

# Pollutants of Concern Reconnaissance Monitoring

Final Progress Report  
Water Years 2015 and 2016

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## Preface

Water Years 2015 and 2016 reconnaissance monitoring was completed with funding provided by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). This report is designed to be updated each year until completion of the study. At least two additional water years (2017 and 2018) are planned for this study. The initial full draft report was submitted to BASMAA in February 2017 in support of materials being submitted on or before March 31<sup>st</sup> 2017 in compliance with the Municipal Regional Stormwater Permit (MRP) Order No. R2-2015-0049. Changes were made to that version in response to SPLWG review comments.

## Acknowledgements

We appreciate the support and guidance from members of the Sources, Pathways and Loadings Workgroup of the Regional Monitoring Program for Water Quality in San Francisco Bay. The detailed work plan behind this work was developed through the Small Tributaries Loading Strategy (STLS) Team during a series of meetings in the summer of 2014, with slight modifications made during the summers of 2015 and 2016. Local members on the STLS Team at that time were Arleen Feng (for the Alameda Countywide Clean Water Program), Bonnie de Berry (for the San Mateo Countywide Water Pollution Prevention Program), Lucile Paquette (for the Contra Costa Clean Water Program), Chris Sommers (for the Santa Clara Valley Urban Runoff Pollution Prevention Program), and Richard Looker and Jan O'Hara (for the Regional Water Board). San Francisco Estuary Institute (SFEI) field and logistical support over the first year of the project was provided by Patrick Kim, Carolyn Doehring and Phil Trowbridge, and in the second year of the project by Patrick Kim, Amy Richey and Jennifer Sun. SFEI's data management team is acknowledged for their diligent delivery of quality-assured well-managed data. Over both years of this project this team comprised: Cristina Grosso, Amy Franz, John Ross, Adam Wong and Michael Weaver. Helpful written reviews of this report were provided by members of BASMAA (Arleen Feng (ACCWP), Lisa Sabin (EOA/ SCVURPPP) and Bonnie de Berry (EOA/ SMCWPPP)), and by SPLWG advisors; Dr. Barbara Mahler (USGS, Austin Texas), Dr. Daniel Cain (USGS, Menlo Park), and Dr. Peter Mangarella (Retired, Geosyntec).

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## Executive Summary

The San Francisco Bay mercury (Hg) and polychlorinated biphenyl (PCB) total maximum daily loads (TMDLs) called for implementation of control measures to reduce PCB and Hg loads entering the Bay via stormwater. Subsequently, the San Francisco Bay Regional Water Quality Control Board (Regional Water Board) issued the first combined Municipal Regional Stormwater Permit (MRP). This first MRP contained provisions aimed at improving information on stormwater pollutant loads in selected watersheds (Provision C.8.) and piloted a number of management techniques to reduce PCB and Hg loading to the Bay from smaller urbanized tributaries (Provisions C.11. and C.12.). In November 2015, the Regional Water Board issued the second MRP. “MRP 2.0” places an increased focus on identifying those watersheds, source areas, and source properties that are potentially most polluted and are therefore most likely to be cost effective areas for addressing load reduction requirements through implementation of control measures.

To support this increased focus, a stormwater characterization monitoring program was developed and implemented in water years (WYs) 2015 and 2016. Most of the sites monitored in WYs 2015 and 2016 were in Alameda, Contra Costa, and San Mateo Counties with a few sites in Contra Costa County. At the 37 sampling sites, time-weighted composite water samples collected during one storm event were analyzed for 40 PCB congeners, total Hg (HgT), suspended sediment concentration (SSC), selected trace metals, organic carbon (OC), and grain size. Sampling efficiency was increased by sampling two sites during a single storm that were near enough to one another that alternating between the two sites was safe and rapid. This same design is being implemented in the winter of WY 2017 and 2018 by the RMP, and with funding independent of the RMP efforts, the San Mateo Countywide Water Pollution Prevention Program and the Santa Clara Valley Urban Runoff Pollution Prevention Program are also implementing the design.

During WYs 2015 and 2016, the RMP began piloting a project to explore the use of alternative un-manned “remote” suspended sediment samplers (the Hamlin and Walling tube samplers). These remote samplers are designed to enhance settling and capture of suspended sediment from the water column. At eight of the sampling sites, a second sample was collected in parallel using a Hamlin remote suspended sediment sampler, and at three sites a second sample was collected in parallel using a Walling tube suspended sediment sampler.

Based on this dataset, a number of sites with elevated PCB and Hg concentrations and particle ratios were identified. Total PCB concentrations measured in the composite water samples collected from the 37 sites ranged 192-fold, from 832 to 159,606 pg/L. The four highest ranking sites for PCB whole water concentrations were Industrial Rd Ditch in San Carlos, Outfall at Gilman St. in Berkeley, Ridder Park Dr SD in San Jose, and Outfall to Lower Silver Ck in San Jose. When normalized by SSC to generate particle ratios, the four sites with highest particle ratios were Industrial Rd Ditch in San Carlos (6,139 ng/g), Gull Dr SD in South San Francisco (859 ng/g), Outfall at Gilman St. in Berkeley (794 ng/g), and Outfall to Lower Silver Ck in San Jose (783 ng/g). Particle ratios of this magnitude are among the most extreme examples in the Bay Area. Previous maximum concentrations were measured at Pulgas Pump Station-

South (8,222 ng/g), Santa Fe Channel (1,295 ng/g), Pulgas Pump Station-North (893 ng/g) and Ettie St. Pump Station (759 ng/g).<sup>1</sup>

Total Hg concentrations in composite water samples collected during WYs 2015 and 2016 ranged over 78-fold, from 5.6 to 439 ng/L. The relative variation between PCBs and Hg is consistent with the conceptual models for these substances (Hg having a higher number of initial commercial uses causing greater initial urban dispersion and a larger influence of atmospheric redistribution in the global cycle relative to PCBs). The greatest HgT concentrations were measured at four Alameda County sites: the Outfall at Gilman St. in Berkeley, Line 9-D-1 PS at outfall to Line 9-D in San Leandro, Line 13-A at end of slough in San Leandro, and Line 3A-M at 3A-D in Union City. By particle ratio, the four most highly ranked sites were Outfall at Gilman St. in Berkeley (5.3 µg/g), Meeker Slough in Richmond (1.3 µg/g), Line 3A-M at 3A-D in Union City (1.2 µg/g), and Taylor Way SD in San Carlos (1.2 µg/g). Particle ratios of this magnitude are similar to the upper range of those observed previously (mainly in WY 2011). The ten highest ranking sites for PCBs based on particle ratios only ranked 14<sup>th</sup>, 11<sup>th</sup>, 1<sup>st</sup>, 19<sup>th</sup>, 26<sup>th</sup>, 3<sup>rd</sup>, 13<sup>th</sup>, 22<sup>nd</sup>, 15<sup>th</sup>, and 8<sup>th</sup>, respectively, in relation to HgT particle ratios.

Results from the two remote suspended sediment sampler types used (Walling tube sampler and Hamlin sampler) generally characterized sites similarly to the composite stormwater sampling methods (higher concentrations matching higher and lower matching lower). However, the match appears to be better for PCBs than for Hg and, based on just three samples, the results suggest that the Walling tube sampler performs better than the Hamlin. These results are overall encouraging, but the data that result from remote samplers are overall less versatile in that it cannot be used for estimating loads without estimates of sediment load and are more challenging to use in model calibration applications. Therefore, one option to consider is using remote samplers to do preliminary screening of sites before doing a more thorough sampling of the water column during multiple storms at selected higher priority sites. Further testing is needed to determine the overall reliability and practicality of deploying these remote instruments instead of, or to augment, manual composite stormwater sampling.

Based on data collated from all sampling programs completed by SFEI since WY 2003 on stormwater in the Bay Area and the use of a Spearman Rank correlation analysis, PCB particle ratios positively correlate with impervious cover ( $r_s = 0.52$ ), old industrial land use ( $r_s = 0.55$ ) and HgT ( $r_s = 0.51$ ). PCB particle ratios inversely correlate with watershed area and trace metals, other than Hg, analyzed (As, Cu, Cd, Pb, and Zn). Total Hg particle ratios do not correlate with any of the other trace metals and showed similar but weaker relationships to impervious cover, old industrial land use, and watershed area than did PCBs. In contrast, the trace metals all correlate with one another more generally. Overall, the data collected to date do not support the use of any of the trace metals analyzed as a tracer for either PCB or HgT pollution sources.

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<sup>1</sup> Note, these particle ratios do not all match those reported in McKee et al. (2012) because of the slightly different method of computing the central tendency of the data (see the methods section of this report above) and, in the case of Pulgas Pump Station – South, because of the extensive additional sampling that has occurred since McKee et al. (2012) reported the reconnaissance results from the WY 2011 field season.

Old industrial land use is believed to contain and yield the greatest load of PCBs in the region. Within the 62 sites that have been sampled for PCBs and HgT in stormwater by SFEI during various field sampling efforts since WY 2003, about 29% of the old industrial land use in the region has been sampled to date. The largest proportion of old industrial area sampled so far in each county has occurred in Santa Clara (96% of this land use has been sampled in this county), followed by San Mateo (43%), Alameda (33%), and Contra Costa (4%). The disproportional coverage in Santa Clara County is due to sampling of a number of large watersheds and the prevalence of older industrial areas upstream in the Coyote Creek and Guadalupe River watersheds. Of the remaining areas with older industrial land use yet to be sampled in the region ( $\sim 100 \text{ km}^2$ ), 46% of it lies within 1 km of the Bay and 67% of it is within 2 km of the Bay. These areas are more likely to be tidal, likely to include heavy industrial areas that were historically serviced by rail and ship based transport, and are often very difficult to sample due to a lack of public rights of way. A different sampling strategy may be needed to effectively determine what pollution might be associated with these areas.

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## Introduction

The San Francisco Bay mercury and polychlorinated biphenyl (PCB) total maximum daily load plans (TMDLs) (SFBRWQCB, 2006; 2007) called for implementation of control measures to reduce stormwater PCB loads from about 20 kg to 2 kg by 2030 and to reduce stormwater total mercury (HgT) loads from about 160 kg to 80 kg by 2028 with an interim milestone of 120 kg of Hg by 2018. Subsequently, the San Francisco Bay Regional Water Quality Control Board (Regional Water Board) issued the first combined Municipal Regional Stormwater Permit (MRP) for MS4 phase I stormwater agencies (SFBRWQCB, 2009; 2011(update)). MRP 1.0, as it came to be known, contained a provision that aimed to improve information on stormwater loads for a number of pollutants in selected watersheds (Provision C.8.) and additional provisions specific to Hg and PCBs (Provisions C.11. and C.12.) that called for piloting a number of management techniques to reduce PCB and Hg loads entering the Bay from smaller urbanized tributaries. To help address these information needs, a Small Tributaries Loading Strategy (STLS) was developed that outlined four key management questions (MQs) about loadings and a general plan to address these questions (SFEI, 2009). These questions were developed to be consistent with Provision C.8.e of MRP 1.0 and to link with the Hg and PCB specific provisions.

MQ1. Which Bay tributaries (including stormwater conveyances) contribute most to Bay impairment from pollutants of concern (POCs);

MQ2. What are the annual loads or concentrations of POCs from tributaries to the Bay;

MQ3. What are the decadal-scale loading or concentration trends of POCs from small tributaries to the Bay; and,

MQ4. What are the projected impacts of management actions (including control measures) on tributaries and where should these management actions be implemented to have the greatest beneficial impact.

During the first term of the MRP (2009-15) for MS4 Phase I stormwater permittees<sup>2</sup>, the STLS Team focused the majority of the STLS-budgeted portion of RMP funds on refining pollutant loadings (Provision C.8.e) with some additional but more minor effort on finding and prioritizing potential “high leverage” watersheds and subwatersheds (those with disproportionately high concentrations or loads with connections to sensitive Bay margins). These RMP efforts with additional contract funds from Bay Area Stormwater Management Agencies Association (BASMAA)<sup>3</sup> resulted in the completion of a number of technical products that were consistent with the implementation plans outlined in the PCBs and Hg policy documents. These technical products in rough order of completion included the

1. 2009/2010 study to explore relationships between watershed characteristics (Greenfield et al., 2010) (RMP funds),

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<sup>2</sup> For a full list of permittees, the reader is referred to the individual countywide program websites or the reissued MRP (SFBRWQCB, 2015).

<sup>3</sup> BASMAA is made up of a number of programs which represent Permittees and other local agencies

2. 2009/2010 study to explore optimal sampling design for loads and trends (Melwani et al., 2010) (RMP funds),
3. reconnaissance study in WY 2011 to characterize concentrations during winter storms at 17 locations (McKee et al., 2012) (RMP funds),
4. completion of a number of “pollutant profiles” describing what is known about the sources and release processes for each pollutant (McKee et al., 2014) (BASMAA funds),
5. the development and operation of a loads monitoring program at six fixed station locations for WYs 2012-2014 (Gilbreath et al., 2015a) (BASMAA and RMP funds),
6. completion of a loads monitoring synthesis report (McKee et al., 2015) (RMP funds), and
7. further refinement of geographic information about land uses and source areas of PCBs and Hg and the development of a regional watershed spreadsheet model (2010-present) (Wu et al., 2016; Wu et al., 2017) (BASMAA and RMP funds).

As a result of these efforts (several million dollars of funding spread over six years and a large number of team members), sufficient pollutant data have been collected at sites with discharge measurements to make computations of pollutant loads with varying degrees of certainty at Mallard Island on the Sacramento River and 11 urban sites (McKee et al. 2015, Gilbreath et al. 2015a). In addition, a reasonable calibration of the regional watershed spreadsheet model (RWSM) has been achieved for water, Cu, Hg, and PCBs (Wu et al., 2016; Wu et al., 2017), although we anticipate further improvements with the inclusion of WY 2016 data and further calibration and testing using 2017 RMP funding.

Discussions between BASMAA and the SFBRWQCB regarding the second term of the MRP, and parallel discussions at the October 2013 and May 2014 Sources Pathways and Loadings Workgroup (SPLWG) meetings, highlighted the need for an increasing focus on finding watersheds and land areas within watersheds that have relatively high unit area load production or high particle ratios or sediment pollutant concentrations at scales paralleling management practices (areas as small as subwatersheds, areas of old industrial land use, or source properties). This changed focus was consistent with the management trajectory outlined in the Fact Sheet (MRP Appendix I) issued with the November 2011 revision of the October 2009 MRP (SFBRWQCB, 2009; 2011). The Fact Sheet described a transition from pilot-testing in a few specific locations during the first MRP term to a greater amount of focused implementation in areas where benefits would be most likely to accrue in the second MRP term.

During 2014 and early 2015, the SPLWG and Small Tributaries Loadings Strategy (STLS) Team discussed alternative monitoring designs that could address this focus and settled upon the “reconnaissance design” described in this report. In November 2015, the Regional Water Board issued the second MRP (SFBRWQCB, 2015). “MRP 2.0” places an increased focus on finding high leverage watersheds, source areas, and source properties that are more polluted and located upstream from sensitive Bay margin areas. Specifically, the permit retains the four Management Question foci from MRP 1.0 but adds a new stipulation that effort should be made to identify which sources or watershed source areas provide the greatest opportunities for reductions of mercury and PCBs in urban stormwater runoff. To help support this focus and also refine information addressing other Management Questions, the SPLWG and the STLS local team developed and implemented a stormwater reconnaissance characterization monitoring program in WYs 2015 and 2016. The methods employed were modified from those first proposed at the

October 2004 SPLWG meeting (study proposal #2), discussed again by the workgroup in 2005/06 as an alternative option to a loading study at Zone 4 Line A in Hayward, Alameda County, and implemented for the first time in WY 2011 (McKee et al., 2012). The nimble design implemented during the winter of WYs 2015 and 2016 benefited from lessons learned during the WY 2011 effort and provides data primarily to support identification of potential high leverage areas as part of multiple lines of evidence being considered by the stormwater programs. The data also support improved calibration of the RWSM being developed to estimate regional scale watershed loads. This same design was implemented in the winter of WY 2016 by the San Mateo Countywide Water Pollution Prevention Program and the Santa Clara Valley Urban Runoff Pollution Prevention Program. It is possible that these highly comparable data will be made available in time for the next calibrations of the RWSM planned for early 2017.

In parallel, the STLS team is designing a sampling program for monitoring stormwater loading trends in response to management efforts. Data collected using the reconnaissance characterization sampling design implemented in WYs 2011, 2015, 2016, and 2017 may provide baseline data for identifying concentration or particle ratio trends through time if the trends monitoring design effort provides evidence of suitability for that purpose.

This report summarizes and provides a preliminary interpretation of data collected during WYs 2015 and 2016. The data collected and presented here is contributing to a broader-based effort to identify potential management areas for pollutant reductions. The report was designed to be updated annually and will be updated again in approximately 12 months to include data from WY 2017 that is being collected currently.

## Sampling Methods

### Methods selection

Water Year 2014 saw the conclusion of three years of pollutant loads monitoring at six fixed locations near the Bay margins for suspended sediment, total organic carbon (TOC), PCBs, HgT, total methylmercury (MeHgT), nitrate ( $\text{NO}_3$ ), phosphate ( $\text{PO}_4$ )<sup>4</sup>, and total phosphorus (TP). In addition, a smaller number of samples were gathered at the loading sites to characterize polybrominated diphenyl ether (PBDEs), polycyclic aromatic hydrocarbons (PAHs), toxicity, pyrethroid pesticides, copper (Cu), and selenium (Se) (Gilbreath et al., 2015a). With the increasing focus of management efforts to identify areas of elevated PCBs (and mercury), a new monitoring design was needed to broaden the spatial coverage of information gathering and to allow for relative comparisons of PCB and mercury concentrations across the region. To collect this information, a reconnaissance design was selected. Although there are weaknesses associated with such low-intensity sampling, to characterize sites this type of design is efficient, cost-effective, allows for a larger number of sites monitored, and can be used

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<sup>4</sup> Is also often referred to as dissolved orthophosphate or dissolved reactive phosphorous (DRP) or dissolved inorganic phosphorous (DIP). All these terms are functionally equivalent and refer to a sample that is filtered before analysis and analyzed using the ascorbic acid + molybdate blue reagents.

on a relative scale for identifying drainages with high PCB and mercury concentrations (McKee et al., 2012; SPLWG, May 2014; McKee et al., 2015).

The design implemented in WYs 2015 and 2016 was based on a previous monitoring design (WY 2011) in which multiple sites were visited during one or two storm events and stormwater samples were collected for analysis of a number of POCs. Based on discussions at the May 2014 SPLWG meeting, modifications were made to the WY 2011 design to increase cost effectiveness. At the SPLWG meeting an analysis of previously collected stormwater sample data from both reconnaissance and fixed station monitoring was presented. An analysis of three sampling designs (sampling just 1, 2, or 4 storms, respectively: functionally 4, 8, and 16 discrete samples) showed that, for Guadalupe River at Hwy 101, PCB particle ratios could vary from 45-287 ng/g (1 storm design), 59-257 ng/g (2 storm design), and 74-183 ng/g (4 storm design). Although the Guadalupe River at Hwy 101 represents an extreme example of variability due to smaller storms causing runoff from just the lower and more urbanized part of the watershed versus larger storms causing runoff from the upper, less contaminated areas of the watershed, this analysis was used to illustrate that the number of storms sampled for a given watershed would have had quite a large influence on the resulting particle ratio and the potential relative ranking among sites.

A similar analysis was then presented for the other fixed loads monitoring sites (Pulgas Pump Station-South, Sunnyvale East Channel, North Richmond Pump Station, San Leandro Creek, Zone 4 Line A, and Lower Marsh Creek) to explore the relative ranking based on a random 1-storm composite or 2-storm composite design. This analysis highlighted the potential for a false negative that could occur due to a lower number of sampled storms especially in smaller and more urban watersheds where transport events can be more acute due to less channel storage (e.g. in Sunnyvale East Channel 3 of the 8 storms represented were < 200 ng/g; these three storms would have ranked it only slightly more polluted than San Leandro Creek, Zone 4 Line A or Guadalupe River at Hwy 101). This analysis also further highlighted the trade-off between generating information about water quality at fewer sites with more certainty or at more sites with less certainty. The SPLWG agreed that a 1-storm composite per site design was preferable since the design allows for a site to be revisited if the measured concentrations were lower than expected, either because a low-intensity storm was sampled or because other information suggested that potential sources exist.

In addition to collection of stormwater composites, a pilot study to test remote suspended sediment samplers based on enhanced water column settling was designed and implemented. Four sampler types were considered: single-stage siphon sampler, the CLAM sampler, the Hamlin sampler, and the Walling tube. After SPLWG discussion, the single-stage siphon sampler was dropped from consideration because it allowed for collection of only a single stormwater sample at a single time point, which offers no advantage over collecting a single manual stormwater sample, yet would require more effort and expense to deploy. The CLAM sampler also had some limitations that affect interpretation of the data, primarily the inability to estimate the volume of water passing through the filters and the lack of performance tests in high turbidity environments. The remaining two sampler types (the Hamlin sampler and the Walling tube) were selected for the pilot study based on previous studies showing use of these devices in similar systems (velocities and analytes). However, there was substantial discussion

about how to analyze the samples and how to ensure their comparability to the composite sampling design. To test the comparability of sampling methods, the SPLWG Science Advisors recommended piloting the samplers at 12 locations<sup>5</sup> where manual water composites would be collected in parallel.

## **Watershed physiography and sampling locations**

At the May 2014 SPLWG meeting sample site selection rationale was discussed. The potential site selection rationales fall into four basic categories.

1. Identifying potential high leverage watersheds and subwatersheds (distributed across Phase I permittees):
  - a. Watersheds with suspected high pollution;
  - b. Sites with ongoing or planned management actions;
  - c. Source identification within a larger watershed of known concern (nested sampling design)
2. Sampling strategic large watersheds with USGS gauges to provide first-order loading estimates and to support calibration of the RWSM
3. Validating unexpected low (potential false negative) concentrations (to address the possibility of a single storm composite poorly characterizing a sampling location)
4. Filling gaps along environmental gradients or source areas (to support the RWSM)

It was agreed that the majority of samples each year (60-70% of the effort) would be dedicated to identifying potential high leverage watersheds and subwatersheds. The remaining resources would be allocated to addressing the other three rationales. To address this focus, SFEI worked with the respective Countywide Clean Water Programs to identify priority drainages for monitoring including storm drains, ditches/culverts, tidally influenced areas, and natural areas. A large number of sites was visited during the summers of 2014 and 2015. Each site was surveyed for safety, logistical constraints, and feasible drainage-line entry points. From this larger set, a final set of about 25 sites were selected each year to form the pool from which field staff would select sampling locations each storm depending on logistics. Of these 25 sites each year, 20 and 17 sites were sampled in WYs 2015 and 2016 respectively (Figure 1; Table 1). The remaining unsampled sites were carried over for possible sampling in WY 2017.

Watershed sites with a wide variety of characteristics were sampled in WYs 2015 and 2016 (Figure 1 and Table 1). Fourteen sites were sampled in Santa Clara County, 13 sites in San Mateo County, nine sites in Alameda County, and just one site in Contra Costa County<sup>6</sup>. The watershed area upstream from each

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<sup>5</sup> Note that in WYs 2015 and 2016 combined, only 8 and 3 locations could be sampled with the Hamlin and Walling samplers, respectively, due to climatic constraints. Five samples using the Walling sampler samples are planned for WY 2017.

<sup>6</sup> This represents a large data gap given the long history of industrial zoning along much of the CCC waterfront. Two additional sites in the county had been identified for WY 2015 but were not sampled because they are tidally influenced with only short sampling windows. Storms in WY 2015 did not align with these short windows.

sampling location ranged from 0.11 km<sup>2</sup> to 17.5 km<sup>2</sup> and typically was characterized by a high degree of imperviousness (21%-88%: mean = 72%). The percentage of the watersheds designated as old industrial<sup>7</sup> ranged from 0% to 79% (mean 29%). Although the sites were primarily selected to address the first site-selection rationale (identifying potential high leverage watersheds and subwatersheds), Lower Penitencia Creek is an example of a site that warranted resampling because concentrations measured previously were unexpectedly low. The wide variety of imperviousness and industrial characteristics of these watersheds will help to broaden the gradient of watershed characteristics, supporting an improved calibration of the RWSM (Wu et al., 2016; 2017). Although a matrix of site characteristics for sampling strategic larger watersheds was also developed (Table 2), none of these could be sampled during WYs 2015 or 2016 because sampling trigger criteria for rainfall and flow were not met.

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<sup>7</sup> Note the definition of “old Industrial” land use used here is based on definitions developed by the Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP) building on GIS development work completed during the development of the RWSM (Wu et al., 2016; 2017).

