Concentrations and Loads of Trace Contaminants in the Zone 4 Line A Small Tributary Hayward, California:

Water Year 2007

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EXECUTIVE SUMMARY

Urban runoff load has been identified in the total maximum daily loads reports (TMDLs) as a large and potentially controllable source of Hg and PCB to San Francisco Bay. The reports encourage further development of loads information to support the adaptive implementation. Here, new information is presented on loads from a small urban watershed in Hayward called Zone 4 Line A (Z4LA). This watershed was chosen as an observation watershed for a Small Tributary Loading Study because it contrasts in size and land use with Guadalupe River, the first observation watershed that was studied between November 2002 and April 2006. The Zone 4 Line A watershed encompasses an area of 4.47 km^2 of completely urbanized landscape. Land use is 38% industrial, 26% commercial, 33% residential, and 2% open space. Sampling during the study was carried out where Cabot Boulevard crosses the open engineered channel, approximately 1.7 km from the Bay and upstream from tidal influence. At this location, collection of rainfall, stage, and turbidity data and automatic sampling for suspended sediment concentrations (SSC) using an ISCO pumping sampler was carried out. Focusing on storms, stormwater was manually sampled between November 1st 2006 and April 30th 2007 using clean hands protocols and analyzed for concentrations of mercury species, PCB concentrations, and other trace contaminants. All analytical results were certified by the RMP data management and quality assurance protocol.

Rainfall during Water Year (WY) 2007 was between 70-80% of mean annual rainfall for the area and flood flows, while flashy, were moderate with storms mostly of less than a 1-year return frequency. Ninety percent of the rainfall occurred in just 25 days or 14% of the time and about 50% and 90% of the runoff occurred in just 5 and 21 days respectively (3% and 12% of the time). Total runoff for the winter season was 0.527 Mm^3. Measured SSC ranged from 1-2,744 mgL^{-1} with a flow-weighted mean concentration (FWMC) of 212 mgL^{-1}. Concentrations of total mercury (HgT) varied over an order of magnitude from 1.85-55.4 ngL^{-1} with a FWMC of 48.1 ngL^{-1}. HgT was correlated with SSC as was total methylmercury (MeHgT). MeHgT concentrations were also variable and on average accounted for 3% of HgT. MeHgT as a portion of HgT was inversely correlated with flow and in general a greater portion of HgT was methylated later in the wet season. Dissolved mercury (HgD) on average comprised 13% of HgT but again there was much variability and an inverse correlation with flow. Dissolved methylmercury (MeHgD) concentrations ranged over an order of magnitude from 0.021-0.27 ngL^{-1} and on average accounted for 26% of MeHgT. Concentrations of other trace elements generally showed much less variability between samples except for aluminum (54x), lead (40x), chromium (24x) and zinc (24x). Total PCB concentrations spanned two orders of magnitude between base flow conditions and storm flow ranging from 0.4 to 46 ng L^{-1} and exhibited a FWMC of 24 ng L^{-1}. In all samples, no single congener comprised more than 10% of t-PCB concentrations. Total PBDE concentrations ranged from 2.8 to 141 ng L^{-1} and exhibited a FWMC of 67 ng L^{-1}. BDE congeners 47, 99, 100, 153, 183, 206, 207, 208 and 209 collectively comprised over 90% of all samples, and congeners 47, 99 and 209 comprised 73-88% of all samples.

Loads were calculated by combining instantaneous runoff with estimated SSC and contaminant concentrations based on regression relationships with turbidity. Suspended sediment, total mercury, methylmercury, PCB, and PBDE loads during the winter of WY 2007 were 112 metric t, 25.4 g, 0.72 g, 14.4g and 40.6 g respectively. Normalizing for area and climatic effects, yields of suspended sediment and total mercury were less than Guadalupe River due to the greater erosion rates on the slopes of the San Cruz Mountains and historic mercury mining wastes near or in the channels, but yields of methylmercury were greater in Z4LA. One unsubstantiated hypothesis is that methylation is occurring in areas that fluctuate in moisture levels perhaps associated with

landscape irrigation wetting and drying drop inlets. Yields of PCBs and PBDEs were similar in both watersheds; however any comparisons should be treated as hypotheses given that sampling took place during such a low rainfall year. It is recommended that further sampling be carried out in Z4LA to provide better data for estimating inter-annual concentrations and loads and long term averages, and to provide data as a baseline for future comparisons.

ACKNOWLEDGEMENTS

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INTRODUCTION

Urban runoff is considered a significant source for a number of pollutants of concern (POCs) found in San Francisco Bay. Some POCs have been determined to be sources of impairment and the San Francisco Bay Regional Water Quality Control Board (Water Board) has initiated or completed TMDLs or some other regulatory response. TMDLs completed or awaiting EPA approval includes San Francisco Bay mercury (Hg) and polychlorinated biphenyl's (PCBs), and Richardson Bay pathogens**.** Site-specific objectives have been developed for copper and cyanide, and conceptual model impairment assessments reports have been written for nickel, dioxins, legacy pesticides, selenium, PBDEs that have identified data needs to support policy decisions. These regulatory documents both assert the need for load reductions for Hg and PCBs and call for improved loads information.

While data from load studies are preferred for preparation of TMDL reports and resulting policy decisions, such data are not always available or may be collected in parallel with TMDL development. For example, mercury (Hg) loads from the greater urban extent of the Bay Area remain uncertain and have been estimated in the TMDL by combining sediment Hg concentrations with annual average suspended sediment loads (Abu-Saba and Tang, 2000: 58-278 kg; KLI, 2002: 96 kg (range 52-226 kg); Looker and Johnson, 2004: 160 kg). Alternatively, one could combine published stormwater Hg concentrations (e.g. McKee et al., 2004) with estimated stormwater flows from urban areas (Davis et al., 2000) to derive an estimate of 150 kg (range 10-1,028 kg) (McKee, 2008). Non-urban runoff average annual loads are equally uncertain (KLI, 2002: 27 kg (range 7-37 kg); Looker and Johnson, 2004: 25 kg). In contrast, initial data from load studies were used to develop the first drafts of PCB TMDL report and the final PCB TMDL did include a best estimate of urban runoff PCBs loads based on field measurements. Despite these uncertainties, the TMDLs assert that reduction of loads over the next 20 years by 50 and 95% for Hg and PCBs respectively is a necessary step towards reducing impairment of beneficial uses in the Bay.

Although improved loading data is still required for some POCs (for example total and dissolved copper, total and methyl-mercury, PCBs, total and dissolved Se, dioxins, PBDEs, PAHs, organochlorine and pyrethroid pesticides, nitrate, and total and dissolved phosphorous), more refined loads studies can also be used to prioritize and inform cost-effective management actions to address a reduction in loads required by the TMDLs. Priority uses now include: 1) Learning about loads entering sensitive areas on the Bay margin, 2) Providing data for tracking trends, and 3) Providing data for selecting urban best management practices (BMPs) for reducing loads and modeling the effects of management. While a Small Tributaries Loading Strategy is now in development to address and prioritize needed information on loads over the 5-10 year time scale, some information (for example to address BMP selection and design) will mostly continue with the majority of funding sourced from outside the RMP. Thus improved local data on loads for policy development and more refined information tailored towards management solutions will develop over the next decade with much communication and collaboration among researchers and agencies.

The Regional Monitoring Program for water quality (RMP) Sources Pathways and Loadings Work Group (SPLWG) began the first *Small Tributaries Loading Study* in Guadalupe River in Water Year (WY[1]) 2002. Guadalupe River watershed is the fourth largest in the Bay Area, it is about 80% urbanized downstream from its five main reservoirs, and it is home to the Quicksilver County Park, formerly the New Almaden Mining District where, since 1850, 6% of the total world production of Hg has occurred. Although it was recognized that the Guadalupe River is unique with respect to Hg, it was deemed to be reasonably typical for PCBs, other trace metals, and OC pesticides (McKee et al., 2004, 2005, 2006). However, it was recognized from the outset that multiple observation watersheds would be necessary over the longer term to characterize loads in a variety of watershed archetypes (Davis et al., 2001; McKee, 2005; McKee et al., 2008). In 2006, the RMP funded a small special study to explore where to locate a second *Small Tributaries Loading Study* (Pearce and McKee, 2006). After much deliberation, Zone 4 Line A, a small 100% urban watershed, was chosen as the next observation watershed for a *Small Tributaries Loading Study* because it represented a good contrast to the Guadalupe River watershed. Here we report on concentrations and loads from the Zone 4 Line A watershed for WY 2007, the first year of study.

METHODS

Watershed Overview

The Zone 4 Line A[2] watershed is located in western Alameda County, California, and debouches directly into the San Francisco Bay approximately 24 km south of Oakland and 19 km north of Newark (Figure 1). It is bounded on the north by the Zone 4 Line B and Sulphur Creek watersheds and on the south and east by Zone 4 Line C and Old Alameda Creek watersheds. Elevation in the watershed ranges from approximately 27 m down to sea level, with a corresponding average watershed surface slope of 0.4%. Geology in the Zone 4 Line A watershed is comprised almost entirely of Holocene alluvial fan and alluvial fan levee deposits, with a few small areas of artificial fill (Witter et al., 2006). Botella loam soils dominate the upper portion of the watershed, and Clear Lake clay and Danville silty clay loam dominate the middle and lower portions (USDA, 2007). The Botella and Danville loams both are well drained soils while Clear Lake clay is poorly drained (USDA, 2007).

The Zone 4 Line A watershed encompasses an area of 4.47 km^2 of completely urbanized landscape. Land use is 38% industrial, 26% commercial, 33% residential, and 2% open space land uses (ABAG, 1995) (Figure 2). The watershed contains 4 km of rail bed and impervious surfaces covering 65-70% of the watershed[3]. The estimated annual average runoff coefficient for the watershed, based on a review and compilation of hydrological

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[1] A water year (WY) starts October 1st and ends September 30th where the year is denoted by the end date.
[2] Zone 4 Line A is an artificial channel that does not correspond with any historic named creek. Alameda County Flood Control and Water Conservation District designated the channel with its name, Zone 4 Line A.
[3] The percent imperviousness for the watershed was determined using the 2001 National Land-Cover Database for the United States. This raster dataset includes the percentage imperviousness for pixels of 30 m^2 resolution. A detailed description and methodology of the dataset is explained in Homer et al. (2004).

and water quality data for the Bay Area (Davis et al., 2000), is 70% (see results for the annual runoff coefficient based on WY 2007 data). The channel of Zone 4 Line A is entirely engineered with approximately one third open to the air and two thirds underground culverts and storm drains.

Figure 1. Regional map.
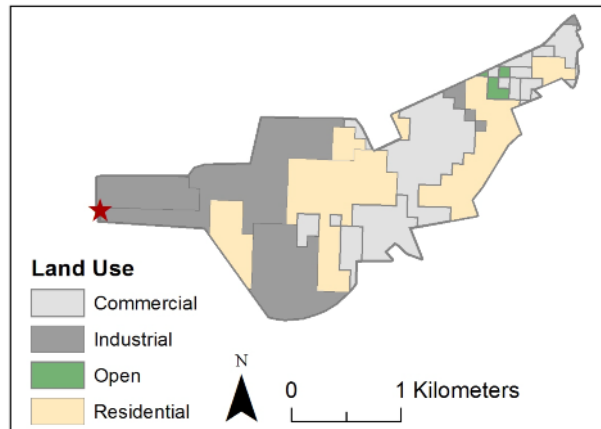
Figure 2. Land use patterns; star indicates sampling location.

Western Alameda County has a Mediterranean marine climate with little variation in temperature throughout the year. Meteorological monitoring stations at Oakland Museum (station 046336) and Newark (station 046144) report average summer maximum temperatures during July at 22.4 and 25.0 ºC, respectively, and average winter maximum temperatures for January at 14 ºC for both stations (WRCC, 2008). For the previous 35-year period (Climatic Years[4] 1973-2007) the average precipitation was 580 millimeters (mm) and 370 mm at the Oakland Museum and Newark rain gauge stations, respectively (WRCC, 2008). At both stations, 95% of rain falls between October 1st and April 30th. Extreme dry years can yield <40% mean annual precipitation (MAP), whereas extreme wet years can exceed 200% MAP.

Sampling Location

Sampling during the study was carried out where Cabot Boulevard crosses the open engineered channel, approximately 1.7 km from the Bay and upstream from tidal influence (Figure 3 and Figure 4). The coordinates at this location are 37º 38' 43'' N and 122º 08' 14'' W. Upstream from the sampling location, Zone 4 Line A is a straight and rip-rap lined channel, with minor amounts of weeds and grasses growing along the banks (Figure 5). The channel is open for 1.5 km upstream from the sampling location, while

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[4] Climate year begins July 1st and end June 30th each year where the year is denoted by the end date.

the rest of the drainage network is underground. Downstream of the sampling location, after flowing through the concrete single-barrel box culvert under Cabot Boulevard, the open air channel looks similar to its upstream form.

