

Concentrations and Loads of Trace Contaminants in a Small Urban Tributary, San Francisco Bay, California

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Acknowledgements

The authors thank Alameda County for access to the sampling location. We thank Rand Eads of RiverMetrics for providing technical assistance specifically in site design and equipment installation and ongoing discussion of discharge, turbidity, and sediment interpretation. We thank Jon Leatherbarrow for his instrumental role in the study design and field work. For their analysis of the water quality samples, we thank Moss Landing Marine Laboratories, AXYS Analytical Laboratories, Brooks Rand Laboratories, East Bay Municipal Utilities District, the Romberg-Tiburon Center, AMS Texas, and Columbia Analytical Services. We also thank Rachel Allen, Nicole David, Jennifer Hunt, Kat Ridolfi, Sarah Pearce, Ben Greenfield, and Katie Harrold (all SFEI staff) for their help in the field. We are indebted to Barbara Mahler, James Kuwabara, Greg Shellenberger, and Peter Mangarella for their thorough and thoughtful review of the manuscript and the many improvements that resulted. This project was funded by the San Francisco Bay Regional Monitoring Program for Water Quality (RMP), and we gratefully acknowledge the support of the Sources Pathways and Loadings Workgroup, the Technical Review Committee, and the Steering Committee of the RMP.

This report can be cited as:

Gilbreath, A., Yee, D., McKee, L., 2012. Concentrations and loads of trace contaminants in a small urban tributary, San Francisco Bay, California. A Technical Report of the Sources Pathways and Loading Work Group of the Regional Monitoring Program for Water Quality: Contribution No. 650. San Francisco Estuary Institute, Richmond, California. pp 40.

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Abstract

Urban runoff has been identified in water-quality policy documents for San Francisco Bay as a large and potentially controllable source of pollutants. In response, concentrations of suspended sediments, mercury and other trace elements, and a range of trace organic compounds were measured in dry and wet weather runoff from a 100% urban watershed. Loads for Water Years 2007-2010 were estimated using regression with turbidity or stratified flow-weighted mean concentration approaches depending on available data and pollutant characteristics. More than 95% of the loads for most pollutants were transported during storm events, along with 90% of the total discharge. Suspended sediment concentrations ranged between 1.4 and 2700 mg/L and varied with storm intensity. The average suspended sediment yield was 30 t/km²/year. Total Hg ranged between 1.4 and 150 ng/L and was on average 92% particulate, 0.9% methylated, and 1.2% acid labile. Total Hg yield averaged 5.7 µg/m²/year. The relative magnitude of loadings for organic contaminant classes were PAHs > pyrethroids > PBDEs > PCBs > OC pesticides > dioxins. Total PCBs ranged between 0.3 and 110 ng/L, and were dominated by the congeners 110, 138, 149, 153 and 180, the sum of which averaged 33% of the total. Less chlorinated congeners were more prevalent during dry weather flows relative to storm flows. PAHs have mixed petroleum and combustion origins mostly associated with automobile activities, and a contribution from coal tar sealcoat might be indicated. This dataset fills an important local data gap for highly urban watersheds of San Francisco Bay. The methods, the uniqueness of the analyte list (e.g., Ag, Se including Se speciation, MeHg, acid labile Hg, dioxins, PBDEs, pyrethroids), and resulting interpretations have applicability for managing pollutant loads in urban watersheds in other parts of the world.

Introduction

Runoff from industrial and other urban developments is often contaminated with mercury (Mason and Sullivan, 1998; Lawson and Mason, 2001; Lawson et al., 2001; Eckley and Branfireun, 2008), other trace elements (Characklis and Wiesner, 1997; Davis et al., 2001; Buffleben et al., 2002; Asaf et al., 2004), trace organic compounds (Horstmann and McLachlan, 1995; Dickhut et al., 2000; Smith et al., 2000; Ngabe et al., 2000; Rossi et al., 2004; Stein et al., 2006; Suarez et al., 2006; Hwang and Foster, 2006, 2008; Weston et al., 2009; Zhang et al., 2010), and nutrients (Line et al., 2002; Coats et al., 2008; Kaushal et al., 2008). Estuaries adjacent to urban and industrial areas are particularly susceptible to impairment and enhanced bioaccumulation because they often have long flushing times (e.g., Nixon et al., 1996), net sediment deposition (e.g., the classic work of Meade, 1969), and high biological productivity (Cloern, 2001; Cloern et al., 2007). San Francisco Bay, the “urbanized estuary” (Conomos, 1979), is a typical example of a system impacted by numerous pollutants of concern emanating from local and globally sourced aerial deposition, wastewater discharge, and runoff from more than 250 urbanized tributaries and the large inland rivers of the Central Valley of California (McKee et al., 2006; David et al., 2009). It represents a quintessential example of the challenges of estuarine management and provides a focal point for voluminous scientific research in support of characterizing water quality issues (Flegal et al., 2007; Cloern et al., 2007; 2010).

San Francisco Bay receives freshwater inputs from the Sacramento-San Joaquin River Delta ($24.9 \times 10^9 \text{ m}^3$), direct precipitation ($0.495 \times 10^9 \text{ m}^3$), and wastewater discharge ($0.87 \times 10^9 \text{ m}^3$) (Oram et al., 2008). Nine counties encircle the Bay with a population of 7.15 million people (US Census Bureau, 2010). Runoff from the nine counties is estimated to be $1.59 \times 10^9 \text{ m}^3$ (Lent and McKee, 2012). Although this volume represents only 6% of the total freshwater input, pollutant loads from the urban landscape are likely disproportionately large because of the legacy of industrial land use and the historic use of many particle reactive, currently banned or restricted substances. These include polychlorinated biphenyls (PCBs), organochlorine pesticides (dichloro-diphenyl-trichloroethane (DDT), chlordane, dieldrin), polybrominated diphenyl ethers (PBDEs), and mercury (Hg).

Urban stormwater runoff has been identified by the San Francisco Bay Regional Water Quality Control Board in the total maximum daily loads reports (TMDLs) and Basin Plan policy documents as a large and potentially controllable source of pollutants (Water Board, 2006; 2008). However, because available data were scarce, the Water Board recommended improved stormwater load estimates as part of the implementation plans to support management decisions and build baseline data against which to measure response to management actions. To this end, a highly urbanized tributary in Hayward, California, called Zone 4 Line A (Z4LA) was chosen for monitoring to represent a class of smaller mixed urban drainages on the Bay margin. The goals of this study are to report on concentrations and loads for pollutants from the Z4LA

watershed for water years (WYs) 2007-2010 and compare these to urban areas in other parts of the world.

Methods

Field Sampling and Loads Calculations

The Z4LA watershed encompasses 4.17 km² of relatively flat (average surface slope 0.4%) urban landscape and flows directly to the Bay (Figure 1). Because of the flat landscape, the channel of Z4LA is entirely engineered. Land use is 19% industrial, 35% commercial, 27% residential, 17% transportation, and 2% open space parks. The channel receives no wastewater and no imported water with the exception of minor landscape irrigation overflow and other dry weather discharge of unknown origin. The watershed has a pronounced wet season and receives 95% of its rainfall between October and April from an average of 51 rain days (defined as ≥ 1 mm at the Alameda County gage, Hayward 541A).

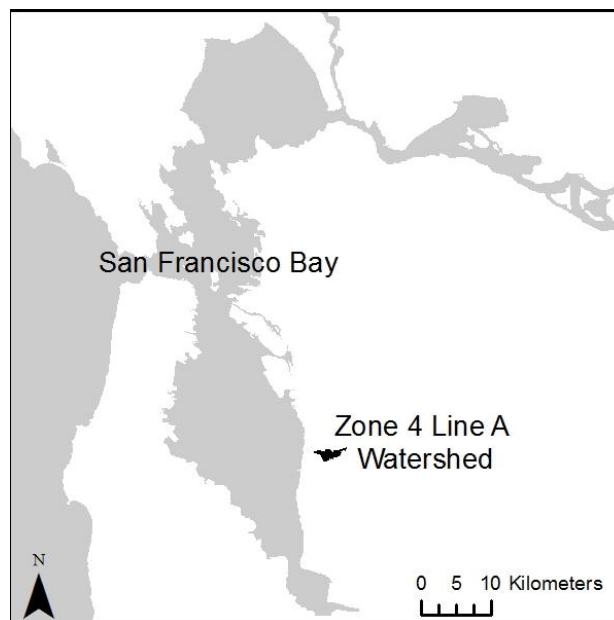


Figure 1: Location of Zone 4 Line A watershed, Hayward, California, USA.

Sampling was carried out where Cabot Boulevard (Hayward, CA) crosses the open engineered channel, approximately 1.7 km from the Bay and upstream from tidal influence. Here, the channel flows through a rectangular box culvert, and the channel is straight and uniform immediately upstream. Flow and suspended sediments (80% <62.5 microns) in this fast flowing turbulent channel were likely well mixed as they passed through the sampling location. Rainfall (Campbell Scientific TE525 tipping bucket rain gauge), stage (INW PS-9805 pressure transducer) and turbidity (Forest Technology Systems Limited DTS-12) data were recorded continuously, initially at 10 minute intervals, and at 5 minute intervals after February 6, 2007 to improve data resolution during flashy storm flow. Water samples were collected with an ISCO 6712 pumping

sampler for analysis of suspended sediment concentration (SSC). The turbidity probe and ISCO intake tube were attached to a boom mounted in the center of the channel using a float to position the equipment approximately mid-depth. The ISCO sampler was triggered when pre-established turbidity thresholds were surpassed (Lewis et al. 2001) so that samples were collected representatively over rising, peak and falling stages. The Campbell Scientific CR10X data logger that controlled all automatic sampling operations was downloaded using a laptop computer at a maximum interval of 17 days.

Manually collected water samples for analysis of pollutants were taken using clean protocols (e.g., USEPA 1996). During high flow, depth-integrated samples were collected by inserting an acid-cleaned 1-L Teflon sample bottle into a D-95 Teflon coated depth-integrating sampler. The sampler was lowered into the channel using a winch and crane from a purpose built sampling platform that spanned the width. During stages sufficiently low for wading (< 0.5 m), samples were collected by hand-dipping sample containers mid-depth, mid-channel. Sampling was focused primarily during storms, during which the majority of contaminants loads are carried into the Bay, and some non-storm flow samples were also collected to characterize low flow conditions. All samples were labeled, placed on ice, and transported to the laboratory for preservation using a consistent chain-of-custody data management system.

Velocity was measured manually using a Marsh-McBirney Model 2000 Flo-Mate portable flowmeter. During wading conditions, the 10-second average velocity was measured at 60% depth at every 0.3 m width increment. At higher flows, velocity was measured in the same width increments at 20%, 60%, and 80% depth. For both protocols, the staff plate readings were recorded during the procedure, and cross referenced with the continuous electronic stage measurements. Velocity measurements were combined with continuously collected stage measurements and cross section dimensions to generate a stage-discharge relationship, and from this, continuous discharge data at 5- or 10-minute intervals was calculated. The resulting high temporal resolution discharge data were the basis for all loads calculations.

Loads calculations for WYs 2007-2010 were made using two well established methods depending on data availability and pollutant characteristics. For most pollutants with a strong affinity to particles during wet weather transport (HgT, Al, Cd, Cr, CuT, Fe, Pb, Ni, Ag, Zn, PCBs, dioxins, PBDEs, polycyclic aromatic hydrocarbons (PAHs), DDT, chlordanes, dieldrin, hexachlorocyclohexane (HCHs), bifenthrin, delta/tralomethrin, and permethrin), continuous short time interval concentrations were calculated using regression with turbidity (often referred to as a regression estimator loads method; Walling and Webb, 1985), then combined with the discharge data to derive “instantaneous” loads which were then summed to any longer time interval desired (storm, daily, monthly, or wet season). The turbidity surrogate regression estimator for Hg has been discussed previously and found to work well for urbanized and mixed land use systems (e.g., Quémérais et al., 1999; Wall et al., 2005).