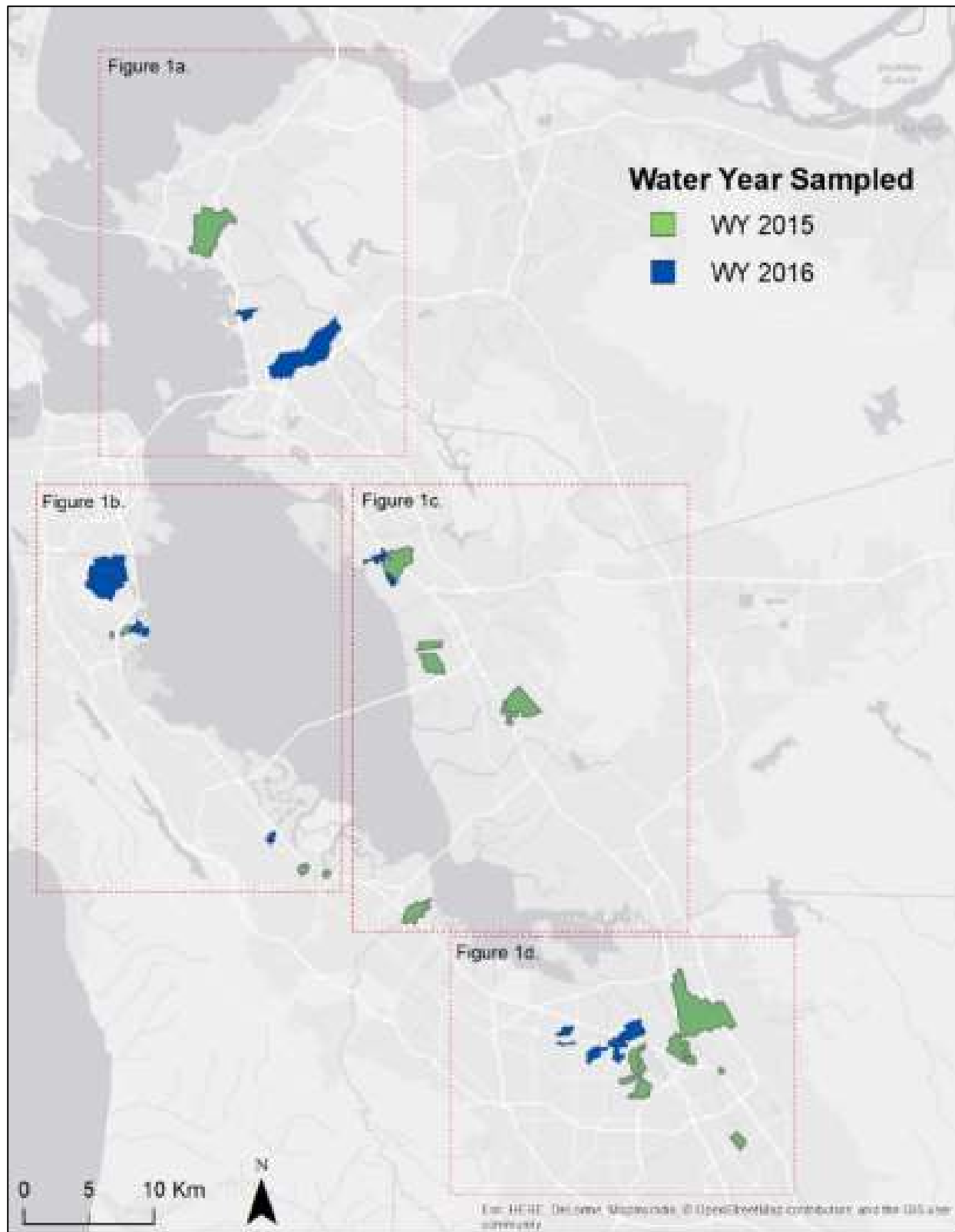


Figure 1. Watersheds sampled in water years 2015 and 2016 (shown in green and blue).



Figure 1a. Sampling locations (marked by the dots) and watershed boundaries (shown in green (water year 2015) and blue (water year 2016)) in northern Alameda and Contra Costa Counties.





Figure 1b. Sampling locations (marked by dots) and watershed boundaries (shown in green (water year 2015) and blue (water year 2016)) in central and northern San Mateo County.



Figure 1c. Sampling locations (marked by dots) and watershed boundaries (shown in green (water year 2015) and blue (water year 2016)) in southern Alameda and San Mateo Counties.

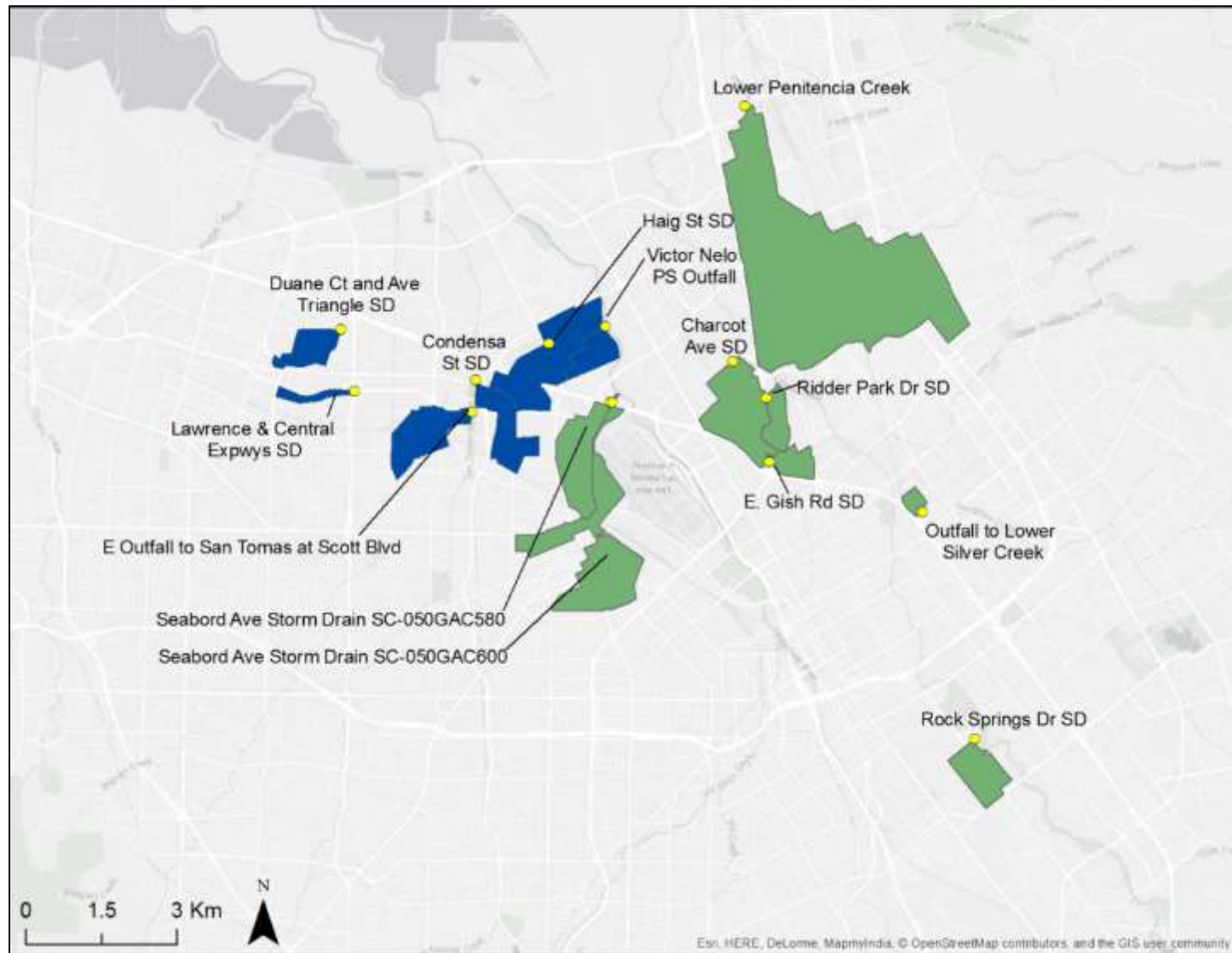


Figure 1d. Sampling locations (marked by dots) and watershed boundaries (shown in green (water year 2015) and blue (water year 2016)) in Santa Clara County.

Table 1. Key characteristics of water years 2015 and 2016 sampling locations.

County	City	Watershed name	Catchment Code	Latitude	Longitude	Sample Date	Area (sq km)	Impervious cover (%)	Old industrial (%)
Alameda	Union City	Line 3A-M-1 at Industrial PS	AC-Line 3A-M-1	37.61893	-122.05949	12/11/14	3.44	78%	26%
Alameda	Union City	Line 3A-M at 3A-D	AC-Line 3A-M	37.61285	-122.06629	12/11/14	0.88	73%	12%
Alameda	Hayward	Line 4-B-1	AC-Line 4-B-1	37.64752	-122.14362	12/16/14	0.96	85%	28%
Alameda	Hayward	Line 4-E	AC-Line 4-E	37.64415	-122.14127	12/16/14	2.00	81%	27%
Alameda	San Leandro	Line 9-D	AC-Line 9-D	37.69383	-122.16248	4/7/15	3.59	78%	46%
Alameda	San Leandro	Line 9-D-1 PS at outfall to Line 9-D	AC-2016-15	37.69168	-122.16679	1/5/16	0.48	88%	62%
Alameda	Berkeley	Outfall at Gilman St.	AC-2016-1	37.87761	-122.30984	12/21/15	0.84	76%	32%
Alameda	Emeryville	Zone 12 Line A under Temescal Ck Park	AC-2016-3	37.83450	-122.29159	1/6/16	17.47	30%	4%
Alameda	San Leandro	Line 13-A at end of slough	AC-2016-14	37.70497	-122.19137	3/10/16	0.83	84%	68%
Contra Costa	Richmond	Meeker Slough	Meeker Slough	37.91786	-122.33838	12/3/14	7.34	64%	6%
San Mateo	Redwood City	Oddstad PS	SM-267	37.49172	-122.21886	12/2/14	0.28	74%	11%
San Mateo	Redwood City	Veterans PS	SM-337	37.49723	-122.23693	12/15/14	0.52	67%	7%
San Mateo	South San Francisco	Gateway Ave SD	SM-293	37.65244	-122.40257	2/6/15	0.36	69%	52%
San Mateo	South San Francisco	South Linden PS	SM-306	37.65018	-122.41127	2/6/15	0.14	83%	22%
San Mateo	East Palo Alto	Runnymede Ditch	SM-70	37.46883	-122.12701	2/6/15	2.05	53%	2%
San Mateo	East Palo Alto	SD near Cooley Landing	SM-72	37.47492	-122.12640	2/6/15	0.11	73%	39%
San Mateo	South San Francisco	Forbes Blvd Outfall	SM-319	37.65889	-122.37996	3/5/16	0.40	79%	0%
San Mateo	South San Francisco	Gull Dr Outfall	SM-315	37.66033	-122.38502	3/5/16	0.43	75%	42%
San Mateo	South San Francisco	Gull Dr SD	SM-314	37.66033	-122.38510	3/5/16	0.30	78%	54%
San Mateo	Brisbane	Tunnel Ave Ditch	SM-350/368/more	37.69490	-122.39946	3/5/16	3.02	47%	8%
San Mateo	Brisbane	Valley Dr SD	SM-17	37.68694	-122.40215	3/5/16	5.22	21%	7%
San Mateo	San Carlos	Industrial Rd Ditch	SM-75	37.51831	-122.26371	3/11/16	0.23	85%	79%
San Mateo	San Carlos	Taylor Way SD	SM-32	37.51320	-122.26466	3/11/16	0.27	67%	11%
Santa Clara	Milpitas	Lower Penitencia Ck	Lower Penitencia	37.42985	-121.90913	12/11/14	11.50	65%	2%
Santa Clara	Santa Clara	Seaboard Ave SD	SC-	37.37637	-121.93793	12/11/14	1.35	81%	68%

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County	City	Watershed name	Catchment Code	Latitude	Longitude	Sample Date	Area (sq km)	Impervious cover (%)	Old industrial (%)
Clara	Clara	SC-050GAC580	050GAC580						
Santa Clara	Santa Clara	Seaboard Ave SD SC-050GAC600	SC-050GAC600	37.37636	-121.93767	12/11/14	2.80	62%	18%
Santa Clara	San Jose	E. Gish Rd SD	SC-066GAC550	37.36632	-121.90203	12/11/14	0.44	84%	71%
Santa Clara	San Jose	Ridder Park Dr SD	SC-051CTC400	37.37784	-121.90302	12/15/14	0.50	72%	57%
Santa Clara	San Jose	Outfall to Lower Silver Ck	SC-067SCL080	37.35789	-121.86741	2/6/15	0.17	79%	78%
Santa Clara	San Jose	Rock Springs Dr SD	SC-084CTC625	37.31751	-121.85459	2/6/15	0.83	80%	10%
Santa Clara	San Jose	Charcot Ave SD	SC-051CTC275	37.38413	-121.91076	4/7/15	1.79	79%	25%
Santa Clara	Santa Clara	Duane Ct and Ave Triangle SD	SC-049CZC200	37.38852	-121.99901	12/13/15 and 1/6/16	1.00	79%	23%
Santa Clara	Santa Clara	Lawrence & Central Expwys SD	SC-049CZC800	37.37742	-121.99566	1/6/16	1.20	66%	1%
Santa Clara	Santa Clara	Condensa St SD	SC-049STA710	37.37426	-121.96918	1/19/16	0.24	70%	32%
Santa Clara	San Jose	Victor Nelo PS Outfall	SC-050GAC190	37.38991	-121.93952	1/19/16	0.58	87%	4%
Santa Clara	Santa Clara	E Outfall to San Tomas at Scott Blvd	SC-049STA550	37.37991	-121.96842	3/6/16	0.67	66%	31%
Santa Clara	San Jose	Haig St SD	SC-050GAC030	37.38664	-121.95223	3/6/16	2.12	72%	10%

Table 2. Characteristics of larger watersheds to be monitored, proposed sampling location, and proposed sampling trigger criteria. None of these watersheds were sampled during water years 2015 or 2016 because sampling trigger criteria for flow and rainfall were not met.

Proposed sampling location							Relevant USGS gauge for 1st order loads computations	
Watershed system	Watershed area (sq km)	Impervious surface (%)	Industrial (%)	Sampling objective	Commentary	Proposed sampling triggers	Gauge number	Area at USGS gauge (sq km)
Alameda Creek at EBRPD Bridge at Quarry Lakes	913	8.5	2.3	2, 4	Operating flow and sediment gauge at Niles just upstream will allow the computation of 1st order loads to support the calibration of the RWSM for a large, urbanizing type watershed.	7" of antecedent rainfall in Livermore (reliable web published rain gauge), after at least an annual storm has already occurred (~2000 cfs at the Niles gauge), and a decent forecast for the East Bay interior valley's (2-3" over 12 hrs).	11179000	906
Dry Creek at Arizona Street (purposely downstream from historic industrial influences)	25.3	3.5	0.3	2, 4	Operating flow gauge at Union City just upstream will allow the computation of 1st order loads to support the calibration of the RWSM for mostly undeveloped land use type watersheds.	7" of antecedent rainfall in Union City, after at least a common annual storm has already occurred (~200 cfs at the Union City gauge), and a decent forecast for the East Bay Hills (2-3" over 12 hrs).	11180500	24.3
San Francisquito Creek at University Avenue (as far down as possible to capture urban influence upstream from tide)	81.8	11.9	0.5	2, 4	Operating flow gauge at Stanford upstream will allow the computation of 1st order loads to support the calibration of the RWSM for larger mixed land use type watersheds. Sample pair with Matadero Ck.	7" of antecedent rainfall in Palo Alto, after at least a common annual storm has already occurred (~1000 cfs at the Stanford gauge), and a decent forecast for the Peninsula Hills (3-4" over 12 hrs).	11164500	61.1
Matadero Creek at Waverly Street (purposely downstream from the railroad)	25.3	22.4	3.7	2, 4	Operating flow gauge at Palo Alto upstream will allow the computation of 1st order loads to support the calibration of the RWSM for mixed land use type watersheds. Sample pair with San Francisquito Ck.	7" of antecedent rainfall in Palo Alto, after at least a common annual storm has already occurred (~200 cfs at the Palo Alto gauge), and a decent forecast for the Peninsula Hills (3-4" over 12 hrs).	11166000	18.8
Colma Creek at West Orange Avenue or further downstream (as far down as possible to capture urban and historic influence upstream from tide)	27.5	38	0.8	2, 4 (possibly 1)	Historic flow gauge (ending 1996) in the park a few hundred feet upstream will allow the computation of 1st order loads estimates to support the calibration of the RWSM for mixed land use type watersheds.	Since this is a very urban watershed, precursor conditions are more relaxed: 4" of antecedent rainfall, and a decent forecast (2-3" over 12 hrs). Measurement of discharge and manual staff plate readings during sampling will verify the historic rating.	11162720	27.5

## Field methods

### Mobilization and preparing to sample

In response to a minimum rainfall weather forecast for at least one-quarter inch<sup>8</sup> over 6 hours, sampling teams were deployed to each of the sampling sites, ideally reaching the sampling site about 1 hour before the onset of rainfall<sup>9</sup>. When possible, one team sampled two sites close to one another to increase sample capture efficiency and decrease staffing costs. On arrival, the team assembled the equipment and carried out final safety checks. Sampling equipment used at a site depended on the characteristics of the access to the drainage line. Some sites were sampled by attaching laboratory-prepared trace-metal-clean Teflon sampling tubing to a painter's pole and a peristaltic pump with laboratory-cleaned silicone pump-roller tubing (Figure 2a). During sampling, the tube was dipped into the channel or drainage line aiming for mid-channel mid-depth (if shallow) or depth integrating if the depth was more than about 0.5 m. In other cases, a DH 84 (Teflon) sampler was used that had also been cleaned prior to sampling, also aiming for mid-channel, mid-depth, or depth integrated depending on channel conditions.

### Manual time-paced composite stormwater sampling procedures

At each site, a time-paced composite sample was collected comprising a variable number of sub-samples, or aliquots. Depending on the weather forecast, prevailing on-site conditions, and radar imagery, staff estimated the duration of the storm and selected an aliquot size and number that ensured that the minimum volume requirements for each analyte would be reached before the storm's end (Table 3). Because the minimum volume requirements were less than the size of the sample bottle, there was flexibility built into the sub-sampling program to add aliquots in the event that the storm continued longer than predicted (e.g., minimally 5 aliquots but up to 10 aliquots could be collected; Table 3). The final decision on the aliquot volume was made just before the first aliquot was taken and remained fixed for the remainder of the event. The final number of aliquots, as long as the minimum volume was reached, was usually adjusted depending upon how rainfall progressed. All aliquots for the sample were collected throughout the storm into the same bottle, which was kept in a cooler on ice.

### Remote suspended sediment sampling procedures

The Hamlin and Walling tube remote suspended sediment samplers were deployed approximately mid-channel/ storm drain. The Hamlin sampler sat flush, or nearly flush, with the bed of either the stormdrain or concrete channel<sup>10</sup>, and was stabilized on the bed either by its own weight (the sampler weighs approximately 25 lbs) or additionally by attaching barbell weight plates to the bottom of the sampler (Figure 2b). The Walling tube could not be deployed in storm drains due to its size and

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<sup>8</sup> Note, this was relaxed due to a lack of larger storms. Ideally, mobilization would only proceed with a 0.5" forecast.

<sup>9</sup> Antecedent dry-weather was not considered prior to deployment. Although this would likely have a bearing on the concentration of certain build-up/wash-off pollutants like metals and perhaps even mercury. For PCBs, antecedent dry-weather is less important than the mobilization of in-situ legacy sources.

<sup>10</sup> In future years, if the Hamlin is deployed within a natural bed channel, elevating the sampler more off the bed may be necessary but was not the case in WY 2015.

requirement for staying horizontal, but was secured in open channels either by being weighted down to a concrete bed with barbell weights secured with hose clamps, or by securing it to a natural bed with hose clamps attached to temporarily installed rebar. To minimize the chances of sampler loss, both samplers were additionally secured by a stainless steel cable to a temporary rebar anchor or another object such as a tree or fencepost.

The remote suspended sediment samplers were deployed for the duration of the manual water quality sampling (Table 4 for site list and success rate). The remote sampler was removed from the channel bed /storm drain bottom shortly after the last water quality sample aliquot was collected. Water and sediment collected in the sediment sampler were decanted into one or two large glass bottles. When additional water was needed to flush the settled sediments from the remote samplers into the collection bottles, site water from the sampled channel was used. Samples were split and placed into laboratory containers and then shipped to the laboratory for analysis. Samples collected by remote samplers from seven locations were analyzed as whole water samples (due to insufficient solid mass to analyze as a sediment sample), and one was analyzed as a sediment sample.



(a)



(b)



(c)



Figure 2. Sampling equipment used in the field. (a) Painter's pole, Teflon tubing and an ISCO used as a slave pump; alternatively a Teflon bottle is attached to the end of a painter's pole (DH84) and used for sample collection rather than using an ISCO as a pump; (b) Hamlin suspended sediment sampler; and (c) the Walling tube suspended sediment sampler.

Table 3. Sub-sample sizes and sample container volumes, by analyte.

Analyte	Bottle size (L)	Minimum volume (L)	Aliquots (sub-samples) (minimum to maximum number, and required volumes (L))			
			3 to 6	4 to 8	5 to 10	6 to 12
HgT/ trace metals	2	0.25	0.33	0.25	0.2	0.17
SSC	1	0.3	0.17	0.13	0.1	0.08
PCBs	2.5	1	0.33	0.25	0.2	0.17
Grain size	2	1	0.33	0.25	0.2	0.17
TOC	1	0.25	0.17	0.13	0.1	0.08

Table 4. Locations where remote sediment samplers were pilot tested.

Site	Date	Sampler(s) deployed	Comments
Meeker Slough	11/2015	Hamlin and Walling	Sampling effort was unsuccessful due to very high velocities. Both samplers washed downstream because they were not weighted down enough and debris caught on the securing lines.
Outfall to Lower Silver Creek	2/06/15	Hamlin and Walling	Sampling effort was successful. This sample was analyzed as a water sample.
Charcot Ave Storm Drain	4/07/15	Hamlin	Sampling effort was successful. This sample was analyzed as a sediment sample.
Cooley Landing Storm Drain	2/06/15	Hamlin	Sampling effort was successful. This sample was analyzed as a water sample.
Duane Ct and Ave Triangle SD	1/6/2016	Hamlin	Sampling effort was successful. This sample was analyzed as a water sample.
Victor Nelo PS Outfall	1/19/2016	Hamlin and Walling	Sampling effort was successful. This sample was analyzed as a water sample.
Forbes Blvd Outfall	3/5/2016	Hamlin	Sampling effort was successful. This sample was analyzed as a water sample.
Tunnel Ave Ditch	3/5/2016	Hamlin and Walling	Sampling effort was successful. This sample was analyzed as a water sample.
Taylor Way SD	3/11/2016	Hamlin	Sampling effort was successful. This sample was analyzed as a water sample.

## Laboratory analytical methods

All samples were labeled, placed on ice, returned back to SFEI, and refrigerated at 4 °C until transport to the laboratory for analysis, except for TOC/DOC. DOC has a 24-hour hold time for filtration. Most samples for analysis of DOC were transported to the analytical laboratory within the 24-hour filtration hold time. In those cases where the laboratory was not open during the 24-hour hold time window, SFEI staff filtered DOC samples using a Hamilton 50-mm glass syringe with a 25-mm, 0.45-µm filter.

Laboratory methods (Table 5) were chosen to ensure the optimal combination of method detection limits, accuracy and precision, and costs (BASMAA, 2011; 2012) (Table 5). At sites where the remote samplers were deployed, Hg, PCBs and OC were analyzed for both particulate and dissolved phases so that results from the remote samplers could be compared to both total water concentrations and particulate-only concentrations in the manually collected water samples.

Table 5. Laboratory analysis methods.

Analysis	Matrix	Analytical Method	Lab	Filtered	Field preservation	Contract Lab / Preservation hold time
PCBs (40)-Dissolved	Water	EPA 1668	AXYS	Yes	NA	NA
PCBs (40)-Total	Water	EPA 1668	AXYS	No	NA	NA
SSC	Water	ASTM D3977	USGS	No	NA	NA
Grain size	Water	USGS GS method	USGS	No	NA	NA
Mercury-Total	Water	EPA 1631E	BRL	No	BrCl	BRL preservation within 28 days
Metals-Total (As, Cd, Pb, Cu, Zn)	Water	EPA 1638 mod	BRL	No	HNO <sub>3</sub>	BRL preservation with Nitric acid within 14 days
Mercury-Dissolved	Water	EPA 1631E	BRL	Yes	BrCl	BRL preservation within 28 days
Organic carbon-Total (WY 2015)	Water	5310 C	EBMUD	No	HCL	NA
Organic carbon-Dissolved (WY 2015)	Water	5310 C	EBMUD	Yes	HCL	NA
Organic carbon-Total (WY 2016)	Water	EPA 9060A	ALS	No	HCL	NA
Organic carbon-Dissolved (WY 2016)	Water	EPA 9060A	ALS	Yes	HCL	NA
Mercury	Particulate	EPA 1631E, Appendix	BRL	NA	NA	
PCBs (40)	Particulate	EPA 1668	AXYS	NA	NA	NA
Organic carbon (WY 2016)	Particulate	EPA 440.0	ALS	NA	NA	NA

## Interpretive methods

### Particle normalized concentrations

Because each site was monitored only at the characterization level, there was no averaging of data for a site across multiple storm events. However, in previous studies of watersheds in which a large number of storms were sampled, great inter-storm variability in PCB and Hg concentrations was measured. Less variability was measured for a watershed when those concentrations were normalized to SSC. It was therefore reasoned that the ratio of PCB or Hg concentrations in stormwater to the suspended sediment concentration in stormwater is likely a better characterization of water quality for a site than a single water concentration, and a better metric of comparison between sites (McKee et al., 2012; Rügner et al., 2013; McKee et al., 2015).