Samples were collected at the upstream entrance to the box culvert that channels the water underneath Cabot Boulevard (Figure 6). The sampling location also is concrete lined since the concrete bed and wingwalls extend just upstream of the Cabot Boulevard crossing. At the sampling location, the channel cross section is approximately 3 m wide and 2.3 m high, and nearly rectangular in shape (Figure 7).
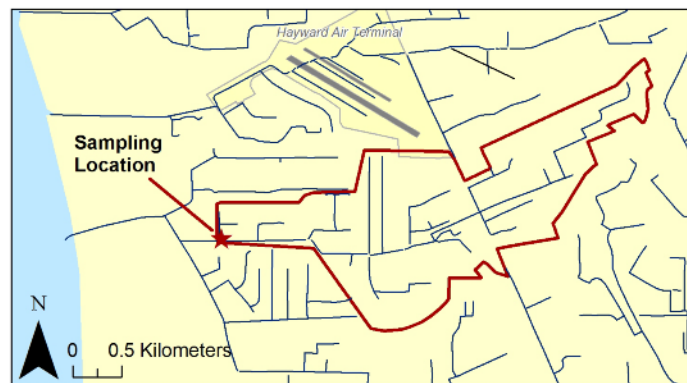
Figure 3. Watershed boundary map and 24-inch or larger storm drain channel network in relation to the sampling location.

Figure 4. Sampling location map view. Star indicates sampling location.

Figure 5. Upstream channel view.

Figure 7. Cross-section of channel at sampling location.
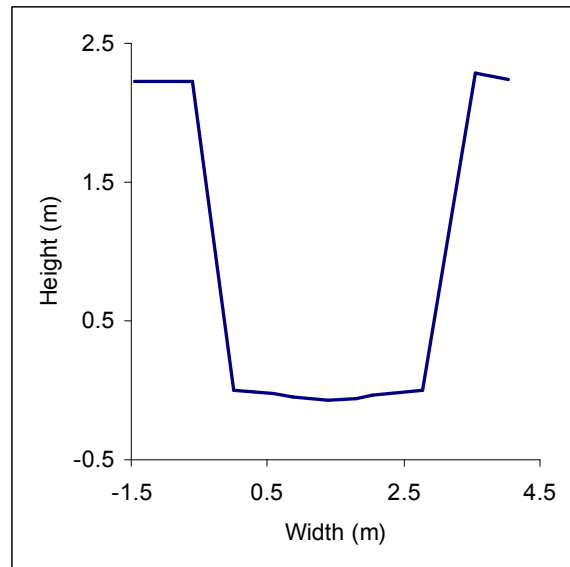
Figure 6. Single-barrel box culvert**.**   **Figure 7.** Cross-section of channel at sampling location.

Study Components

The study incorporated three semi-separate sampling components that together formed a comprehensive integrated sampling methodology for estimating the concentrations and loads of suspended sediments, PCBs, mercury and ancillary parameters in this small urban drainage. The three components were:

1. Real-time continuous measurement of stage and turbidity, and periodic turbidity-triggered suspended sediment concentration (SSC) sampling,

2. Manual sampling for SSC and mercury, other trace elements and trace organics using "clean hands" techniques,

3. Manual velocity measurements.

Real-Time Continuous Turbidity Measurement and SSC Sampling
Rand Eads, RiverMetrics LLC, led this component of the study. A Forest Technology Systems Limited (FTS) DTS-12 turbidity sensor (Figure 8a) was installed at the Zone 4 Line A sampling location and connected to a Campbell Scientific CR10X data logger (Figure 8b). The turbidity sensor and pumping sampler intake was deployed in the center of the channel using a bridge-mounted sampling boom that was attached to a wooden sampling platform above the sampling location (Figure 9). The boom was intended to position the sensor and intake at about mid-depth in the water column. Resistance to the

flow raising the boom in the water column was controlled with a weight. During flows above 0.7 m the boom experienced hydroplaning and some data were lost. The DTS-12 has a wiper that reduces optical fouling and is activated before each measurement. Field crews removed larger organic debris lodged near the sensor during field visits. An INW PS-9805 pressure transducer was installed on the left bank wall opposite the staff plate. Average water stage (150 readings) and the median turbidity (100 readings) from each 5- or 10-minute interval were stored in the data logger's memory. The DTS-12 records turbidity in formazine nephelometric units (FNU) and is auto-scaling from 0-200 and 0-1600. The DTS-12 measurements were periodically compared to grab samples taken near the sensor and measured in the field with a Hach 2100P portable turbidimeter (widely considered a standard device for field measurements). Although the relation is not 1:1 (due a difference in optical measurement methods), the fit is linear providing assurance that the DTS-12 sensor was operating correctly.

Automatic SSC samples were collected with an ISCO 6712 pumping sampler under control of the data logger program (Figure 10). The ISCO was housed in a metal box on the right bank, and Teflon intake suction tubing was routed in conduit sloping downward towards the channel and terminating near the turbidity sensor on the sampling boom. The ISCO sampler was triggered when pre-established turbidity thresholds (9 rising and 13 falling) were measured by the turbidity sensor under control of a modified Turbidity Threshold Sampling program (Lewis et al. 2001). The instrumentation set-up is shown in Figure 11, with the metal box housing the ISCO sampler, CR10X data logger, and battery on the right bank, the wooden sampling platform across the channel, and a Campbell Scientific TE525 tipping bucket rain gauge and Campbell Scientific SP10R solar panel immediately adjacent to the metal box housing. A Redwing 100 CDMA cellular modem/SC105 was also connected to the data logger to allow the data to be transmitted back to the office at midnight each day or in response to stage and turbidity criteria during storms.

(a)   (b)
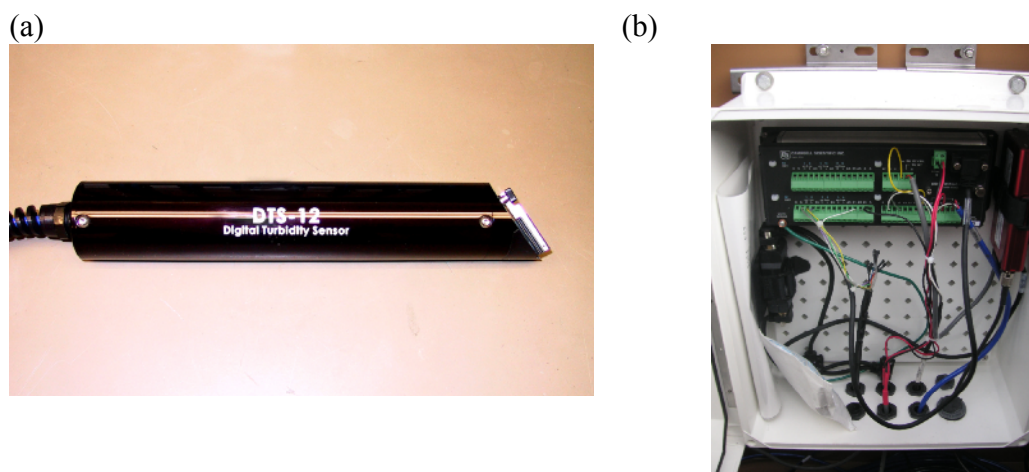
Figure 8. a) The DTS-12 Turbidity Sensor. Note the wiper on the right side of the instrument. b) The Campbell Scientific CR10X data logger.

(a)

(b)
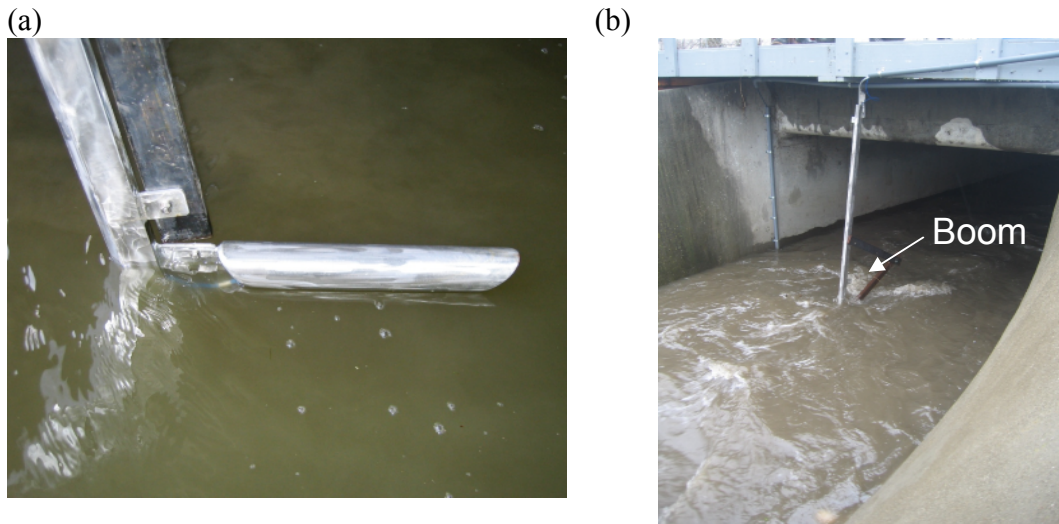
Figure 9. a) The DTS-12 Turbidity Sensor housing. b) The stabilizing counter weight. The turbidity housing and sensor attached at the bottom of the counter weight is under water in this picture.
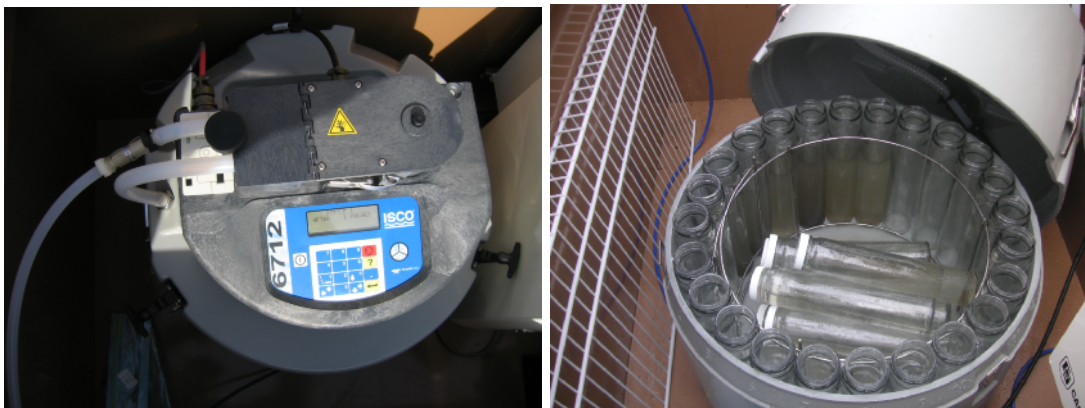
Figure 10. The automated ISCO 6712 full-size portable pumping sampler.

Figure 11. The instrumentation set-up at Zone 4 Line A, including the metal box housing the ISCO pumping sampler, datalogger and battery, the wooden sampling platform, the sampling boom, solar panel and tipping-bucket rain gauge.

Stage and turbidity were measured every 10 minutes during the period from November 10th 2006 through February 6th 2007, and every 5 minutes thereafter through May 30th 2007 after it was determined that a shorter time interval would improve the resolution of stage and turbidity during rapidly changing conditions. Data were collected for seven months for a total of 36,661 data records. Samples were collected from every storm event using the ISCO pumping sampler and a selection of these samples was analyzed for SSC (n=90).

Manual Sampling for Suspended Sediment and Trace Contaminant Concentrations

SFEI field scientists took the lead on this component of the project. Sampling was carried out using two protocols. Both protocols involved the use of two persons (one designated "clean hands" and the other designated "dirty hands"). Double-bagged (Ziploc™) sample bottles prepared for mercury and other trace elements were supplied by Moss Landing Marine Laboratory. During high flow, samples were taken by inserting an acid-cleaned 1-L Teflon sample bottle into a D-95 depth-integrating sampler (Figure 12). The "dirty hands" person did not touch the trace-element clean bottles, but opened the outer Ziploc™ bags without touching anything but the outside of the bag. The "clean hands" person, wearing a pair of trace-element clean polyethylene gloves, did not touch anything

with her/his hands except the inner Ziploc™ bag and trace-element clean sampling bottle and components. The "clean hands" person loaded the bottle into the D-95 sampler. The "dirty hands" person then lowered the D-95 sampler into the water column using a USGS Type A crane mounted on a 4-wheel truck (Model 4350) and B-reel manual winch for lowering and raising the sampler (Figure 13). The bottle was filled by passing it evenly through the water column (single vertical) without touching the bottom of the channel, aiming to fill the bottle completely by the time it reached the surface again. Once the sample bottle was filled the "clean hands" person retrieved it. The "dirty hands" person then secured the winch and D-95 before assisting the "clean hands" person to remove the sample bottle and decant the sample into shipping containers. To fill all of the shipping containers, the 1-L Teflon sampling bottle had to be lowered and filled multiple times. Once all the shipping bottles were filled, the "dirty hands" person helped the "clean hands" person to double-bag the 1-L Teflon sample bottle.

