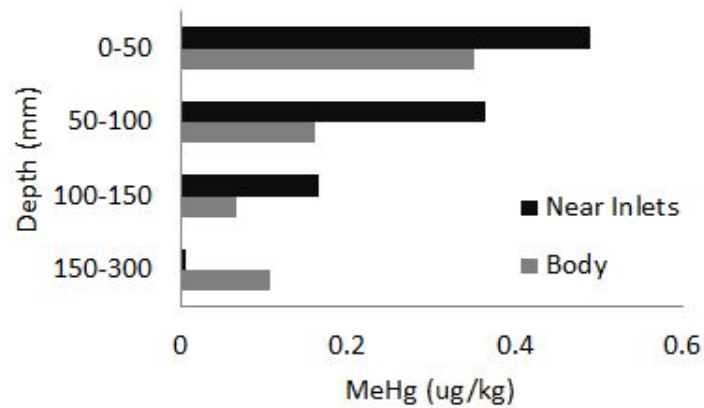
Using the composite concentration data from this study and the soil mass in the unit, total pollutant mass in each depth interval of the soil profile was estimated (Figure 9). A greater proportion of the overall Hg and MeHg mass is present in the lower soil depths than for PCBs (Figure 9). In light of the PCB and Hg fractionation data collected by Geosyntec Consultants (described previously 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 in front of 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.



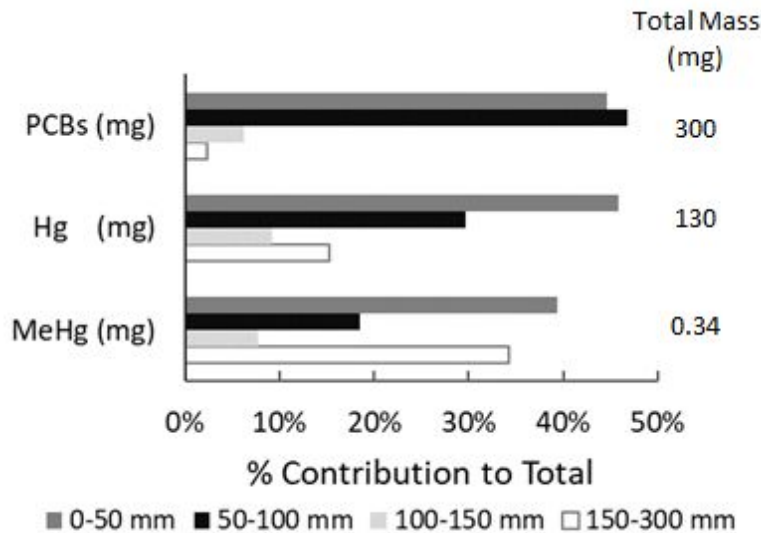
**Figure 6.** Soil PCB concentrations ( $\mu\text{g}/\text{kg}$ ) at various depths (0-300 mm) in the bioretention unit.



**Figure 7.** Soil Hg concentrations ( $\mu\text{g}/\text{kg}$ ) at various depths (0-300 mm) in the bioretention unit.



**Figure 8.** Soil MeHg concentrations ( $\mu\text{g}/\text{kg}$ ) at various depths (0-300 mm) in the bioretention unit.



**Figure 9.** Estimation of mass (mg) of contaminants by depth throughout the entire rain garden (including both the inlets and the main bioretention unit by area).

### Management Implications

Several implications for stormwater management can be drawn from these results. This study shows 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 may possibly be due to the proportion in the dissolved phase and on particles smaller than 10  $\mu\text{m}$ .

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, 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 light 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 4).

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. If the unit were to be held to the residential screening concentrations, it appears that build-up in the inlet surface areas may exceed such concentrations in just one year. In contrast, the surface of the entire unit would reach an average 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 concentration of concern in about 31 years. These estimates all assume that the pollutants accumulate at a constant rate, which may not be the case.

**Table 4.** Comparison between the EPA's screening concentrations (EPA, 2017) of residential and industrial surface soil contaminant concentrations to the concentrations of contaminants in the El Cerrito rain garden's surface and body.