Although normalizing for SSC increases our ability to compare relative contamination between sites, the effects of climate cannot be as easily removed. Climatic conditions can influence the interpretations of relative ranking between watersheds, although the absolute nature of that influence may differ between watershed locations depending on source characteristics. For example, dry years or lower storm intensity might result in a greater particle ratio for some watersheds if transport of the polluted sediments are triggered but are less diluted by erosion of less contaminated particles from other parts of the watershed. This is most likely to occur in mixed land use watersheds with large amounts of pervious area. For other watersheds, the source may be a patch of polluted soil that can only be eroded and transported when antecedent conditions and/or rainfall intensity reach some threshold. In this instance, a false negative could occur during a dry year. Only with many years of data during many types of storms can such processes be teased out.

These climatic challenges acknowledged, the particle ratio (PR) (mass of a given pollutant of concern in relation to mass of suspended sediment) was computed for each composite water sample collected for each analyte at each site by dividing the total water concentration (mass per unit volume) by its suspended sediment concentration (mass of suspended sediment per unit volume) (Equation 1).

Equation 1 (example PCBs):  $PR (ng/mg) = (PCB (ng/L))/(SSC (mg/L))$

These PRs were used as the primary comparison method between sites without regard to climate or rainfall intensity. Such comparisons may be sufficient for providing evidence to differentiate a group of sites with higher pollutant concentrations from a contrasting group with lower pollutant concentrations (acknowledging the risk that some data for watersheds in this group will be false negatives). However, to generate information on the absolute relative ranking between individual sites, a much more rigorous sampling campaign sampling many storms over many years would be required (c.f. the Guadalupe River study: McKee et al., 2006, or the Zone 4 Line A study: Gilbreath et al., 2012a).

### Derivations of central tendency for comparisons with past data

Mean, median, geometric mean (geomean), time-weighted mean or flow-weighted mean can be used as measures of central tendency of a dataset. Previously, most of these measures of central tendency have been used by the RMP in POC studies in which discrete stormwater samples were collected rather than

composites. To best compare WYs 2015 and 2016 composite results with previously-collected discrete sample data, a slightly different approach was used to compute the central tendency of those discrete stormwater samples. It was reasoned that a timed interval water composite collected over a single storm, such as was the case for WYs 2015 and 2016, is equivalent to mixing all discrete samples collected during a storm into a single bottle for analysis. To calculate this equivalency to the water composite results for WYs 2015 and 2016, for previously sampled watersheds, the sum all of the pollutant water concentration discrete samples was divided by the sum of all suspended sediment concentration discrete samples (Equation 3). Note: this method is mathematically not equivalent to averaging together the PRs of each discrete sample paired with its SSC.

Equation 2 (example PCBs): 
$$PR (ng/mg) = (\Sigma PCB (ng/L))/(\Sigma SSC (mg/L))$$

Due to the use of this alternate method for estimating the central tendency, PRs reported here differ slightly from those reported previously for the same site (e.g., McKee et al., 2012; McKee et al., 2014; Wu et al., 2016).

## Results and Discussion

This section presents the data in the context of two key questions:

- a) What are the concentrations and PRs observed at each of the sites based on the composite water samples?
- b) How do the PRs measured at each of the sites based on the composite water samples compare to PRs derived from the remote suspended-sediment samplers?

The data collected and presented here contributes to a broader based effort to identify potential management areas. The rankings provided here based on either stormwater concentration or PRs are part of a weight-of-evidence approach being used for locating, prioritizing and managing areas in the landscape that may be disproportionately impacting downstream water quality.

### PCBs concentrations and particle ratios

Total PCB concentrations measured in the composite water samples across the 37 sampling sites ranged almost 200-fold, from 832 to 159,606 pg/L (Table 6) (note that the Duane Ct and Ave Triangle SD site was sampled twice to avoid the potential for a false negative, given that the first storm sampled was very low intensity). The highest concentration was measured in Industrial Rd Ditch in San Carlos, located downstream from Delta Star, a known PCB contamination site, for which 79% of the estimated drainage area is old industrial land use. This concentration (159,606 pg/L) was relatively high in relation to previous measurements in the Bay Area (e.g., Zone 4 Line A FWMC = 14,500 pg/L: Gilbreath et al., 2012a; Ettie Street Pump Station mean = 59,000 pg/L; Pulgas Pump Station-North: 60,300 pg/L: McKee et al., 2012). Based on PRs, the three highest ranking sites were the Industrial Rd Ditch in San Carlos (6,140 ng/g) (79% old industrial), Gull Dr Storm Drain in South San Francisco (859 ng/g) (54% old industrial), and the Outfall at Gilman St. in Berkeley (794 ng/g) (32% old industrial). Particle ratios of this magnitude are among the highest measured in the Bay Area (Pulgas Pump Station-South (8,222 ng/g) (54% old industrial), Santa Fe Channel (1,295 ng/g) (3% old industrial), Pulgas Pump Station-North (893 ng/g) (52% old industrial), Ettie St. Pump Station (759 ng/g) (22% old industrial): McKee et al., 2012; Gilbreath et al., 2016)<sup>11</sup>. The sample collected at Lower Penitencia Creek is consistent with a previous finding (McKee et al., 2012). Similarly, two samples taken at the Duane Ct and Ave Triangle SD site during separate storm events on December 13, 2015, and January 6, 2016, have relatively consistent and low PRs (Table 6). In general, the PRs for the WYs 2015 and 2016 sampling effort were larger than those from WY 2011 (McKee et al., 2012). This likely resulted because the WYs 2015 and 2016 sites were selected to have a higher likelihood of PCB discharge to stormwater, based on the much greater proportion of old industrial land use in the catchment areas, and on stakeholder knowledge of potential sources.

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<sup>11</sup> Note, inconsistencies between the PRs reported herein and those reported in McKee et al. (2012) stem from the slightly different method of computing the central tendency of the data (see the methods section of this report above) and, in the case of Pulgas Pump Station – South, because of the extensive additional sampling that has occurred since McKee et al. (2012) reported the reconnaissance results from the WY 2011 field season.

Table 6. Concentrations of total mercury, sum of PCBs (RMP 40), and ancillary constituents measured at each of the sites during winter storms of water years 2015 and 2016. The sum of PCBs and HgT are also expressed as a particle ratio (mass of pollutant divided by mass of suspended sediment). The table is sorted from high to low PCB particle ratios.

Watershed / Catchment	County	City	Sample Date	Number of Aliquots collected	SSC (mg/L)	DOC (mg/L)	TOC (mg/L)	PCBs				Total Hg			
								(pg/L)	Rank	(ng/g)	Rank	(ng/L)	Rank	(µg/g)	Rank
Industrial Rd Ditch	San Mateo	San Carlos	3/11/16	4	26			159,606	1	6,140	1	13.9	29	0.535	14
Gull Dr SD	San Mateo	South San Francisco	3/5/16	5	10			8,592	20	859	2	5.62	38	0.562	11
Outfall at Gilman St.	Alameda	Berkeley	12/21/15	9	83			65,670	2	794	3	439	1	5.31	1
Outfall to Lower Silver Ck	Santa Clara	San Jose	2/6/15	6	57	8.6	8.3	44,643	4	783	4	24.1	24	0.423	19
Ridder Park Dr SD	Santa Clara	San Jose	12/15/14	5	114	7.7	8.8	55,503	3	488	5	37.1	17	0.326	26
Line 3A-M at 3A-D	Alameda	Union City	12/11/14	5	74	9.5	7.3	24,791	8	337	6	85.9	4	1.17	3
Seaboard Ave SD SC-050GAC580	Santa Clara	Santa Clara	12/11/14	5	85	9.5	10	19,915	9	236	7	46.7	12	0.553	13
Line 4-E	Alameda	Hayward	12/16/14	6	170	2.8	3.6	37,350	5	219	8	59.0	9	0.346	22
Seaboard Ave SD SC-050GAC600	Santa Clara	Santa Clara	12/11/14	5	73	7.9	8.6	13,472	13	186	9	38.3	15	0.528	15
South Linden PS	San Mateo	South San Francisco	2/6/15	5	43	7.4	7.4	7,814	22	182	10	29.2	20	0.679	8
Gull Dr Outfall	San Mateo	South San Francisco	3/5/16	5	33			5,758	25	174	11	10.4	35	0.315	27
Taylor Way SD	San Mateo	San Carlos	3/11/16	5	25	4.5	9.1	4,227	29	169	12	28.9	22	1.16	4
Line 9-D	Alameda	San Leandro	4/7/15	8	69	5	4.6	10,451	15	153	13	16.6	26	0.242	32
Meeker Slough	Contra Costa	Richmond	12/3/14	6	60	4.4	5.3	8,560	21	142	14	76.4	6	1.27	2
Rock Springs Dr SD	Santa Clara	San Jose	2/6/15	5	41	11	11	5,252	26	128	15	38	16	0.927	5
Charcot Ave SD	Santa Clara	San Jose	4/7/15	6	121	20	20	14,927	11	123	16	67.4	8	0.557	12
Veterans PS	San Mateo	Redwood City	12/15/14	5	29	5.9	6.3	3,520	30	121	17	13.7	30	0.469	16
Gateway Ave SD	San Mateo	South San Francisco	2/6/15	6	45	9.9	10	5,244	27	117	18	19.6	25	0.436	17
Line 9-D-1 PS at outfall to Line 9-D	Alameda	San Leandro	1/5/16	8	164			18,086	10	110	19	118	2.5	0.720	7

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Watershed / Catchment	County	City	Sample Date	Number of Aliquots collected	SSC (mg/L)	DOC (mg/L)	TOC (mg/L)	PCBs				Total Hg			
								(pg/L)	Rank	(ng/g)	Rank	(ng/L)	Rank	(µg/g)	Rank
Tunnel Ave Ditch	San Mateo	Brisbane	3/5/16	6	96	5.8	11.3	10,491	14	109	20	73.0	7	0.760	6
Valley Dr SD	San Mateo	Brisbane	3/5/16	6	96			10,442	16	109	21	26.5	23	0.276	30
Runnymede Ditch	San Mateo	East Palo Alto	2/6/15	6	265	16	16	28,549	7	108	22	51.5	11	0.194	36
E. Gish Rd SD	Santa Clara	San Jose	12/11/14	5	145	12	13	14,365	12	99.2	23	84.7	5	0.585	10
Line 13-A at end of slough	Alameda	San Leandro	3/10/16	7	357			34,256	6	96.0	24	118	2.5	0.331	24
Line 3A-M-1 at Industrial PS	Alameda	Union City	12/11/14	6	93	4.2	4.5	8,923	18	95.8	25	31.2	19	0.335	23
Forbes Blvd Outfall	San Mateo	South San Francisco	3/5/16	5	23	3.4	7.9	1,840	36	80.0	26	14.7	28	0.637	9
SD near Cooley Landing	San Mateo	East Palo Alto	2/6/15	6	82	13	13	6,473	24	78.9	27	35.0	18	0.427	18
Lawrence & Central Expwys SD	Santa Clara	Santa Clara	1/6/16	3	58			4,506	28	77.7	28	13.1	31.5	0.226	33
Condensa St SD	Santa Clara	Santa Clara	1/19/16	6	35			2,602	32	74.4	29	11.5	34	0.329	25
Oddstad PS	San Mateo	Redwood City	12/2/14	6	148	8	7.5	9,204	17	62.4	30	54.8	10	0.372	20
Line 4-B-1	Alameda	Union City	12/16/14	5	152	2.8	3.1	8,674	19	57	31	43.0	13	0.282	29
Zone 12 Line A under Temescal Ck Park	Alameda	Emeryville	1/6/16	8	143			7,804	23	54.4	32	41.5	14	0.290	28
Victor Nelo PS Outfall	Santa Clara	San Jose	1/19/16	9	45	4.0	10.5	2,289	33	50.9	33	15.8	27	0.351	21
Haig St SD	Santa Clara	San Jose	3/6/16	6	34			1,454	37	42.8	34	6.61	36	0.194	35
E Outfall to San Tomas at Scott Blvd	Santa Clara	Santa Clara	3/6/16	6	103			2,799	31	27.2	35	13.1	31.5	0.127	37
Duane Ct and Ave Triangle SD (Dec 13)*	Santa Clara	Santa Clara	12/13/15	5	79			1,947	35	24.6	36	5.91	37	0.0748	38
Duane Ct and Ave Triangle SD (Jan 6)*	Santa Clara	Santa Clara	1/6/16	3	48	4.2	12	832	38	17.3	37	12.9	33	0.268	31
Lower Penitencia Ck	Santa Clara	Milpitas	12/11/14	7	144	5.9	6.1	2,033	34	14.1	38	29.0	21	0.202	34
Minimum				3	10	2.8	3.1	832		14.1		5.62		0.0748	
Maximum				9	357	20	20	159,606		6,140		439		5.31	



## Mercury concentrations and particle ratios

Total Hg concentrations in composite water samples varied 78-fold between the 37 watershed sampling sites, from 5.62 to 439 ng/L (Table 6). This relatively large range among sites is similar to that from a previous reconnaissance effort in WY 2011, when mean HgT concentrations ranged from 13.9 to 503 ng/L among sites (McKee et al., 2012). The greatest concentration of HgT measured during the sampling in WYs 2015 and 2016 was measured at the Outfall at Gilman Street (439 ng/L), which is 32% old industrial upstream from the sampling point. Other sites with high HgT concentrations were Line 9-D-1 PS at outfall to Line 9-D and Line 13-A at end of the slough, both in San Leandro (62% and 68% old industrial respectively), Line 3A-M at 3A-D in Union City (12% old industrial), Gish Rd Storm Drain in San Jose (71% old industrial), and Meeker Slough in Richmond, which now ranks sixth but has just 6% old industrial land use area upstream from the sampling location. This helps to illustrate that mercury concentrations do not appear to have a strong relationship with old industrial land use, in contrast to PCBs, which have a weak, positive relationship between concentrations measured in water and industrial land use.

When the HgT data were normalized to SSC, the five most highly ranked sites were Outfall at Gilman Street (32% old industrial), Meeker Slough in Richmond (6% old industrial), Line-3A-M at 3A-D in Hayward (12% old industrial), Taylor Way Storm Drain in San Carlos (11% Old Industrial), and Rock Springs Dr. Storm Drain in San Jose (10% old industrial). Particle ratios at these sites were 5.3, 1.3, 1.2, 1.2, and 1.0 µg/g, respectively. Particle ratios of this magnitude exceed the upper range of those measured during the WY 2011 sampling campaign (Pulgas Pump Station-South: 0.83 µg/g, San Leandro Creek: 0.80 µg/g, Ettie Street Pump Station: 0.78 µg/g, and Santa Fe Channel: 0.68 µg/g) (McKee et al., 2012).<sup>see footnote 11 above</sup> On a regional basis, there is no discernible relationship between old industrial land use and HgT PRs whereas, in contrast, there is a weak relationship between PCB PRs and old industrial land use.

When making comparisons between data collected in the Bay Area to date, the PR method of normalization remains the most reliable tool for ranking sites for potential management follow-up. It provides a mechanism for accounting for both flow of water and sediment erosion. Another important issue during the ranking process is to consider the combined ranks of PCBs and Hg to determine whether management effort might address both pollutants together. However, there was only a weak but positive relationship between PCB and HgT concentrations. The six highest ranking sites for PCBs based on PRs ranked 14<sup>th</sup>, 11<sup>th</sup>, 1<sup>st</sup>, 19<sup>th</sup>, 26<sup>th</sup>, and 3<sup>rd</sup>, respectively, for HgT. This observation contrasts with the conclusions drawn from the WY 2011 dataset, where there appeared to be more of a general correlation between the two contaminants (McKee et al., 2012). This difference might reflect a stronger focus on PCBs during the WYs 2015 and 2016 site-selection process and the resulting focus on smaller watersheds with higher imperviousness and old industrial land use, or perhaps it might still be an artifact of small datasets. This observation is explored further below.

## Trace metal (As, Cd, Cu, Pb, and Zn) concentrations

The respective ranges in concentrations of As, Cd, Cu, Pb, and Zn measured during WYs 2015 and 2016 were less than the reporting limit (RL)-2.66 µg/L (As), 0.023-0.55 µg/L (Cd), 3.63-52.7 µg/L (Cu), 0.910-

21.3 µg/L (Pb), and 39.4-337 µg/L (Zn) (Table 7). Total As concentrations of this magnitude have been measured in the Bay Area before (Guadalupe River at Hwy 101: mean=1.9 µg/L; Zone 4 Line A: mean=1.6 µg/L) but are much lower than were measured at the North Richmond Pump Station (mean=11 µg/L) (see Appendix A3 in McKee et al., 2015). The Cd concentrations measured at sites during WYs 2015 and 2016 also are similar to mean concentrations of Cd measured at Guadalupe River at Hwy 101 (0.23 µg/L), North Richmond Pump Station (0.32 µg/L), and Zone 4 Line A (0.25 µg/L) (see Appendix A3 in McKee et al., 2015). Similarly, Cu and Pb concentrations measured during WYs 2015 and 2016 also are typical of those measured in other Bay Area watersheds (Guadalupe River at Hwy 101: Cu 19 µg/L, Pb 14 µg/L; Lower Marsh Creek: Cu 14 µg/L; North Richmond Pump Station: Cu 16 µg/L, Pb 1.8 µg/L; Pulgas Pump Station-South: Cu 44 µg/L; San Leandro Creek: Cu 16 µg/L; Sunnyvale East Channel: Cu 18 µg/L; and Zone 4 Line A: Cu 16 µg/L, Pb 12 µg/L) (see Appendix A3 in McKee et al., 2015). Similarly, Zn measurements at 26 of the sites sampled during WYs 2015 and 2016 were comparable to the mean concentrations measured in the Bay Area previously (Zone 4 Line A: 105 µg/L; Guadalupe River at Hwy 101: 72 µg/L) (see Appendix A3 in McKee et al., 2015). In WY 2016, measurements of Mg (528-7350 µg/L) and Se (<RL-0.39 µg/L) were added to the analytical schedule. Both of these analytes largely reflect geologic sources in watersheds. No measurements of Mg have been previously reported in the Bay Area but the measured concentrations of Se are on the lower side of mean concentrations reported previously in the Bay Area (North Richmond Pump Station: 2.7 µg/L; Walnut Creek: 2.7 µg/L; Lower Marsh Creek: 1.5 µg/L; Guadalupe River at Hwy 101: 1.3 µg/L; Pulgas Creek Pump Station - South: 0.93 µg/L; Sunnyvale East Channel: 0.62 µg/L; Zone 4 Line A: 0.48 µg/L; Mallard Island: 0.46 µg/L; Santa Fe Channel - Richmond: 0.28 µg/L; San Leandro Creek: 0.22 µg/L) (Table A3: McKee et al., 2015). Given the high proportion of Se transported in the dissolved phase (e.g., 81% in the Guadalupe River system) and the inverse correlation with flow (David et al., 2012; Gilbreath et al., 2012a), it is reasonable that our sampling design, which focused on high flow, measured lower concentrations than those measured with sampling designs that included low-flow and base-flow samples (North Richmond Pump Station: 2.7 µg/L; Guadalupe River at Hwy 101: 1.3 µg/L; Zone 4 Line A: 0.48 µg/L; Mallard Island: 0.46 µg/L). Concentrations of Se measured during this current study should not be used to estimate regional loads due to this sampling bias.

### Comparison between composite water and remote sampling methods

The 11 results from remote suspended-sediment samplers in WYs 2015 and 2016 were compared to the results from water composite samples collected in parallel at those sites for the same storm events (Table 8). Results for the remote samplers are all compared on a PR basis.

Samples were collected using the Hamlin samplers at eight sites, and a Walling tube was simultaneously deployed at three of these sites. Grain size distribution was measured in a subset of the samples. Results show that the grain size distribution captured by the Walling tube samplers is a better representation of the grain size distribution in the water composite samples (Figure 3). Relative to the other two sampling methods, the Hamlin sampler captures a portion of coarser grained near-bed or bedload sediment. This finding could be caused by the positioning of the samplers in the water column. The manually collected water composite samples were collected in a way that aimed to be representative of the water column as a whole. The Walling tube can be positioned at any height in the

Table 7. Concentrations of selected trace elements measured during winter storms of water years 2015 and 2016. The highest and lowest concentration for each trace element is bolded.

Watershed/Catchment	As (µg/L)	Cd (µg/L)	Cu (µg/L)	Pb (µg/L)	Mg (µg/L)	Se (µg/L)	Zn (µg/L)
Outfall to Lower Silver Ck	2.11	0.267	21.8	5.43			<b>337</b>
Ridder Park Dr SD	<b>2.66</b>	0.335	19.6	11.0			116
Line 3A-M at 3A-D	2.08	0.423	19.9	17.3			118
Seabord Ave SD SC-050GAC580	1.29	0.295	27.6	10.2			168
Line 4-E	2.12	0.246	20.6	13.3			144
Seabord Ave SD SC-050GAC600	1.11	0.187	21	8.76			132
South Linden PS	0.792	0.145	16.7	3.98			141
Line 9-D	0.47	0.053	6.24	<b>0.91</b>			67
Meeker Slough	1.75	0.152	13.6	14.0			85.1
Rock Springs Dr SD	0.749	0.096	20.4	2.14			99.2
Charcot Ave SD	0.623	0.0825	16.1	2.02			115
Veterans PS	1.32	0.093	8.83	3.86			41.7
Gateway Ave SD	1.18	0.053	24.3	1.04			78.8
Runnymede Ditch	1.84	0.202	<b>52.7</b>	<b>21.3</b>			128
E. Gish Rd SD	1.52	<b>0.552</b>	23.3	19.4			152
Line 3A-M-1 at Industrial PS	1.07	0.176	14.8	7.78			105
SD near Cooley Landing	1.74	0.100	9.66	1.94			48.4
Oddstad PS	2.45	0.205	23.8	5.65			117
Line 4-B-1	1.46	0.225	17.7	8.95			108
Lower Penitencia Ck	2.39	0.113	16.4	4.71			64.6
Condensa St SD	1.07	0.055	6.66	3.37	3,650	<b>0.39</b>	54.3
Forbes Blvd Outfall	1.5	0.093	31.7	3.22	<b>7,350</b>	<0.34	246
Gull Dr SD	<b>&lt;0.34</b>	<b>0.023</b>	<b>3.63</b>	1.18	<b>528</b>	<0.34	<b>39.4</b>
Line 9-D-1 PS at outfall to Line 9-D	1.07	0.524	22.5	20.9	2,822	0.2	217
Taylor Way SD	1.47	0.0955	10.0	4.19	5,482	<0.34	61.6
Victor Nelo PS Outfall	0.83	0.140	16.3	3.63	1,110	<b>0.04</b>	118
Minimum	<0.34	0.023	3.63	0.91	528	0.04	39.4
Maximum	2.66	0.552	52.7	21.3	7,350	0.39	337

Table 8. Remote suspended-sediment sampler data and comparison with manually collected composite water data.