During stages sufficiently low for wading (< 0.5 m), samples were collected by hand-dipping at approximately mid-depth in the water column using "clean hands" and "dirty hands" techniques. Field personnel did not to enter the channel during the measurement of turbidity, stage, or during the automatic collection of SSC samples. All samples were labeled, placed on ice, and transported to the laboratory for preservation and analysis. In WY 2007, 40 samples were collected from the Zone 4 Line A sampling location using the methods described above. Samples were collected over a range of stages and primarily during storm events for analysis of mercury, PCBs and other trace substances.
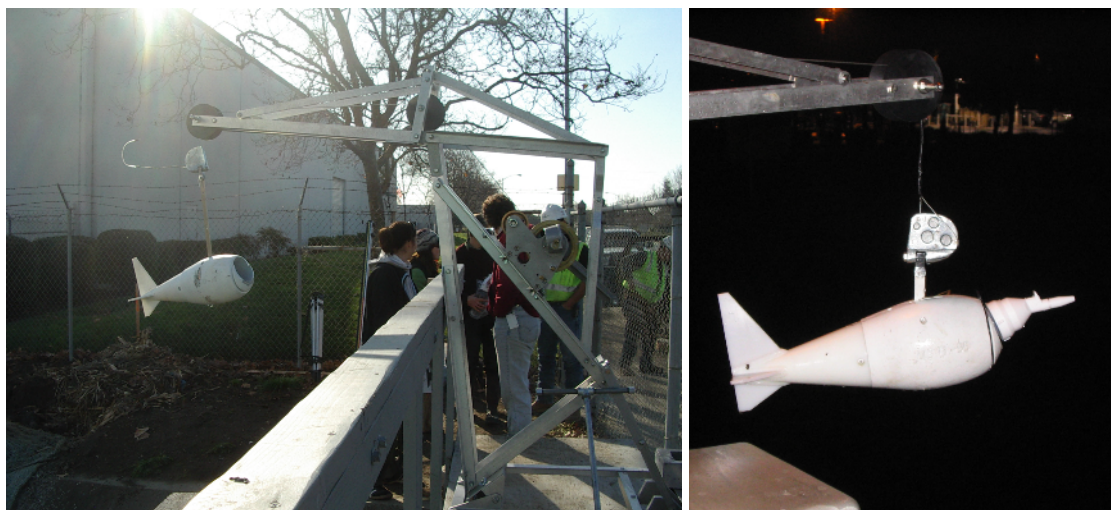
Figure 12. USGS Type A Crane, Type A Four-Wheel Truck, B-reel, and D-95 depth-integrating sampler empty in the photo on the left and with a bottle inserted in the photo on the right.

Figure 13.   Lowering the D-95 sampler loaded with a 1-L Teflon sampling bottle into the channel during flood flow (picture at left), and decanting the bottle into an organics shipping bottle (picture at right).

Manual Velocity Measurements

To develop a stage-discharge rating curve, SFEI field personnel measured velocity manually using a Marsh-McBirney Model 2000 Flo-Mate portable flowmeter during storm events. During wading conditions (stage <0.5 m), field personnel stood behind and to the side of the flowmeter sensor, which was attached a top-setting wading rod (Figure 14). The 10-second average velocity was measured at 60% depth at every 0.3 m (1 foot) increment starting at 0.15 m (0.5 feet) from the right bank. At stages greater than 0.5 m, velocity was measured from the sampling platform by attaching the flowmeter sensor to a 32-kg USGS Columbus-Type sounding weight and lowering the sensor into the channel using the crane assembly. Ten-second average velocity measurements at 20%, 60%, and 80% depth were recorded at every 0.3 m increment, starting at 0.15 m from the right bank. For both protocols, the staff plate readings were recorded during the procedure, and cross referenced with the electronic stage measurements.

Figure 14. Measuring velocity at wading stage.

Analytical and Interpretation Methods

Laboratory Analysis of Mercury, Trace Elements, SSC and Organic Carbon

Water samples were analyzed for total mercury (HgT), dissolved Hg (HgD), total methylmercury (MeHgT), and dissolved methylmercury (MeHgD), other total trace elements (silver (Ag), aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn)), and SSC (Table 1) by Moss Landing Marine Laboratory (MLML), Moss Landing, California. Upon receipt at the lab, trace metal, mercury and methylmercury sample aliquots were filtered in the laboratory. When samples were received beyond the 48-hour preservation holding time, only aliquots of HgT were retained. HgT and HgD water samples were preserved to a final concentration of 0.5% v/v bromine monochloride (BrCl), MeHg samples to 0.5% v/v HCl, and other trace element analysis samples were acidified to a final concentration of 1% v/v nitric acid (HNO$_3$). MeHg and SSC samples were refrigerated at 4°C in the dark until the analysis was performed. Mercury samples were analyzed with cold vapor atomic fluorescence following U.S. EPA method 1631e (USEPA, 2002). Other trace element samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following U.S. EPA method 1638 (USEPA, 1996). SSC was measured gravimetrically following the methods of Guy (1969).

Total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed by Applied Marine Sciences Inc., League City, Texas. POC and DOC analyses were performed in accordance with EPA guidelines (EPA method 415.1), the 2006 Dept. of Defense (DoD) Quality Systems Manual for Environmental Laboratories, Version 3 and the 2003 NELAC Standard.

Table 1. Analyses completed on water samples collected at Zone 4 Line A during water year 2007.

Analyte	Sample Count (n)	Analyte	Sample Count (n)
Hg (Total)	40	Mn	21
Hg (Dissolved)	20	Ni	21
MeHg (Total and dissolved)	20	Pb	21
POC and DOC	16	Se	21
Ag	21	Zn	21
Al	21	PCBs	20
As	21	PBDEs	20
Cd	21	PAHs	7
Cr	21	OC Pesticides	7
Cu	21	SSC	120

Mercury, Trace Elements, SSC and Organic Carbon Quality Assurance

Samples were received in generally good condition between mid-November and late-April, 2007. The mercury and other trace-element analytical methods were chosen to ensure the method detection limits (MDL) were below the expected concentrations, and selenium was the only parameter analyzed that repeatedly had concentrations less than the MDL. Relative percent difference (RPD) was within the target range of ±25% with the exception of one batch for selenium that was marginally outside the desirable range (Appendix A1).

The percent recoveries for standard reference materials were within the target range (75 – 125%, 70 – 130% for MeHg) without exception. The percent recoveries for matrix spikes were within the target range (75 - 125%, 70 – 130% for MeHg) for all samples except one batch of aluminum (Appendix Table A1). Trace element concentrations in the method blanks were not detected. In cases where minor SSC was detected in the method blank, samples were corrected using the average blank concentration for the batch.

See Appendix A for more detailed description of the Quality Assurance data for mercury, trace elements, SSC and organic carbon.

Laboratory Analysis of PCBs, PBDEs, PAHs, and Pesticides

Twenty grab samples were analyzed for PCBs and PBDEs. Concentrations of 38 individual and co-eluting PCB congeners were measured and summed to derive total PCB (t-PCB) concentrations in water samples. This group of congeners comprised the 40 PCB congeners that are typically measured by the RMP. Total PBDE (t-PBDE) concentrations were comprised of 42 individual and co-eluting PBDEs. Seven grab samples were additionally analyzed for organochlorine (OC) pesticides and PAHs. Total DDT (t-DDT) concentrations accounted for concentrations of o,p' and p,p'-isomers of DDD, DDE, and DDT. Total chlordane (t-chlordane) concentrations were comprised of alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide. Dieldrin also was measured as part of this study. Twenty-five PAH congeners

comprised the total PAH (t-PAH) concentrations, which included 13 low-molecular weight PAHs (LPAHs) and 12 high-molecular weight PAHs (HPAHs).

Trace organic contaminants were analyzed by AXYS Analytical Services Limited, Sidney, British Columbia, Canada. Prior to analysis, approximately 8 liters for each sample were spiked with $^{13}C_{12}$-labeled standards and filtered. The filtrate was liquid/liquid extracted with dichloromethane (DCM), and the particulate was soxhlet extracted with DCM. Ideally, laboratory analysis would be performed on the particulate fraction separately from the dissolved phase to learn more about the transport process, but at this time costs are prohibitive. Sample extracts were combined and the extract quantitatively split. Approximately one-quarter of the extract was used for PAH analysis, and the remaining three-quarters was used for analyses of PCBs and OC pesticides. PCBs, OC pesticides, and PBDEs were analyzed using high resolution gas chromatography/ high resolution mass spectrometry (HRGC/ HRMS) following EPA method 1668 revision A for PCBs and OC pesticides (USEPA, 1999) and EPA method 1614 for PBDEs (AXYS Analytical Services, 2002; USEPA 2007).

PAHs were analyzed using high resolution gas chromatography/ low resolution mass spectrometry (HRGC/ LRMS) following AXYS's own method MLS-021. The PAH portion of the extracts was reduced in volume, solvent-exchanged to hexane, treated for sulphur and columned on deactivated silica. The extracts were spiked with a labeled recovery (internal) standard prior to instrumental analysis. PAH analyses were performed on extracts using HRGC/LRMS performed on an Agilent 6890N GC equipped with an Agilent 5973 MS, an Agilent 7683 Series Autosampler, and an HP Chemstation. A Restek Rtx-5 chromatography column (30 m, 0.25mm i.d., 0.25mm film thickness) was coupled directly to the MS source. The MS was operated at a unit mass resolution in the electron ionization (EI) mode using multiple ion detection (MID) acquiring two characteristic ions for each target analyte and surrogate standard. A splitless/split injection sequence was used.

PCBs, PBDEs, PAHs, and Pesticides Analysis Quality Assurance
Quality assurance and quality control criteria were based on protocols outlined in the RMP Quality Assurance Program Plan (Lowe *et al.*, 1999) and in EPA Method 1668, Revision A (USEPA, 1999). Quality assurance samples included laboratory blanks, matrix spikes, $^{13}C_{12}$-labeled surrogates, and duplicate field samples.

No PCB measurements were below detection. Relative percent differences (RPD, calculated as the difference in concentration of a pair of analytical duplicates divided by the average of the duplicates) of PCB congeners measured in the field duplicate sample ranged from 3 to 37% (Appendix Table B1). Approximately one-half of the PBDE congeners were detected less than 100% of the time, and three were never detected. The RPDs of PBDE field duplicates ranged from 0 to 40%. All PAHs analyzed were detected in all samples and only the pesticide Aldrin was not detected in one sample. The RPDs ranged between 0.21 and 21% for PAHs and between 0 and 57.6% for pesticides.

See Appendix B for more detailed description of the Quality Assurance data for PCBs, PBDEs, PAHs, and pesticides.

Loads calculation methods and error analysis
Loads were calculated by combining nearly continuous (5- or 10-minute interval) estimates of suspended sediment and contaminant concentrations with discharge derived from the rating equation. While there is some argument that linear regression might be more appropriate, an annual SSC load estimate was generated from discrete SSC turbidity pairs using a locally weighted LOESS regression (linear, power, log, and LOESS had nearly identical statistics for annual load computations, but no single model provides the best fit for individual storm events). The choice of regression will be further discussed in a future report when more years of data area available. Nearly continuous concentrations of total trace elements and trace organics were determined by developing regression relationships between SSC and individual contaminants. Loads were summed to daily, monthly or wet season totals. In the cases of As and Se, there were no regression relationships with SSC and therefore loads were calculated by combining the flow-weighted mean concentration based on the instantaneous data with total annual discharge. In the cases of HgD and MeHgD, loads were estimated as a fraction of total loads based on the flow-weighted mean of each fraction (HgD: 13%; MeHgD: 25%).

The total error 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 (±10%), SSC-Turbidity regressions (±10%), interpolation / SSC-trace contaminant specific regressions (3%-36%) (Table 2), and the mean coefficient of variation (CV) of duplicate field samples (0%-21%) (Table 2). In the cases of As and Se, the errors were set arbitrarily at ±50% (slightly greater than the maximum error of any other analyte load. In the cases of HgD and MeHgD, the errors were set the same as HgT and MeHgT respectively. The total estimated errors for mass loads calculations ranged between (15%-50%). Note that we have found no other papers in the literature that have quantified errors in mass loads calculations, yet clearly the error associated with the measurements is such that claims of mass load variation between years may not be valid. In most cases differences between years of less than 25% likely are not statistically significant (quantifiable with certainty).

Table 2.   Errors (+/-%) associated with loads calculations.