The total error in our loads calculations using the turbidity surrogate regression methodology was estimated using the reasonable maximum error associated with each source of uncertainty in the analyses and calculations. Errors accounted for during mass loads estimation were flow ($\pm 10\%$), turbidity ($\pm 2\%$), trace contaminant specific regressions with turbidity (3% for aluminum to 20.5% for nickel and permethrin) and the mean coefficient of variation (CV) of duplicates (0.4%-51%, from the greater of laboratory or field replicates). Therefore, the total estimated errors for mass loads calculations ranged between 14 and 72%.

Loads for some pollutants of interest are not transported on particles and were laboratory measured in dissolved phase (total dissolved N (TDN), total dissolved P (TDP), nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$), PO_4 , NH_4). Yet others were laboratory measured on whole water samples as total concentrations but were likely mostly dissolved or had more complex seasonal processes (Se, methylmercury (MeHg)). In these cases, the data were averaged by weighting for flow (often referred to as a flow-weighted-mean-concentration (FWMC)) (Walling and Webb, 1985). To increase the accuracy of these load estimates, the data were stratified into low and storm flow regimes (threshold set at $0.05 \text{ m}^3/\text{s}$). Stratification of the data in this manner has been previously applied for Chesapeake Bay tributaries and found to improve the accuracy of loading estimates (Lawson et al., 2001). The FWMC for each flow stratum was then combined with flow data to derive 5- or 10-minute interval loads.

The errors for the FWMC loads were estimated in the same manner as for the regression method, except substituting the regression error component with an error associated with flow weighting (37-142%) (see below for further explanation). Because no field or laboratory duplicates were measured in this study for nutrients, replicate uncertainty was estimated from data published previously by McKee et al. (2000) using the same laboratory methods. The total estimated errors for mass loads calculations using the FWMC approach ranged between 55% and 167%.

To illustrate the potential error associated with FWMC estimates using only two strata, loads were calculated for HgT and PCBs (two of our most sampled analytes) using FWMC estimates to compare to the loads estimated by the turbidity surrogate regression method. The average bias (the relative difference between the two methods) for the four water years ranged between 67% and 120% (mean 101%) of the load estimated by regression for HgT. The range was less favorable for PCBs (98.6% to 156%; mean 134% of the load estimated by regression) but still within the errors of the loads calculations. The high and low flow FWMCs themselves also have some uncertainties in their estimates. The flow-weighted standard deviations for pollutants excluding SeT and $\text{NO}_3 + \text{NO}_2$ ranged from 16 to 63% of their respective FWMCs, however SeT returned flow-weighted standard deviations of 113% for low flow samples and 127% for storm flow samples, and $\text{NO}_3 + \text{NO}_2$ was only sampled during storm flow and returned a flow-weighted standard deviation of 142%. Typically the uncertainties around the high-flow FWMCs were

larger than those around the low-flow FWMCs because the range of events in that stratum was wider.

Additional uncertainties might arise from the representativeness of the events sampled for the FWMC estimate. For the period for which estimated loads were calculated using the storm flow FWMC, 0% (for arsenic) to 30% of the samples for each analyte were collected during high flow intervals accounting for the top 25% of cumulative flow ($>2.66 \text{ m}^3/\text{s}$), 40-67% of the samples for each analyte were collected from the middle 50% of total flow (0.51 to $2.66 \text{ m}^3/\text{s}$), and 25-60% (again for arsenic) of samples for each analyte were collected from periods accounting for the lowest 25% of cumulative flow ($<0.51 \text{ m}^3/\text{s}$). This distribution suggests that on average all the flow regimes were sampled proportionately for most analytes, and adds to our confidence that application of the FWMC methodology to intermediate and moderately low flows (down to $0.05 \text{ m}^3/\text{s}$) might be performing well for the annual load for individual contaminants.

Because there were no long term runoff measurements for the watershed, climatically adjusted “long term average loads” were calculated by regressing monthly calculated loads against monthly rainfall recorded at the Alameda County gage, Hayward 541A for a 12 year period.

Analytical Methods & QA/QC

Samples were analyzed for SSC by Moss Landing Marine Laboratories (MLML), California, using the laboratory’s method MPSL-108, a filtration and drying method similar to Standard Methods 2540 D for total suspended solids (TSS), except avoiding subsampling variability by filtering the entire volume in a sample container. No samples were reported as non-detects. Laboratory replicates were not possible for SSC as the entire volume was consumed for each analysis. Field sample replicates were collected and were variable as expected (sometimes $>10\%$ relative standard deviation (RSD)) given typically rapid changes in storm flood flow. Samples for those batches were flagged but not censored (because they were still within double the target range, i.e., 20%) for uncertainty in precision.

Samples were analyzed for Hg and MeHg by MLML using laboratory-specific variants of EPA Method 1631 Revision E (Hg) and 1630 (MeHg) and cold-vapor atomic fluorescence spectrometer (CVAFS) detection. Dissolved samples were filtered at the laboratory within 48 hours of collection through a $0.45\text{-}\mu\text{m}$ capsule filter or filter unit prior to preservation by addition of 0.5% v/v bromine monochloride (BrCl) solution for HgD or HCl for MeHgD. Brooks Rand Laboratory (BRL), Washington, analyzed “acid labile Hg”, the inorganic component that is easily reducible to Hg^0 using SnCl_2 (Mason and Sullivan, 1998). Data quality was ensured through routine calibration and testing of the entire analytical system. Detection limits for Hg (0.2 ng/L) and MeHg (0.02 ng/L) were sufficient in all field samples, with no non-detects. Total mercury results were reported corrected by subtraction of the average blank due to a consistent low level blank signal, with blank variability (standard deviation around the subtracted mean) below

detection limits. Methylmercury results were not blank corrected, because raw blank signals were typically below detection limits. Recoveries were well within target range (<35% average error), and precision on laboratory replicates were all within the desired range (<35% RSD). Analyses of acid labile mercury had acceptable QC on blanks, replicates, and blank spike recoveries, with only method sensitivity (one-third to one-half of results being non-detects) being an area that could be improved.

Samples were analyzed for trace elements (other than mercury species) by MLML, using a laboratory-specific variation of EPA Method 1638 and inductively coupled plasma mass spectrometer (ICP-MS) after a light acid digest (gentle refluxing with nitric and hydrochloric acids; note this will be referred to in the results section when discussion iron). Samples for dissolved analytes were filtered at the laboratory prior to digestion. Analyses were sufficiently sensitive so that only silver had non-detects (20%). Trace element results were blank corrected; the variation (stdev) of mean blank concentrations was less than detection limits for all analytes except iron and selenium—more than one-half of the iron batches were flagged for blank variation greater than the detection limit. However, variation in blanks was always <1/3 the lowest sample concentrations, so no selenium or iron results were censored. Recoveries on certified reference materials (CRMs) was good, averaging <25% error (35% for selenium). Variability in sampling and analysis were evaluated via both field and laboratory replicates, showing good consistency for all analytes reported with average RSDs for all analytes <25%.

In Water Year 2010, samples were analyzed for total and dissolved selenium (SeT, SeD) by BRL, with a small subset of samples analyzed for selenium species (selenate, selenite). Total and dissolved selenium samples were analyzed using method BR-0060, a laboratory-specific implementation variant of EPA Method 1638 (generally described previously for other trace elements). Selenium species were analyzed by Brooks Rand method BR-0061, using high performance liquid chromatography (HPLC) separation, followed by in-line introduction to an ICP-MS operating in a dynamic reaction cell mode for detection and quantitation. Detection limits for SeT analysis (~0.02 µg/L) were sufficient so that no results were reported as non-detects. Selenium species detection limits were somewhat higher (averaging 0.04-0.05 µg/L), and those analytes were not detected in one-half or more of the field samples. Total selenium results were blank corrected, but variation in blanks was greater than the detection limit in one batch, so about 30% of the selenium results were flagged but not censored for variable blanks possibly affecting results. None of the speciated selenium analytes in blanks were measured above detection limits. No CRMs are available for selenium species in water, so recoveries were evaluated on blank spikes and matrix spikes. Where concentrations were in a quantitative range (>3 time detection limits), precision on laboratory replicate analyses was good (<35% RSD), and recoveries on matrix spikes were good (well below target 35% error). Recoveries on selenium species were within the target average error of <35%.

Dissolved, particulate, and total organic carbon was analyzed using EPA Method 415.1 or Method 9060A at AMS Texas and Columbia Analytical, Washington. TOC was obtained from unfiltered water samples, DOC and POC from filtrate and filtered material respectively. Method sensitivity was sufficient such that only one particulate result was reported non-detect (<0.4 mg/L). Concentrations of TOC and DOC in blanks all were below the detection limit, but some POC blank samples had detected carbon, greater than one-third the field sample concentration in around 5% of samples, which were censored. Higher concentration field samples in those batches were less affected and were flagged but not censored. Recoveries for spiked blank samples were good, averaging within the <10% target. Variability in laboratory replicates was good with average RSD within the <5% target for DOC, but POC variability averaged slightly over the target 10% RSD and was flagged but not censored (10 to 20% RSD) in about one-third of the samples. The POC variability could have arisen, in part, from subsampling, similar to the variability in subsampling shown in TSS measurement (Gray et al. 2000).

Nutrients in filtered samples were analyzed at the San Francisco State University Romberg Tiburon Center for Environmental Studies. Concentrations of nitrate (NO_3), nitrite (NO_2), and phosphate (PO_4) were analyzed with a Bran and Luebbe AutoAnalyzer II with MT-19 manifold chemistry module. Ammonium (NH_4) was analyzed using a colorimetric method (Solorzano 1969, summarized in Standard Methods 4500-NH3 F). Total dissolved nitrogen (TDN) was measured using a Shimadzu TOC-V with a Shimadzu TNM detector (Sugimura and Suzuki, 1988; Sharp et al., 2004). Total dissolved phosphorus (TDP) was measured using a colorimetric method (Bran and Luebbe G-175-96, Standard Methods 4500-P F equivalent). Blanks were non-detect for all analytes. Recoveries of certified nitrate and nitrite standards were good, with <10% error. Measurement precision could not be evaluated because none of the samples were run in replicate by the laboratory, and no field replicates were collected.

Samples were analyzed for PCB congeners by AXYS Analytical (AXYS), British Columbia, Canada using Method MLA-010, a laboratory-specific variant of EPA Method 1668 Revision A using a high-resolution mass spectrometer (HRMS) coupled to a high-resolution gas chromatograph (HRGC) equipped with a SPB-Octyl chromatography column (30 m, 0.25 mm i.d., 0.25 μm film thickness). For most samples, 40 congeners historically reported by RMP were included, but for a subset of 8 samples, all 209 PCB congeners that could be quantified were reported. Detection limits for the 40-congener analyses were sufficiently low that only PCB 132 was not detected, in <10% of the samples. In analyses of 209 congeners, about one-third of the compounds were occasionally not detected, generally in samples with the lowest concentrations of total PCBs. About one-fourth of the congeners were detected in blanks, but of the 40 PCB congeners, only PCB 8 was censored in over 10% of the field samples for blanks contributing >one-third of that congener. There are no CRMs for PCBs in water, so recoveries were evaluated on blank spikes, with <35% average errors for all analytes. Sampling and analytical variability were evaluated using field replicates collected in quick succession, with good results (<35% average RSD) for all but a few congeners (PCB 52, 87, 99, 101), which were flagged but not censored.