Site	Remote Sampler Used	Manual Water Composite Data								Remote Sampler Data	
		SSC (mg/L)	Total PCBs (pg/L)	PCBs Particulate (pg / Liter filtered)	PCBs Dissolved (pg/L)	% Dissolved	PCBs Particle Concentration (lab measured on filter) (ng/g)	Total PCBs Particle Ratio (ng/g)	Bias (particle ratio: lab measured )	Total PCBs Particle Ratio (ng/g)	Bias (Remote Sampler particle ratio : Manual Composite particle ratio)
Duane Ct and Ave Triangle SD (Jan 6)	Hamlin	48	832	550	282	34%	11	17	151%	43	246%
Victor Nelo PS Outfall	Hamlin	45	2,289	2,007	283	12%	45	51	114%	70	137%
Taylor Way SD	Hamlin	25	4,227	3,463	764	18%	139	169	122%	237	140%
Tunnel Ave Ditch	Hamlin	96	10,491	9,889	602	6%	103	109	106%	150	137%
Forbes Blvd Outfall	Hamlin	23	1,840	1,794	47	3%	78	80	103%	42	53%
Charcot	Hamlin	121	14,927	No data				123	No data	142	115%
Outfall to Lower Silver Ck	Hamlin	57	44,643					783		1767	226%
SD near Cooley Landing	Hamlin	82	6,473					79		68	87%
Outfall to Lower Silver Ck	Walling	57	44,643					783		956	122%
Victor Nelo PS Outfall	Walling	45	2,289	2,007	283	12%	45	50.9	114%	100	197%
Tunnel Ave Ditch	Walling	96	10,491	9,889	602	6%	103	109	106%	96	88%
Median						12%			114%		137%
Mean						15%			119%		141%

Site	Remote Sampler Used	Manual Water Composite Data								Remote Sampler Data	
		SSC (mg/L)	Total Hg (ng/L)	Hg Particulate (ng / Liter filtered)	Hg Dissolved (ng/L)	% Dissolved	Hg Particle Concentration (lab measured on filter) (ng/g)	Total Hg Particle Ratio (ng/g)	Bias (particle ratio: lab measured )	Total Hg Particle Ratio (ng/g)	Bias (Remote Sampler particle ratio : Manual Composite particle ratio)
Duane Ct and Ave Triangle SD (Jan 6)	Hamlin	48	13	11	1.88	15%	229	268	117%	99	37%
Victor Nelo PS Outfall	Hamlin	45	16	12.1	3.71	23%	269	351	131%	447	127%
Taylor Way SD	Hamlin	25	29	17.9	11	38%	716	1156	161%	386	33%
Tunnel Ave Ditch	Hamlin	96	73	65.8	7.23	10%	685	760	111%	530	70%
Forbes Blvd Outfall	Hamlin	23	15	12.2	2.45	17%	530	637	120%	125	20%
Charcot	Hamlin	121	67	No data				557	No data	761	137%
Outfall to Lower Silver Ck	Hamlin	57	24					423		150	36%
SD near Cooley Landing	Hamlin	82	35					427		101	24%
Outfall to Lower Silver Ck	Walling	57	24					423		255	60%
Victor Nelo PS Outfall	Walling	45	16	12.1	3.71	23%	269	351	131%	483	138%
Tunnel Ave Ditch	Walling	96	73	65.8	7.23	10%	685	760	111%	577	76%
Median						17%			120%		60%
Mean						21%			128%		69%

water column, and was typically deployed 1 to 2 ft above the channel bed, which placed it at approximately mid-depth position during storm flow conditions. In contrast, the Hamlin samplers were positioned either on the bed or slightly elevated (~3 cm) above the bed when attached atop a weighted plate. It is likely that securing the Hamlin samplers closer to the bed increased the capture of coarser grained sediment mass (Figure 3). Grain sizes were analyzed for a select number of sites and the results show that the grain size distribution for the Hamlin samplers was typically coarser than for the Walling tube samples, and the grain size distribution for the Walling tube samples better approximated the grain size distribution for the manual water composite samples.

The PR results for the remote suspended-sediment samplers and manual water composites were evaluated to compare the measurement techniques. Following the Bland-Altman approach (Bland and Altman, 1986; and explained in Dallal, 2012), results were first plotted against one another for a basic visual inspection of scatter about the 1:1 line, and then the differences between the methods were plotted against the mean of the two measurements to evaluate symmetric grouping around zero and systematic variation of the differences with the mean. Results for Hg showed that much of the remote sampler data had lower PRs than those obtained from the composited stormwater samples (Figure 4). However, the Walling tube samples are much closer to the 1:1 line than the Hamlin samples, and have no obvious bias (two samples are lower than the 1:1 line and one is higher). The mean and standard deviation of the paired sample differences (remote samples minus the water composite samples) for the Hamlin sampler were -248 ng/g (mean) and 311 (standard deviation), whereas the mean for the Walling tube sampler was -73 ng/g with a standard deviation of 178.

That the remote sampler Hg PRs are typically lower than the manual composites is conceptually in concordance with the findings in Yee and McKee (2010), with more Hg in dissolved and slower settling fractions than PCBs. This is consistent with the data (Table 8), which indicate that, on average, 19% of the HgT was in the dissolved form (range 10-38%) compared to a slightly lower tendency for dissolved phase for PCBs (mean = 15%; range = 3-34%). Thus, these composited stormwater samples would be expected to have higher PRs than would the remote samplers, due to lower sediment content and thus a greater relative proportion of Hg in the dissolved phase or on fine particles. Although the Hg results for the Walling tube samples may appear better correlated, this may just be coincidental; the Hamlin samples at the same sites performed almost as well as the Walling tubes. In future testing of the remote samplers, it will be necessary to include more side-by-side Hamlin and Walling tube sites to better compare results directly between the methods and confirm whether the Walling tubes perform well even in circumstances in which the Hamlin sampler does not perform well.

The differences in Hg PR between the remote samplers and the composite water samples were lowest for Victor Nelo PS Outfall (RPD 31%), which could be due to subsampling and analytical variation. However, the PRs for Hg at other sites differed up to 5-fold (as noted previously, with the composited stormwater samples biased higher). This difference is not easily accounted for through subsampling or analytical variation, as both the composite sample (time paced with just 3 to 9 sub-samples) and remote sampler methods collect time-integrated samples, which reduce the influence of momentary spikes in concentration. The lower Hg PRs from the remote samplers than the manual water composites might be caused by a larger proportion of Hg in the dissolved phase. If instead more samples collected in the

future continue to show good agreement for the Walling tube samplers, then the difference may be more the result of the Hamlin samplers collecting a larger proportion of coarser sediment.

Generally there was better agreement between the remote and manual water composite methods for PCBs (Figure 4). Consistently higher remote sampler PRs were measured for sites with higher PRs obtained from composite stormwater samples. In contrast to the results for Hg, the remote samples for PCBs were biased higher than for the manual water composites, a result that is conceptually reasonable, though somewhat surprising. Described earlier, the Hamlin remote samplers preferentially sample heavier and larger particles as compared to the manual water composite samples. A prior settling experiment using collected runoff (Yee and McKee, 2010) showed that 50-75% of PCBs in a sediment phase settled out of a 30-cm water column within 20 minutes or less (in contrast to the results for HgT

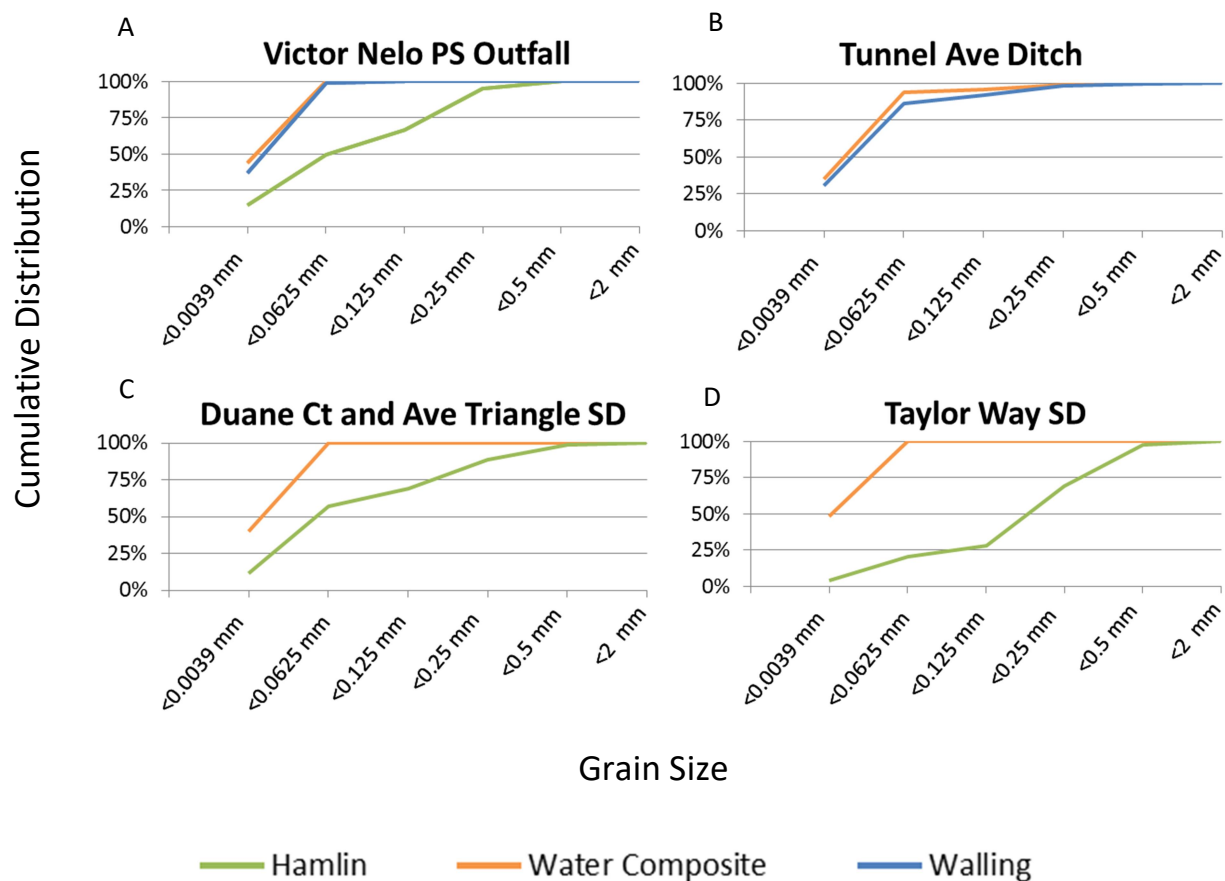


Figure 3. Cumulative grain size distribution in the Hamlin suspended-sediment sampler, Walling tube suspended-sediment sampler, and water composite samples at four sampling locations. At Victor Nelo PS Outfall (Figure 3A), both suspended-sediment samplers were deployed, whereas only one sampler was deployed at the other three locations.

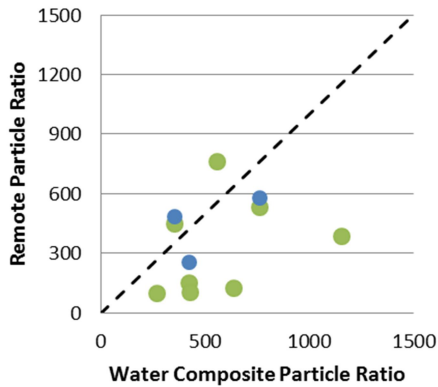
which showed generally lower settling rates). The average residence time for particles passing through the Walling tube is about 4 minutes, though we cannot provide such an estimate for the Hamlin sampler due to its more complicated flow-through structure. It may be conceptually reasonable that PCBs on sediment are settling out in the remote samplers at a rate efficient enough to accurately characterize the PR for the site. The surprising aspect of these results is that, by using the manual water composite PR (total PCBs/SSC), the dissolved proportion (mean 15%, median 12%; Table 8) is included in the ratio and therefore the PR is biased high. And yet, as compared to the water composite PRs, the remote sampler PRs are still mostly higher (mean of the differences (remote sampler PRs minus the manual water composite PRs) is +138 ng/g for the Hamlin and +70 ng/g for the Walling tube). Additional sampling in future years is expected and may help to improve the interpretation of these general patterns.

The PCB remote sampler dataset has one interesting high outlier in which the Hamlin remote sampler PR (1767 ng/g) is elevated well above the manual water composite PR (783 ng/g). One hypothesis is that the remote samplers captured a time-limited pulse of PCBs during the storm which the manual water composite subsampling did not capture. That hypothesis is not strong, however, since the Walling tube sampler was only slightly elevated above the manual water composite. A key difference between the Hamlin sampler and the other two methods is that it disproportionately captures heavier and larger grain sizes, suggesting that a substantial portion of the PCBs flowing through this catchment were on these larger particles.

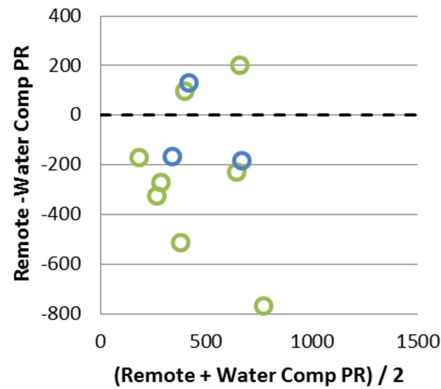
When normalized to grain size, improvement was marginal and more promising for Hg than PCBs, particularly when normalized to a <0.125-mm particle size (Figure 5). The comparison between the two sample types for the Hg sample with the highest PR in a manual composite sample, which had a correspondingly low remote-sampler PR was greatly improved by normalizing to particles <0.125 mm. This Hamlin-collected sample had a high percentage of medium and coarse sands (see grain size distribution for this Hamlin sample in Figure 3D). On the other hand, PCBs for same sample (which had the highest manual composite PR for PCBs as well as Hg) had a better agreement when not normalized to particle size. This result is not entirely expected because conceptually a sample with a larger proportion of sand would result in a lower PR and would have better agreement with the water composite sample when normalized to finer grain sizes. Five subsamples comprised the manual water composite sample and it is possible that this density of aliquots was insufficient to represent the average storm concentration that may have been better captured by the Hamlin sampler (which stayed in the water through the duration of the storm). Exploration into normalizing by grain size and TOC will continue in the next progress report with WY 2017 data (expected spring 2018).

These remote sampling methods could be applied in a way as to save staff time and potentially be deployed in situations that are not feasible for manual sampling (discussed in greater detail in the following section), yet there are certainly some challenges interpreting the data and comparing it to the manual water composites. Whereas the remote methods collect primarily a concentrated, whole storm integrated suspended sediment sample, the manually composited water samples include some proportion of dissolved concentration, which conflates the metric of comparison (PR) between the methods. Also, the data collected thus far using the Hamlin sampler has a largely different grain size

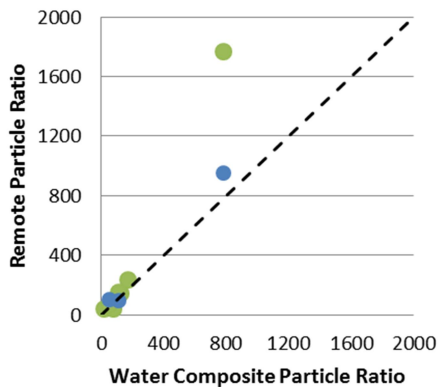
4A – Hg



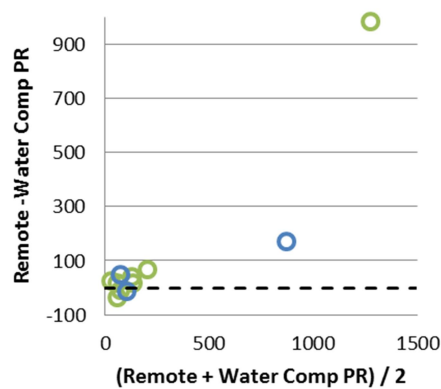
4B – Hg



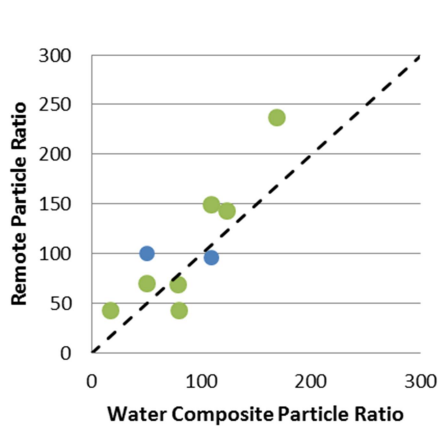
4C – PCBs



4D – PCBs



4E – PCBs



4F – PCBs

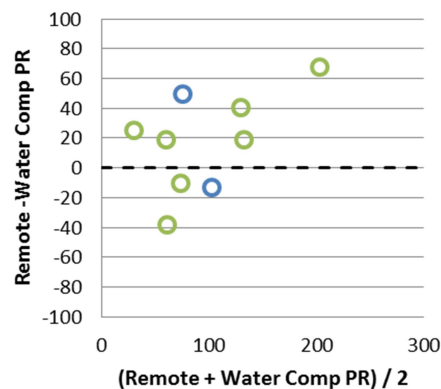


Figure 4. Particle ratio comparisons between remote suspended-sediment samples versus manually collected composite samples, and comparisons of the differences between the methods against their means. Data for Hg is plotted in 4A and 4B. Data for PCBs is plotted in 4C and 4D. PCB data is also shown in 4E and 4F but excludes the high outlier. Figures 4A, 4C and 4E show the 1:1 line (dashed black line), and Figures 4B, 4D and 4F show the 0 line as dashed. Data for samples collected with the Hamlin sampler are green, and data for samples collected using the Walling tube are blue.



distribution than that collected by the manual water composite method. Another challenge with these sample data gathered using the remote samplers is that the data cannot be used to estimate loads without corresponding sediment load estimates and we don't currently have a regional model calibrated for suspended sediment (McKee et al., 2014). In summary, the remote sampling method comes with tradeoffs: they may have value as a cost-effective reconnaissance and prioritization tool, but they cannot be used for loads calculations and the error around direct comparisons to manually collected water composite samples is still uncertain.

With these concerns raised, the sampling program for WY 2017 will continue to build out the dataset for comparing samples derived from composite and remote suspended sediment sampling methods. The five additional Walling tube samples planned should provide more confidence in the importance of bias and in the range of differences among methods. They may also shed light on causes of bias and difference, either generally or specific to a site (e.g., land use) or event (e.g., storm intensity, duration, sample grain size, organic carbon). If, after the eight-sample pilot study is completed, the data do not show reasonable comparability or explainable differences between the composite and remote sampler methods, additional factors, such as site cross-sectional variation, and contribution of near-bed load to contaminant loading, will be considered.

In summary, the data obtained to date from remote samplers show some promise as a relative ranking or prioritization tool. This pilot study will continue into WY 2017 and possibly beyond. The additional data collected should aim to confirm whether these samplers have value as a reconnaissance tool. If that proves to be the case, these samplers can be used as a low-cost screening and ranking tool to identify watersheds where greater investment in manual sampling and other methods of investigation is warranted.

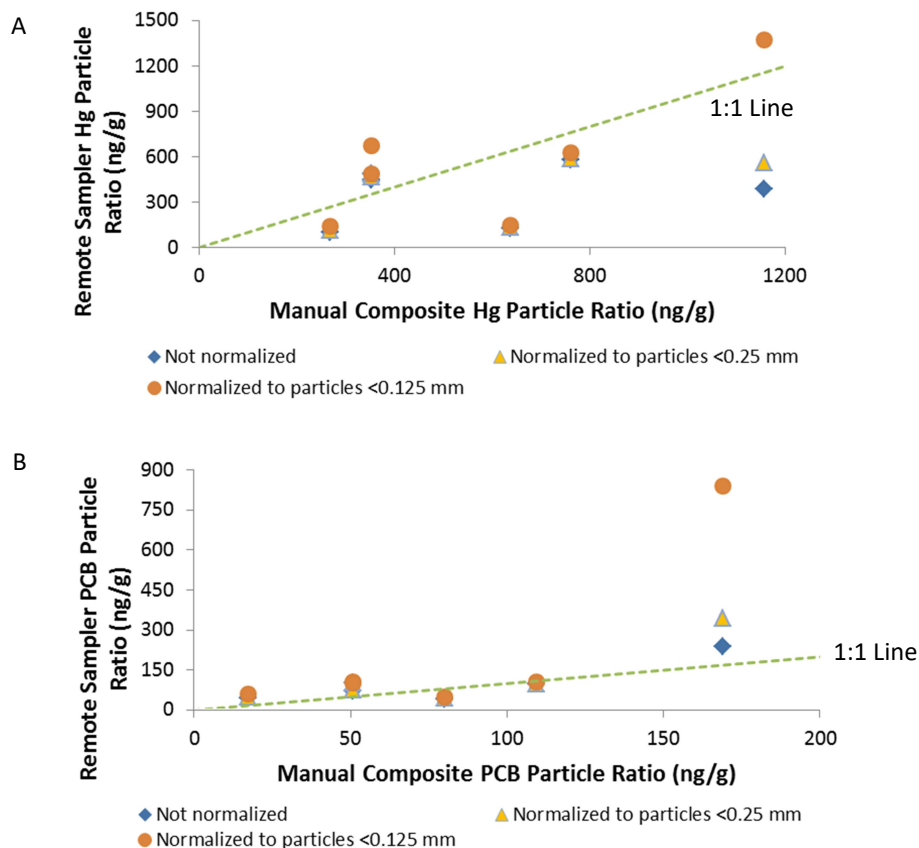


Figure 5. Grain size normalized particle ratio comparisons between remote (sediment) versus composite (water) samples for A) Hg and B) PCBs. Only samples in which grain size was analyzed (n=5) are shown in these graphs; the other remote samples were not analyzed for grain size.

### Pros and cons of the remote sampling method

The pilot study to assess effectiveness of remote samplers is still in progress. The samplers have been successfully deployed at eight locations, in which the Hamlin sampler was tested at all eight and the Walling tube sampler was tested at three. During the winter of WY 2017 we intend to focus remote sampling using the Walling tube; a more comprehensive analysis of effectiveness and cost versus benefit of this method will be completed after that sampling effort. A preliminary comparison is presented in Table 9a and 9b below. Generally speaking, it is anticipated that remote sampling methods will be more cost effective. Conceptually, this method would allow multiple sites to be monitored during a single storm event where devices are deployed prior to the storm and retrieved after the storm. There would be initial costs to purchase the equipment, and labor would be required to deploy and process samples. In addition, there will always be logistical constraints (such as turbulence or tidal influences) that complicate use of the remote devices and require manual monitoring at a particular site. As mentioned above, the data derived from the remote sampling methodologies may be less straightforward to

interpret than water grab or composite samples, and overall would have somewhat less versatility or greater complications for uses other than ranking sites for relative pollution. Used as a companion to manual monitoring methods, however, costs would most likely be reduced and data suitable for other purposes would continue to be collected. Factoring in the more limited data uses in the cost-effectiveness analysis will be challenging.

Table 9a. Preliminary comparison of the advantages and disadvantages of the remote sampling method compared to the manual sampling method for the characterization of sites.

Category	Remote Sampling Relative to Manual Sampling	Notes
Cost	Less	Both manual and remote sampling include many of the same costs, though manual sampling generally requires more staff labor related to tracking the storm carefully in order to deploy field staff at just the right time. The actual sampling also requires more labor for manual sampling, especially during long storms. There are some greater costs for remote sampling related to having to drive to the site twice (to deploy and then to retrieve) and then slightly more for post-sample processing, but these additional costs are minimal relative to the amount of time required to track storms and sample on site during the storm. See additional details in Table 11b below.
Sampling Feasibility	Some advantages, some disadvantages	Remote sampling has a number of feasibility advantages over manual sampling. With remote sampling, manpower is less of a constraint; there is no need to wait on equipment (tubing, Teflon bottle, graduated cylinder) cleaning at the lab; the samplers can be deployed for longer than a single storm event, if desired; the samplers composite more evenly over the entire hydrograph; and conceivably, with the help of municipalities, remote samplers may be deployed in storm drains in the middle of streets. On the contrary, at this time there is no advantage to deploy remote samplers (and perhaps it is easier to just manually sample) in tidal locations since they must be deployed and retrieved within the same tidal cycle, although we are beginning to think of solutions to this challenge.
Data Quality	Assessment incomplete	Comparison between the remote sampler and manual sampling results are being assessed in this study. If remote samplers can be used consistently over multiple storm events, it is reasonable to think that the extended sample collection would improve the representativeness of the sample.
Data Uses	Equivalent or slightly lower	At this time, both the remote and manual sampling collects data for a single storm composite which is then used for characterization purposes. Although not a high quality estimate, the water concentration data from the manual water composites may also be used to estimate loads if the volume is known or can be estimated (e.g., using the RWSM).
Human stresses and risks associated with sampling program	Much less	Manual sampling involves a great deal of stressful planning and logistical coordination to sample storms successfully; these stresses include irregular schedules and having to cancel other plans; often working late and unpredictable hours; working in wet and often dark conditions after irregular or insufficient sleep and added risks under these cumulative stresses. Some approaches to remote sampling (e.g., not requiring exact coincidence with storm timing) could greatly reduce many of these stresses (and attendant risks).

Table 9b. Detailed preliminary labor and cost comparison between the remote sampling method compared to the manual composite sampling method for the characterization of sites.

Task	Remote Sampling Labor Hours Relative to Manual Sampling	Manual Composite Sampling Task Description	Remote Sampling Task Description
Sampling Preparation in Office	Equivalent	Cleaning tubing/bottles; preparing bottles, field sampling basic materials	Cleaning sampler; preparing bottles, field sampling basic materials
Watching Storms	Much less	Many hours spent storm watching and deciding if/when to deploy	Storm watching is minimized to only identifying appropriate events with less/little concern about exact timing
Sampling Preparation at Site	Equivalent	Set up field equipment	Deploy sampler
Driving	More (2x)	Drive to and from site	Drive to and from site 2x
Waiting on Site for Rainfall to Start	Less	Up to a few hours	No time since field crew can deploy equipment prior to rain arrival
On Site Sampling	Much less	10-20 person hours for sampling and field equipment clean up	2 person hours to collect sampler after storm
Sample Post-Processing	Slightly more (~2 person hours)	NA	Distribute composited sample into separate bottles; takes two people about 1 hour per sample
Data Management and Analysis	Equivalent	Same analytes and sample count (and usually same matrices)	Same analytes and sample count (and usually same matrices )

### Preliminary site rankings based on all available data

The PCB and HgT load allocations of 2 and 80 kg, respectively, translate to a mean concentration of 1.33 ng/L (PCBs) and 53 ng/L (HgT) (assuming an annual average flow from small tributaries of 1.5 km<sup>3</sup> (Lent et al., 2012)) and mean annual PR of 1.4 ng/g (PCBs) and 58 ng/g (HgT) (assuming an average annual suspended sediment load of 1.4 million metric tons) (McKee et al., 2013). Keeping in mind that the estimates of regional flow and regional sediment loads are subject to change as further interpretations are completed, only two sampling locations observed to date (Gellert Park bioretention influent stormwater and the storm drain at the corner of Duane Ct. and Triangle Ave.) have a composite averaged PCB concentration of < 1.33 ng/L (Table 12) and none of 62 sampling locations have composite averaged PCB PRs <1.4 ng/g (Table 12; Figure 6 and 7). The lowest PCB PR measured to date is for Marsh Creek (2.9 ng/g).