	Error Accounted for in Mass Loads Estimation: (%)		
Flow	10		
SSC-Turbidity Regression	10		
	Interpolation/SSC-Trace-Contaminant Specific Regression:	Mean Coefficient of Variation (CV) of Duplicated Field Samples:	Total Estimated Errors for Mass Loads Calculations:
SSC			16
Ag	15	14	25
Al	18	3	23
As		6	
Cd	21	2	25
Cr	18	21	31
Cu	25	1	29
Mn	14	1	20
Ni	8	12	20
Pb	12	1	18
Se		ND	
Zn	16	2	21
HgT	36	15	41
HgD		21	
MeHgT	19	11	26
MeHgD		5	
PCBs	4	8	17
PBDEs	9	11	20
PAHs	5	8	17
DDT	3	4	15
Chlordane	29	0	32
Dieldrin	5	6	16

RESULTS AND DISCUSSION

Hydrological Processes

Rainfall and runoff are the primary sources of energy in the Zone 4 Line A watershed that transmit sediments and contaminants from sources into waterways and past the sampling location at Cabot Boulevard. Watershed loads were described using the temporal scales of annual, monthly, daily, and instantaneous. In addition, the loads were described for specific storm events to better understand the process of transport as it relates to runoff. The following sections place the 2007 water year (WY) (the year beginning October 1st, 2006, and ending September 31st, 2007) and the 2007 climatic year (CY) (the rainfall

year beginning July 1st, 2006, and ending June 30th, 2007) into the context of the period of record using the range of temporal scales listed above.

Runoff and the Stage-Discharge Rating Curve

Prior to the installation of the Z4LA instrumentation discharge was only available from the Alameda County Public Works Department gage located upstream of the sampling location. Because the data record was not reliable we constructed a discharge rating curve using stage and velocity measurements that were collected during the study, and applied the results of this rating curve to the nearly continuous stage data collected during the study period (Figure 15). The resulting discharge information was the basis for calculating the loads presented in later sections.
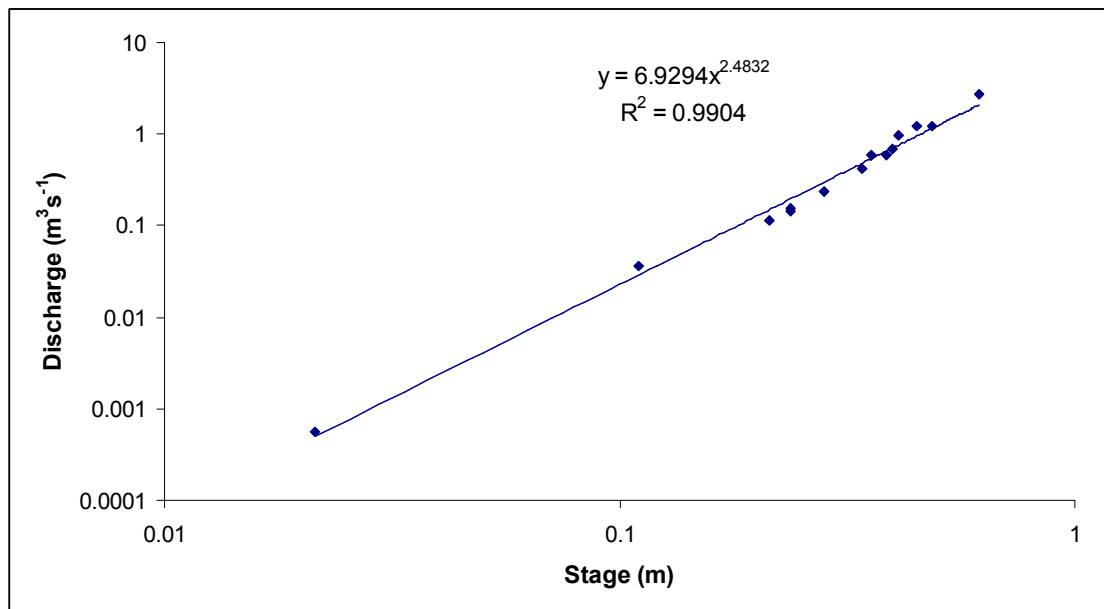
Figure 15. Rating curve for Zone 4 Line A during WY 2007.

Annual Rainfall

The Alameda County Public Works Agency has two rain gauges (Stations: 541A and 544G) near the Zone 4 Line A watershed, one south of Zone 4 Line A in Fremont (Station: 50 dly), and the Western Regional Climate Center has long-term gauging stations nearby in Newark and Oakland (Figure 16). Rainfall in the Zone 4 Line A watershed probably is best represented by gauge data from 541A, and secondarily by gauge 544G. However, these two gauges may overestimate the total annual rainfall averaged throughout the watershed based on data from 2007, in which measured total

annual rainfall at the sampling location lower in the watershed was 50-64 mm less than either of the Alameda County Public Works gauges, located higher and just outside the watershed. This is further supported by rainfall isohyets developed by Alameda County in 1993, which indicate a clear gradient of increasing average rainfall from the lower to the upper watershed (Figure 17). Based on these isohyets, the watershed as a whole receives between 365 and 380 mm per year on average. Oakland Museum typically receives 10-15% more rain than 541A and 541G, and Newark typically receives 30-35% less rain (Figure 18). During the period of record (2000-2007) at gauge 541A, the average total annual rainfall was 490 mm. The greatest annual rainfall on record was 670 mm in CY 2005 and the driest year on record was CY 2007 with a total of 330 mm.

The return interval analysis based on the 8 years of data recorded at station 541A directly overlaps with that at gauge 50 dly in Fremont (Figure 18). In the 45 years of record for gauge 50 dly, the average total annual rainfall was 465 mm, with a return period of about 2.3 years (Figure 19). The driest year on record in CY 1992 when 188 mm of rain fell, and the wettest year on record was in CY 1983, when 988 mm of rain fell at this station. Rainfall at the 50 dly gauge in CY 2007 was 360 mm, and was 77% of the average total annual rainfall over the 45-year record. An annual rainfall of this magnitude has a return period of about 1.6 years (Figure 19).

Figure 16. Map of nearby rain gauge stations.
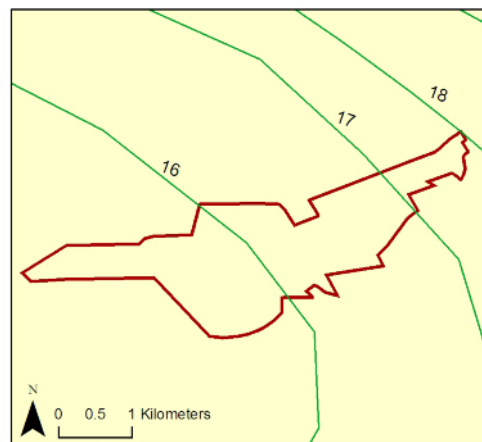
Figure 17. Isohyets (inches)[5] in the Z4LA Watershed. After Goodridge, 1992.

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[5] Note, these isohyets are in inches in contrast to the rest of the report which discusses rainfall using metric units (mm). Information from James D. Goodridge, P.E., 1992 . "Alameda County Design Rainfall Study Report". Appendix B in: Hydrologic Modeling Evaluation Summary Report for Alameda County, California. Alameda County Public Works Agency, Hayward, 1994.
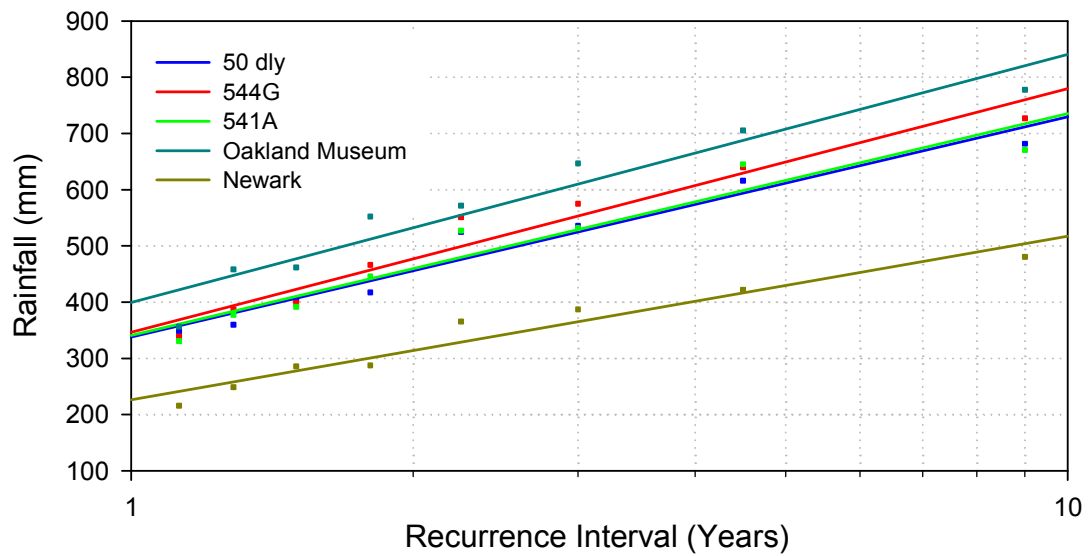
Figure 18. Return intervals of annual rainfall at five nearby rain gauges based on data for the period 2000-2007 Data for gauges 541A, 544G and 50 dly provided by Alameda County Public Works, 2008; Newark and Oakland Museum data downloaded from the Western Region Climate Center web location, WRCC, 2008.
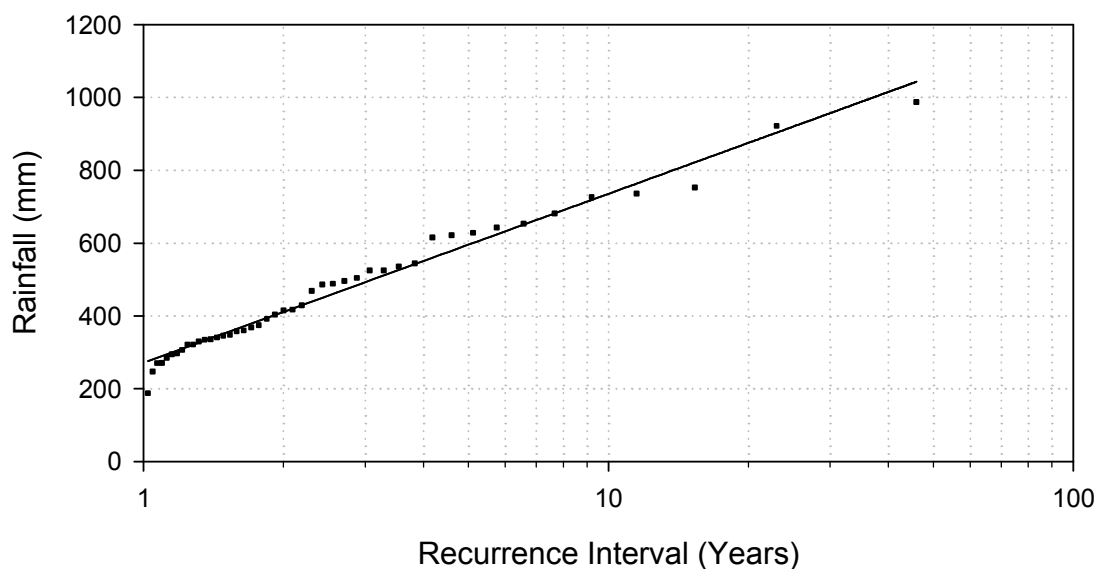
Figure 19. Return interval of annual rainfall at Alameda County's rain gauge 50 dly based on 45 years of record (1953-1969; 1980-2007) Data provided by Alameda County Public Works, 2008.

Monthly Rainfall and Runoff

The majority of rainfall (89-91%) and runoff (87-99%) in Bay Area watersheds occurs on average during the wet season months of November to April inclusive (McKee et al., 2003). Rainfall on the Zone 4 Line A watershed also follows this pattern. At the Hayward rain gauge 541A, on average during the period 2000-2007, 95% of rainfall occurred during the wet season months. At the Oakland Museum rain gauge, on average from 1971-2007, 95% of rainfall occurred during the wet season. During the CY 2007 study year, 99% of the annual rainfall at Gauge 541A and 97% of the rainfall at Oakland Museum occurred during the months November to April (Table 3). Monthly runoff totals calculated from stage measurement at the location are provided (Table 3), however only a portion of the year is represented as the period of record begins on November 11, 2006, and ends on April 30, 2007. The fact that monthly runoff measured during this study tracks monthly precipitation at gauge 541A (r^2=0.98) provides a first order indication of the high quality of both rainfall and runoff data.

Daily Rainfall and Runoff

The accumulation of rainfall and runoff in the Zone 4 Line A watershed during the study period was punctuated by a number of maritime storm systems that impacted the watershed. As a result, the majority of the rainfall and runoff occurred over relatively short periods of time (hours) with rather longer periods in between (many days to weeks) (Figure 20). During the period November 10th, 2006, to May 30th, 2007, the cumulative rainfall at the site was 269 mm which fell over a total of 45 rain days (defined as a rainfall of >0.01 inches, or 0.25 mm). Over 50% of the rainfall fell in just 7 days or 4% of the time (Figure 20). Ninety percent of the rainfall occurred in just 25 days or 14% of the time. In terms of runoff, about 50% and 90% of the runoff occurred in just 5 and 21 days respectively (3% and 12% of the time) (Figure 21).