Dioxins and furans were analyzed using AXYS Method MLA-017, a laboratory-specific variant of EPA Method 1613B. Analysis was by HRGC/HRMS with a DB-5 capillary chromatography column (60 m, 0.25 mm i.d., 0.1 µm film thickness). A second column, DB-225 (30 m, 0.25 mm i.d., 0.15 µm film thickness), was used for confirmation of 2,3,7,8-TCDF identification. Through concentration by liquid-liquid extraction of large-volume samples (typically 4 L), detection limits for dioxins and furans were low, ranging from 0.06 to 0.30 pg/L. There was at most one sample (out of 14) that contained each isomer at a concentration less than the detection limit. Nearly all the congeners were detected in the blank for at least one batch; however, only 2,3,7,8-TCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8,9-HxCDF, each had one or two samples with concentrations where the blank could account for > one-third of the total. There are no CRMs for dioxins and furans in water, so blank spike samples were analyzed to check recovery, which was good (average error <35%). Analytical and sampling variability were evaluated using replicate field samples, with results within targets (35% RPD or RSD) aside from less quantitative samples near the MDL.

Samples were analyzed for PBDEs using AXYS Method MLA-033, a laboratory-specific implementation of EPA Method 1614, with HRMS/HRGC using a DB-5HT chromatography column (30 m, 0.25 mm i.d., 0.10 µm film thickness), generally having higher average detection limits. Most congeners were detected (detection limits from 0.3 pg/L, up to 350 pg/L for more substituted compounds (e.g. PBDE 209)) in nearly all samples, but some less abundant compounds (e.g. PBDE 10, 105, 205) were not detected in most samples. Many of the PBDEs were detected in blanks, including some of the most abundant (47, 99, 100), but concentrations were less than 1/3 of those in reported field samples. For less abundant congeners with blank concentrations >one-third of those in field samples (typically less than 25% of the samples, usually samples with concentrations near the detection limit), the results were censored. Precision on field replicate samples was generally good, with only a few PBDEs (especially higher substituted congeners 206, 207, 209) showing variation outside of the target range (35% RSD). As there are no CRMs for PBDEs in water, recoveries in matrix spikes were within the target of 35% average error, except for PBDE 209, which was outside of that range but <70% and thus not censored.

Twenty five PAHs (Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Biphenyl, Chrysene, Dibenz(a,h)anthracene, 2,6-Dibenzothiophene, Dimethylnaphthalene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d)pyrene, 1-Methylnaphthalene, 2-Methylnaphthalene, 1-Methylphenanthrene, Naphthalene, Perylene, Phenanthrene, Pyrene, 2,3,5-Trimethylnaphthalene) were analyzed using AXYS Method MLA-021, a variant of EPA Methods 1624 and 8270 using high resolution gas chromatography/low resolution mass spectrometry (HRGC/ LRMS) performed on an Agilent 6890N GC / 5973 MS / 7683 Autosampler. Detection limits between 0.5 and 10 ng/L were sufficient to detect most PAHs. Many of the PAHs were detected in blanks for one or more batches, but concentrations were < one-third

those in all reported (uncensored) field samples. PAHs in samples at concentrations less than 3 times those in blanks were censored and not reported. Some results were qualified for precision outside of targets (35% RPD or RSD) on duplicates (field sample replicates), but not censored. Field sample replicates showed sampling variability, but given highly dynamic flows in the system, variation between sequential samples was expected. No analytes were qualified for accuracy problems based on recoveries in blank spike samples (average errors <35%).

Legacy organochlorine pesticides were analyzed using AXYS Method MLA-028 (HRGC/HRMS). Pyrethroids were analyzed by AXYS using Method MLA-046 by HRGC (DB-5 capillary) and using voltage selected ion detection. Detection limits were sufficient to quantify DDTs and chlordanes in most samples, but HCHs were not detected in up to half the samples. Many of the pyrethroids were also not detected in most samples. Many of the organochlorine pesticides aside from DDTs were found in blanks, but mostly at concentrations <one-third those in field samples. Delta-HCH in blanks was >one-third of sample concentrations in 25% or more of the samples. No CRMs were available for pesticides in water, so recoveries were analyzed in blank spike samples, with good results (average error <35%). Variability in sample collection and laboratory analysis was measured in field replicates, with <35% average RSD for most analytes, with exception of cis- and trans-chlordane and deltamethrin/tralomethrin, which were flagged for being between 35 to 70% but not censored.

Results and Discussion

Rainfall and Runoff

Annual rainfall during the 4-year study period at the Alameda County gage, Hayward 541A ranged from 337 to 573 mm and was 72%, 81%, 84% and 123% (in WY 2007 to 2010, respectively) of mean for the area (466 mm; 1999-2010). Based on the maximum 1-hr rainfall for each event, storms were mostly of less than a 0.5-year return frequency, with only three storms greater than a 1-year return frequency. Monthly rainfall during the study varied from 10% to 325% of monthly normals and included a rare large early-season storm during October 2009, which had an estimated return frequency of 3.3 years (based on the maximum 1-hr rainfall for the event), with discharge peaking just 40 minutes after the onset of rainfall, and a return frequency of 30 years based on a 12 hour duration for the whole event; as discussed below, this event was well sampled.

Runoff in Z4LA was primarily aligned with rainfall events during winter storms (Figure 2). Storm flows began to rise within 15 minutes in response to as little as 1 to 2 mm of rain, and the centroid lag (center of mass of rainfall to the center of mass of discharge) during typical storms was 45 to 120 minutes. Total annual discharge measured at Z4LA for WYs 2007-2010 averaged 720,000 m³ (equivalent to 0.023 m³/s average flow), varying between 600,000 and 1,010,000 m³ (0.019 – 0.032 m³/s average flow). These variations in flow are similar to the variations in rainfall

because of the impervious nature of the watershed; watersheds with a greater area of pervious landscape in the Bay Area have greater discharge variability between wetter and drier years. During the study 90% of the discharge occurred during storm flow ($>0.05 \text{ m}^3/\text{s}$) which occurred just 2.9% of the time. Instantaneous discharge in Z4LA varied over 4 orders of magnitude, averaging $0.003 \text{ m}^3/\text{s}$ during the monitored low flow conditions and peaking at $7.0 \text{ m}^3/\text{s}$ during the most intense rainstorm on October 19, 2009.

Turbidity and Suspended Sediment Concentration

Turbidity ranged between 0 and 1040 Formazine Nephelometric Units (FNU) for the sampling period, and variation was primarily driven by rainfall induced runoff (Figure 2). For the majority of storms, turbidity was less than 500 FNU. In contrast, for a one-year return frequency storm event on February 12, 2007, turbidity peaked at 1040 in response to an intense thunderstorm. In this instance, the increase in turbidity was very rapid, increasing from < 300 to over 1000 FNU in just 20 minutes, similar to patterns reported for other urban systems with extensive observations (e.g., Old et al., 2003). Turbidity had clockwise hysteresis, with the turbidity peak usually preceding that of the peak in discharge, and there were no systematic changes with

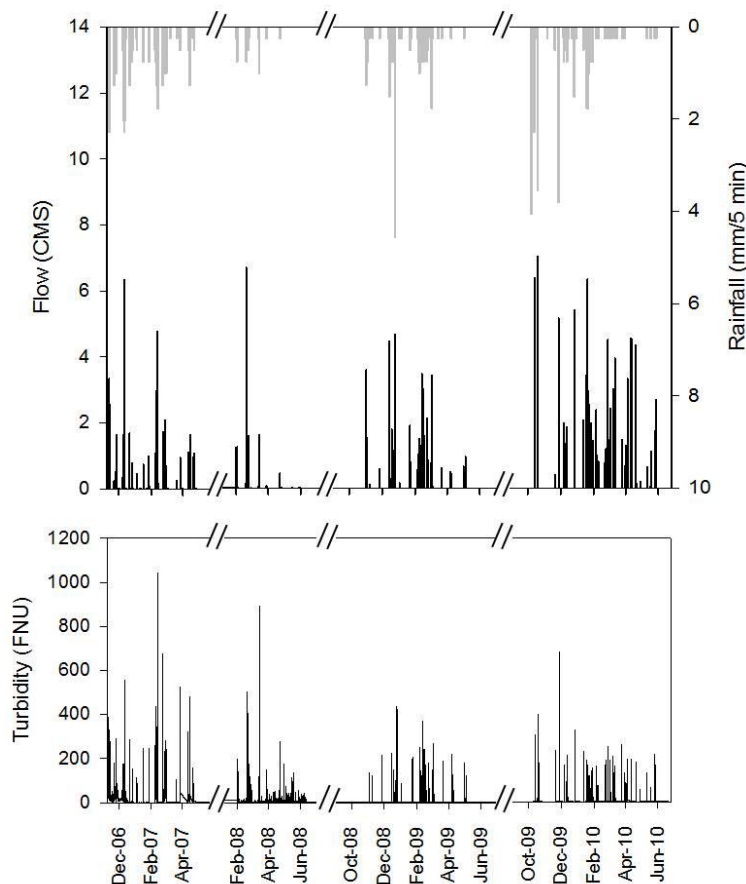


Figure 2: Flow, rainfall, and turbidity during the four year study period.

progression of the water year. SSC measured from grab samples ranged between 1.4 and 2700 mg/L (Table 1). Averaged over the four years of observations, the flow-weighted mean concentration (FWMC) for SSC was 170 mg/L. These results are within the range of concentrations reported in Southern California (70-380 mg/L; Buffleben et al., 2002) and other parts of the world for urban systems (e.g., review by Taylor and Owens, 2009). The rainfall-

Table 1. Pollutant concentrations in Z4LA stormwater during storm and low flow conditions (excluding mercury species, addressed later).