	EPA Screening Levels		Bioretention Media 0-150mm Depth		Bioretention Media 150-300 mm Depth	
	Residential Soil	Industrial Soil	Near Inlet	Throughout Body	Near Inlet	Throughout Body
Mercury (mg/kg)	11	46	0.18	0.15	0.025	0.017
Methyl Mercury (mg/kg)	7.8	120	0.00049	0.00035	0.000007	0.00011
PCBs (mg/kg)	0.23	0.94	4.8	0.21	0.021	0.006

In this unit alone, replacing the top 50 mm of soil equates to only 0.3 m<sup>3</sup> of soil, 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, 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 metric t of soil would need replacement annually (or, 1,350 metric t of soil when capturing 3 kg annually).

These estimates assume 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. Thirteen hundred fifty metric tons of soil is neither trivial nor insurmountable, but it is something to plan for. However, note that the residential and industrial screening levels are well-below the Department of Toxic Substance Control's (DTSC; the relevant state agency) classification of hazardous waste for PCBs ( $\geq 50$  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 one major management tool for meeting TMDL targets.

## **Conclusions**

The findings in this study support the use of bioretention as one 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, Hg and MeHg were moderately well-captured (37 - 68%), likely because they were present in greater portions in the dissolved phase or on finer particles. 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 down 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.

## **Acknowledgements**

Funding was provided by the California Department of Water Resources via Proposition 84. Support and oversight for this study was provided by the San Francisco Estuary Partnership. We acknowledge the work of Geosyntec Consultants (funded by an EPA grant to the Bay Area Stormwater Management Agencies Association Clean Watersheds for a Clean Bay project) in collecting and analyzing data from the WYs 2014-15 sampling effort. The authors would like to acknowledge the City of El Cerrito for their cooperation and collaboration in this study. Internal



and external review comments from Josh Bradt, Luisa Valliela, Margaret Sedlak, Phil Trowbridge, and Rebecca Sutton greatly strengthened the resulting publication.

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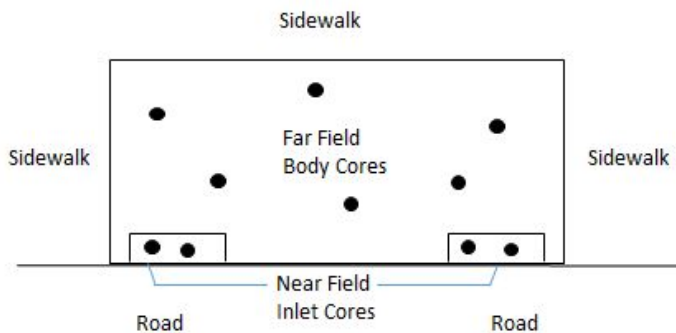
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## Supplemental Data



**Figure 2.** Diagram (approximately to-scale) illustrating near and far field samples on the horizontal surface plane of the bioretention rain garden.

### Quality Assurance

This section presents the QA data for WYs 2012 and 2017 only (the years for which the authors collected the data). All data were subjected to quality assurance/quality control (QA/QC) procedures prescribed by the Regional Monitoring Program (RMP) for Water Quality (Yee et al., 2017). Quality control for SSC was assessed by the percentage of non-detected samples and the relative standard deviation (RSD) of field replicates. Only one SSC sample from the outlet was below the method detection limit (MDL) of 0.5 mg/L. Laboratory replicates were not possible for SSC as the entire volume was consumed for each analysis. The average RSD of the field replicate samples was 8.5%.

Quality control of PCBs was assessed by the percentage of non-detected samples, detections in blanks, blank spike recoveries and RSDs of field replicates. AXYS Analytical lab reported sample specific detection limits for each analyte determined during the analysis. The sampling methods, including volume choices, extraction and analytical methods, allowed most analytes to be detected in field samples most of the time with some exceptions for the less abundant PCBs (only one out of 16 samples for congeners PCB 049, PCB 060, and PCB 128 were not detected). About one-half of the congeners were detected in the method blank, which resulted in censoring 3% of the data. Precision on field sample replicates was generally good with RSDs less than 16%. There are no certified reference materials (CRMs) for PCBs in water so recoveries were evaluated on blank spikes with errors less than 18%. The sum of PCBs was deemed robust for all sample analyzed.