Although there are always challenges associated with interpreting data in relation to highly variable factors, including antecedent conditions, storm specific rainfall intensity, and watershed specific source-release-transport processes, the objective here is to provide evidence to help identify watersheds that might have disproportionately elevated PCB or Hg concentrations or PRs. Given the nature of the reconnaissance sampling design, the absolute rank is much less certain but it is unlikely that the highest rank locations would drop in ranking much if more sampling was conducted. With these caveats in mind, a relative ranking was generated for PCBs and Hg based on both water concentrations and PRs for all the available data, most of which was collected during WY 2011 (a slightly wetter than average year), WY 2015 (a slightly drier than average year), and WY 2016 (about average).

Based on water composite concentrations for all available data, the 10 most polluted sites for PCBs are (in order from higher to lower): Pulgas Pump Station-South, Santa Fe Channel, Industrial Rd Ditch, Sunnyvale East Channel, Outfall at Gilman St., Pulgas Pump Station-North, Ettie Street Pump Station, Ridder Park Dr Storm Drain, Outfall to Lower Silver Creek, and Line 4-E (Figure 7). The locations span a range in land use from 3-79% old industrial, illustrating the challenge in using land use alone as a tool for locating areas of high leverage. Using PCB PRs, the ten most polluted sites are: Pulgas Pump Station-South, Industrial Rd Ditch, Santa Fe Channel, Pulgas Pump Station-North, Gull Dr SD, Outfall at Gilman St., Outfall to Lower Silver Creek, Ettie Street Pump Station, Ridder Park Dr Storm Drain and Sunnyvale East Channel. Nine sampling sites were among the top 10 based on both water concentrations and PRs, but one site (Line 4-E) with elevated water concentrations had a lower PR due to its high sediment production, and a different site (Gull Dr SD) which did not have particularly high PCB water concentrations was ranked in the top ten for PCB PRs due to its very low suspended sediment mass. In addition to identifying three new top-10 ranked PCB PR sites, the WY 2016 stormwater sampling efforts also identified a large number of sites with moderate PRs (Figure 7). This additional large cohort of sites with moderately elevated PRs was likely a result of a site selection process that targeted watershed areas with greater older industrial influences.

Table 10. PCB and HgT concentrations and PRs measured in the Bay area based on all data collected in stormwater since water year 2003 and that focused on urban sources (62 sites in total for PCBs and HgT). This dataset is sorted high to low for PCB PR to provide preliminary information on potential leverage.

Watershed/ Catchment	County	Water Year sampled	Area (km2)	Impervious cover (%)	Old Industrial land use (%)	Polychlorinated biphenyls (PCBs)				Total Mercury (HgT)			
						Particle Ratio		Composite /mean water concentration		Particle Ratio		Composite /mean water concentration	
						(ng/g)	Rank	(pg/L)	Rank	(µg/g)	Rank	(ng/L)	Rank
Pulgas Pump Station-South	San Mateo	2011-2014	0.58	87%	54%	8222	1	447984	1	0.35	31.5	19	46
Industrial Rd Ditch	San Mateo	2016	0.23	85%	79%	6139	2	159606	3	0.53	22	14	52
Santa Fe Channel	Contra Costa	2011	3.3	69%	3%	1295	3	197923	2	0.57	17.5	86	10.5
Pulgas Pump Station-North	San Mateo	2011	0.55	84%	52%	893	4	60320	6	0.4	28	24	43.5
Gull Dr SD	San Mateo	2016	0.30	78%	54%	859	5	8592	34	0.56	19	6	59
Outfall at Gilman St.	Alameda	2016	0.84	76%	32%	794	6	65670	5	5.31	1	439	4
Outfall to Lower Silver Creek	Santa Clara	2015	0.17	79%	78%	783	7	44643	9	0.42	27	24	43.5
Ettie Street Pump Station	Alameda	2011	4.0	75%	22%	759	8	58951	7	0.69	13	55	22.5
Ridder Park Dr Storm Drain	Santa Clara	2015	0.50	72%	57%	488	9	55503	8	0.33	35	37	35
Sunnyvale East Channel	Santa Clara	2011	15	59%	4%	343	10	96572	4	0.2	49	50	26
Line-3A-M at 3A-D	Alameda	2015	0.88	73%	12%	337	11	24791	14	1.17	5	86	10.5
North Richmond Pump	Contra	2011-	2.0	62%	18%	241	12	13226	23	0.81	10	47	27.5

Watershed/ Catchment	County	Water Year sampled	Area (km2)	Impervious cover (%)	Old Industrial land use (%)	Polychlorinated biphenyls (PCBs)				Total Mercury (HgT)			
						Particle Ratio		Composite /mean water concentration		Particle Ratio		Composite /mean water concentration	
						(ng/g)	Rank	(pg/L)	Rank	(µg/g)	Rank	(ng/L)	Rank
Station	Costa	2014											
Seabord Ave Storm Drain SC-050GAC580	Santa Clara	2015	1.4	81%	68%	236	13	19915	17	0.55	21	47	27.5
Line4-E	Alameda	2015	2.0	81%	27%	219	14	37350	10	0.35	31.5	59	19
Glen Echo Creek	Alameda	2011	5.5	39%	0%	191	15	31078	12	0.21	48	73	15
Seabord Ave Storm Drain SC-050GAC600	Santa Clara	2015	2.8	62%	18%	186	16	13472	22	0.53	23	38	33.5
South Linden Pump Station	San Mateo	2015	0.14	83%	22%	182	17	7814	37	0.68	14	29	40
Gull Dr Outfall	San Mateo	2016	0.43	75%	42%	174	18	5758	41	0.32	37	10	57
Taylor Way SD	San Mateo	2016	0.27	67%	11%	169	19	4227	46	1.16	6	29	41
Line 9-D	Alameda	2015	3.6	78%	46%	153	20	10451	27	0.24	43.5	17	47.5
Meeker Slough	Contra Costa	2015	7.3	64%	6%	142	21	8560	35	1.27	4	76	14
Rock Springs Dr Storm Drain	Santa Clara	2015	0.83	80%	10%	128	22	5252	42	0.93	8	38	33.5
Charcot Ave Storm Drain	Santa Clara	2015	1.8	79%	24%	123	23	14927	20	0.56	20	67	17
Veterans Pump Station	San Mateo	2015	0.52	67%	7%	121	24	3520	48	0.47	24	14	51
Gateway Ave Storm Drain	San Mateo	2015	0.36	69%	52%	117	25	5244	43	0.44	25	20	45

Watershed/ Catchment	County	Water Year sampled	Area (km2)	Impervious cover (%)	Old Industrial land use (%)	Polychlorinated biphenyls (PCBs)				Total Mercury (HgT)			
						Particle Ratio		Composite /mean water concentration		Particle Ratio		Composite /mean water concentration	
						(ng/g)	Rank	(pg/L)	Rank	(µg/g)	Rank	(ng/L)	Rank
Guadalupe River at Hwy 101	Santa Clara	2003-2006, 2010, 2012-2014	233	39%	3%	115	26	23736	15	3.6	3	603	1
Line 9-D-1 PS at outfall to Line 9-D	Alameda	2016	0.48	88%	62%	110	27	18086	19	0.72	12	118	6.5
Tunnel Ave Ditch	San Mateo	2016	3.0	47%	8%	109	28	10491	26	0.76	11	73	16
Valley Dr SD	San Mateo	2016	5.2	21%	7%	109	29	10442	28	0.28	41	27	42
Runnymede Ditch	San Mateo	2015	2.1	53%	2%	108	30	28549	13	0.19	51	52	25
E. Gish Rd Storm Drain	Santa Clara	2015	0.45	84%	70%	99	31	14365	21	0.59	16	85	12
Line 3A-M-1 at Industrial Pump Station	Alameda	2015	3.4	78%	26%	96	32	8923	30	0.34	33	31	38
Line 13-A at end of slough	Alameda	2016	0.83	84%	68%	96	33	34256	11	0.33	34	118	6.5
Zone 4 Line A	Alameda	2007-2010	4.2	68%	12%	82	34	18442	18	0.17	53	30	39
Forbes Blvd Outfall	San Mateo	2016	0.40	79%	0%	80	35	1840	54	0.64	15	15	50
Storm Drain near Cooley Landing	San Mateo	2015	0.11	73%	39%	79	36	6473	39	0.43	26	35	36
Lawrence & Central Expwys SD	Santa Clara	2016	1.2	66%	1%	78	37	4506	45	0.23	45	13	53.5



Watershed/ Catchment	County	Water Year sampled	Area (km2)	Impervious cover (%)	Old Industrial land use (%)	Polychlorinated biphenyls (PCBs)				Total Mercury (HgT)			
						Particle Ratio		Composite /mean water concentration		Particle Ratio		Composite /mean water concentration	
						(ng/g)	Rank	(pg/L)	Rank	(µg/g)	Rank	(ng/L)	Rank
Condensa St SD	Santa Clara	2016	0.24	70%	32%	74	38	2602	52	0.33	36	12	56
San Leandro Creek	Alameda	2011-2014	8.9	38%	0%	66	39	8614	33	0.86	9	117	8
Oddstad Pump Station	San Mateo	2015	0.28	74%	11%	62	40	9204	29	0.37	29	55	22.5
Line 4-B-1	Alameda	2015	0.96	85%	28%	57	41	8674	32	0.28	39.5	43	30
Zone 12 Line A under Temescal Ck Park	Alameda	2016	17	30%	4%	54	42	7804	38	0.29	38	42	31
Victor Nelo PS Outfall	Santa Clara	2016	0.58	87%	4%	51	43	2289	53	0.35	30	16	49
Haig St SD	Santa Clara	2016	2.12	72%	10%	43	44	1454	56	0.19	50	7	58
Lower Coyote Creek	Santa Clara	2005	327	22%	1%	30	45	4576	44	0.24	43.5	34	37
Calabazas Creek	Santa Clara	2011	50.1	44%	3%	29	46	11493	25	0.15	56	59	19
E Outfall to San Tomas at Scott Blvd	Santa Clara	2016	0.67	66%	31%	27	47	2799	51	0.13	57	13	53.5
San Lorenzo Creek	Alameda	2011	125	13%	0%	25	48	12870	24	0.18	52	41	32
Stevens Creek	Santa Clara	2011	26	38%	1%	23	49	8160	36	0.22	46.5	77	13
Guadalupe River at Foxworthy Road/ Almaden Expressway	Santa Clara	2010	107	22%	0%	19	50	3120	49	4.09	2	529	2
Duane Ct and Ave Triangle SD	Santa Clara	2016	1.0	79%	23%	17	51	832	58	0.27	42	13	55

Watershed/ Catchment	County	Water Year sampled	Area (km2)	Impervious cover (%)	Old Industrial land use (%)	Polychlorinated biphenyls (PCBs)				Total Mercury (HgT)			
						Particle Ratio		Composite /mean water concentration		Particle Ratio		Composite /mean water concentration	
						(ng/g)	Rank	(pg/L)	Rank	(µg/g)	Rank	(ng/L)	Rank
Lower Penitencia Creek	Santa Clara	2011, 2015	12	65%	2%	16	52	1588	55	0.16	54.5	17	47.5
Borel Creek	San Mateo	2011	3.2	31%	0%	15	53	6129	40	0.16	54.5	58	21
San Tomas Creek	Santa Clara	2011	108	33%	0%	14	54	2825	50	0.28	39.5	59	19
Zone 5 Line M	Alameda	2011	8.1	34%	5%	13	55.5	21120	16	0.57	17.5	505	3
Belmont Creek	San Mateo	2011	7.2	27%	0%	13	55.5	3599	47	0.22	46.5	53	24
Walnut Creek	Contra Costa	2011	232	15%	0%	7	57	8830	31	0.07	59	94	9
Lower Marsh Creek	Contra Costa	2011-2014	84	10%	0%	3	58	1445	57	0.11	58	44	29
San Pedro Storm Drain	Santa Clara	2006	1.3	72%	16%	No data				1.12	5	160	4
El Cerrito Bioretention Influent	Contra Costa	2011	0.004	74%	0%	442	NR <sup>a</sup>	37690	NR <sup>a</sup>	0.19	NR <sup>a</sup>	16	NR <sup>a</sup>
Fremont Osgood Road Bioretention Influent	Alameda	2012, 2013	0.0008	76%	0%	45	NR <sup>a</sup>	2906	NR <sup>a</sup>	0.12	NR <sup>a</sup>	10	NR <sup>a</sup>
Gellert Park Daly City Library Bioretention Influent	San Mateo	2009	0.015	40%	0%	36	NR <sup>a</sup>	725	NR <sup>a</sup>	1.01	NR <sup>a</sup>	22	NR <sup>a</sup>

<sup>a</sup>NR = site not included in ranking. All sites that are not included in the ranking are very small catchments with unique sampling designs for evaluation of green infrastructure.

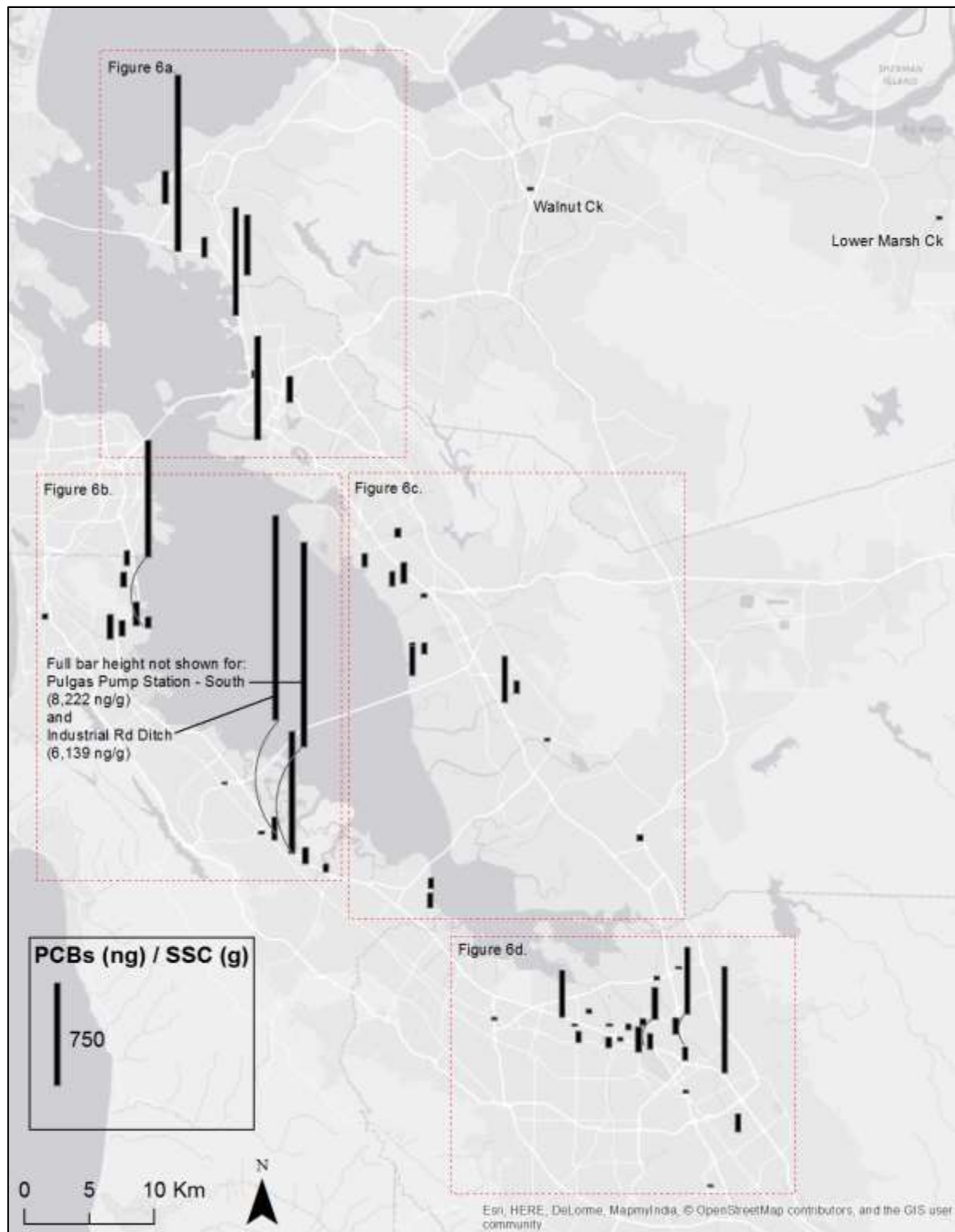


Figure 6. Regional distribution of PCB particle ratios in stormwater samples collected by the RMP to date (water years 2003-2016).

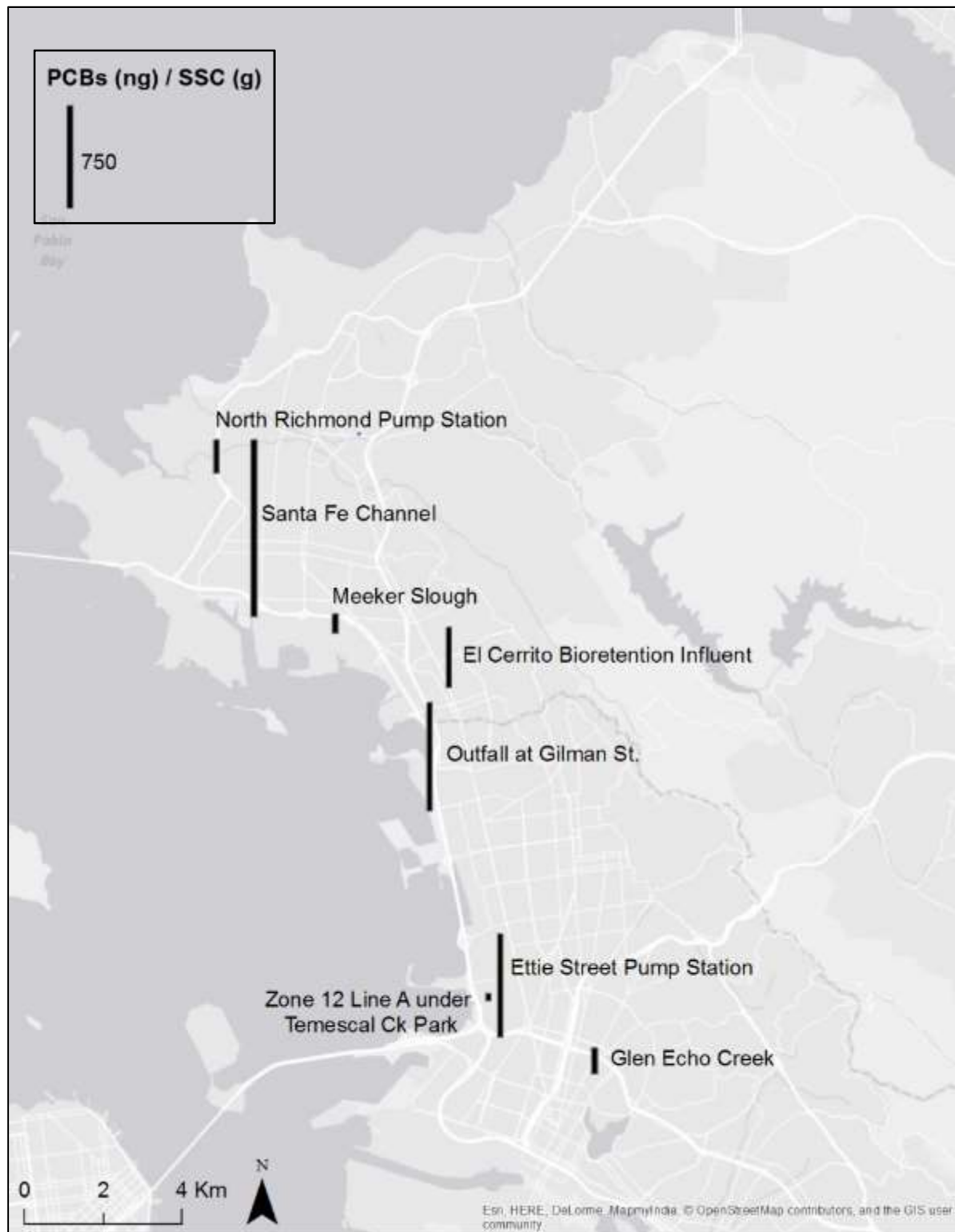


Figure 6a. Distribution of PCB particle ratios in stormwater samples collected by the RMP to date (water years 2003-2016) in northern Alameda and Contra Costa counties.

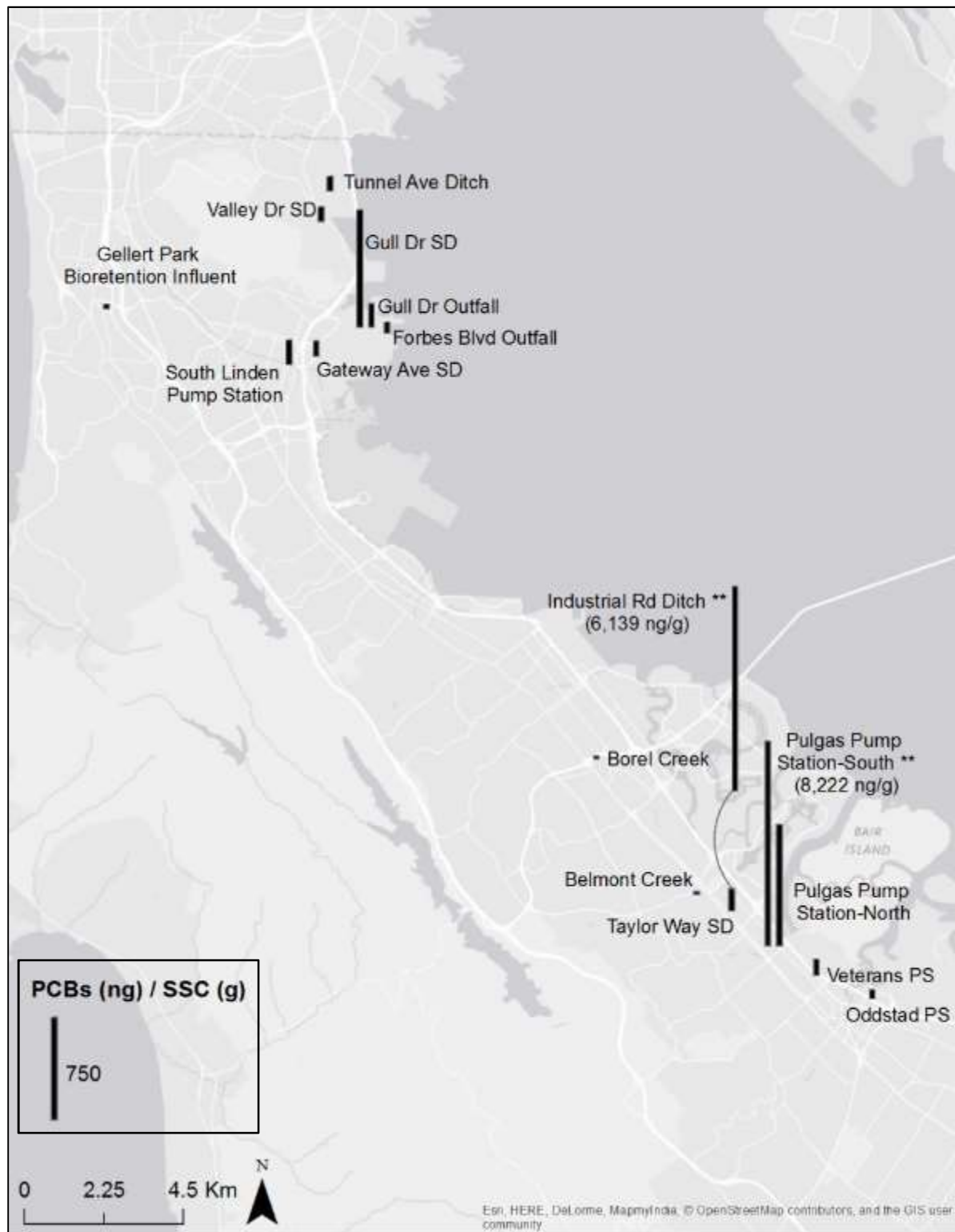


Figure 6b. Distribution of PCB particle ratios in stormwater samples collected by the RMP to date (water years 2003-2016) in central and northern San Mateo County.