Individual Storms in WY 2007

Twenty-one individual storm events occurred over the Zone 4 Line A watershed in water year 2007 during the course of the study (November 11, 2006 – May 30, 2007) (Figure 20). These individual storm events are reflected by the stepwise nature of the cumulative rainfall and runoff (Figure 21). Due to its small drainage area and high percentage of impervious surfaces, the watershed responds rapidly to rainfall, seen both on the rising and recession limbs of the individual storm hydrographs. The largest storm event occurred on December 12, when the stage in the channel was 0.92 m and the calculated maximum discharge was 8.7 m³/s (Figure 22). The discharge peaked just less than 2 hours after the initial onset of rainfall, and the lag to peak (time difference between the center of mass of rainfall and peak runoff rate) was 35 minutes. The recession limb is only slightly more gradual than the rising limb, and the discharge receded back below 0.85 m³/s just 2 hours after the runoff peaked (this hydrograph is not continued to baseflow because another similarly punctuated storm immediately followed this one). The sharp rising and recession limbs and very brief lag time are typical of runoff

hydrographs in Zone 4 Line A (see Figure 23 for the hydrograph from another characteristic storm event).

Table 3. Monthly rainfall and runoff in the Hayward watershed during the study compared to longer term averages in Hayward and Oakland. Rainfall data supplied by the Alameda County Public Works Agency (2008) and the Western Region Climate Center (2008). Runoff data for WY 2007 were recorded at the sampling location.

	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Annual
[6] Hayward Rainfall at 541A (mm)													
2000-2007	0.0	0.7	2.7	24.5	46.7	121	67.4	100	62.5	43.3	17.7	3.1	490
%Annual	0.0	0.1	0.6	5.0	9.5	24.7	13.8	20.5	12.7	8.8	3.6	0.6	100
Jul 1st 2006-Jun 30th 2007	0.0	0.0	0.0	11.9	51.3	80.0	17.3	128	7.6	31.2	3.3	0.0	331
%Annual	0.0	0.0	0.0	3.6	15.5	24.2	5.2	38.7	2.3	9.4	1.0	0.0	100
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Annual
[7] Oakland Rainfall at Oakland Museum (mm)													
1971-2007	1.3	2.0	6.6	30.2	78.5	96.5	111.0	105.3	86.7	34.8	13.9	2.5	569
%Annual	0.2	0.4	1.2	5.3	13.8	16.9	19.5	18.5	15.2	6.1	2.4	0.4	100
Jul 1st 2006-Jun 30th 2007	0.0	0.0	0.0	15.2	42.4	95.8	14.0	128.5	11.2	39.9	9.7	0.0	357
%Annual	0.0	0.0	0.0	4.3	11.9	26.9	3.9	36.0	3.1	11.2	2.7	0.0	100
	Oct	Nov*	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Wet season*
Zone 4 Line A runoff at sampling location (Mm^3)													
Nov 11 2006-April 30th 2007	NR	0.069	0.158	0.016	0.233	0.008	0.043	NR	NR	NR	NR	NR	0.527

* Period of record begins on Nov. 11, 2006 and ends April 30, 2007. NR = "No Record".

Figure 20. Cumulative rainfall (mm) and discharge (m^3s^{-1}) during the study period.
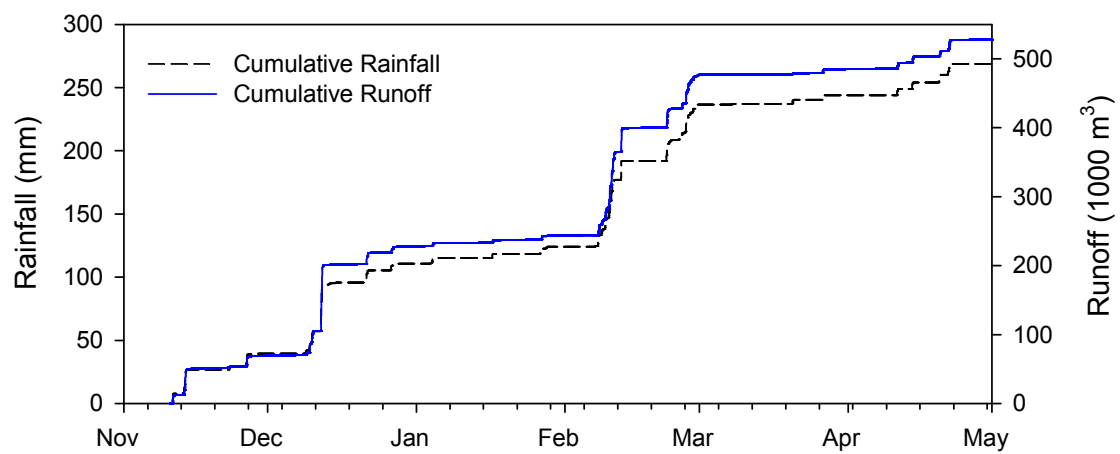
Figure 21. Cumulative rainfall and runoff curves for Zone 4 Line A watershed during WY 2007. Both datasets were collected at the sampling location by SFEI for this study.
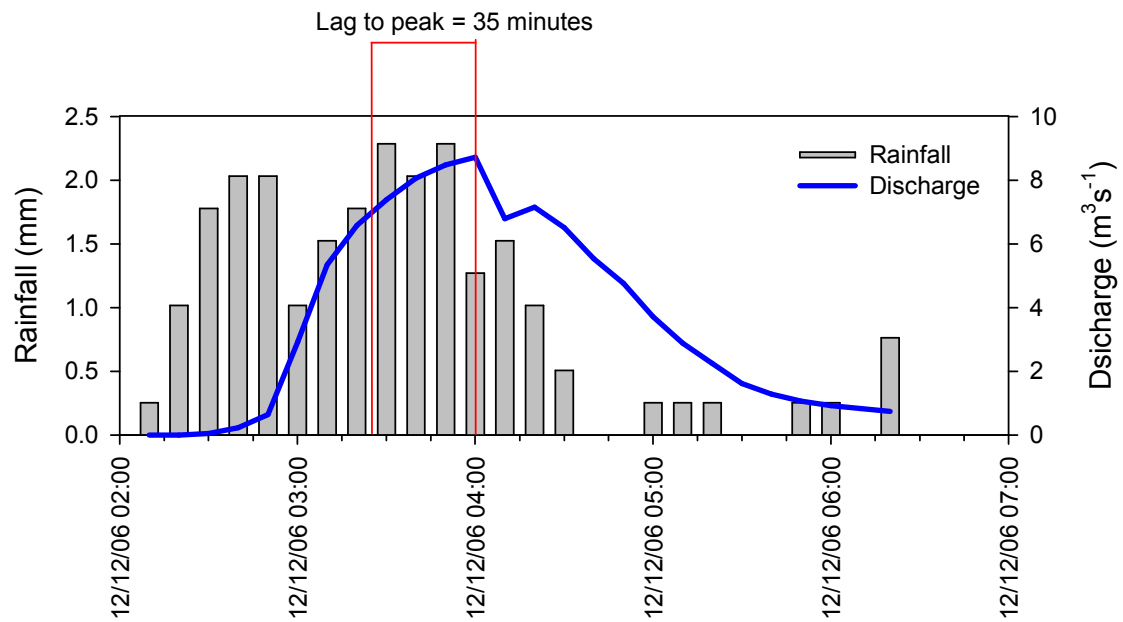
Figure 22. Discharge and rainfall during the largest storm event in WY 2007 on December 12, 2006.
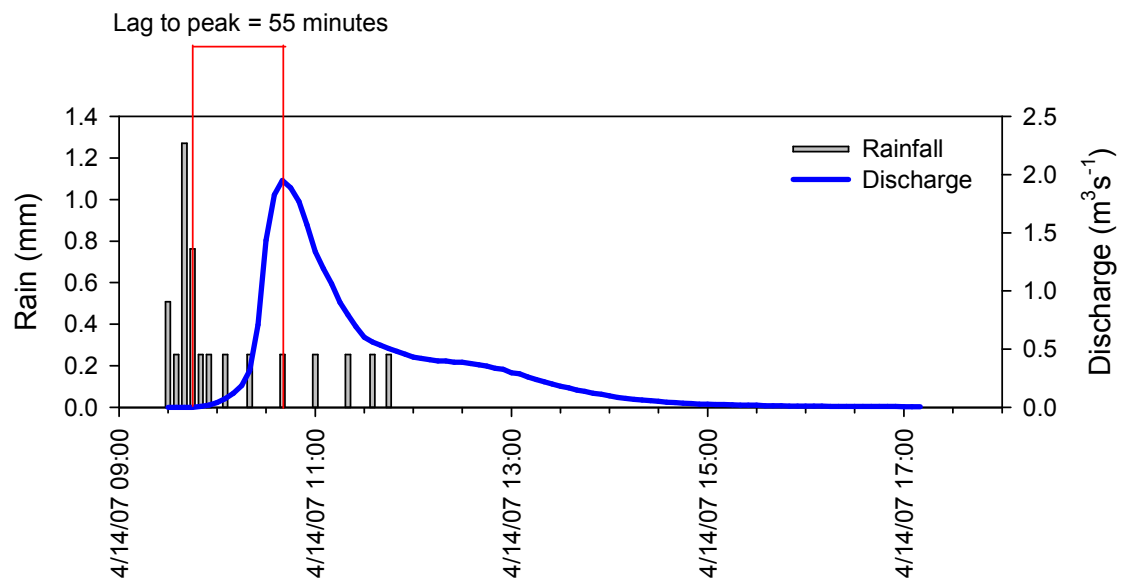
Figure 23. Discharge and rainfall during a small storm event in April 2007.

Suspended Sediment Processes

Continuous Turbidity and Suspended Sediment Concentration WY 2007

Turbidity was measured at the sampling location where Zone 4 Line A crosses Cabot Boulevard every 10 minutes during the period November 10th, 2006-February 6th, 2007, and every 5 minutes from February 6th, 2007-May 30th, 2007 (almost 7 months, or 36,661 data points). Turbidity ranged from 0 to 1041 FNU and varied during the study period mainly in response to discharge. Water samples (n=90 using the ISCO pumping sampler and n=30 grab samples) also were collected and analyzed for SSC (Figure 24). Measured SSC ranged from 1 to 2,744 mg/L with a flow-weighted mean concentration of 212 mg/L. A nearly continuous SSC record was estimated for the season by developing storm specific relationships between instantaneous turbidity and instantaneous SSC and applying the loess regression equations to the un-sampled periods (see Figure 25 for several examples).
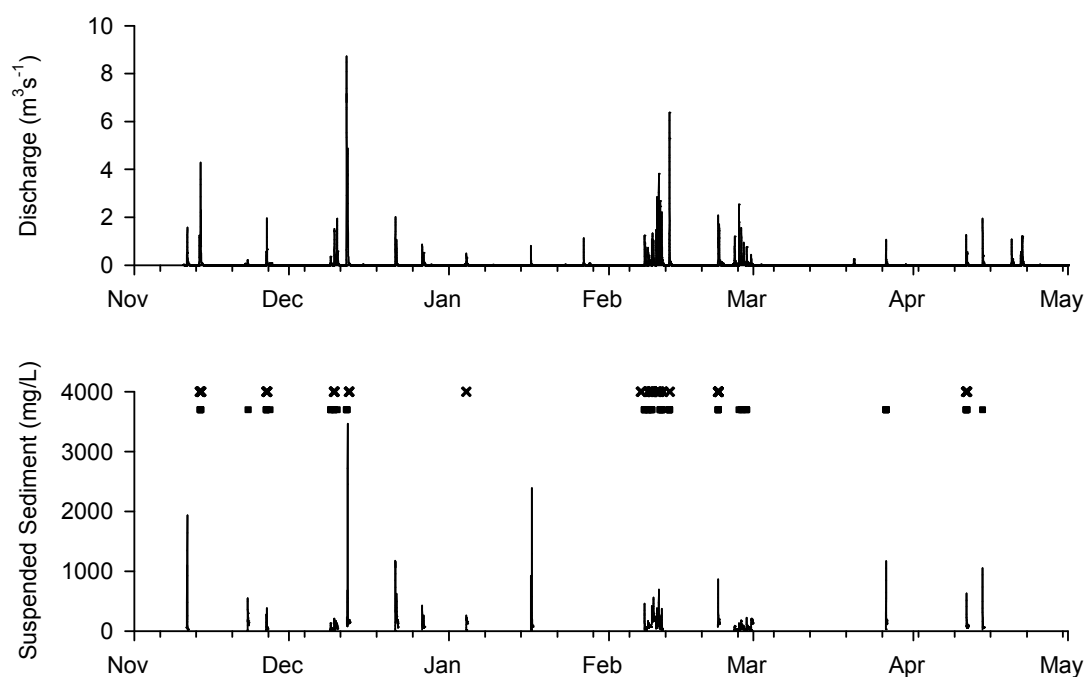
Figure 24. Hydrology and SSC variation during the study period (WY 2007). The water sampling periods are noted at the top of the SSC graph using a square to indicate ISCO automatic pump samples from which SSC was analyzed, and an "x" to indicate where SFEI personnel collected samples from which mercury, organics, SSC, and other ancillary measurements were analyzed.