The PCB data for soils were analyzed using the same method as for water. Method detection limits were sufficient such that all congeners were detected above the MDLs. Again about half of the congeners were detected in the method blank but were not greater than one-third of the concentration of the field samples, and therefore no data were censored. Accuracy was evaluated using the laboratory control samples for PCB 105, PCB 118, and PCB 156, and was generally good with an average percentage error of 12%, 26.5% and 10%, respectively. Precision was evaluated using the laboratory replicate of the field sample. Average RSDs for the congeners measured, ranged from 0.69% to 45%. PCB 008, PCB 018, PCB 028, PCB 031, PCB 033, and PCB 060 all had RSDs between 35 and 45%, which was greater than the 35% target. These congeners combined comprise less than 1% of the sum of PCBs and therefore had negligible impact on the sum of PCBs, and do not affect the interpretations of the data because, as seen in the results section, there are large variations observed in concentrations between cores, as well as vertically in each core profile.

Detection limits for total Cu samples were sufficiently low such that all samples were detected. Field precision in replicate samples was good with an average RSD of 2.4%. Copper concentration in the field blank was approximately three times the MDL, however the lowest field concentration was 17 times greater than the field blank, so contamination associated with any of the field, storage, transportation and sample preparation procedures was minimal. No laboratory blank contamination was observed and RSDs on laboratory replicates averaged 2.2%. Recoveries were good for both CRMs (average recovery was 102%) and matrix spikes (average recovery was 103%).

All Hg and MeHg samples were detected and no laboratory blank contamination was observed, negating the need for blank correcting the results. Field precision was good for Hg, with the average RSD 7%, but for MeHg the average RSD was 37%, and was therefore qualified. The sample is still reported. In general, the field replicate RSDs were larger than typical for stormwater sampling because the field replicate set (set ordered PCBs, SSC, HgT, HgD, MeHg, Cu) was collected sequentially, in time, after the entire parent set was collected. This sequential collection can offset the field replicate from its parent sample by up to 10 minutes, which can lead to substantially different concentrations in flow from such a small drainage area. The average CRM recovery for Hg was 102%, and 110% for methylmercury, both well within the target range (less than 35%). Matrix spike recoveries averaged 98% for Hg and 101% for MeHg.

Total Hg and MeHg were detected in all soil samples with the exception of one MeHg sample. Laboratory precision was good for both Hg and MeHg, with RSDs of 11% and 14%, respectively. CRM recoveries for Hg and MeHg were 101% and 119% respectively, and matrix spike recoveries were 97% and 83% respectively, all within target ranges.

Methods for characterizing microplastic contamination are rapidly evolving and rigorous and standardized quality assurance measures for microplastic sample collection and analysis are an important data gap in the field. As part to the laboratory method development for extracting, enumerating, and characterizing microplastics, lab-prepared model stormwater samples were spiked with microplastic particles with range of sizes, morphologies, and polymers designed to provide the varying levels that might be associated with diverse particles. Table S1 summarizes the recovery for different particle types in model stormwater spikes.

Table S1. Recovery of spiked microplastic particles in model stormwater sample. The model stormwater matrix consisted of water treated with reverse osmosis, to which was added soil and leaf fragments. Replicates 1 and 2 were sieved first using a 500  $\mu\text{m}$ , then subjected to density separation, while Replicates 3 and 4 were subjected to density separation without pre-sieving.

Particle Type	Particle Size	Replicate 1 Recovery	Replicate 2 Recovery	Replicate 3 Recovery	Replicate 4 Recovery
Polyethylene terephthalate fragment (clear/white)	1 mm	4 (40%)	8 (80%)	9 (90%)	10 (100%)
Polystyrene fragment (brown)	2 mm	5 (50%)	7 (70%)	4 (40%)	6 (60%)
Cellulose acetate bead (red)	1 mm	3 (100%)	3 (100%)	3 (100%)	3 (100%)
Polyethylene bead (green)	250-300 micron	10 (100%)	10 (100%)	5 (50%)	9 (90%)
Polyester fiber (red)	3 mm in length	6 (60%)	6 (60%)	1 (10%)	3 (30%)

Two lab method blanks analyzed with the field samples indicated 2 and 3 fibers per sample. Using a 70L sample volume estimate (which is the smallest field sample volume rounded to the nearest 10), this is calculated to be a particle contamination concentration of 4 particles/100 L. Field method blanks were also collected during 2 of the 3 storms. The particle counts in the two field blanks indicated 12 and 13 particles per sample, which was similar to the number of particles counted in the outlet field samples during the same storm, which had particle counts of 13 and 16. Unidentified anthropogenic fibers represented the dominant particle type in the



field blank, method blank, and field samples. Using a 70 L sample volume to calculate the particle concentration would give a 17 - 19 particles/100 L in field blanks.