Analyte	Unit	Low Flow (<0.05 CMS)			Storm Flow (≥ 0.05 CMS)			Low Flow FWMC ^a	Storm Flow FWMC ^a	4 Yr Avg FWMC ^b
		Min	Max	n	Min	Max	n			
SSC	mg/l	1.4	300	30	8	2700	329	70	270	160
Aluminum	µg/l	66	980	8	940	11000	26	860	2400	1800
Arsenic	µg/l	0.99	3.2	8	0.68	2.8	26	1.5	1.1	1.2
Cadmium	µg/l	0.010	0.20	8	0.11	0.67	26	0.089	0.27	0.22
Chromium	µg/l	0.57	3.3	8	4.0	39	26	2.7	8.9	5.8
Copper	µg/l	2.3	10	9	6.9	50	36	5.9	15	14
Copper - Dissolved	µg/l	5.9	5.9	1	1.4	11	10	pilot data ^c	pilot data ^c	pilot data ^c
Iron	µg/l	27	250	6	2400	75000	17	110	5000	8000
Lead	µg/l	0.18	4.6	8	4.5	40	26	2.7	12	10
Nickel	µg/l	3.3	10	8	5.1	60	26	3.5	12	10
Selenium	µg/l	0.11	2.9	8	ND ^f	1.2	32	0.32	0.13	0.14
Selenium(IV)	µg/l	NS ^d	NS ^d	0	ND ^f	0.027	6	pilot data ^c	pilot data ^c	pilot data ^c
Selenium(VI)	µg/l	NS ^d	NS ^d	0	ND ^f	0.085	6	pilot data ^c	pilot data ^c	pilot data ^c
Selenium - Dissolved	µg/l	NS ^d	NS ^d	0	0.041	0.10	6	pilot data ^c	pilot data ^c	pilot data ^c
Silver	µg/l	ND ^f	0.020	8	0.020	0.11	26	0.020	0.046	0.030
Zinc	µg/l	2.4	62	8	39	280	26	48	120	91
DOC	mg/l	0.0020	7.5	6	0.11	12	34	4.9	4.4	4.4
POC	mg/l	0.15	1.2	6	0.060	16	34	0.45	7.7	7.0
TOC	mg/l	3.4	9.4	6	4.0	23	34	5.8	12	12
Nitrogen - Dissolved	mg/l	NS ^d	NS ^d	0	0.31	1.3	10	NS ^d	0.42	0.42
Phosphorous - Dissolved	mg/l	NS ^d	NS ^d	0	0.038	0.23	10	NS ^d	0.069	0.069
NO3+NO2 - Dissolved	mg/l	NS ^d	NS ^d	0	0.012	0.67	10	NS ^d	0.091	0.091
PO4 - Dissolved	mg/l	NS ^d	NS ^d	0	0.024	0.24	10	NS ^d	0.063	0.063
Ammonium - Dissolved	mg/l	NS ^d	NS ^d	0	0.056	0.17	10	NS ^d	0.080	0.080
Sum of PCBs	ng/l	0.33	11	16	4.0	110	69	7.1	24	16
Sum of Dioxins and Furans	ng/l	0.23	0.23	1	0.98	6.3	12	0.23 ^e	3.7	3.6
Sum of PBDEs	ng/l	0.35	25	11	9.4	430	27	17	81	50
BDE 47	ng/l	0.11	2.5	11	0.75	20	27	1.8	5.1	3.1
BDE 209	ng/l	ND ^f	14	11	5.0	240	27	9.4	47	29
Sum of PAHs	ng/l	14	1400	8	1400	23000	13	730	9600	6400
Sum of DDTs	ng/l	0.41	7.4	8	5.1	59	12	4.8	21	15
Sum of Chlordanes	ng/l	0.35	6.4	8	2.5	16	12	3.8	9.4	6.7
Sum of HCHs	ng/l	ND ^f	0.40	8	0.30	0.89	12	0.36	0.43	0.40
Dieldrin	ng/l	0.28	0.85	8	0.74	4.6	12	0.68	1.8	1.4
Bifenthrin	ng/l	0.18	12	7	2.2	46	7	6.1	18	22
Cyhalothrin	ng/l	ND ^f	ND ^f	7	ND ^f	6.1	7	ND ^f	NR ^g	NR ^g
Delta/Tralomethrin	ng/l	ND ^f	0.64	7	0.46	5.5	7	0.64	2.6	2.9
Permethrin	ng/l	1.6	26	7	4.6	290	7	7.0	77	89

^a The FWMC for each strata was calculated using the sample data.

^b The 4-year average FWMC was back-calculated as the total four year load divided by the total four year flow.

^c pilot data = few samples of these analytes were collected for primarily characterization purposes rather than FWMC or loads estimation.

^d NS = no sample collected in flow condition.

^e Only one sample comprising this FWMC.

^f ND = Not detected.

^g NR = Detection too infrequent to report FWMC.

weighted annual average load of suspended sediment in Z4LA was 130 t, equivalent to 30 t/km² (Table 3). These results are at the lower end of observations in other urban systems and are perhaps more typical of older built out urban areas with little recent disturbance (Taylor and Owens, 2009). Rapid changes in flow, turbidity, and SSC were a primary driver for transport of most pollutants discussed below.

Mercury

Concentrations of HgT varied over two orders of magnitude from 1.4-150 ng/L with a FWMC of 29 ng/L (Table 2). These are similar to or greater than concentrations measured in other urban systems. For example, maximum concentrations in Z4LA were consistent with those reported by Mason and Sullivan (1998) for an urban watershed in the Washington D.C. area, but much greater than those in three urban watersheds in Wisconsin (Hurley et al., 1995), urban influenced watersheds in the Chesapeake Bay region (Lawson et al., 2001), and two mostly urban sub-catchments in the Toronto area (Eckley and Branfirheun, 2008). HgT was strongly correlated with turbidity ($r^2=0.75$, Table 3, Figure 3) indicating the sources and processes that mobilize mercury from the watershed involve fine sediments and allowing for the calculation of very accurate loads from this watershed.

MeHgT concentrations were not correlated with turbidity, SSC or flow at the annual scale. The sources and processes that influence concentrations in runoff are more complex than those of HgT. On average (plus or minus relative standard error; the relative standard error is the error statistic used consistently throughout this paper unless otherwise noted) MeHgT accounted for $1.1\pm 10\%$ of HgT during storm flows and $7.8\pm 25\%$ of HgT during low flows. In general the portion of total mercury in methylated forms is similar to that measured for other urban systems during wet- and dry-weather flow (e.g., Mason and Sullivan, 1998). Although the concentrations of acid labile (reactive) Hg (HgR) have a pattern opposite that previously reported by Mason and Sullivan (1998) where greater concentrations during storm flow than base flow were measured, the portion of total Hg in acid labile forms under each flow regime in Z4LA is consistent with Mason and Sullivan's results in which a greater proportion of Hg was acid labile during low flow. This occurred because the relative variation of the magnitude in each of the paired sample sets was different in each of the datasets.

Dissolved Hg, MeHgT, and MeHgD as a portion of HgT were all inversely correlated with flow; at lower flows more of the mercury is transported in dissolved and methylated forms. In addition, concentrations were usually higher during early season storms decreasing as the wet season progressed and again increasing during base flow spring and early summer conditions. This same kind of seasonal pattern has been observed in agriculturally dominated Minnesota watersheds where seasonal changes in temperature, discharge, reservoir production, stream algal productivity, and leaf matter were speculated to play a role (Balogh et al., 2003; 2005). This pattern was also present in several western Maryland watersheds (Lawson and Mason, 2001)

and Wisconsin Rivers (Babiarz et al., 1998), but it is less commonly reported for urban systems. One of the proposed management measures in the stormwater permit for urban runoff to San Francisco Bay is to route dry-weather flows to wastewater treatment; success will be challenged by the fact that dry weather flow contains a greater component of the mercury load in dissolved, methylated, and acid labile forms that will likely be more difficult to treat.

Table 2. Concentrations of mercury species and percentages in relation to total mercury.

	Unit	HgT	HgD	MeHgT	MeHgD	HgR
Low Flow Concentrations ^a	ng/l	1.4 - 23	0.74 - 2.6	0.09 - 0.34	0.025 - 0.17	0.17 - 1.9
Low flow n/DF ^b		17/100%	7/100%	7/86%	7/100%	9/89%
Storm Flow Concentrations	ng/l	8.1 - 150	0.83 - 7.6	0.032 - 1.3	0.021 - 0.27	0.17 - 0.44
Storm Flow n/DF ^b		94/100%	48/100%	50/100%	47/96%	18/50%
Low Flow FWMC ^c	ng/l	12	2.0	0.13	0.049	1.3
High Flow FWMC ^d	ng/l	29	2.4	0.28	0.054	0.25
4-year FWMC ^e	ng/l	29 ^f	2.4 ^g	0.27 ^g	0.054 ^g	0.34 ^g
Low Flow % of HgT ^h			43 - 59	1.7 - 15	0.73 - 7.3	2.2 - 77
High Flow % of HgT ^h			1.6 - 36	0.16 - 4.3	0.05 - 0.99	0.36 - 1.7

^a Concentrations not detected are not reported in the range.

^b n is the number of samples within the flow strata, and DF is the frequency of detection.

^c Calculated by flow weighting individual samples collected during flows <0.05 CMS.

^d Calculated by flow weighting individual samples collected during flows >0.05 CMS.

^e Calculated by dividing total estimated annual load by total annual discharge.

^f Turbidity surrogate regression used to estimate annual total load.

^g FWMC method used to estimate annual total load.

^h Calculated using only sample pairs.

On average Z4LA emits about 24 g HgT and about 0.22 g of MeHgT annually. Normalized to area, these equate to 5.7 µg/m²/y HgT and 0.052 µg/m²/y for MeHgT, within the range reported for a similar sized urban system (Herring Run) tributary to Chesapeake Bay (Lawson et al., 2001). The yield for HgT is similar to the atmospheric wet deposition rates reported for Central coastal California (4.4 µg/m²/y: Steding and Flegal, 2002).

Other Trace Elements

Given our focus on high flow water sampling, we measured a large range of trace element concentrations; the most variable was Fe which varied from 27-75000 µg/L (a ~2800x range). The least variable element in stormwater was As which varied by a factor of just five. The elements measured listed from greatest to least variability were Fe>Pb>Al>Zn>Cr>Cd>Se≈Mg>Cu≈Ni>Ag≈As. The variation of turbidity in relation to stormwater flow explained >86% of the variation in trace element concentrations with the exceptions of Se,

Ni, Ag and As. Correlations between Ni, Ag, and turbidity were positive, and turbidity accounted for 59 and 74% of the variation during storm flow for these two elements, respectively.

Environmental concentrations of Ag were challenging to measure because many concentrations were near the method detection limit (0.01 µg/L). Other than this study, very few authors have reported Ag concentrations. For example, Domagalski and Deleanis (2000) measured but did not report Ag concentrations because most of the concentrations were low or less than the level of detection. The concentrations we measured were similarly low and near detection limits, but our confidence in the data quality was bolstered by the correlation of Ag with turbidity (seldom reported in other studies). Nickel, in contrast, is well studied in urban systems. The concentrations reported here are similar to those reported by Lawson et al. (2001) for a 5.5 km² mixed land use urban watershed and by Asaf et al. (2004) for a number of small (<5.1 km²) urban watersheds. However, concentrations in Z4LA are slightly greater than reported for several other California urban systems (e.g., Buffleben: 6.5-8 µg/L; Domagalski and Deleanis, 2000: 2-4 µg/L) and in several urban watersheds of similar size (6 km²) by Rule et al. (2006). Loads of Ag and Ni were respectively 0.024 and 8.3 kg/y on average, equivalent to yields of 0.0057 and 2.0 mg/m²/y respectively. We are not aware of any other reports of loads or yields for Ag (used in x-ray film photography, electronics including batteries, deodorants, catalytic converters, clothing manufacture, jewelry and many other urban uses), but the yield of Ni is similar to another California urban system (1.2 mg/m²/y; Sabin et al., 2005) and about half that of the Potomac (4.73 mg/m²/y) and Susquehanna (4.23 mg/m²/y), two large watersheds draining to Chesapeake Bay (Lawson et al., 2001). This similarity to other systems suggests that our local serpentine geological sources (Anderson, 1998) are not dominating urban sources (automotive batteries, chemical industrial feedstock, electrical equipment including household and industrial appliances, and fabricated metal products for construction) in the Z4LA watershed.

Selenium is seldom measured in urban stormwater but occurs naturally in California soils at concentrations that contribute to water quality concerns in the northern reaches of San Francisco Bay, leading to efforts to monitor loads in recent years (David et al., in review). Detected Se concentrations in Z4LA ranged from 0.053-2.9 µg/L (flow-weighted mean = 0.14 µg/L). Selenium concentrations seem to be diluted during high flow, consistent with the hypothesis that the main sources of Se are groundwater and dry-weather flows. Selenium was mostly in the dissolved phase (25-77%, mean 61±20%) and thus was the only pollutant in the study with greater than 20% of its load transported during low flows (<0.5 m³/s); even MeHgT was mostly transported during high flows. We found no information on selenium speciation in urban literature. However, our small pilot-level dataset is consistent with speciation data from nearby agricultural systems with soils of marine sedimentary origin, where selenate (Se (VI)) is the dominant species. In Z4LA, Se was dominantly Se(VI), with detected results ranging from 0.027-0.085 µg/L (mean 0.048 µg/L), with Se(IV) only detected in one sample (0.027 µg/L). Using the FPMC specific to each flow strata, rainfall-weighted (see methods section) estimated long

term average Se loads were 0.11 kg (equivalent to 0.027 mg/m²/y), about five times lower than measured in two small forested watersheds (Lawson and Mason, 2001), 10 times lower than reported by Miller et al. (2003) for an agricultural dominated watershed and about four times lower than measured in the large Sacramento River at Mallard Island (David et al., in review).