(a)

(b)
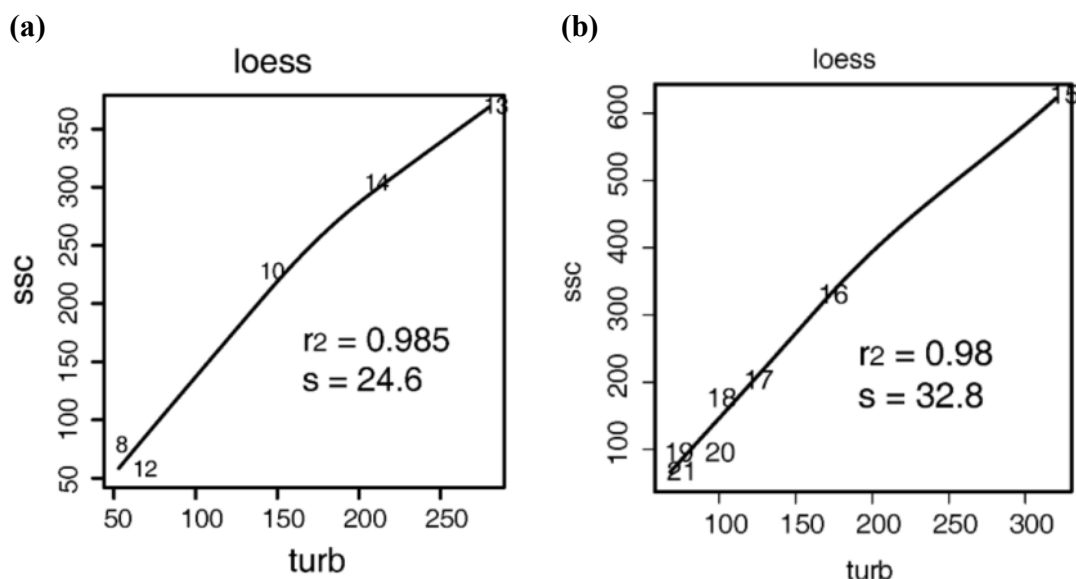
Figure 25. Examples of regression models used to calculate continuous suspended sediment concentrating in Zone 4 Line A. (a) Storm 4 regression model. (b) Storm 20 regression model.

Concentrations of Mercury Species, Trace Elements and Ancillary Parameters

Between November 10th, 2006, and April 30th, 2007, 40 samples were collected during seven storms and analyzed for HgT (Figure 26). A subset of 20 samples also was analyzed for HgD, MeHgT, and MeHgD, and 21 samples were analyzed for other trace elements. The mercury and other trace element analytical methods were chosen to ensure the method detection limits (MDL) were below the expected concentrations. Selenium was the only parameter analyzed that repeatedly had concentrations less than the MDL (>50% of the samples were below the MDL). Of the other trace elements analyzed (excluding Hg), only silver had a concentration below the MDL (one sample). Dissolved MeHg concentrations were close to the detection limit with 10% of the data below the detection limit (MDL) of 0.02 ngL^{-1} and 30% of the data <3x the MDL. In the case of HgT, all samples were above the MDL, and over 50% of the samples collected recorded Hg concentrations >100x the MDL.

Concentrations of total mercury varied over an order of magnitude (30x) from 1.85-55.4 ng/L with a flow-weighted average of 48.1 ng/L (Table 4). HgT was correlated with SSC (Figure 27) as was MeHgT. MeHgT concentrations also were variable and on average accounted for 3% of HgT. MeHgT as a portion of HgT was inversely correlated with flow and in general a greater portion of HgT was methylated later in the wet season. HgD on average comprised 13% of HgT but again there was much variability and an inverse correlation with flow. MeHgD concentrations ranged over an order of magnitude from 0.021-0.27 ngL^{-1} and on average accounted for 26% of MeHgT. Concentrations of other
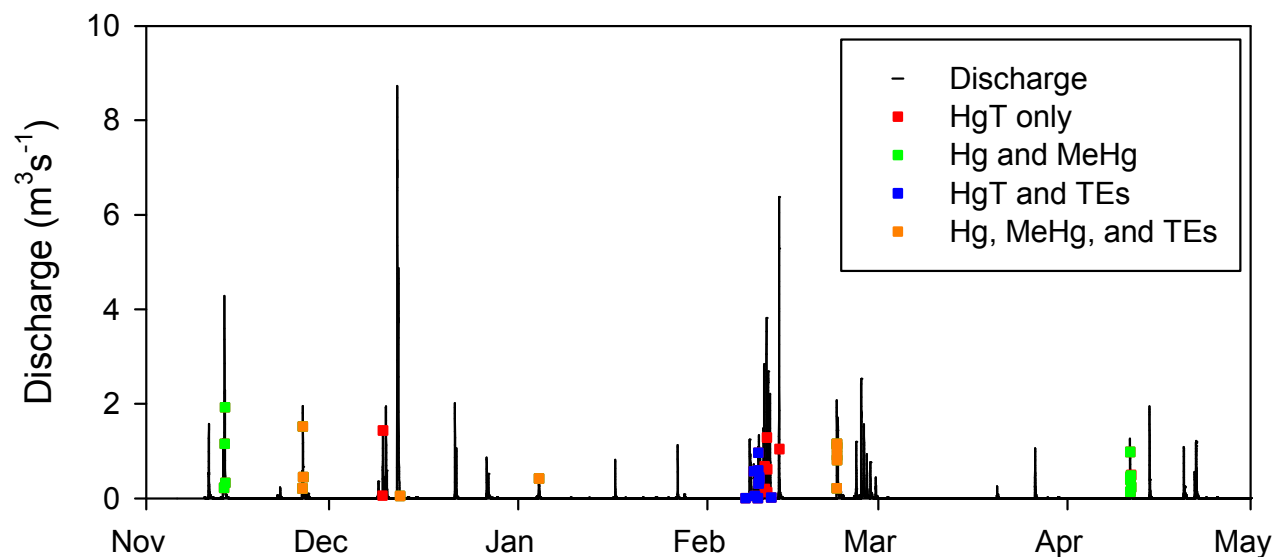
Figure 26. Mercury and trace-element sampling events at Zone 4 Line A, WY 2007. Red squares on the hydrograph indicate sampling events that were analyzed for total mercury only. Green squares indicate samples analyzed for total and dissolved mercury, as well as total and dissolved methyl mercury. Blue squares indicate samples analyzed for total mercury and trace elements. Orange squares indicate samples analyzed for total and dissolved mercury, total and dissolved methylmercury, and trace elements.

Table 4. Mercury speciation, trace element concentrations and ancillary parameters measured during discrete sampling at Zone 4 Line A from November 2006-April 2007.

	SSC (mg/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Zn (µg/L)
Min.	1.42	1.85	0.83	0.08	<MDL	<MDL	82.5	0.66	0.04	0.98	3.24	11.1	3.26	0.56	<MDL	7.45
Max.	2,744	55.4	7.61	1.3	0.27	0.08	4,491	2.38	0.42	39.2	27.6	192	49	22.2	1.17	181
Number	120	40	20	20	20	21	21	21	21	21	21	21	21	21	21	21
FWMC	212	48.1	-	1.4	-	0.07	3,735	1.10	0.36	12.1	21.5	172	15.1	14.9	0.20	175

trace elements generally showed much less variability between samples except for Al (54x), Pb (40x), Cr (24x) and Zn (24x) (Table 4). Concentrations of most other trace elements (except As, Cr, and Se) also correlated with discharge and SSC (Figure 27). However, Al, Cd, Cu, Ni and Zn appear to have 2-4 data points that fall above the general trend in the data. At this point we do not have a good hypothesis for the cause but the data points are the same for each of these trace metals indicating a single source or release process is most likely. Average concentrations of Se in Z4LA were similar to those commonly observed concentrations in San Francisco Bay (SFEI, 2007).

A Spearman Rank correlation analysis was performed using the whole data set to determine the relative significance of correlations between parameters (Table 5). The analysis yielded numerous significant correlations between metals. There were significant correlations between most of the trace elements and between instantaneous discharge (Q) and SSC. HgT correlated with SSC and instantaneous Q. Organic carbon does not appear to strongly influence the transport of mercury and most other trace elements, with the exception of aluminum and manganese. However, since SSC has such a large effect on metal concentrations, high correlations between individual pairs of metals may occur due to variations in SSC and not necessarily as a result of similar metal sources or transport behavior (except for the fact that they are carried by suspended sediment). Therefore, this analysis is effective at showing how metals correlate to the "independent" variables like SSC, Q, POC, and DOC, but is not useful for determining correlations between individual pairs of metals independent of those other variables.

A Spearman Partial correlation analysis was then completed which controlled for the effect of SSC on correlations between individual pairs of metals (Cu vs. Ni, Cu vs. Hg, etc.) by treating SSC as a partial variable in the analysis. This analysis gives more realistic information on similar sources and/or transport of the different metals. For example, Ni and Cr are highly correlated as expected (r = 0.95); however, they are not correlated to any other metals after removing the effect of SSC (Table 6). In the initial Spearman Rank correlation, HgT was correlated to most metals, but in the partial correlation, significant HgT correlations were observed only with the more anthropogenic metals: Ag, Cd, Cu, Pb, and Zn. In contrast to the Guadalupe River system, HgT was not correlated with Se, Cr, or Ni. In the Guadalupe system, a common geological origin was hypothesized as the cause for correlations.
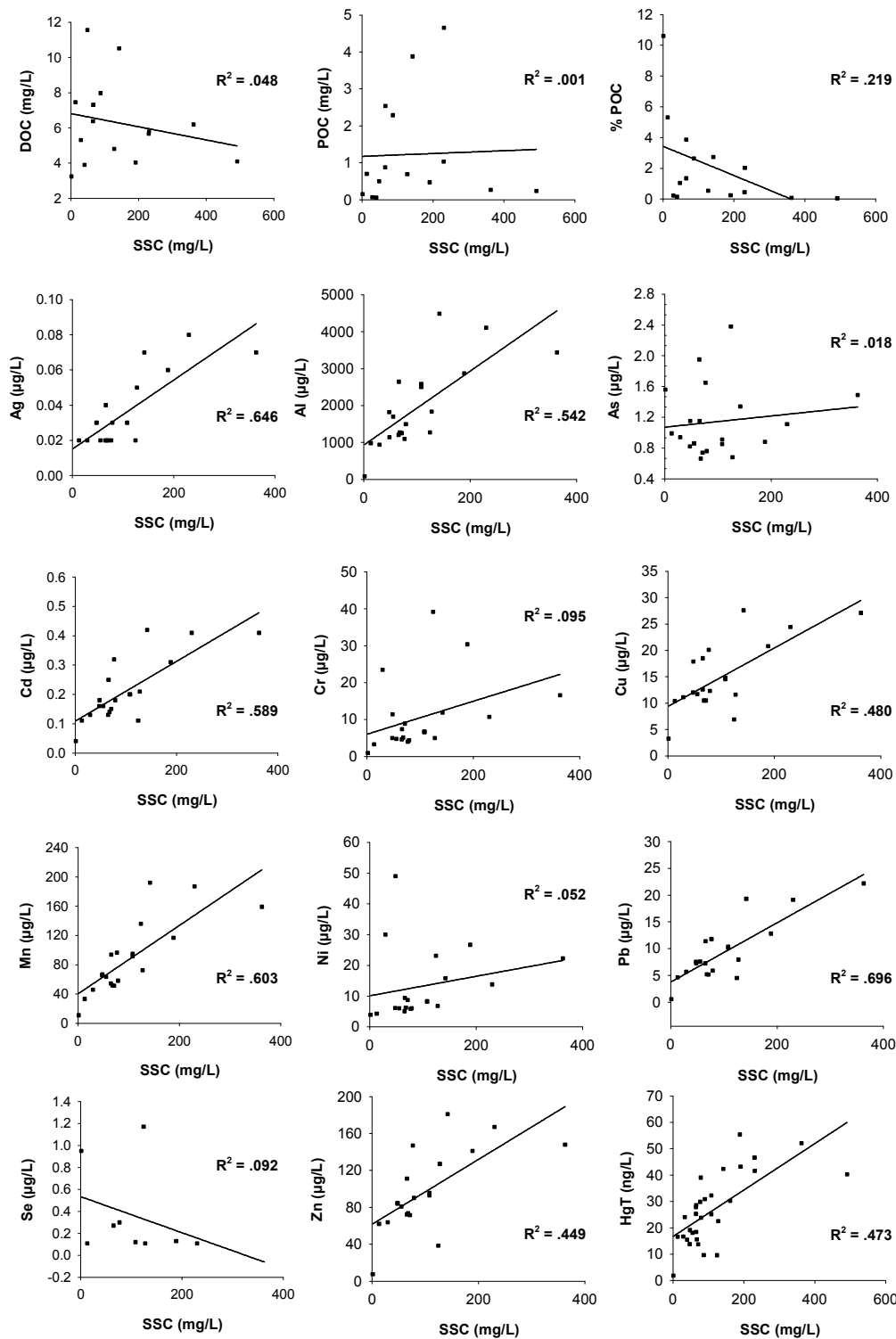
Figure 27. Relationships between suspended sediment and dissolved organic carbon, particulate organic carbon, other total trace elements, and total mercury during water year 2007. Regressions are simple linear regressions.