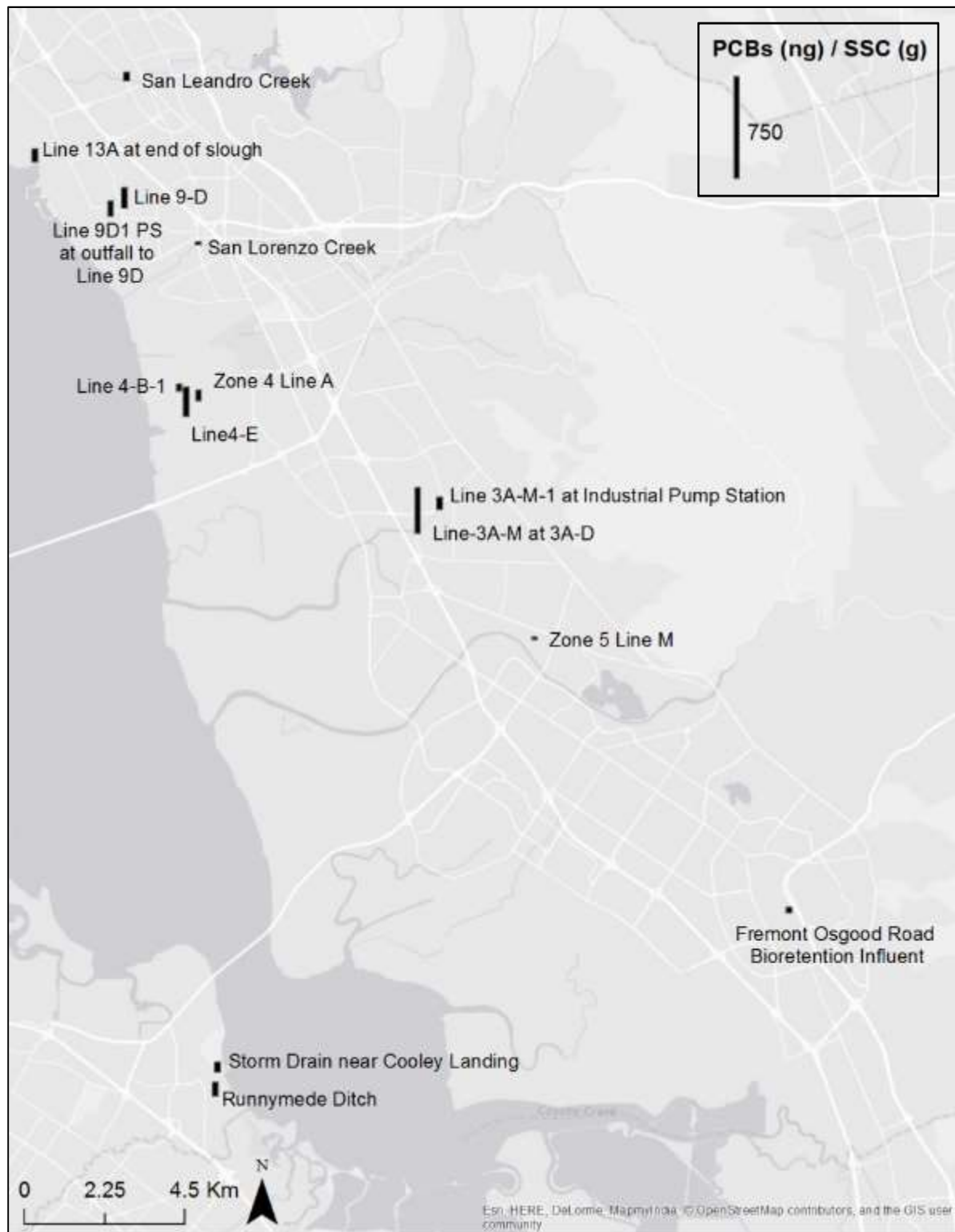


Figure 6c. Distribution of PCB particle ratios in stormwater samples collected by the RMP to date (water years 2003-2016) in southern Alameda and San Mateo counties.



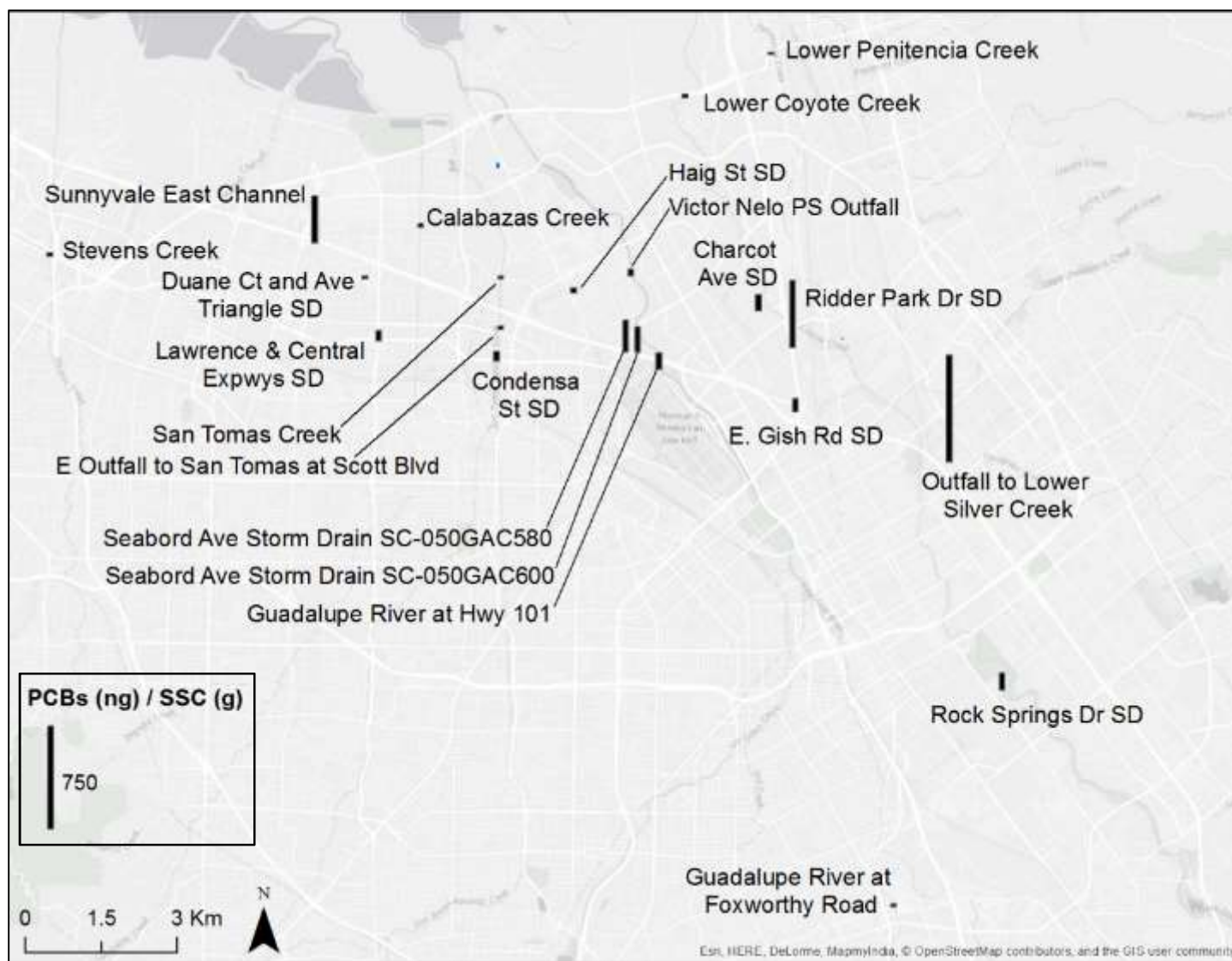


Figure 6d. Distribution of PCB particle ratios in stormwater samples collected by the RMP to date (water years 2003-2016) in Santa Clara County.

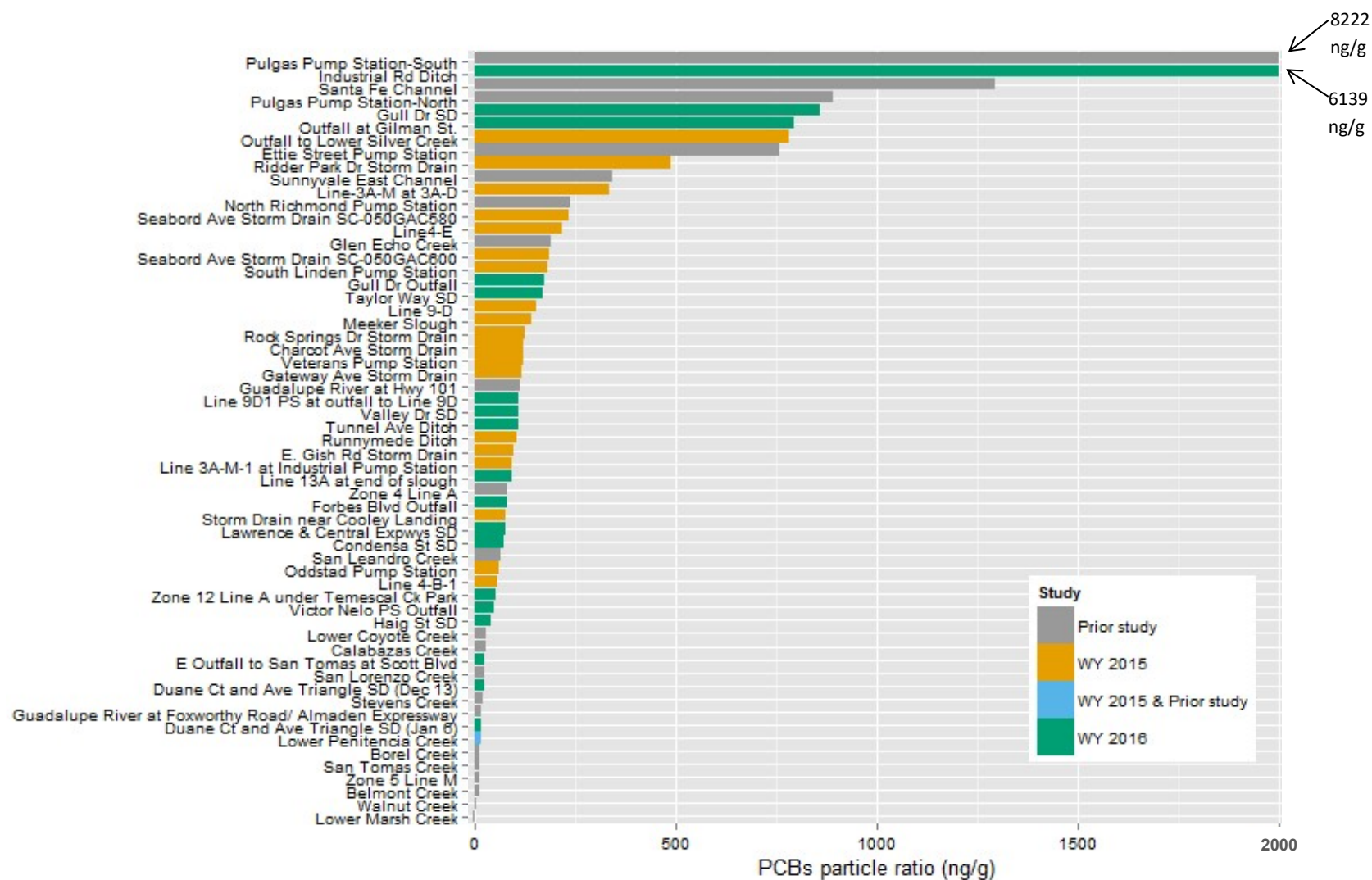


Figure 7. PCB particle ratios for watershed sampling sites measured to date (water years 2003-2016). Note that PCB PRs for Pulgas Pump Station-South (8,222 ng/g) and for Industrial Road Ditch (6,139 ng/g) are beyond the extent of this graph. The sample count represented by each bar in the graph is provided in Appendix B.



To a large degree, sites that rank high for PCB water concentrations also rank high for PRs (Figure 8). Watersheds that rank high in water concentration but low in PR suggest that there are sources present but the PR is diluted by relatively higher rates of clean sediment. Conversely, those watersheds that rank high in PR but not high in water concentration suggest that PCB mobilization is high relative to sediment mobilization. This latter scenario is more likely to occur in watersheds that are highly impervious with little input of clean sediment.

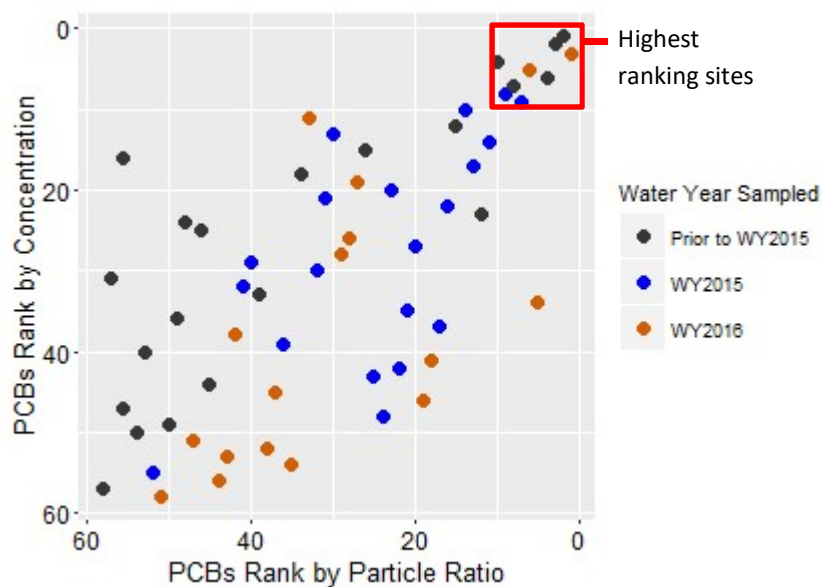


Figure 8. Comparison of site rankings for PCBs based on particle ratios versus water concentrations. 1 = highest rank; 58 = lowest rank.

There are a number of watersheds that have relatively low Hg concentrations (Table 12). In contrast to PCBs, 38 of 62 sampling locations have composite averaged HgT water concentrations less than 53 ng/L (Table 12), the regionally averaged concentration derived from the TMDL target. These lower ranking sites based on water concentrations range in impervious cover from 10 to 87%, with a median of 72%, and likely have very few Hg sources in the watersheds outside of atmospheric deposition<sup>12</sup>. Seventeen sites measured to date (Walnut Creek, Lower Marsh Creek, E Outfall to San Tomas at Scott Blvd, Calabazas Creek, Lower Penitencia Creek, Borel Creek, Zone 4 Line A, San Lorenzo Creek, Runnymede Ditch, Haig St SD, Sunnyvale East Channel, Glen Echo Creek, Stevens Creek, Belmont Creek, Lawrence & Central Expressways SD, Lower Coyote Creek, and Line 9-D) do have PRs <0.25 µg/g, which, given a

<sup>12</sup> Multiple studies in the Bay Area on atmospheric deposition rates for HgT reported very similar wet deposition rates of 4.2 µg/m<sup>2</sup>/y (Tsai and Hoenicke, 2001) and 4.4 µg/m<sup>2</sup>/y (Steding and Flegal, 2002), and Tsai and Hoenicke reported a total (wet + dry) deposition rate of 18-21 µg/m<sup>2</sup>/y. Tsai and Hoenicke computed volume-weighted mean mercury concentrations in precipitation based on 59 samples collected across the Bay Area of 8.0 ng/L. They reported that wet deposition contributed 18% of total annual deposition; scaled to volume of runoff, an equivalent stormwater concentration is 44 ng/L (8 ng/L/0.18 = 44 ng/L).

reasonable expectation of error bars of 25% around the measurements, could be considered equivalent to or less than 0.2 µg/g of Hg on suspended solids, the particulate Hg concentration that was specified in the Bay and Guadalupe River TMDLs (SFBRWQCB, 2006; 2008).

On the other end of the spectrum, there are some watersheds that have elevated HgT concentrations that, if the sources could be found and treated, would reduce HgT loads entering the Bay (Table 12). Based on composite averaged HgT water concentrations, the 10 most polluted sites (ranked in order from high to low) are the Guadalupe River at Hwy 101, Guadalupe River at Foxworthy Road/ Almaden Expressway, Zone 5 Line M, Outfall at Gilman St., San Pedro Storm Drain, Line 13-A at end of slough, Line 9-D-1 PS at outfall to Line 9-D, San Leandro Creek, Walnut Creek, and Santa Fe Channel (Figure 10). Just two of these (Santa Fe Channel and the Outfall at Gilman St.) are also ranked in the top 10 for PCB concentrations in water. Ten watersheds rank in the top 20 for both Hg and PCBs.

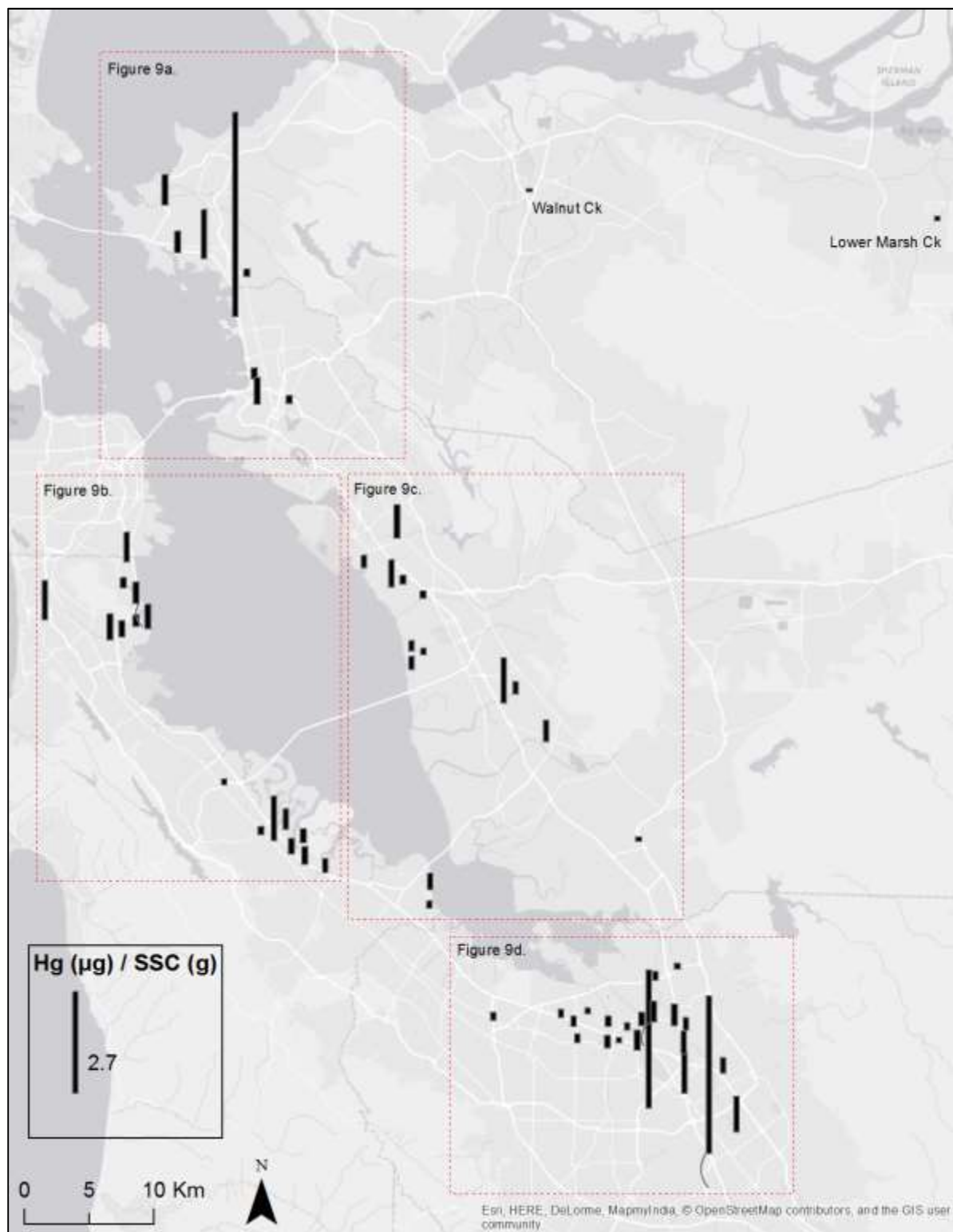


Figure 9. Regional distribution of sites and particle ratios of total mercury (HgT) in stormwater samples collected to date (water years 2003-2016).

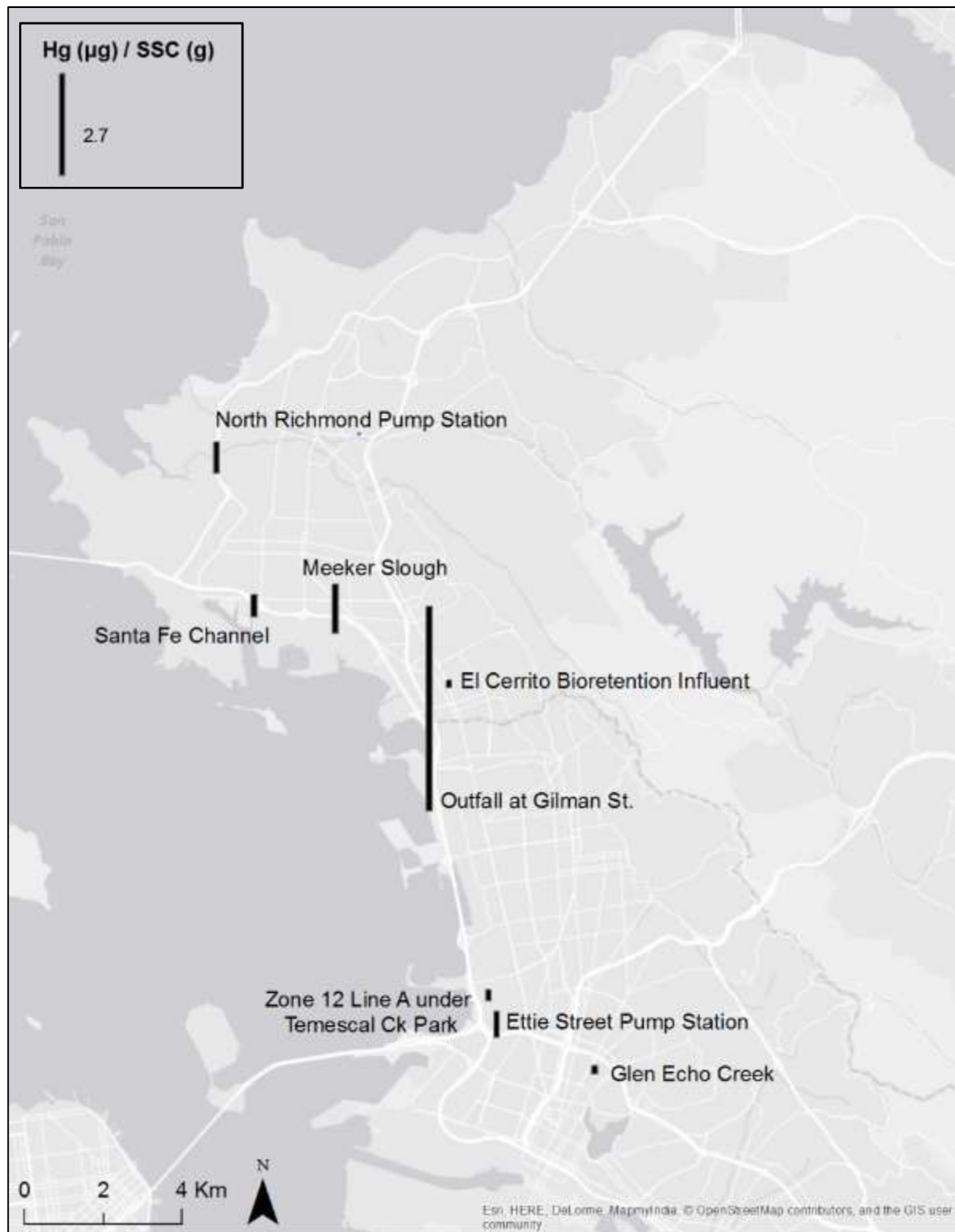


Figure 9a. Distribution of sites and particle ratios of total mercury (HgT) in stormwater samples collected to date (water years 2003-2016) in northern Alameda and Contra Costa Counties.