Concentrations of Al, Fe, and Pb were most strongly correlated with turbidity, likely because of the dominantly (>90%) particulate nature of these elements in urban runoff (e.g., Buffleben et al., 2002; Asaf et al., 2004). Average annual loads were estimated to be 1500 kg for Al or on average about 1.1% of the suspended sediment load, less than California soil composition (3-10.6%; average = 7.3%) (Bradford, 1996) probably because the laboratory methods used in this study did not totally digest all siliceous minerals present. Iron also is a large component of the earth's crust and makes up between 1-8.7% (average=3.7%) of California soils (Bradford, 1996); in Z4LA, the average Fe load was 6200 kg equating to suspended sediment composition of 5% Fe. Given these are primary use metals for human civilization, it seems likely that Al and Fe should be anthropogenically enhanced in urban systems relative to natural weathering, however the light acid digest used during the laboratory analysis was more able to digest oxyhydroxide and other Fe corrosion byproducts rather than aluminosilicate compounds and byproducts – perhaps future studies could incorporate some mineralogical studies or a fluoric acid digest.

Lead is used in lighting applications, batteries, wired telecommunications, radiation shielding, solder (for pipe joints, wiring, canning, and printed circuit boards), balance weights, ammunitions, and preservatives (Davis and Burns, 1999). Lead makes up a much smaller component of California soils (average = 23.9 mg/kg, Bradford, 1996) than do Al and Fe. The strong correlation with turbidity is most likely because of the strong affinity of lead (the adsorbate) for sediment particles in environmental samples (e.g., Buffleben et al., 2002) that include carbon compounds and iron and aluminum oxyhydroxides (the adsorbents), widespread distribution via atmospheric pathways, and ubiquitous historic and current urban use. The concentrations measured were greater than those recently reported for some urban watersheds of similar size (e.g., Lawson and Mason, 2001; Lawson et al., 2001; Asaf et al., 2004), but less than those measured in a 6 km² light industrial watershed (Rule et al., 2006). Overall, there is a downward trend in environmental concentrations of lead in U.S.A. evident in urban lake cores (Mahler et al., 2006). Normalizing the load of 8.3 kg to watershed area, Z4LA released Pb at a rate of 2.0 mg/m²/y, similar to other systems (1.64 mg/m²/y (Potomac River), 1.15 mg/m²/y (Susquehanna River): Lawson et al., 2001; 1.86 mg/m²/y: Sabin et al., 2005). The bans of lead in paint and gasoline (two of the largest uses) occurred at different times in countries across the world, and therefore it is likely that a more thorough review would reveal more variability in recently published yields. For example, yields of 60-326 mg/m²/y were reported in Korea (Choe et al., 2002), and 51 mg/m²/y was reported for a residential area in Brazil (Prestes et al., 2006).

Copper, like lead, might be considered ubiquitous in the urban environment; the many uses including heating, plumbing, roofing, and cladding; batteries, wiring, and circuit boards; jewelry,

utensils, and coins; industrial catalysts and cathodes; brake pads and other automobile components; alloys such as brass; plating; fertilizers, herbicides, fungicides, and pesticides; pigments; and dietary supplements (Boulay and Edwards, 2000). A California law enacted in 2010, SB 346 (Kehoe), provides an approach to reduce environmental Cu concentrations substantially over the coming decade, and hence potential down gradient toxicological effects. Copper concentrations range between 2.3-50 µg/L and are similar to concentrations reported for other urban watersheds (Lawson et al., 2001; Lawson and Mason, 2001; Buffleben et al., 2002; Rule et al., 2006).

Urban emissions and uses of Cd include batteries, stabilizers, plating, tires, brakes, combustion of fossil fuels, paint, fertilizers (Bergbäck et al., 2001). The concentrations measured in Z4LA (0.010-0.67 µg/L) are in the middle of the range reported for other urbanized systems, slightly but not significantly less on average than the Herring Run watershed tributary to Chesapeake Bay, USA (Lawson et al., 2001), and slightly but not significantly greater on average than measured in Ballona Creek, Southern California (Buffleben et al., 2002).

In contrast to Cd, our Cr observations in Z4LA (0.57-39 µg/L) are in the upper range of those reported recently for other systems (Domagalski and Deleanis, 2000; Lawson et al., 2001; Lawson and Mason, 2001; Buffleben et al., 2002; Asaf et al., 2004; Rule et al., 2006). Cr is used in stainless steel, chrome plated products, paint, and some wood and leather preservatives (Sörme et al., 2001). We have not identified specific sources to explain why Cr might be greater in Z4LA relative to other watersheds.

As with previously discussed metals, Zn has many uses in the urban environment, some of which are very susceptible to release by corrosion and abrasion (galvanizing, vehicles tires, and paint). Perhaps the most commonly considered uses for Zn are brass (an alloy of Cu and Zn) and galvanized steel, where Zn is a sacrificial surface coating, but zinc is also used in car tires and batteries (Sörme et al., 2001) and, more recently, in wheel balancing weights in which lead was formerly used. There is greater variability in concentrations between urban systems for Zn compared to other trace metals. For example, Lawson et al. (2001) reported concentrations of just 11 µg/L for a 5.5 km² mixed urban watershed in the Chesapeake Bay Area, not dissimilar to concentrations reported by Domagalski and Dileanis (2001) for urban Sacramento, California, and Ashley and Napier (2005) reported a concentration of 47 µg/L for a 20 km² dominantly urban system in Port Macquarie, Australia. In contrast, concentrations >155 µg/L have been reported for urban systems (1-330 km²) in Houston, Texas, USA (Characklis and Wiesner, 1997), in Southern California, USA (Buffleben et al., 2002), in Ashdod, Israel (Asaf et al., 2004), and in the United Kingdom (Rule et al., 2006). The concentrations we measured fall in the upper range of the literature and were similar to the southern California example, and we have not identified any specific industrial sources prevalent in the Z4LA watershed.

Table 3. Loads calculation methods, equations for regression against turbidity, loads, and yields by analyte measured in Z4LA. All regression equations are significant to <0.001 except the sum of dioxins and furans which is significant to <0.005.

	Regression Equations				Annual Loads			Annual Yields	
	Slope	Intercept	r ²	Unit	Mean 4 Monitoring Years	Estimated Long Term Average	Unit		Unit
SSC	0.0014x ² + 1.374x		0.84	mg	110	130	t	30	t/km ²
HgT	0.277	3.23	0.75	ng	21	24	g	5.7	µg/m ²
MeHgT	FWMC method				0.19	0.22	g	0.052	µg/m ²
Aluminum	18.6	81.7	0.94	µg	1300	1500	kg	360	mg/m ²
Arsenic	FWMC method				0.85	0.95	kg	0.23	mg/m ²
Cadmium	0.00186	0.0408	0.86	µg	0.16	0.18	kg	0.042	mg/m ²
Chromium	0.0528	0.814	0.87	µg	4.2	4.7	kg	1.1	mg/m ²
Copper - Total	0.109	4.11	0.86	µg	10	12	kg	2.8	mg/m ²
Iron	81.2		0.97	µg	5500	6200	kg	1500	mg/m ²
Lead	0.109		0.87	µg	7.4	8.3	kg	2.0	mg/m ²
Nickel	0.0655	4.10	0.59	µg	7.4	8.3	kg	2.0	mg/m ²
Selenium	FWMC method				0.10	0.11	kg	0.027	mg/m ²
Silver	0.000264	0.00517	0.74	µg	0.021	0.024	kg	0.0057	mg/m ²
Zinc	0.755	19.4	0.87	µg	65	74	kg	18	mg/m ²
TOC	FWMC method				8.3	9.5	t	2.3	t/km ²
Total Nitrogen - Dissolved	FWMC method				300	340	kg	82	mg/m ²
Total Phosphorous - Dissolved	FWMC method				49	56	kg	13	mg/m ²
NO3+NO2 - Dissolved	FWMC method				65	73	kg	18	mg/m ²
PO4 - Dissolved	FWMC method				45	51	kg	12	mg/m ²
Ammonium - Dissolved	FWMC method				57	65	kg	15	mg/m ²
Sum of PCBs	168		0.77	pg	11	13	g	3.1	µg/m ²
Sum of Dioxins and Furans	28.6	868	0.62	pg	2.6	2.9	g	0.69	µg/m ²
Sum of PBDEs	531		0.88	pg	36	41	g	9.7	µg/m ²
BDE 47	29.0	320	0.90	pg	2.2	2.5	g	0.60	µg/m ²
BDE 209	307		0.86	pg	21	23	g	5.6	µg/m ²
Sum of PAHs	67513		0.67	pg	4.6	5.2	kg	1.2	mg/m ²
Sum of DDTs	163		0.79	pg	11	12	g	3.0	µg/m ²
Sum of Chlordanes	59.4	1069	0.78	pg	4.8	5.4	g	1.3	µg/m ²
Sum of HCHs	2.34	155	0.69	pg	0.29	0.33	g	0.078	µg/m ²
Dieldrin	11.4	319	0.77	pg	1.0	1.1	g	0.27	µg/m ²
Bifenthrin	232		0.84	pg	16	18	g	4.3	µg/m ²
Delta/Tralomethrin	30.6		0.88	pg	2.1	2.3	g	0.56	µg/m ²
Permethrin	439		0.67	pg	64	72	g	17	µg/m ²

Organic Carbon and Nutrients

Organic carbon and nutrients are delivered to or mobilized in runoff from urban watersheds by atmospheric deposition, landscaping fertilizers, phosphate detergents, vegetation senescence and pet and other animal wastes. San Francisco Bay has long been considered a nutrient enriched, low productivity estuary (Cloern, 2001). However, in the last 12 years, the balance of

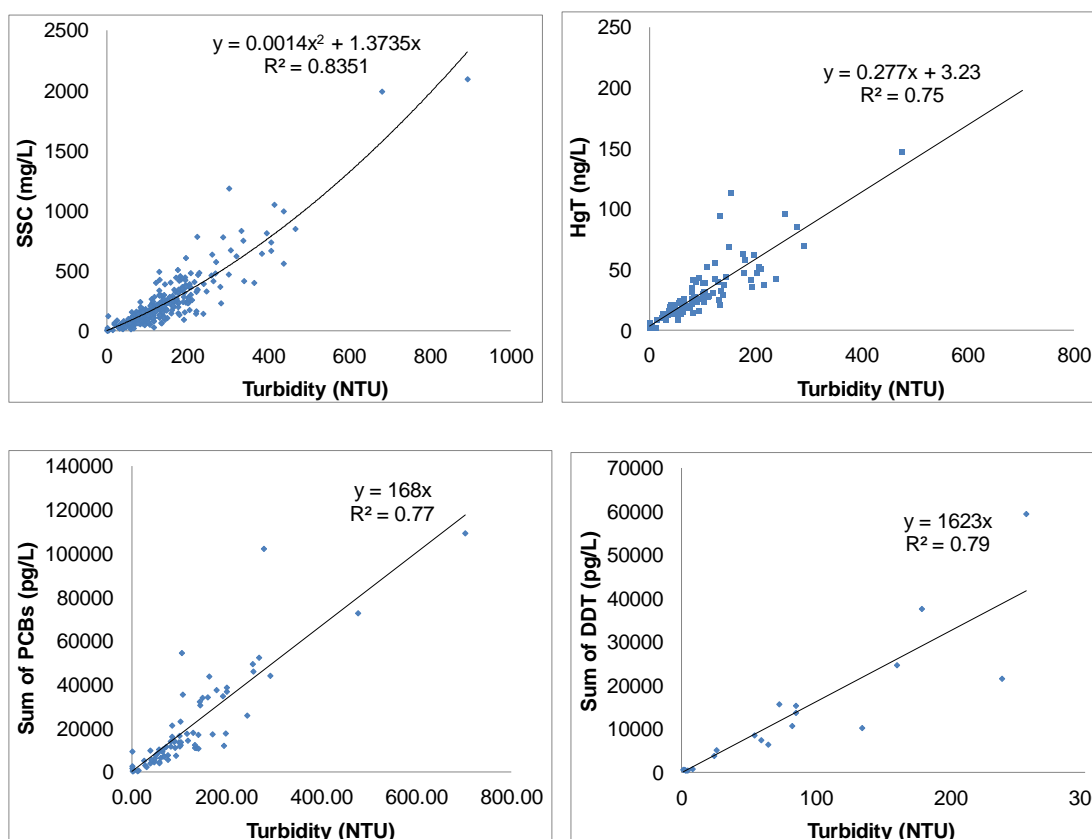


Figure 3. Relationships between turbidity and suspended sediment concentration, HgT, PCBs, and DDT.

organic production has been changing, especially in the southern reaches of the Bay, as indicated by increased spring bloom chlorophyll-a concentrations and the appearance of autumn blooms (Cloern et al., 2007). Should management intervention become necessary, nutrient loads from wastewater and urban runoff will need to be investigated more fully; here we report on a beginning data set for nutrients.