Table 5. Spearman Correlation matrix comparing trace element concentrations and instantaneous discharge (Inst. Q), suspended sediment concentrations (SSC), dissolved organic carbon (DOC), and particulate organic carbon (POC).

	SSC	DOC	POC	Inst. Q	HgT	Ag	Al	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
Spearman Correlation Coefficients																
Prob > |r| under H_0: Rho=0																
SSC	---	.	.	0.48**	0.63***	0.73***	0.81***	.	0.77***	0.57**	0.66**	0.86***	0.51*	0.72***	.	0.75***
DOC		---	0.67**	.	.	.	.	.	.	.	.	.	.	.	.	.
POC			---	.	.	.	0.71*	.	.	.	.	0.63*	.	.	.	.
Inst.Q				---	0.59***	0.57**	0.59**	-0.48*	0.62**	0.49*	0.49*	0.47*	0.46*	0.54*	.	0.61**
HgT					---	0.81***	0.76***	.	0.91***		0.93***	0.77***	0.44*	0.93***	.	0.92***
Ag						---	0.88***	.	0.85***	0.50*	0.80***	0.76***	0.53*	0.81***	.	0.86***
Al							---	.	0.82***	0.52*	0.74**	0.81***	0.47*	0.83***	.	0.81***
As								---	.	.	.	.	.	.	0.59*	.
Cd									---	.	0.92***	0.83***	0.45*	0.95***	.	0.99***
Cr										---	0.44*	0.61**	0.96***	.	.	.
Cu											---	0.80***	0.47*	0.94***	.	0.92***
Mn												---	0.58**	0.82***	.	0.80***
Ni													---	.	.	.
Pb														---	.	0.95***
Se															---	.
Zn																---

A dot (▪) indicates p>0.05
* p<0.05
** p<0.01
*** p<0.001

Table 6. Spearman Partial Correlation matrix comparing relationships between trace element concentrations, with the effect of SSC controlled for as a partial variable.

	HgT	Ag	Al	As	Cd	Cr	Cu	Mn	Ni	Pb	Se	Zn
	Spearman Partial Correlation Coefficients, N = 21											
	Prob > |r| under H_0: Partial Rho=0											
HgT	---											
Ag	0.57 **	---										
Al	▪	0.72 ***	---									
As	▪	▪	▪	---								
Cd	0.80 ***	0.66 **	0.51 *	▪	---							
Cr	▪	▪	▪	▪	▪	---						
Cu	0.88 ***	0.61 **	0.48 *	▪	0.87 ***	▪	---					
Mn	▪	▪	▪	0.51 *	0.52 *	▪	0.61 **	---				
Ni	▪	▪	▪	▪	▪	0.95 ***	▪	▪	---			
Pb	0.85 ***	0.60 **	0.60 **	▪	0.90 ***	▪	0.90 ***	0.58 **	▪	---		
Se	▪	-0.46 *	-0.53 *	0.59 **	▪	▪	▪	▪	▪	▪	---	
Zn	0.82 ***	0.69 ***	0.51 *	▪	0.98 ***	▪	0.86 ***	0.47 *	▪	0.90 ***	▪	---

A dot (▪) indicates $p > 0.05$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

Concentrations of PCBs, PBDEs, OC Pesticides, and PAHs

PCBs and PBDEs

Twenty grab samples collected over a range of Q were analyzed for PCBs and PBDEs (Figure 28). Samples collected at the same time also were analyzed for POC and DOC. Total PCB (t-PCB) concentrations spanned two orders of magnitude between base flow conditions and storm flow ranging from 0.4 to 46 ng L^{-1} and exhibited a flow-weighted mean concentration (FWMC) of 24 ng L^{-1} (Table 7). The maximum t-PCB concentration sampled was collected on February 22nd, 2007, at 4:37 AM when discharge was 1.9 m^3/s and SSC was 189 mg L^{-1}. In all samples, no single congener comprised more than 10% of t-PCB concentrations (Figure 29). Concentrations of all individual PCB congeners are listed in the Appendix. Total PBDE (t-PBDE) concentrations ranged from 2.8 to 141 ng L^{-1} and exhibited a FWMC of 67 ng L^{-1} (Table 7). The maximum t-PBDE concentration sampled was collected on February 9th, 2007 at 8:00 AM when discharge was 1.0 m^3/s and SSC was 230 mg L^{-1}. BDE congeners 47, 99, 100, 153, 183, 206, 207, 208 and 209 collectively comprised over 90% of all samples, and congeners 47, 99 and 209 comprised 73-88% of all samples (Figure 30). Concentrations of all individual BDE congeners are listed in the Appendix.
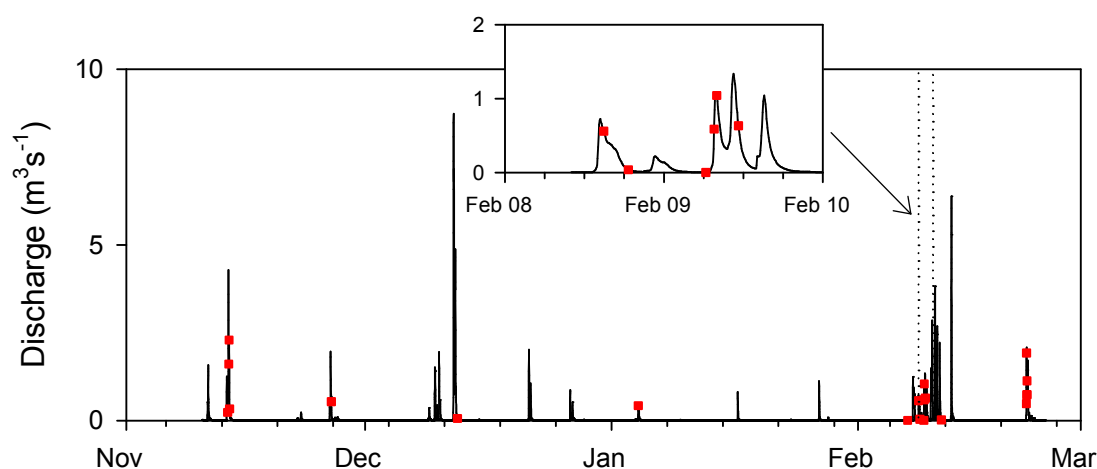
Figure 28. PCB and BDE sampling events at Zone 4 Line A, WY 2007. Sampling events are depicted as red squares on the hydrograph.

Table 7. PCB, PBDE, OC pesticide and PAH concentrations and ancillary parameters measured during discrete sampling at Zone 4 Line A from November 2006-April 2007. FWMC = flow-weighted mean concentration.

	SSC (mg/L)	DOC (mg/L)	POC (mg/L)	PCBs (ng/L)	BDEs (ng/L)	PAHs (ng/L)	DDTs (ng/L)	Chlordanes (ng/L)	Dieldrin (ng/L)
Min.	1.42	3.24	0.06	0.4	2.8	1.4	7.4	3.5	0.7
Max.	2,744	11.6	4.66	46	141.2	19.7	59.5	16.4	4.6
N=	120	16	16	20	20	7	7	7	7
FWMC	212	5.52	1.24	27	77	10	31	11	2.5
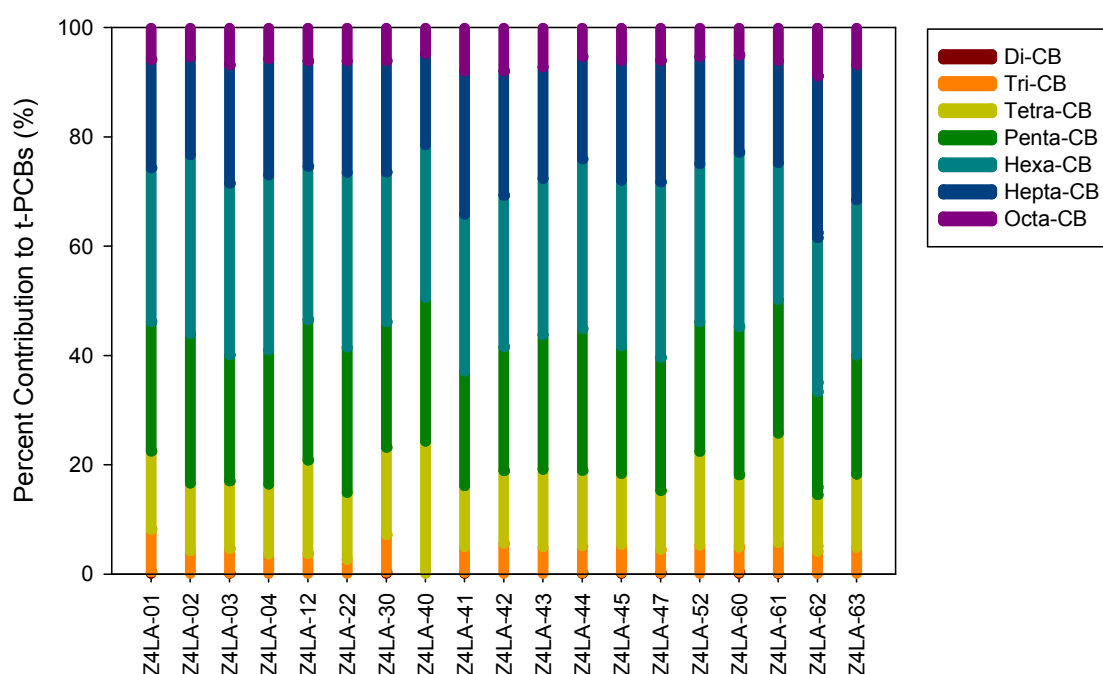
Figure 29. Relative abundance of PCB homologs in Zone 4 Line A water samples.
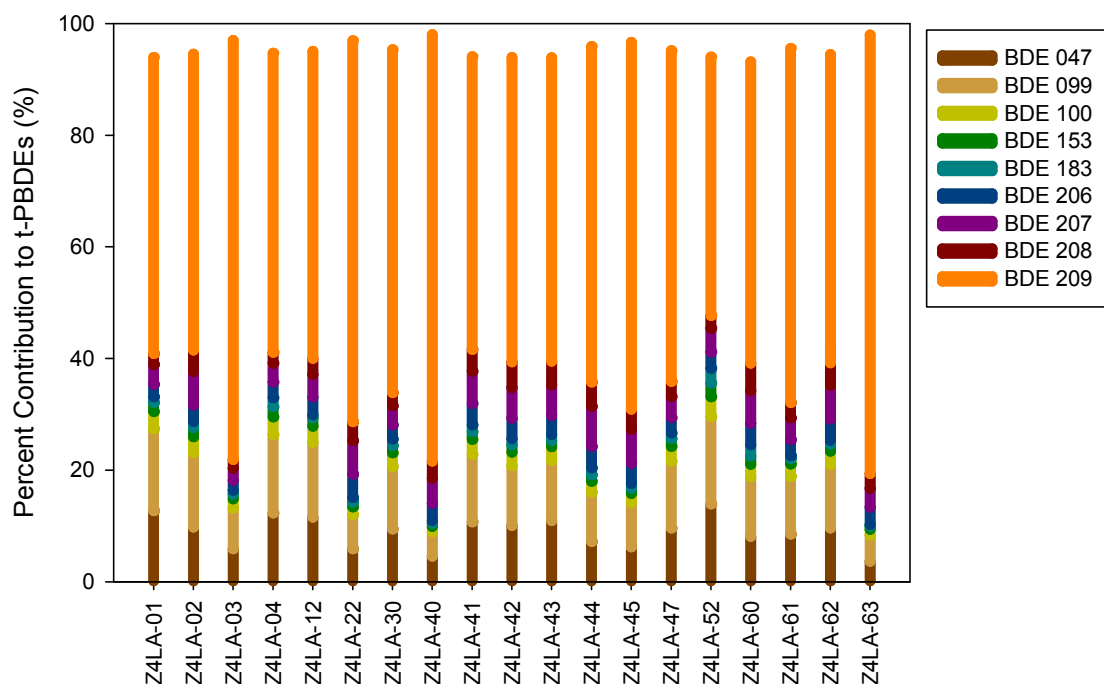
Figure 30. Relative abundance of select BDE congeners in Zone 4 Line A water samples. Congener profiles do not sum to 100% because only a subset of all the BDE congeners is chosen for representation in this figure.