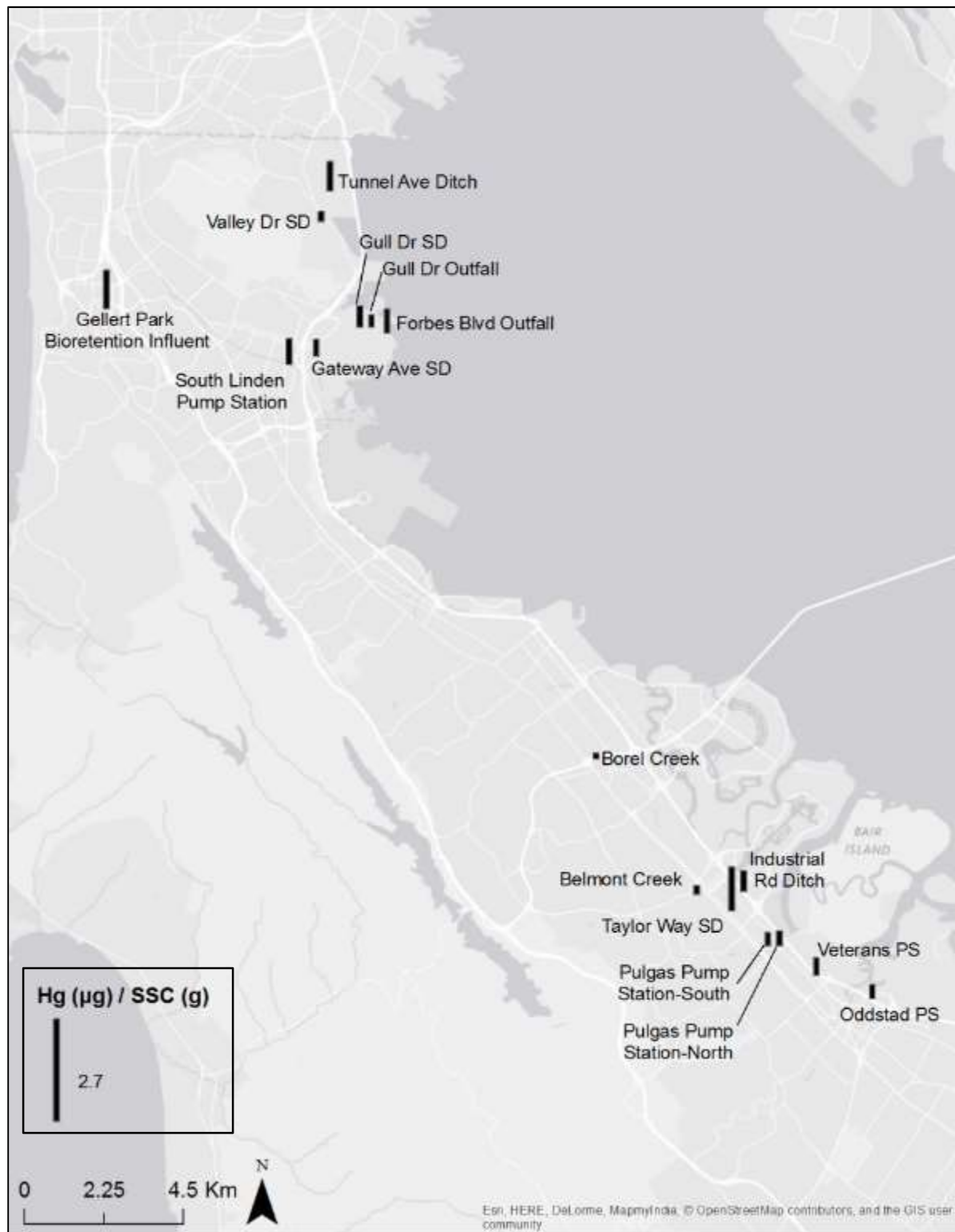


Figure 9b. Distribution of sites and particle ratios of total mercury (HgT) in stormwater samples collected to date (water years 2003-2016) in central and northern San Mateo County.

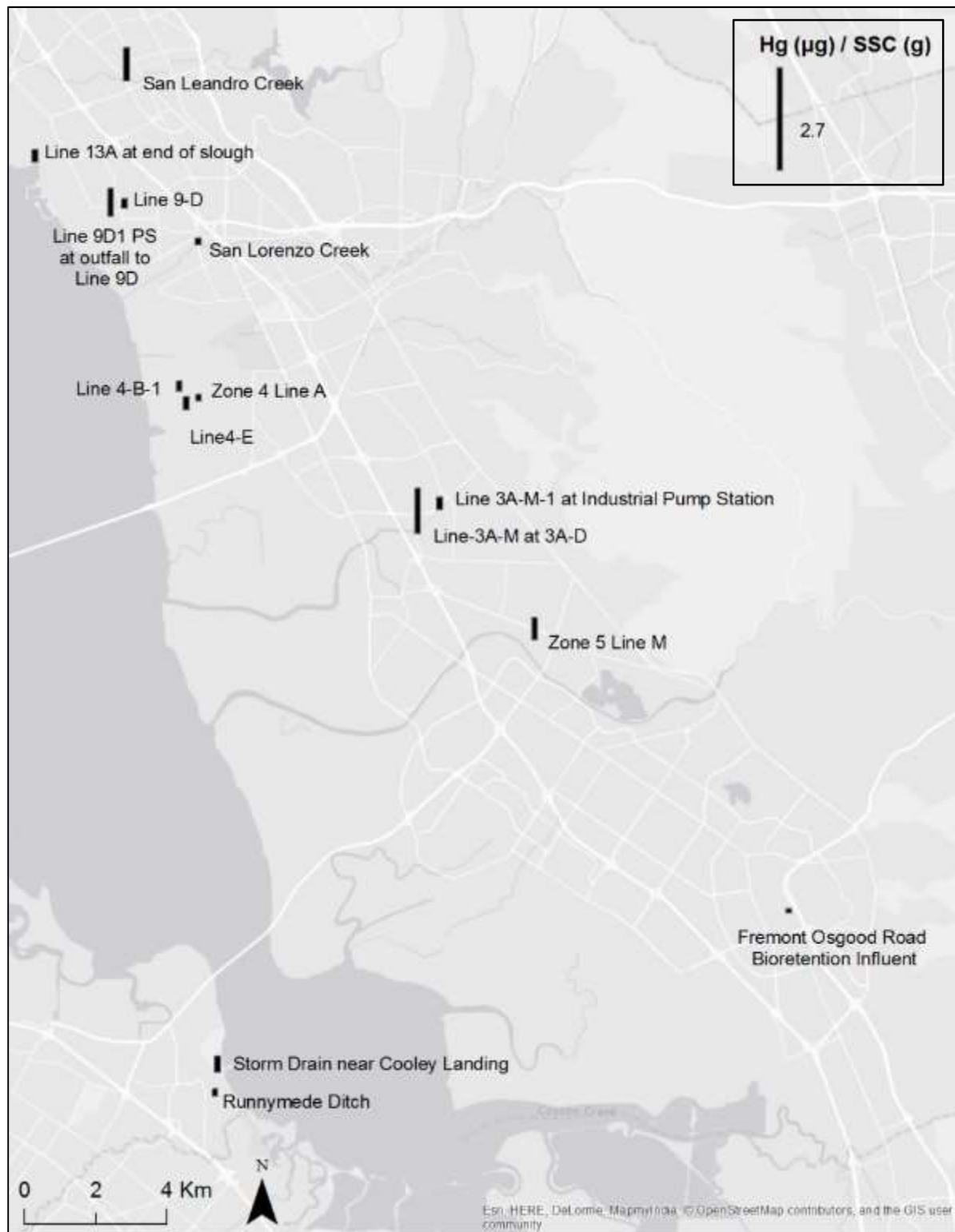


Figure 9c. Distribution of sites and particle ratios of total mercury (HgT) in stormwater samples collected to date (water years 2003-2016) in southern Alameda and San Mateo counties.



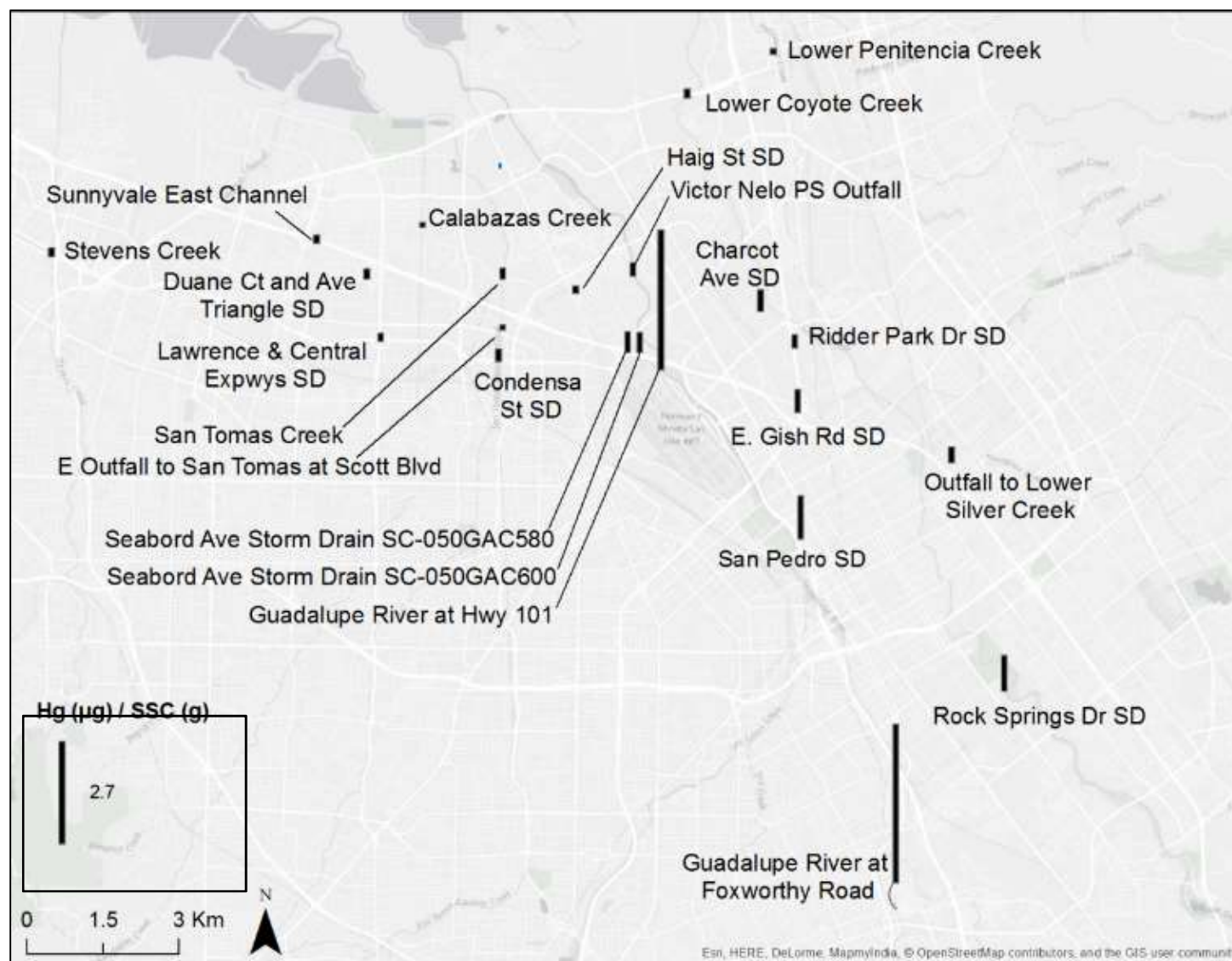


Figure 9d. Distribution of sites and particle ratios of total mercury (HgT) in stormwater samples collected to date (water years 2003-2016) in Santa Clara County.

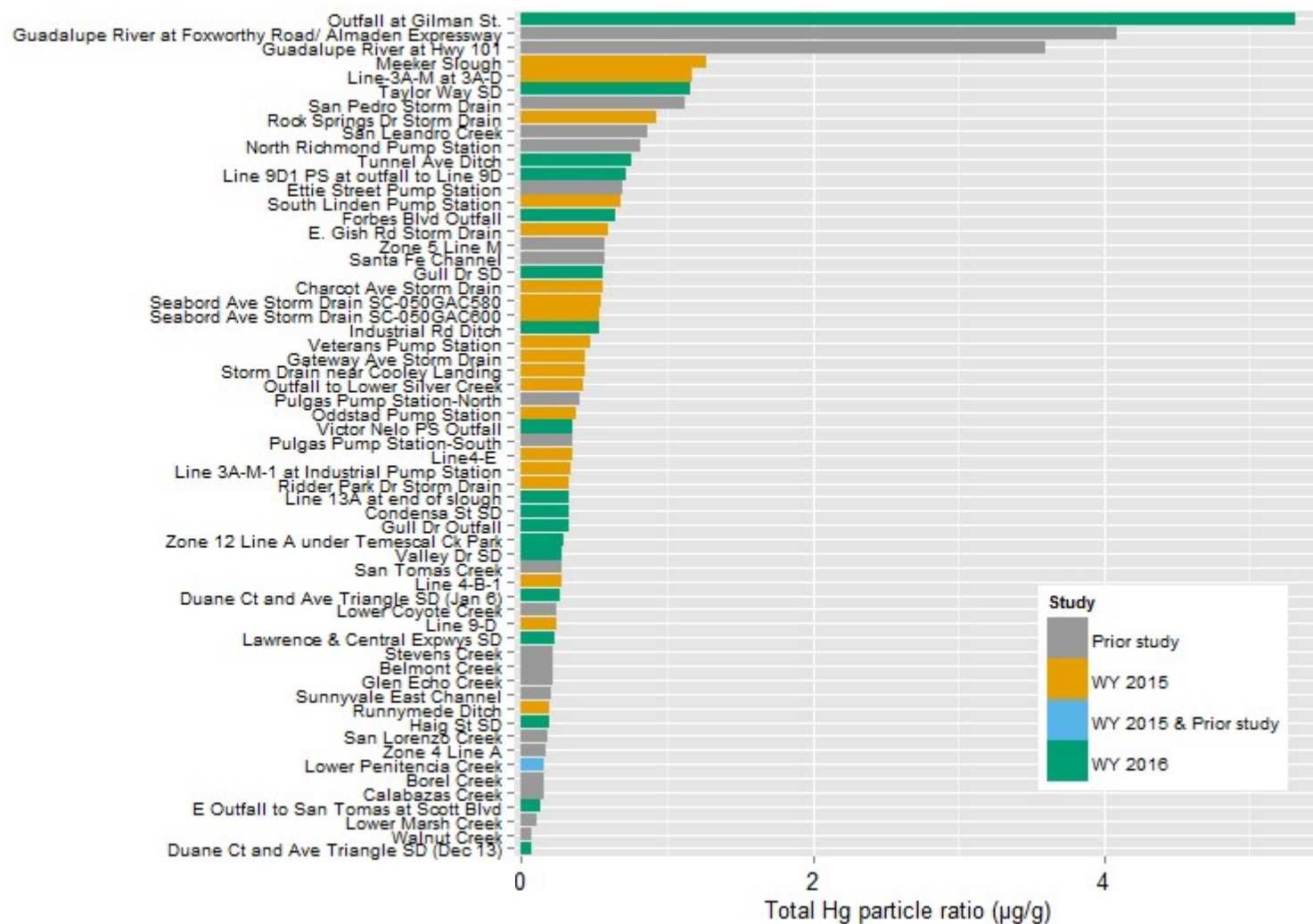


Figure 10. All watershed sampling locations measured to date (water years 2003-2016) ranked by total mercury (HgT) particle ratios. The sample count represented by each bar in the graph is provided in Appendix B.



In contrast to PCBs, sites ranking high for HgT concentration in water are not necessarily ranked high for PR with the exception of a few sites with high HgT (Guadalupe River at Hwy 101, Guadalupe River at Foxworthy Road/ Almaden Expressway, Outfall at Gilman St., San Pedro Storm Drain, and San Leandro Creek) (Figure 11). As discussed above and introduced by McKee et al. (2012), given the atmospheric deposition of Hg across the landscape, and the highly variable sediment erosion in Bay Area watersheds, it is possible to have very elevated HgT stormwater concentrations but very low PRs. The best example of this is Walnut Creek, which was ranked 9<sup>th</sup> highest for stormwater composite averaged concentrations but lowest (59<sup>th</sup> out of 62 ranked watershed locations) for PRs (other examples include Zone 5 Line M, Line 13-A at end of slough, Stevens Creek, Glen Echo Creek, Calabazas Creek, Guadalupe River at Hwy 101). Thus, much more care is needed when ranking the sites for HgT than for PCBs (for which the atmospheric pathway plays less of a role in dispersion). This is consistent with the relative results from the most recent calibrations of the RWSM based on hydrology, for which better calibrations were achieved for PCBs than for Hg (Wu et al., 2016; Wu et al., 2017). A RWSM based on sediment may be more successful for Hg.

Based on PRs (the preferred method), the 10 most polluted sites for HgT are (in addition to the two Guadalupe River mainstem sites): Outfall at Gilman St., Meeker Slough, Line 3A-M at 3A-D, Taylor Way SD, San Pedro Storm Drain, Rock Springs Dr Storm Drain, San Leandro Creek, North Richmond Pump Station, Tunnel Ave Ditch, and Line 9-D-1 PS at outfall to Line 9-D (Table 12; Figure 10). Management in these watersheds might be most cost effective for HgT. The Daly City Library bioretention demonstration project (at Gellert Park), with a PR of 1.0 µg/g, seems to have been placed (quite by accident) in a cost-effective manner and appears to be functioning reasonably well for HgT removal, although there were some concerns about methylmercury production (David et al., 2015). Only one of these top 10 HgT locations was also identified as elevated for PCB PRs (Outfall at Gilman St.), but eight additional watersheds rank in the top 20 for both pollutants (Figure 12)), providing the opportunity for multiple benefits.

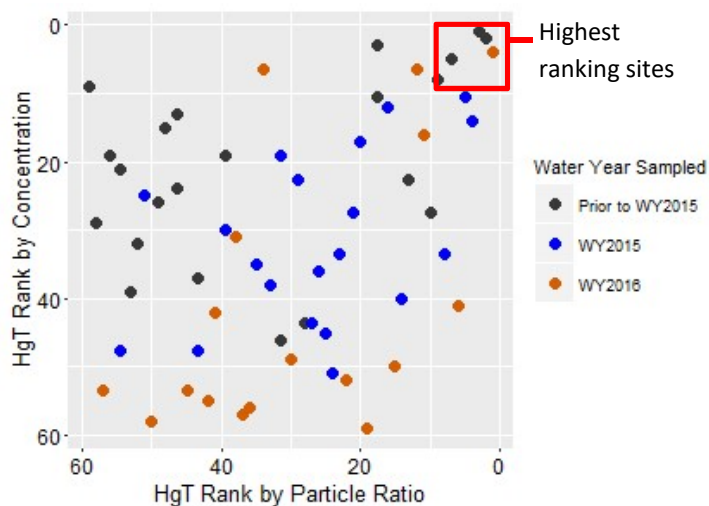


Figure 11. Comparison of site rankings for HgT particle ratios and water concentrations. 1 = highest rank; 59 = lowest rank.

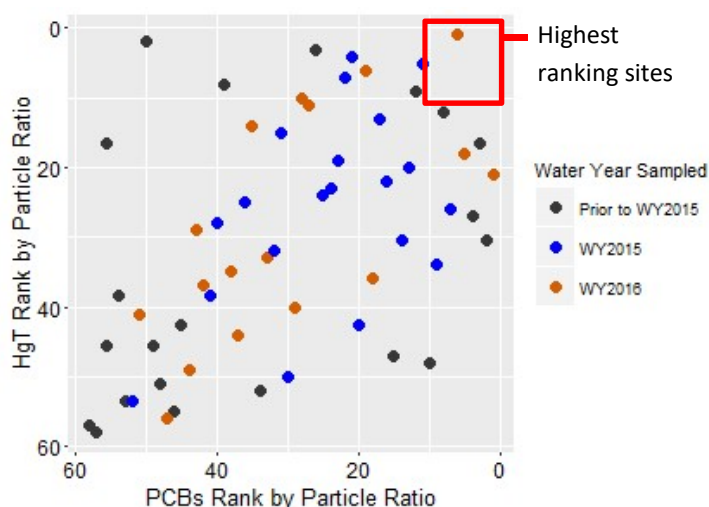


Figure 12. Comparison of site rankings for PCB and HgT particle ratios. 1 = highest rank; 58 = lowest rank. One watershed ranks in the top 10 for both PCBs and HgT, and nine watersheds rank in the top 20 for both pollutants.

### Relationships between PCBs and Hg and other trace substances and land-cover attributes

Beginning in WY 2003, numerous sites have been evaluated for a range of trace elements in addition to PCBs and HgT. These sites include the fixed station loads monitoring sites on Guadalupe River at Hwy 101 (McKee et al., 2006), Zone 4 Line A (Gilbreath et al., 2012a), North Richmond Pump Station (Hunt et al., 2012) and at four sites for which only Cu was measured (Lower Marsh Creek, San Leandro Creek, Pulgas Pump Station-South, and Sunnyvale East Channel) (Gilbreath et al., 2015a). Copper data were also collected at the inlets to several pilot performance studies for bioretention (El Cerrito: Gilbreath et al., 2012b; Fremont: Gilbreath et al., 2015b), and Cu, Cd, Pb, and Zn data were collected at the Daly City Library Gellert Park demonstration bioretention site (David et al., 2015). In addition, during WYs 2015 and 2016, trace element data were collected at an additional 26 locations (See Table 6 earlier in this report). All these data (n=36 sites for Cu; n=30 for Cd, Pb, and Zn; n=28 for As; Mg and Se not included due to small sample size) were pooled to complete a Spearman Rank correlation analysis of relationships between PRs of PCBs and HgT, trace elements, and impervious land cover and old industrial land use (Table 13). In the case of Guadalupe River, the HgT data were removed from the analysis because of historic mining influence in the watershed<sup>13</sup>. Particle ratios were chosen for this analysis for the same reasons as described above and in McKee et al. (2012): the influence of variable sediment production across Bay Area watersheds is best normalized out so that variations in the influence of pollutant sources and mobilization can be more easily observed between sites.

<sup>13</sup> Historic mining in the Guadalupe River watershed caused a unique positive relationship between Hg, Cr, and Ni, and there are unique inverse correlations between Hg and other typically urban metals such as Cu and Pb (McKee et al., 2005).

Based on the available PR data, PCBs correlate positively with impervious cover, old industrial land use and HgT, and inversely correlate with watershed area (Table 13). These observations are consistent with previous analysis (McKee et al., 2012), and make conceptual sense given that larger watersheds tend to have mixed land use and thus a lower proportional amount of PCB source areas. The positive but relatively weak correlation between PCBs and HgT also makes sense given the general relationships between impervious cover and old industrial land use and both PCBs and Hg. However, the weakness of the relationship is probably associated with the larger role of atmospheric recirculation in the mercury cycle and large differences between the use history of each pollutant (PCBs is a legacy contaminant that was used as dielectrics, plasticizers, and oils; Hg was used in electronic devices, pressure and heat sensors, pigments, mildewcides, and dentistry and has a strong contemporary signal in addition to legacy usage). Total Hg also has relationships to impervious cover, old industrial land use, and watershed area that are similar to but weaker than those for PCBs and these geospatial variables. Neither PCBs nor Hg have strong correlations with other trace metals. Based on this analysis using the available pooled data, there is no support for the use of trace metals as a surrogate investigative tool for either PCB or HgT pollution sources. To further explore these relationships, the PCB data were examined graphically (Figure 13). The graphs show that all high PCB concentrations are in small watersheds that have a high proportion of impervious cover and old industrial area. But the lack of a strong correlation between these metrics indicates that not all small, highly impervious watersheds have high PCB concentrations. The data also indicate the presence of outliers that may be worth exploring once additional data are obtained in WY 2017.

Table 11. Spearman Rank correlation matrix based on stormwater samples collected in the Bay Area since water year 2003 (see text for data sources and exclusions). Sample size in correlations ranged from 16 to 61. Values shaded in light blue:  $p < 0.05$ .