Dissolved organic carbon concentrations varied from 0.002-12 mg/L depending on flow conditions. Particulate organic carbon concentrations ranged from 0.060-16 mg/L, the combined effect leading to TOC concentrations that varied by a factor of about six. During low to moderate flows ($<2 \text{ m}^3/\text{s}$), organic carbon concentrations were dominated by DOC. This trend is notable because DOC stimulates mercury methylation, particularly under suboxic and anoxic conditions (Graham et al., 2012). However, on average, particulate organic carbon was 61% of TOC and suspended sediment was on average 4.2% organic carbon. Total dissolved nitrogen ranged from 0.31-1.3 mg/L with a flow-weighted average of 0.42 mg/L. Organic forms dominated and nitrate + nitrite ($\text{NO}_3 + \text{NO}_2$) and ammonia concentrations only varied from 0.012-0.67 and 0.056-0.17 mg/L respectively. In contrast, total dissolved phosphorus was dominantly inorganic, as

phosphate. Long term average loads of NO_3+NO_2 and PO_4 were estimated from the one year of data to be 73 kg and 51 kg respectively or about 18 and 12 $\text{g/m}^2/\text{y}$. Although these loads are greater than reported for other small urban systems (Coats et al., 2008) and nitrate exports are much less than for several other systems (Line et al., 2002; Kaushal et al., 2008), our nutrient data set is too limited at this time to draw strong conclusions.

PCBs

PCBs are persistent organic chemicals historically used in numerous industrial applications, and PCB contamination in the San Francisco Bay is high (Davis et al., 2007). Although banned from production since the late 1970's, PCBs are still utilized in completely enclosed systems, and at least 260,000 kg of PCBs are still in use in San Francisco Bay Area electrical equipment (EPA, 2011). Because of legacy contamination of PCBs across the landscape and accidental spills from current-use applications, stormwater runoff from local tributaries accounts for a significant portion of the loading into San Francisco Bay (Davis et al., 2007). Therefore PCBs were a strong driver for this study, and a total of 78 samples were collected over the four years, across the full range of flows (8.5×10^{-5} -5.9 m^3/s) and turbidities (0.9-703 FNU).

Flow and seasonal factors might be affecting PCB concentrations and congener distributions. Total PCB concentrations ranged from 0.33-11 ng/L during low flow and from 4.0-110 ng/L during storm flow. Although there was a general tendency toward higher concentrations measured during periods with high flows, there was no consistent pattern in congener distributions associated with flow only (Figure 4). Typically around 50% or more of total PCBs in collected samples were hexa- and heavier chlorinated congeners, a pattern present in all years. However, in samples collected in the late spring and early summer (May and June) 2008, all with low flows and lower total PCB concentrations, hexa- and heavier congeners often contributed a smaller proportion of total PCBs, in some samples less than 40%. This is consistent with the lower solubility of the higher chlorinated congeners. In lower flow scenarios, although concentrations of all congeners would decrease, the contribution of dissolved phase (lower chlorinated) congeners to total PCBs would increase relative to those of particulate PCBs. However, wet season samples with PCB concentrations in a similar range (<10 ng/L) did not show the same pattern, so seasonal differences also likely affect the relative contribution of dissolved versus particulate associated PCBs. The net impact of these seasonal differences on food web uptake depend on various environmental factors such as temperature, DOC, POC, and target organism lipid content (Gobas and Wilcockson, 2003); some of the information provided in the present study can serve as inputs to apply to such (pseudo-)equilibrium food web models.

Concentrations in Z4LA are similar to or marginally lower than those reported for urban systems elsewhere (2.0-28.9 ng/L: Foster et al., 2000b; 27-179 ng/L: Marsalek and Ng, 1989; 26.9-1,120 ng/L: Walker et al., 1999). The average FWMC during the monitoring years (16 ng/L) and even

the maximum sampled concentration in the dataset (110 ng/L) are lower than event mean concentrations (EMCs) reported in other studies. Hwang and Foster (2008) reported a maximum EMC of 211 ng/L in a study of six urban catchments in Washington D.C., and Rossi et al. (2004) reported EMCs up to 403 ng/L for urban areas in Switzerland.

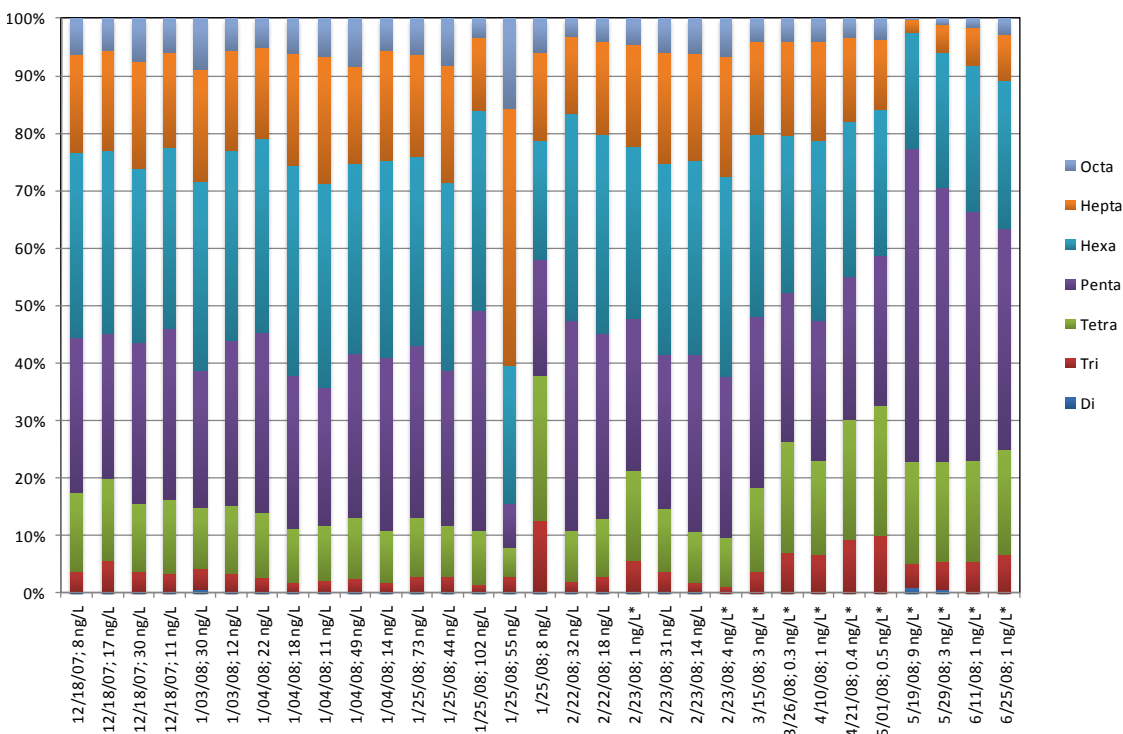


Figure 4. PCB Homolog Profiles in Z4LA during WY 2008. * = low flow sampling event.

Changes in total PCB concentrations in Z4LA were well explained by changes in turbidity ($r^2=0.77$; Figure 3). The long-term estimated average annual load was 13 g, with a yield of $3.1 \mu\text{g}/\text{m}^2/\text{y}$. This yield estimate is on the low end of that reported for the Guadalupe watershed ($3.0 - 5.0 \mu\text{g}/\text{m}^2/\text{y}$; Davis et al., 2007), also a tributary to San Francisco Bay, perhaps because of the history of PCB manufacturing and industrial use in the Guadalupe River watershed. Foster et al. (2000b) also reported much higher yields, between 9 and $10 \mu\text{g}/\text{m}^2/\text{y}$, for two watersheds in Washington DC that are only 60% urban. These results indicate that percent urban or percent impervious might not be the strongest predictors of PCB yield for modeling unmonitored watersheds. Other factors, such as the total area of older industrial landscape (9.4 km^2 in Guadalupe versus 0.6 km^2 in Z4LA) or the presence of specific historic industries, such as manufacture of PCBs and production of transformers and larger capacitors, might have greater explanatory strength.

Dioxins

Dioxins and furans are byproducts of the synthesis or combustion of chlorine-based compounds; they are persistent and bioaccumulative, and include some of the most toxic chemical substances known (Fisher et al., 1999). The San Francisco Bay Regional Water Quality Control Board estimates stormwater runoff as the greatest source of dioxins to the San Francisco Bay, with air emissions being the ultimate source of most dioxins in stormwater runoff (Gervason and Tang, 1998). Consequently, dioxins are widely dispersed throughout the urban environment. Surprisingly few studies have reported concentrations of dioxins in urban runoff (Suarez et al., 2006). The Z4LA study included 13 dioxin samples collected over a diverse range of discharges, but all were for events with less than a 1.7 year return, with a relatively low maximum turbidity of 161 FNU. Dioxins were detected in all 13 samples and ranged in concentration from 0.23-6.3 ng/L. Concentrations had a moderate relationship with turbidity ($r^2=0.62$), and storm flow concentrations were 4-28 times higher than the single low-flow measurement. Concentrations in Z4LA fall in the mid-range of other urban study sites in the Bay Area (Wenning et al., 1999), but are two orders of magnitude greater than measured in the large Sacramento River watershed at the head of the Bay (David et al., in review). World Health Organization 2005 toxic equivalency (TEQ, where TEQ refers to toxic equivalency with 2378-TCDD; Van den Berg et al., 2006) concentrations ranged from 4.5-44 pg TEQ/L during storm flows, with one outlier of 125 pg TEQ/L. This sample contained an abnormally high concentration of 12378-PeCDD, one of the most toxic dioxins. It is unclear why this was the case, but batch QC data did not indicate any reasons to reject the result. The single low-flow sample yielded a 0.8 pg TEQ/L. The two congeners with the greatest toxic equivalency (toxic equivalency factor of 1.0), 2378-TCDD and 12378-PeCDD, were detected in all samples, except that 2378-TCDD was not detected in the low flow sample, and contributed an average of $5\pm12\%$ and $32\pm8\%$ to the total TEQ for each sample, respectively.

The TEQ concentrations in this study are very similar to those reported by Fisher et al. (1999) in watersheds with greater than 60% urbanization (0.8-1.6 pg TEQ/L during dry weather ($n=7$) and 6.5-53 TEQ pg/L during wet weather ($n=4$)) in the Santa Monica Bay region, although generally higher than those reported internationally (Horstmann and McLachlan, 1995; Kueh and Lam, 2008). Suarez et al. (2006) collected high volume samples (700 liters over 7 hours) in the Houston area and reported total dioxin concentrations of 0.0052-2.3 ng/L. Although not strictly comparable because of differences in study design, the 4-year FWMC (3.6 ng/L) in Z4LA is higher than the highest sample reported in Houston. This might be because the Houston watersheds have less urban development (14-89%), or because Suarez et al. failed to capture the peak discharge in all but two of the 10 samples. The estimated long-term total annual load of dioxins from Z4LA is 2.9 g, or 0.69 g/km²/year. During monitoring years, storm flows transported 95-99% of the total dioxin load. We found no other studies that reported estimated yields of dioxins from other urban areas.

PBDEs

Polybrominated diphenyl ethers are commonly used as flame retardants in clothing, children's toys, building materials, carpet, matrices, some kinds of paints, and some uses (e.g., tent fabrics) are even required by law in California. Because of their wide usage, PBDEs are now ubiquitous in the environment (see review by Oram et al., 2008). Studies of the San Francisco Bay Area in particular have reported some of the highest PBDE concentrations measured in wildlife anywhere in the world (She et al., 2002; Oros et al., 2005). To our knowledge, only two articles have previously published data on whole-water concentrations of PBDEs in stormwater, one for the Pearl River Delta, China (Guan et al., 2007), and the other for the San Francisco Bay, USA (Oram et al., 2008). In the present study, total PBDE concentrations ranged from 0.35-25 ng/L during low flow, and from 9.4-430 ng/L during storm flow, with a FWMC of 50 ng/L. PBDE concentrations strongly correlated with turbidity ($r^2=0.88$), with >99% of the total load transported during storm flows. The maximum concentration (430 ng/L) was sampled at a peak turbidity of 702 FNU, and was up to six times greater than the maximum concentrations reported by Guan et al. (2007) for eight urban watersheds in the Pearl River Delta, a global electronic-waste hot spot. Similar to the Chinese study, BDE congeners 47, 99 and 209 together dominated the sum, comprising an average of $70\pm4\%$ of PBDEs in all storm flow samples.

BDE-47 is one of the more dominant congeners in the Bay (Oram et al., 2008) and is often elevated in biota (Hites, 2004 from Oram et al., 2008). It is a lower-brominated, more highly soluble congener that is believed to easily transfer from surface sediments to the aqueous phase (Muresan et al., 2010). BDE-47 concentrations varied from 0.11-20 ng/L, comprised on average $9\pm9\%$ of total PBDEs, and are much higher than those reported by Guan et al. (0.003-0.143 ng/L: 2007) but similar to Oram et al. (0.6-26.5 ng/L: 2008) for two other San Francisco Bay watersheds. The FWMC of BDE 47 for Z4LA is 3.1 ng/L, nearly 10 times greater than the ambient concentration in the Bay (a maximum of 0.34 ng/L: Oram et al., 2008).

Oram et al. (2008) published a mass budget of BDE-47 and BDE-209 for the San Francisco Bay, and described local tributaries as the dominant source of BDE 209 loading to the Bay (71-77% of the total annual load). Indeed, BDE-209 was, on average, the largest contribution to the sum of PBDEs in Z4LA samples, with detected concentrations ranging 0.58-240 ng/L, and a FWMC of 29 ng/L, 55 times higher than maximum ambient concentrations in the Bay (0.53 ng/L: Oram et al., 2008). BDE 209 sorbs tightly to particles (Muresan et al., 2010) and therefore unsurprisingly comprised a larger proportion of samples collected during storm flow ($56\pm4\%$) than during low flow conditions ($20\pm65\%$). BDE 209 concentrations in Z4LA are higher than those reported in the other two studies citing whole water concentrations in China and the San Francisco Bay (0.33-65.2 ng/L: Guan et al., 2007; 1.7-119.0 ng/L: Oram et al., 2008).

Z4LA data were not available at the time that the PBDE mass budget for the San Francisco Bay was developed (Oram et al., 2008), and could now be used to further refine the previous

regional loadings estimated in that study. Annual BDE 209 yield from Z4LA is $5.6 \mu\text{g}/\text{m}^2$, which extrapolated to the entire Bay Area conurbation (excluding areas upstream from reservoirs = $5,050 \text{ km}^2$), yields an estimated total annual BDE 209 load to the San Francisco Bay from local tributaries of $28.3 \text{ kg}/\text{year}$ (versus 17.3 kg previously estimated). Because it is a more urbanized watershed, Z4LA might not be any more representative of the Bay Area landscape than the Guadalupe or Coyote Creek watersheds, from which the data was used to generate the 2008 mass budget. The results of this study support the magnitude of the prior mass budget estimate, but indicate the total load might be slightly higher than previously estimated because many of the more highly urbanized watershed areas surrounding the Bay could be better characterized by yields estimated in the present study.

PAHs

PAHs are a large class of suspected cancer-causing hydrophobic contaminants produced by incomplete combustion of petroleum, oil, coal, organic materials and wood, and are present, at lower concentrations, in unburned petroleum and some plant materials. PAHs are widespread in the environment, though the highest levels on the West Coast, where coal combustion and the use of coal tar sealcoat is rare, are primarily associated with traffic activities in urban areas (Van Metre and Mahler, 2010). San Francisco Bay currently has amongst the highest PAH sediment concentrations on the U.S. Pacific Coast (McCain et al., 2000), and the projected increase in population (ABAG, 2009) and associated traffic activity in the nine county Bay Area might continue to increase that contamination. PAH samples were collected in all monitoring years except 2009, during flow conditions ranging from $0.0001\text{--}6.1 \text{ m}^3/\text{s}$ in relation to turbidity from 1–256 FNU. Flow and turbidity exceeded these maxima during only 0.006% and 0.04% of the time, respectively, during our observation period; but without long-term data, we have no knowledge of what maximum flows would be during storms of higher rainfall intensity and duration.

Total PAH concentrations reported represent the sum of 25 individual PAHs routinely reported by the RMP (see methods section for the list of PAHs measured). On average for the samples measured in this study, the sum of the EPA's 16 Priority PAHs account for $85 \pm 1\%$ of the sum of 25 PAHs reported here. In Z4LA, PAH concentrations were below $1,400 \text{ ng}/\text{L}$ during low flow, with a FPMC of $730 \text{ ng}/\text{L}$. This low flow FPMC is 28 times the average water column PAH concentration in the San Francisco Bay ($26 \text{ ng}/\text{L}$; Greenfield and Davis, 2004). Storm flow FPMC was $9,600 \text{ ng}/\text{L}$, with concentrations spanning two orders of magnitude (Table 1). These concentrations are similar to those reported in urban watersheds elsewhere (Chesapeake Bay watersheds: Hwang and Foster, 2006; South Carolina watersheds: Ngabe et al., 2000; Southern California watersheds: Stein et al., 2006). The maximum PAH concentration measured for this study was $23,000 \text{ ng}/\text{L}$ and was for a sample collected during the rising stage of an intense first-of-season storm event in WY 2010. Elevated concentrations during the first flush, or initial period of stormwater runoff, are reported in other studies (Lee et al., 2002; Smith et al., 2000). Shinya et al. (2000) measured PAH concentrations up to $30,020 \text{ ng}/\text{L}$, with concentrations in the

first runoff sample collected up to 13 times greater than the event mean concentrations. Although the first-of-season flush phenomenon is not evident for all types of watersheds, pollutants, and rainfall events (Soller et al., 2005), Stein et al. (2006) reported a strong correlation between PAH concentrations and loads and antecedent dry period, in which early season storms with typically longer dry intervals had significantly higher loads than later-season storm events. On the basis of linear regression, the samples from the one first-flush event monitored in this study for PAHs (October 2009) had a concentration of total PAHs per unit of turbidity that was twice that for non-first-of-season samples from the same year (collected February through June, 2010). Of the other analytes that could be evaluated for first-of-season flush effects based on the data collection, a similar phenomenon was present for total PDBEs, but not for HgT, PCBs, OC Pesticides and dioxins.

As commonly reported in other studies of urban runoff, PAH composition was dominated by high molecular weight PAHs (HPAHs; having 4, 5, or 6 aromatic rings) (Stein et al., 2006; Hwang and Foster, 2006). However, the relative contributions of low molecular weight PAHs (LPAHs; having 2 or 3 aromatic rings) and HPAHs shifted substantially from low-flow conditions to storm-flow conditions. During low flows, LPAHs comprised an average of $40 \pm 26\%$ of the total, with naphthalene and phenanthrene as major LPAH contributors (on average $7 \pm 39\%$ and $14 \pm 28\%$, respectively), and flouranthene, pyrene and chrysene (12 ± 7 , 10 ± 16 , and $8 \pm 20\%$ respectively) accounting for the majority of HPAHs. However, during storm flows, HPAHs comprised an average of $90 \pm 1\%$ of all PAHs measured, again with flouranthene, pyrene and chrysene (13 ± 3 , 12 ± 3 , and $11 \pm 3\%$) as the highest contributors, and benzo(e)pyrene and benzo(b)flouranthene (11 ± 18 and $8 \pm 4\%$) also providing sizable contributions. HPAHs sorb more tightly to sediments, and so the shift towards HPAHs contributing a greater percentage during storm flow is expected with the increase in particle transport during storm flows.

The estimated total PAH load in Z4LA varied between 3.0- 5.5 kg during the study period, and the long-term average annual load is estimated at 5.2 kg, which translates to a yield of 1.2 mg/m^2 . Storm flows dominated the transport process, conveying >99% of the total load each year. As would be expected, the estimated yield for Z4LA is lower than reported by Smith et al. (2000) for four targeted traffic and gas station land uses in Virginia ($32.3\text{-}2,240 \text{ mg/m}^2/\text{y}$) and much greater than reported for the very large, rurally dominated Susquehanna River ($0.069 \text{ mg/m}^2/\text{y}$; Foster et al., 2000a), but similar to the predominantly urban Anacostia River watershed ($1.7 \text{ mg/m}^2/\text{y}$; Foster et al., 2000b).

Ratios of PAH isomers were investigated in the dataset to help distinguish possible sources. Ratios of benzo(b)flouranthene to benzo(k)flouranthene (0.86-1.48, average 1.09) and benzo(a)anthracene to chrysene (0.24-0.51, average 0.33) resembled ratios typical of vehicle operation (1.26 and 0.53, respectively: Dickhut et al., 2000) more so than other sources (e.g., coal/coke, wood, or smelter sources). Yunker et al. (2002) reviewed a number of isomer pair

ratios for various sources found in the literature. Based on the framework provided by that review, sources in Z4LA have mixed origins of petroleum and combustion.

Following methods and source profiles used in Van Metre and Mahler (2010) for preliminary indication of potential sources, a Chi-square correlation was calculated between known PAH profiles of common urban sources and the mean Z4LA profiles stratified by low flows and storm flows. The results of the Chi-square, in which the lower the Chi-square statistic the better the correlation, corroborated the findings of the benzo[b]fluoranthene to benzo[k]fluoranthene isomer ratio results based on the work of Dickhut et al. (2000), and additionally indicated coal tar sealcoat as a potential source. In stormwater, the dominant transport vector, the sources that are most similar to the storm flow profiles included coal tar sealcoat products ($X^2 = 0.06$), coal tar dust ($X^2 = 0.14$), traffic tunnel air ($X^2 = 0.11$) and gasoline ($X^2 = 0.19$). Note that the Chi-square correlation only provides a preliminary indication of sources that might be in the watershed. A more thorough investigation would be required to verify the presence of coal tar sealcoat, and a contaminant mass balance model (also used in Van Metre and Mahler, 2010) would help to indicate actual contributions of various sources.