	PCBs (pg/mg)	HgT (ng/mg)	Arsenic (ug/mg)	Cadmium (ug/mg)	Copper (ug/mg)	Lead (ug/mg)	Zinc (ug/mg)	Area (sq km)	% Imperviousness	% Old Industrial	% Clay (<0.0039 mm)	% Silt (0.0039 to <0.0625 mm)	% Sands (0.0625 to <2.0 mm)
HgT (ng/mg)	0.51												
Arsenic (ug/mg)	-0.57	0.00											
Cadmium (ug/mg)	-0.35	0.24	0.77										
Copper (ug/mg)	-0.14	0.14	0.78	0.77									
Lead (ug/mg)	-0.29	0.17	0.73	0.90	0.71								
Zinc (ug/mg)	-0.32	0.27	0.63	0.78	0.90	0.68							
Area (sq km)	-0.41	-0.36	-0.14	-0.24	-0.40	-0.06	-0.41						
% Imperviousness	0.52	0.35	-0.23	0.03	0.13	-0.13	0.22	-0.68					
% Old Industrial	0.55	0.35	-0.44	-0.26	-0.29	-0.32	-0.21	-0.46	0.70				
% Clay (<0.0039 mm)	0.28	0.18	-0.12	0.06	-0.22	-0.04	-0.15	-0.41	0.15	0.30			
% Silt (0.0039 to <0.0625 mm)	-0.04	0.11	-0.11	-0.18	0.26	0.00	0.19	0.30	-0.07	-0.14	-0.11		
% Sands (0.0625 to <2.0 mm)	-0.26	-0.14	0.13	-0.07	0.12	0.01	0.04	0.25	-0.17	-0.33	-0.87	-0.50	
TOC (mg/mg)	0.20	0.37	0.69	0.59	0.88	0.47	0.76	-0.53	0.47	0.19	-0.24	0.24	0.20

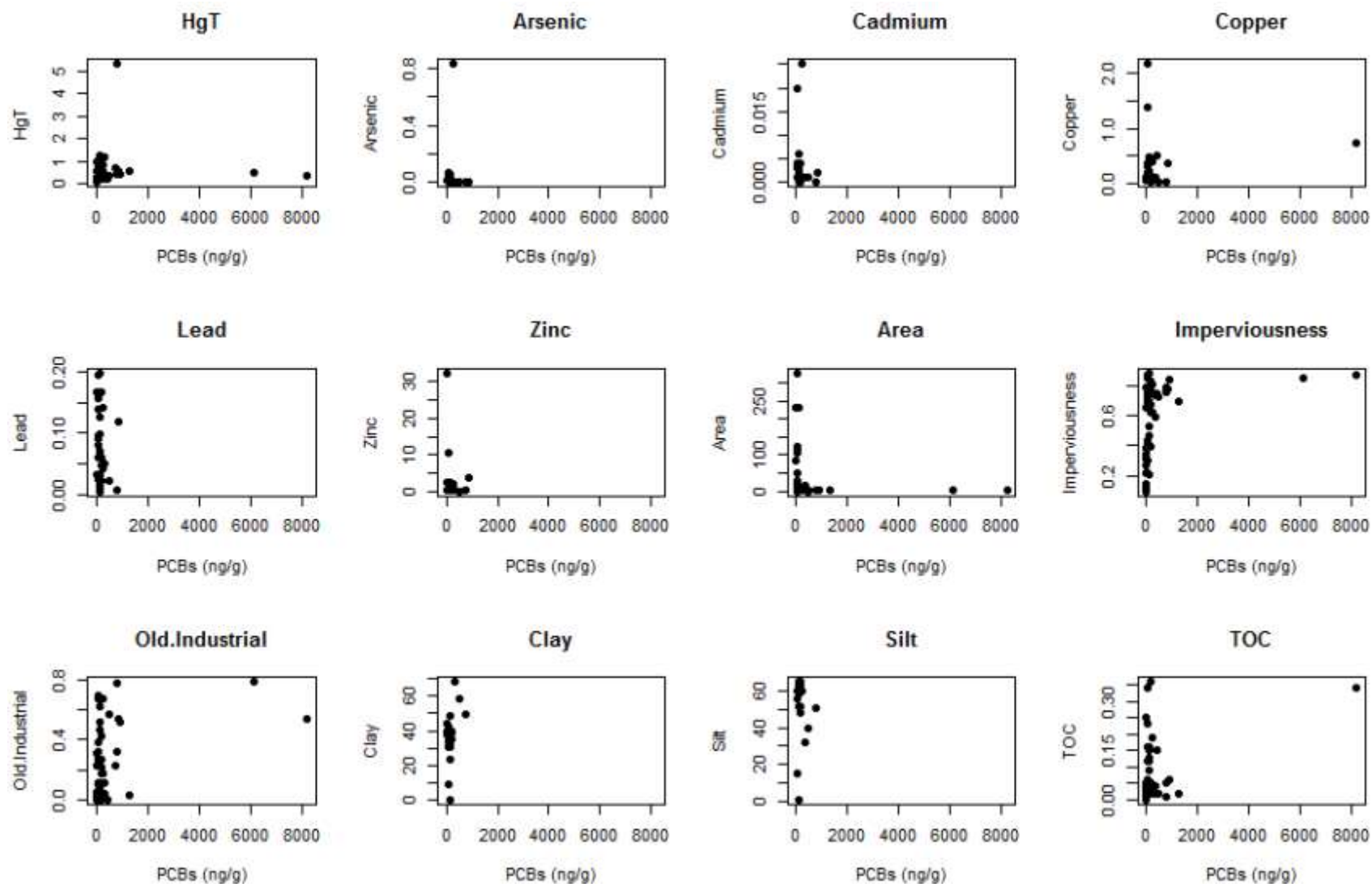


Figure 13. Relationships between observed particle ratios of PCBs and HgT, trace elements, and impervious land cover and old industrial land use.

## Sampling progress in relation to data uses

Sampling completed in older industrial areas can be used as an indicator of progress towards identifying areas for potential management. It has been argued previously that old industrial land use and the specific source areas found within or in association with older industrial areas are likely to have higher concentrations and loads of PCBs and HgT (McKee et al., 2012; McKee et al., 2015).

Regional Monitoring Program sampling for PCBs and HgT since WY 2003 has included 29% of the old industrial land use in the region. The best effort so far has occurred in Santa Clara County (96% of this land use has been sampled), followed by San Mateo County (43%) and Alameda County (33%). In Contra Costa County, only 4% of old industrial land use has been sampled. The disproportional coverage in Santa Clara County is due to sampling of a number of larger watersheds (Lower Penitencia Creek, Lower Coyote Creek, Guadalupe River at Hwy 101, Sunnyvale East Channel, Stevens Creek and San Tomas Creek) that have older industrial land use areas upstream from their sampling points. Of the remaining older industrial land use yet to be sampled, 46% of it lies within 1 km and 67% of it within 2 km of the Bay. These areas are more likely to be tidal, likely to include heavy industrial areas that were historically serviced by rail and ship based transport and military areas, and are often very difficult to sample due to a lack of public rights of way. A different sampling strategy may be needed to effectively determine what pollution might be associated with these areas to better identify areas for potential management.

One objective of data collection is to calibrate the RWSM (Wu et al., 2016). The present version of the model was calibrated using data from 37 watershed areas. Parameterization of the model is currently limited because many of the key source areas are not present in sufficient amounts within the calibration watersheds to strongly influence the calibration procedures. For example, various forms of waste recycling (general waste, metals, auto, drum) only produce an estimated <1.5% of the runoff within the calibration watersheds and were present in <16 of the 37 watersheds (Wu et al., 2017). Based on the extended dataset (now 62 watersheds), the number of sampled watersheds where these types of source areas are present will likely increase. In addition, many of the new watersheds characterized in WY 2016 (described for the first time in this current report) are smaller in size ( $0.23\text{--}17.5\text{ km}^2$ ; mean =  $2.1\text{ km}^2$ ) than those from previous sampling efforts ( $0.0008\text{--}327\text{ km}^2$ ; mean =  $31\text{ km}^2$ ). These watersheds therefore are likely to have more homogeneous land uses and source areas. Addition of these watersheds may help the model to better calibrate by placing stronger constraints on the calibration process for key source areas. Also, the larger range of watershed sizes and land-use characteristics now available provides an opportunity to continue to question and evaluate the most appropriate set of calibration watersheds for estimating regional-scale loads.

## Summary and Recommendations

Despite climatically challenging conditions that resulted in a limited number of storms of appropriate magnitude for sample capture, 37 sites were sampled during WYs 2015 and 2016. At these sites, composite water samples collected during one storm event were analyzed for PCBs, HgT, SSC, selected trace metals, organic carbon and grain size. Sampling efficiency was increased by sampling two sites during a single storm that were near enough to one another that alternating between the two sites was

safe and rapid. At eight of the sampling sites, a second sample was collected in parallel using a Hamlin remote suspended sediment sampler, and at three sites a second sample was collected in parallel using a Walling tube suspended sediment sampler. Based on this dataset, a number of sites with elevated PCB and Hg concentrations and PRs were identified, in part based on an improved effort of site selection focusing on older industrial landscapes. The remote sampler trial showed mixed results and, therefore, needs further testing. Based on the WYs 2015 and 2016 results, the following recommendations were made:

- Continue to select sites based on the four main selection rationales (Section 2.2). The majority of the samples located to assist in identifying areas of potential high leverage (indicated by high unit area loads or PRs/ concentrations relative to other sites). The remaining sites should be allocated to sampling potentially cleaner and variably sized watersheds to help broaden the dataset for regional model calibration and to inform consideration of cleanup potential. Selecting sites of potentially higher leverage by focusing on older industrial and highly impervious landscapes appears successful and should continue.
- Continue to use the composite water-sampling design as developed and applied during WYs 2015 and 2016 with no further modifications. In the event of a higher-rainfall wet season, there might be greater success at tidally influenced sites as, with a greater range of storms to choose from, there will be a greater likelihood that more storm events will fall within the required tidal windows.
- In the next progress report, present an improved analysis of the statistical potential of the composite, single-storm sampling design to return false negative results (low or moderate concentrations when high concentrations are possible). Make recommendations for a procedure to select and resample sites that return lower than expected concentrations or PRs.
- Preliminary results from the remote sampler pilot study indicate that the samplers show promise as a characterization tool for PCBs, but less so for Hg. We recommend continuation of the trial with a focus on collecting samples using the Walling tube remote suspended sediment samplers to amass an equally sized dataset to that already collected for the Hamlin. This will allow comparison of both samplers to the manual composite water sampling design, with the objective of evaluating usefulness and comparability of the data obtained in relation to the management questions.
- Although the Spearman rank analysis did not support the use of other trace metals as good indicators of PCB or Hg sources, the analysis revealed positive and negative correlations that were perplexing and encourage of further investigation that could be completed in the next technical report.

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## Appendices

### Appendix A – Quality assurance

The sections below report quality assurance reviews on WYs 2015 and 2016 data only. The data were reviewed using the quality assurance program plan (QAPP) developed for the San Francisco Bay Regional Monitoring Program for Water Quality (Yee et al., 2015). That QAPP describes how RMP data are reviewed for possible issues with hold times, sensitivity, blank contamination, precision, accuracy, comparison of dissolved and total phases, magnitude of concentrations versus concentrations from previous years, other similar local studies or studies described from elsewhere in peer-reviewed literature and PCB (or other organics) fingerprinting. Data handling procedures and acceptance criteria can differ among programs, however, for the RMP the underlying data were never discarded. Because the results for “censored” data were maintained, the effects of applying different QA protocols can be assessed by a future analyst if desired. Quality assurance (QA) summary tables can be found in Appendix A in addition to the following narrative.

#### *Suspended Sediment Concentration and Particle Size Distribution*

The SSC and particle size distribution (PSD)<sup>14</sup> data from USGS-PCMSC were acceptable, aside from failing hold-time targets. SSC samples were all analyzed outside of hold time (between 9 and 93 days after collection, exceeding the 7-day hold time specified in the RMP QAPP); hold times are not specified in the RMP QAPP for PSD. Minimum detection limits (MDLs) were generally sufficient, with <20% non-detects (NDs) reported for SSC and the more abundant Clay and Silt fractions. Extensive NDs (>50%) were generally reported for the sand fractions starting as fine as 0.125 mm and larger, with 100% NDs for the coarsest (Granule + Pebble/2.0 to <64 mm) fraction. Method blanks and spiked samples are not typically reported for SSC and PSD. Blind field replicates were used to evaluate precision in the absence of any other replicates. The relative standard deviation (RSD) for two field blind replicates of SSC were well below the 10% target. Particle size fractions had average RSDs ranging from 12% for Silt to 62% for Fine Sand. Although some individual fractions had average relative percent difference (RPD) or RSDs >40%, suspended sediments in runoff (and particle size distributions within that SSC) can be highly variable, even when collected by minutes, so results were flagged as estimated values rather than rejected. Fines (clay and silt) represented the largest proportion (~89% average) of the mass.

In 2016 samples, SSC and PSD was analyzed beyond the specified 7-day hold time (between 20 and 93 days after collection) and qualified for holding-time violation but not censored. No hold time is specified for grain-size analysis. Method detection limits were sufficient to have some reportable results for nearly all the finer fractions, with extensive NDs (> 50%) for many of the coarser fractions. No method blanks or spiked samples were analyzed/reported, common with SSC and PSD. Precision for PSD could not be evaluated as no replicates were analyzed for 2016. Precision of the SSC analysis was evaluated

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<sup>14</sup> Particle size data were captured for % Clay (<0.0039 mm), % Silt (0.0039 to <0.0625 mm), % V. Fine Sand (0.0625 to <0.125 mm), % Fine Sand (0.125 to <0.25 mm), % Medium Sand (0.25 to <0.5 mm), % Coarse Sand (0.5 to <1.0 mm), % V. Coarse Sand (1.0 to <2.0 mm), and % Granule + Pebble (>2.0 mm). The raw data can be found in appendix B.

using the field blind replicates and the average RSD of 2.12% was well within the 10% target Method Quality Objective (MQO). PSD results were similar to other years, dominated by around 80% Fines. Average SSC for whole-water samples (excluding those from passive samplers) was in a reasonable range of a few hundred mg/L.

### *Organic Carbon in Water*

Reported TOC and DOC data from EBMUD and ALS were acceptable. TOC samples were field acidified on collection, DOC samples were field or lab filtered as soon as practical (usually within a day) and acidified after, so were generally within the recommended 24-hour holding time. MDLs were sufficient with no NDs reported for any field samples. TOC was detected in only one method blank (0.026 mg/L), just above the MDL (0.024 mg/L), but the average blank concentration (0.013 mg/L) was still below the MDL, so results were not flagged. Matrix spike samples were used to evaluate accuracy, although many samples were not spiked high enough for adequate evaluation (must be at least two times the parent sample concentration). Recovery errors in the remaining DOC matrix spikes were all below the 10% target MQO. TOC errors in WY 2015 averaged 14%, above the 10% MQO, and TOC was therefore qualified but not censored. Laboratory replicate samples evaluated for precision had an average RSD of <2% for DOC and TOC, and 5.5% for POC, within the 10% target MQO. RSDs for field replicates were also within the target MQO of 10% (3% for DOC and 9% for TOC), so no precision qualifiers were needed.

POC and DOC were also analyzed by ALS in 2016. One POC sample was flagged for a holding time of 104 days (past the specified 100 days). All OC analytes were detected in all field samples and were not detected in method blanks, but DOC was detected in filter blanks at 1.6% of the average field sample and 5% of the lowest field sample. The average recovery error was 4% for POC evaluated in LCS samples, and 2% for DOC and TOC in matrix spikes, within the target MQO of 10%. Precision on POC LCS replicates averaged 5.5% RSD, and 2% for DOC and TOC field sample lab replicates, well within the 10% target MQO. No recovery or precision qualifiers were needed. The average 2016 POC was about three times higher than 2014 results. DOC and TOC were 55% and 117% of 2016 results, respectively.

### *PCBs in Water and Sediment*

Water (whole water and dissolved) and sediment (separately analyzed particulate) PCB data from AXYS were acceptable. EPA 1668 methods for PCBs recommend analysis within a year, and all samples were analyzed well within that time (maximum 64 days). MDLs were sufficient with no NDs reported for any of the PCB congeners measured. Some blank contamination was detected in method blanks for about 20 of the more abundant congeners, with only two PCB 008 field sample results censored for blank contamination exceeding one-third the concentration of PCB 008 in those field samples. Many of the same congeners detected in the method blank also were detected in the field blank, but at concentrations <1% the average measured in the field samples and (per RMP data quality guidelines) always less than one-third the lowest measured field concentration in the batch. Three target analytes (part of the "RMP 40 congeners"), PCBs 105, 118, and 156, and numerous other congeners were reported in laboratory control samples (LCS) to evaluate accuracy, with good recovery (average error on target compounds always <16%, well within the target MQO of 35%). A laboratory control material (modified NIST 1493) was also reported, with average error 22% or better for all congeners. Average RSDs for congeners in the field replicate were all <18%, within the MQO target of 35%, and LCS RSDs

were ~2% or better. PCB concentrations have not been analyzed in remote sediment sampler sediments for previous POC studies, so no inter-annual comparisons could be made. PCBs in water samples were similar to those measured in previous years (2012-2014), ranging from 0.25 to 3 times previous averages, depending on the congener. Ratios of congeners generally followed expected abundances in the environment.

AXYS analyzed PCBs in dissolved, particulate, and total fraction water samples for 2016. Numerous congeners had several NDs, but extensive NDs (>50%) were reported for only PCBs 099 and 201 (both 60% NDs). Some blank contamination was detected in method blanks, with results for some congeners in field samples censored due to concentrations that were less than 3 times higher than the highest concentration measured in a blank. This was especially true for dissolved-fraction field samples with low concentrations. Accuracy was evaluated using the laboratory control samples. Again, only three of the PCBs (PCB 105, PCB 118, and PCB 156) reported in the field samples were included in LCS samples (most being non-target congeners), with average recovery errors for those of <10%, well below the target MQO of 35%. Precision on LCS and blind field replicates was also good, with average RSDs <5% and <15%, respectively, well below the 35% target MQO. Average PCB concentrations in total fraction water samples were similar to those measured to previous years, but total fraction samples were around 1% of those measured in 2015, possibly due to differences in the stations sampled.

### *Trace Elements in Water*

Overall the 2015 water trace elements (As, Cd, Pb, Cu, Zn, Hg) data from Brooks Rand Labs (BRL) were acceptable. MDLs were sufficient with no NDs reported for any field samples. Arsenic was detected in one method blank, and mercury in four method blanks; the results were blank corrected, and blank variation was <MDL. No analytes were detected in the field blank. Recoveries in certified reference materials (CRMs) were good, averaging 2% error for mercury to 5% for zinc, all well below the target MQOs (35% for arsenic and mercury; 25% for all others). Matrix spike and LCS recovery errors all averaged below 10%, well within the accuracy MQOs. Precision was evaluated in laboratory replicates, except for mercury, which was evaluated in certified reference material replicates (no mercury lab replicates were analyzed). RSDs on lab replicates ranged from <1% for zinc to 4% for arsenic, well within target MQOs (35% for arsenic and mercury; 25% for all the other analytes). Mercury CRM replicate RSD was 1%, also well within the target MQO. Matrix spike and laboratory control sample replicates similarly had average RSDs well within their respective target MQOs. Even including the field heterogeneity from blind field replicates, precision MQOs were easily met. Average concentrations were up to 12 times higher than the average concentrations of 2012-2014 POC water samples, but whole water composite samples were in a similar range those measured in as previous years.

For 2016 the quality assurance for trace elements in water reported by Brooks Applied Lab (BRL's name post merger) was good. Blank corrected results were reported for all elements (As, Cd, Ca, Cu, Hardness (as CaCO<sub>3</sub>), Pb, Mg, Hg, Se, and Zn). MDLs were sufficient for the water samples with no NDs reported for Cd, Cu, Pb, Hg, and Zn. Around 20% NDs were reported for As, Ca, Hardness, and Mg, and 56% for Se. Mercury was detected in a filter blank, and in one of the three field blanks, but at concentrations <4% of the average in field samples and (per RMP data quality guidelines) always less than one-third the lowest measured field concentration in the batch. Accuracy on certified reference materials was good,



with average %error for the CRMs ranging from 2 to 18%, well within target MQOs (25% for Cd, Ca, Cu, Pb, Mg, Zn; 35% for As, Hg, and Se). Recovery errors on matrix spike and LCS results on these compounds was also good, with the average errors all below 9%, well within target MQOs. The average error of 4.8% on a Hardness LCS was within the target MQO of 5%. Precision was evaluated for field sample replicates, except for Hg, where matrix spike replicates were used. Average RSDs were all < 8%, and all below their relevant target MQOs (5% for Hardness; 25% for Cd, Ca, Cu, Pb, Mg, Zn; 35% for As, Hg, and Se). Blind field replicates were also consistent, with average RSDs ranging from 1% to 17%, all within target MQOs. Precision on matrix spike and LCS replicates was also good. No qualifiers were added. Average concentrations in the 2016 water samples were in a similar range of POC samples from previous years (2003-2015), with averages ranging 0.1x to 2x previous years' averages.

### *Trace Elements in Sediment*

A single sediment sample was obtained in 2015 from fractionating one Hamlin sampler and analyzing for As, Cd, Pb, Cu, Zn, and Hg concentration on sediment. Overall the data were acceptable. MDLs were sufficient with no NDs for any analytes in field samples. Arsenic was detected in one method blank (0.08 mg/kg dw) just above the MDL (0.06 mg/kg dw), but results were blank corrected and the blank standard deviation was less than the MDL so results were not blank flagged. All other analytes were not detected in method blanks. CRM recoveries showed average errors ranging from 1% for copper to 24% for mercury, all within their target MQOs (35% for arsenic and mercury; 25% for others). Matrix spike and LCS average recoveries were also within target MQOs when spiked at least 2 times the native concentrations. Laboratory replicate RSDs were good, averaging from <1% for zinc to 5% for arsenic, all well within the target MQOs (35% for arsenic and mercury; 25% for others). Matrix spike RSDs were all 5% or less, also well within target MQOs. Average results ranged from 1 to 14 times higher than the average concentrations for the RMP Status and Trend sediment samples (2009-2014). Results were reported for Mercury and Total Solids in one sediment sample analyzed in two laboratory batches. Other client samples (including lab replicates and Matrix Spike/Matrix Spike replicates), a certified reference material (CRM), and method blanks were also analyzed. Mercury results were reported blank corrected.

In 2016, a single sediment sample was obtained from a Hamlin sampler, which was analyzed for total Hg by BAL. MDLs were sufficient with no NDs reported, and no target analytes were detected in the method blanks. Accuracy for mercury was evaluated in a CRM sample (NRC MESS-4). The average recovery error for mercury was 13%, well within the target MQO of 35%. Precision was evaluated using the laboratory replicates of the other client samples concurrently analyzed by BAL. Average RSDs for Hg and Total Solids were 3% and 0.14%, respectively, well below the 35% target MQO. Other client sample matrix spike replicates also had RSDs well below the target MQO, so no qualifiers were needed for recovery or precision issues. The Hg concentration was 30% lower than the 2015 POC sediment sample.

## Appendix B – Figures 7 and 10 Supplementary Info

Table Appendix B: Sample counts for data displayed in Figures 7 and 10 bar graphs. For samples with a count of 2 or more, the central tendency was used which was calculated as the sum of the pollutant water concentrations divided by the sum of the SSC data.

Catchment	Year Sampled	PCB sample count	HgT sample count
Belmont Creek	Prior to WY2015	3	4
Borel Creek	Prior to WY2015	3	5
Calabazas Creek	Prior to WY2015	5	5
Charcot Ave Storm Drain	WY2015	1	1
Condensa St SD	WY2016	1	1
Duane Ct and Ave Triangle SD	WY2016	1	1
E Outfall to San Tomas at Scott Blvd	WY2016	1	1
E. Gish Rd Storm Drain	WY2015	1	1
Ettie Street Pump Station	Prior to WY2015	4	4
Forbes Blvd Outfall	WY2016	1	1
Gateway Ave Storm Drain	WY2015	1	1
Glen Echo Creek	Prior to WY2015	4	4
Guadalupe River at Foxworthy Road/ Almaden Expressway	Prior to WY2015	14	46
Guadalupe River at Hwy 101	Prior to WY2015	119	261
Gull Dr Outfall	WY2016	1	1
Gull Dr SD	WY2016	1	1
Haig St SD	WY2016	1	1
Industrial Rd Ditch	WY2016	1	1
Lawrence & Central Expwys SD	WY2016	1	1
Line 13A at end of slough	WY2016	1	1
Line 3A-M-1 at Industrial Pump Station	WY2015	1	1
Line 4-B-1	WY2015	1	1
Line 9-D	WY2015	1	1
Line 9D1 PS at outfall to Line 9D	WY2016	1	1
Line-3A-M at 3A-D	WY2015	1	1
Line4-E	WY2015	1	1
Lower Coyote Creek	Prior to WY2015	5	6
Lower Marsh Creek	Prior to WY2015	28	31
Lower Penitencia Creek	WY2015	4	4
Meeker Slough	WY2015	1	1
North Richmond Pump Station	Prior to WY2015	38	38
Oddstad Pump Station	WY2015	1	1
Outfall at Gilman St.	WY2016	1	1



Catchment	Year Sampled	PCB sample count	HgT sample count
Outfall to Lower Silver Creek	WY2015	1	1
Pulgas Pump Station-North	Prior to WY2015	4	4
Pulgas Pump Station-South	Prior to WY2015	29	26
Ridder Park Dr Storm Drain	WY2015	1	1
Rock Springs Dr Storm Drain	WY2015	1	1
Runnymede Ditch	WY2015	1	1
San Leandro Creek	Prior to WY2015	39	38
San Lorenzo Creek	Prior to WY2015	5	6
San Pedro Storm Drain	Prior to WY2015		3
San Tomas Creek	Prior to WY2015	5	5
Santa Fe Channel	Prior to WY2015	5	5
Seabord Ave Storm Drain SC-050GAC580	WY2015	1	1
Seabord Ave Storm Drain SC-050GAC600	WY2015	1	1
South Linden Pump Station	WY2015	1	1
Stevens Creek	Prior to WY2015	6	6
Storm Drain near Cooley Landing	WY2015	1	1
Sunnyvale East Channel	Prior to WY2015	42	41
Taylor Way SD	WY2016	1	1
Tunnel Ave Ditch	WY2016	1	1
Valley Dr SD	WY2016	1	1
Veterans Pump Station	WY2015	1	1
Victor Nelo PS Outfall	WY2016	1	1
Walnut Creek	Prior to WY2015	6	5
Zone 12 Line A under Temescal Ck Park	WY2016	1	1
Zone 4 Line A	Prior to WY2015	69	94
Zone 5 Line M	Prior to WY2015	4	4