Table 4. Chi-square difference between sources and mean low-flow and storm-flow profiles for Zone 4 Line A. Better correlated values (Chi-square of less than 0.2) are in bold.

Source category	PAH source	Zone 4 Line A Storm Flow s,	Zone 4 Line A Low Flow s,	Reference
		mean	mean	
Coal combustion	Power plant emissions	0.42	0.32	Li et al., 2003
	Residential heating emissions	0.95	0.27	Li et al., 2003
	Coke oven emissions	0.20	0.70	Li et al., 2003
	Coal averaged (defined in Li et al.)	0.30	0.25	Li et al., 2003
Vehicle-related	Diesel vehicle emissions	0.74	0.15	Li et al., 2003
	Gasoline vehicle emissions	0.19	0.64	Li et al., 2003
	Traffic tunnel air	0.11	0.39	Li et al., 2003
	Traffic averaged (defined in Li et al.)	0.26	0.13	Li et al., 2003
	Used motor oil 1	1.17	0.72	Wang et al., 2000
	Used motor oil 2	0.89	0.36	Boonyatumanond et al., 2007
	Tire particles	0.64	0.80	Boonyatumanond et al., 2007
	Asphalt	0.29	0.25	Boonyatumanond et al., 2007
	NIST diesel particles	1.03	0.21	NIST, 2000
	Gas-soot	0.50	1.15	Boonyatumanond et al., 2007
	Diesel-soot	0.66	0.18	Boonyatumanond et al., 2007
	Tire Fire	0.28	0.97	Wang et al., 2007
Fuel-oil combustion	Fuel oil combustions particles	0.68	0.45	Li et al., 2003
Wood burning	Pine-wood soot particles	0.46	0.56	Schauer et al., 2001
Coal tar seal coat related	NIST coal tar	0.78	0.26	NIST, 1992
	Coal tar sealcoat south	0.06	0.55	Van Metre and Mahler, 2010
	Coal tar sealcoated pavement dust	0.14	0.36	Van Metre and Mahler, 2010

OC Pesticides

With the exception of very limited uses of gamma-HCH (lindane), the organochlorine insecticides (DDT, chlordane, HCHs and dieldrin) are all now banned from use in the United States and most other countries around the world. However, these chemicals are persistent and

continue to flush from our urban watersheds years after their approved usage ended. In this study, samples were collected in all monitoring years except 2009. Total DDT (the sum of isomers and degradation products) concentrations ranged from 0.41-7.4 ng/L during low flows and from 5.1-59 ng/L during storm flows. These concentrations are higher than those reported by Foster et al. (2000b) for an urban catchment in Washington DC, where the maximum sum of DDTs measured was 7.7 ng/L. The 4-year FWMC in Z4LA was 15 ng/L, similar to the range of EMCs reported for three urban catchments in China (1.29-26.3 ng/L, average 12.3 ng/L for 29 events: Zhang et al., 2010). In Z4LA, total DDT concentrations were composed on average of $40\pm4\%$ DDE isomers, $31\pm13\%$ DDD isomers, and $29\pm12\%$ DDT isomers. DDD and DDE are degradation products of DDT. Although concentrations of all the isomers increased in storm flow, DDE and DDT isomer contributions increased from an average of $46\pm8\%$ of total DDTs at turbidities below 20 FNU up to an average of $79\pm3\%$ of total DDTs at high turbidity. Storm flow, transporting the bulk of the DDT loads, was therefore more abundant in the undegraded or unweathered DDT and the aerobic degradation product, DDE. Perhaps under California's climatic conditions, degradation rates of DDT are slow because surficial soils are dry most of the year and what degradation does occur, occurs under unsaturated soil conditions and aerobic conditions (Nowell et al., 1999).

HCHs measured in this study included the alpha-, beta-, delta-, and gamma-HCH isomers, and were detected in 17 of 20 samples analyzed. The sum of HCHs for detected results ranged from 0.087-0.40 ng/L during low flow and 0.30-0.89 ng/L during storm flow. These concentrations are much lower than reported by Foster et al. (2000b) (maximum of 7.4 ng/L). The overall FWMC was 0.40 ng/L, much lower than the EMCs reported by Zhang et al. (2010) for three urban catchments in China (6.46-107 ng/L, average 35 ng/L for 29 storm events). Gamma-HCH (lindane), the only isomer still in use today in the US, comprised on average the greatest proportion of total HCHs ($41\pm6\%$), closely followed by alpha-HCH ($40\pm6\%$). Beta-HCH, which has the greatest toxicological significance, comprised an average of $19\pm17\%$, whereas delta-HCH was detected in only one sample.

Chlordanes measured in this study included cis- and trans-chlordane, heptachlor, heptachlor epoxide, cis- and trans-nonachlor, and oxychlordane. All of these chlordanes were detected in all 20 samples, with the exception of oxychlordane and heptachlor, which were not detected in the seven lowest flow samples ($<0.002\text{ m}^3/\text{s}$). Concentrations of total chlordane ranged from 0.35-6.4 ng/L during low flow and 2.5-16 ng/L during storm flow. These concentrations are much lower than reported by Foster et al. (maximum 49.2 ng/L: 2000b). Alpha- and gamma-chlordane each comprised an average of $30\pm3\%$, of the total, followed by trans-nonachlor ($24\pm2\%$), cis-nonachlor ($11\pm4\%$), heptachlor epoxide ($4.6\pm19\%$), heptachlor ($0.7\pm28\%$), and oxychlordane ($0.6\pm25\%$).

Concentrations of dieldrin ranged from 0.28-0.85 ng/L in samples collected during low flow and from 0.74-4.6 ng/L in samples collected during storm flow, with a 4-year FWMC of 1.4 ng/L.

These concentrations are similar to those reported for the urban and suburban Anacostia River basin (maximum 4.8 ng/L: Foster et al. 2000b).

Overall, total DDT (including all isomers and degradation products) loading to the Bay exceeded that of any other organochlorine pesticide measured, with an estimated long-term average load of 12 g/year, and an estimated yield of 3.0 $\mu\text{g}/\text{m}^2/\text{y}$. Chlordanes represent the next largest class (5.4 g/year, 1.30 $\mu\text{g}/\text{m}^2/\text{y}$), followed by dieldrin (1.1 g/year, 0.27 g/year/ km^2) and HCHs (0.33 g/year, 0.078 $\mu\text{g}/\text{m}^2/\text{y}$). Storm flows transported 94-99% of the load for all of these contaminants in each water year studied.

Pyrethroids

Pyrethroid insecticides largely have replaced the use of organophosphate insecticides (e.g., diazinon, chlorpyrifos) in the United States, and currently are used on the urban landscape by professional and non-professional users, primarily for structural treatment and landscape maintenance. Pyrethroids are toxic to sensitive aquatic organisms, and although studied frequently in sediments, concentrations and loads have rarely been reported for urban stormwater runoff (Weston et al., 2009). Pyrethroids were sampled on 14 occasions in WYs 2008 and 2010, one-half of which were during storm flow and one-half during low flow. Three pyrethroids (permethrin, bifenthrin, and delta/tralomethrin) are discussed here, chosen based on their detection in more than 50% of the samples. Cyhalothrin was detected in two of the 14 samples (concentrations reported in Table 1). Other pyrethroids analyzed but for which there was 0% detection included: allethrin, cyfluthrin, cypermethrin, fenpropathrin, fenvalerate, phenothrin, prallethrin, resmethrin, and tetramethrin).

Permethrin was measured at the highest concentrations for the pyrethroids and was detected in all samples. The maximum concentration in storm flow was 290 ng/L, four and six times greater than the maximum storm flow concentrations reported by Weston et al. (2009) and Weston and Lydy (2010), respectively, for primarily residential neighborhoods in the greater Sacramento area. The highest storm-flow concentration was measured in a sample collected during the rising stage of a first-of-season storm (290 ng/L; FNU = 161) and is a high outlier that we have some uncertainty about because the second-highest concentration was only 80 ng/L (turbidity of 144 FNU), which was more consistent with concentrations measured in the Sacramento area (maximums of 48.5 ng/L and 66.1 ng/L). The high outlier was excluded from load calculations because of its influence on the regression with turbidity. Additional samples collected during conditions when turbidity is higher would help determine whether the high concentration in this study is an anomaly or is typical of a first-of-season flush phenomenon in the Z4LA watershed. Bifenthrin was also detected in all samples, and delta/tralomethrin was detected in 8 of the fourteen samples. Both were measured at much lower concentrations than permethrin, though within a range similar as reported for residential neighborhoods in the greater Sacramento area (Weston et al., 2009; Hladik and Kuivila, 2009; Weston and Lydy, 2010). Unlike permethrin,

concentrations of bifenthrin and delta/tralomethrin correlated well with turbidity ($r^2=0.84$ and $r^2=0.88$, respectively).

Stormwater runoff was the key vector in transporting pyrethroids to the Bay. Loading was estimated at 72, 18, and 2.3 g/year for permethrin, bifenthrin, and delta/tralomethrin, respectively. Storm flows accounted for >99% of the total load for each analyte. A single 6-hour storm event in WY2007 (1.5-year return frequency) discharged an estimated 14 times as much bifenthrin to the Bay as that discharged during the entire low flow period of 2007 (97% of the year). In addition to minimizing their use, proper disposal and care in the application of pyrethroids, especially prior to or during the wet season, could be critical for minimizing negative impacts.

Conclusions

Urban runoff is an important source of pollutants of concern to the San Francisco Bay. In all cases except some pyrethroids, pollutants of concern measured in the study were detected in at least some samples, even in cases in which the pollutant has been banned for several decades. Flow rates change rapidly in Zone 4 Line A as one might expect over the less permeable surfaces of urbanized areas. Because of the land use characteristics, non-point contaminant source characteristics, and the climatic and sediment transport characteristics in Zone 4 Line A, pollutant exports also were flashy and mostly occurred during wet-weather flows of larger volume. This finding has important management implications for regulators and municipalities, because collection and treatment of low-flow runoff is technically much more feasible than storm flows at the present time but likely will capture only a small percentage of the annual contaminant load for most pollutants of concern.

When pollutants were measured during the dry season, concentrations generally were low relative to storm-flow concentrations (with the exception of methyl- and reactive Hg), and included a greater proportion in the dissolved phase. Because some pollutants (e.g., Cu and Hg) are more bioavailable in the dissolved phase, there could be the opportunity to spatially identify the source areas for these during dry weather and manage at source and/or selectively manage and treat this runoff before it adversely affects sensitive biota in the Bay.

This study utilized continuous measurements of turbidity as a surrogate for a wide range of predominantly particle-associated pollutants. Uncertainties in our load calculations were influenced by the scatter about the pollutant concentration to turbidity regressions for each pollutant. However, concentrations in most pollutant classes were well explained by changes in turbidity, and there is great value using a loads calculation method that preserves flow and concentration independently from one another. Only a few contaminants required use of a stratified FWMC method to estimate loads; in these cases, our confidence was improved by a

methods comparison for HgT and PCBs that demonstrated acceptable bias between the two methods. The sampling design focused on collection during flashy storm-flow runoff to ensure that sample collection occurred over a broad range of flow and turbidity conditions for most pollutants. For these reasons, we have very high confidence in the reported loadings estimates and the range of potential error in these estimates. These findings are particularly important for some of the more rarely reported urban contaminants such as Ag, Se (including speciation), MeHg, acid labile Hg, dioxins, PBDEs, and pyrethroids. Assuming Zone 4 Line A is a reasonable surrogate watershed for urban areas in general, the data and interpretations presented here likely have far reaching applicability for managing pollutant loads in urban watersheds in other parts of the world.

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