PAHs and Organochlorine Pesticides

Seven of the 20 samples analyzed for PCBs and PBDEs also were analyzed for PAHs and OC pesticides (Figure 31). All of these samples were collected over a period of less than one month and at flows less than 2 $m^3 s^{-1}$, and therefore may not be representative of concentrations that might be sampled during larger storm events. Total PAH concentrations ranged from 1.4 to 19.7 ng L^{-1} and had a FWMC of 8.9 ng L^{-1} (Table 7). Chrysene, pyrene, and fluoranthene each comprised 10% or more of the PAH profile of every sample, and benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene and indeno[1,2,3-*c,d*]pyrene generally each comprised just under 10% of the profile in all samples (PAH concentrations listed in the Appendix). LPAHs, those with two or three rings) and HPAHs (those with four or more rings) were analyzed in this study (Table 8). LPAHs comprised from 5 to 14% of total PAH concentrations, and HPAHs comprised from 86 to 95% of total PAH concentrations. Concentrations of individual PAH compounds are listed in Appendix C.

Total DDT concentrations ranged from 7.4 to 59.5 ng L^{-1} and had a FWMC of 31 ng L^{-1} (Table 7). Total DDT concentrations were comprised primarily of p,p'-DDT (28 to 37%), p,p'-DDE (22 to 36%), and p,p'-DDD (12 to 32%). Total chlordane concentrations ranged from 3.5 to 16.4 ng L^{-1} and had a FWMC of 11 ng L^{-1}. Abundant chlordane components were gamma-chlordane (31 to 35%), alpha-chlordane (29 to 31%), trans-nonachlor (22 to 25%) and cis-nonachlor (10 to 12%). Dieldrin concentrations ranged

from 0.7 to 4.6 ng L^{-1} and exhibited a FWMC of 2.5 ng L^{-1}. Maximum concentrations of t-DDT, t-chlordane, and dieldrin were measured in a sample collected on February 22nd, 2007, at 4:37 AM (the same sample in which the maximum PCB concentration was measured) when Q was 1.9 m^3/s and SSC was 189 mg L^{-1}. Concentrations of all individual pesticides are listed in Appendix C.

Table 8. Low molecular weight (LPAHs) and high molecular weight PAHs (HPAHs) measured in Zone 4 Line A in Water Year 2007.

LPAHs analyzed	HPAHs analyzed
1-Methylnaphthalene	Benz[*a*]anthracene
2,3,5-Trimethylnaphthalene	Chrysene
2,6-Dimethylnaphthalene	Fluoranthene
2-Methylnaphthalene	Perylene
Biphenyl	Benzo[*a*]pyrene
Naphthalene	Pyrene
1-Methylphenanthrene	Benzo[*e*]pyrene
Acenaphthene	Benzo[b]fluoranthene
Acenaphthylene	Benzo[*k*]fluoranthene
Anthracene	Dibenz[*a,h*]anthracene
Fluorene	Benzo[*g,h,i*]perylene
Phenanthrene	Indeno[1,2,3-*c,d*]pyrene
Dibenzothiophene	
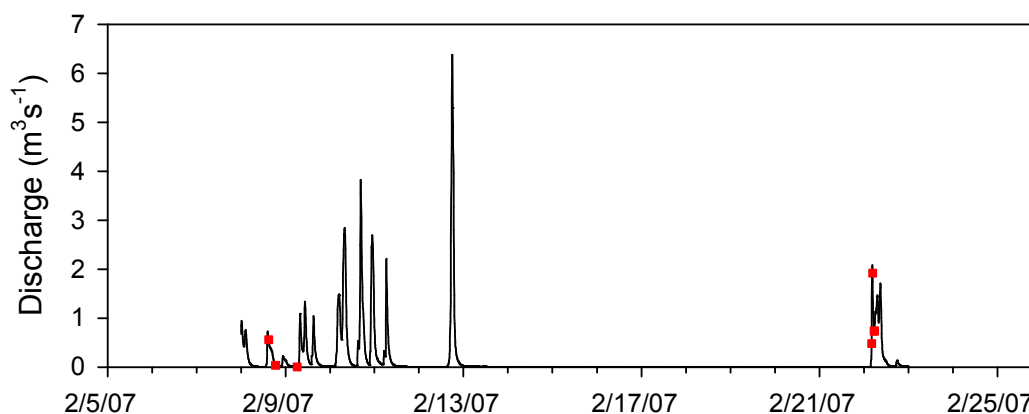
Figure 31. Twenty day hydrograph and PAH and OC Pesticide sampling events at Zone 4 Line A WY 2007. Sampling events are depicted as black circles on the hydrograph.

Suspended Sediment and Trace Contaminant Loads

Characteristic of Bay Area watersheds, the load of suspended sediment varied considerably in response to rainfall and runoff. Instantaneous suspended sediment load (in this case the load transported within a 5 minute period) varied from 0.048 g to 1.5 metric t spanning eight orders of magnitude. Daily loads varied from 32 g to 26.3 metric t spanning five orders of magnitude. The maximum daily load of 26.3 metric t occurred on December 12th, 2006, in response to a storm of 36.6 mm rainfall. Based on the magnitude-frequency-duration analysis for the Bay Area (Rantz, 1971), it is estimated that a storm of this magnitude and duration has a return frequency of 2 years. Monthly loads varied from 2.06 to 40.5 metric t for a total of 112 metric t during the study period (Table 9). Loads for months with no observations and total annual loads were estimated using a regression between monthly rainfall and loads. Given that there was a small amount of rainfall prior to the beginning of our study, we estimated suspended sediment loads for October based on a regression relationship between rainfall and suspended sediment load (Figure 33). The relationship was surprisingly good ($r^2 = 0.9$) probably because the watershed is almost 100% urbanized and because there is a low variability in runoff coefficient between storms and months relative to less urban Bay Area watersheds. Including the loads for October 2006 and May 2007 estimated in this manner increased the total sediment mass by only 3%. At this time it was decided not to adjust the loads for all the analytes because 3% is much less than the errors in the calculations. Normalized to the watershed area, the observed sediment yield was equivalent to 24.9 metric t/km^2 (Table 9).

Loads of mercury and other trace elements varied similarly month to month in relation to rainfall. Overall, 87% of HgT was transported through Zone 4 Line A in particulate forms. The concentration of Hg associated with suspended sediment (mg/kg) was very similar to the average of California soils (Bradford, 1996) (Table 9). Aluminum, a major component of the earths crust was by far the largest load of a single trace metal constituting about 1.76% of the sediment load but less than California soil composition (3-10.6%; average = 7.3%) (Bradford, 1996). With the exceptions of Ag and Cr, all other trace elements normalized to suspended sediment (mass TE per unit mass sediment) were greater than average California soil concentrations, despite below normal runoff in WY 2007.

Annual loads of organic carbon averaged 0.58% of the suspended sediment load during the period of observations (Table 10). Overall, an estimated 14.4 g of PCBs passed into the Bay through Z4LA; PBDE loads were about 2.8 times greater. Sediment-mass normalized concentrations of PCBs averaged 0.13 mg/kg, more than an order of magnitude greater than concentrations in Bay sediments (0.001-0.01 mg/kg) (SFEI, 2007). Similarly, PBDE concentrations in Zone 4 Line A suspended sediment (0.36 mg/kg) are about an order of magnitude greater than those in Bay sediments (maximum concentrations in the Bay sediments are around 0.01 mg/kg; SFEI, 2007). The load of PAHs for the WY 2007 wet season was 5.4 g, equivalent to a yield of 1.20 ng/m^2, much lower than that of PCBs and PBDEs. PAHs sources in the urban environment include used motor oil, wood, coal, and oil burning, tire wear particles and vehicle exhausts (see Van Metre e al., 2009 and references therein. Data collected to-date in Zone 4 Line A

appears to most closely resemble automobile exhaust, brakelining particles and tire wear particles in terms of the ratio of benzo[a]pyrene: benzo[e]pyrene with a measure of diesel exhaust in the mix based on the Fluoranthene:pyrene ratio (Figure 32). Consistent with the finings of Van Metre et al. (2009), coal tar uses to not appear to be a major contributor. PCBs have been banned from production since the late 1970s yet there are still large loads entering the Bay. Similarly, there are still large loads of legacy pesticides in urban stormwater despite bans in the late 70s and early 80s (Table 10).

1. Coal tar, NIST standard 1597a
2. Petroleum crude oil, NIST standard 1582a
3. Diesel particulate matter, NIST standard 1650b
4. Tire-wear particles (see references in Van Metre et al. (2009)
5. Brake-lining particles (see references in Van Metre et al. (2009)
6. Automobile exhaust (see references in Van Metre et al. (2009)
7. Diesel truck exhaust (see references in Van Metre et al. (2009)

Figure 32. Comparison of ratios of indicator PAHs in data from Z4LA (blue diamonds) to characteristic ratios of a range of sources. After Van Metre et al., 2009.

Comparisons Between Zone 4 Line A and Other Bay Area Locations

Concentrations in water

Concentrations of Hg species, PCBs, PBDEs, OC pesticides and other trace elements have been collected in a variety of settings in the Bay Area beginning in the Guadalupe River in Water Year 2003. Since then, a small number of samples have been collected from Coyote Creek at Hwy 237 and a storm drain on San Pedro Road in San Jose

Table 9. Monthly and wet season suspended sediment, mercury and trace element loads in Zone 4 Line A during Water Year 2007.

Month	SSC (t)	HgT (g)	HgD (g)	MeHgT (g)	MeHgD (g)	Ag (g)	Se (g)	As (g)	Cd (g)	Al (kg)	Cr (kg)	Cu (kg)	Mn (kg)	Ni (kg)	Pb (kg)	Zn (kg)
Nov	24.7	6.75		0.117	-	7.42	-	-	37.9	403	1.25	2.04	18.5	1.70	1.57	17.7
Dec	40.5	8.44		0.283	-	12.7	-	-	66.5	700	1.99	3.74	32.1	2.60	2.70	32.0
Jan	2.81	0.636		0.0198	-	0.886	-	-	5.43	48.7	0.145	0.321	2.40	0.190	0.217	2.60
Feb	36.4	7.92		0.242	-	12.2	-	-	67.8	676	2.53	4.32	31.2	2.90	2.79	33.0
Mar	2.06	0.433		0.0145	-	0.651	-	-	3.40	35.8	0.102	0.192	1.64	0.133	0.138	1.64
Apr	5.71	1.24		0.0418	-	1.98	-	-	11.2	109	0.35	0.729	5.03	0.437	0.456	5.52
Wet season	112	25.4	3.30	0.718	0.179	35.9	106	581	192	1,970	6.36	11.3	90.9	7.96	7.88	92.5
Sediment normalized concentration (mg/kg)	-	0.23	-	-	-	0.32	0.94	5.18	1.72	1.76%	57	101	812	71	70	825
California soils (Bradford (1996)		0.20				0.41	0.03	2.80	0.26	7	76	24	592	36	22	236
Yield (µg/m^2)	24.9 (t/km^2)	5.65	0.73	0.159	0.04	7.97	23.5	129	42.7	438,000	1,410	2,520	20,200	1,770	1,750	20,600

Table 10. Monthly organic carbon, PCB, PBDE, OC pesticide, and PAH loads in Zone 4 Line A during Water Year 2007.

Month	DOC (kg)	POC (kg)	t-PCBs (g)	t-PBDEs (g)	t-PAHs (g)	t-DDTs (g)	t-Chlordanes (g)	Dieldrin (g)
Nov	-	-	2.80	6.98	1.19	3.66	1.06	0.282
Dec	-	-	5.35	15.5	1.95	6.01	1.99	0.473
Jan	-	-	0.378	1.08	0.136	0.418	0.165	0.034
Feb	-	-	4.85	14.0	1.74	5.38	2.28	0.445
Mar	-	-	0.273	0.792	0.100	0.307	0.102	0.024
Apr	-	-	0.767	2.21	0.276	0.848	0.399	0.072
Wet season	2,920	655	14.4	40.6	5.40	16.6	5.99	1.33
Sediment normalized concentration (mg/kg)	-	0.58%	0.13	0.36	0.048	0.15	0.053	0.012
Yield (ng/m^2)	650	145	3.21	9.02	1.20	3.69	1.33	0.296
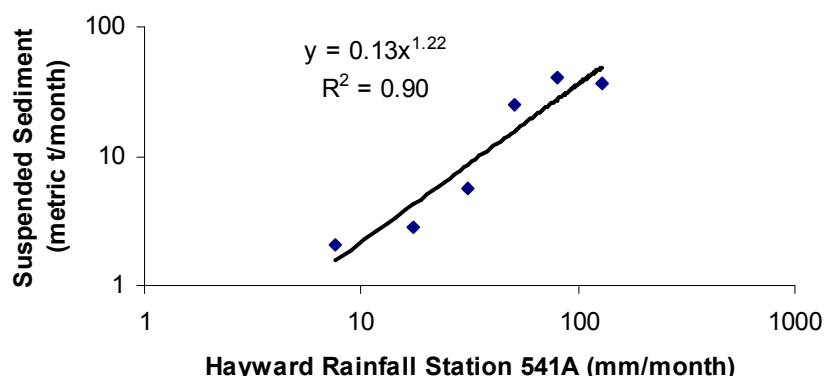
Figure 33. Relationship between rainfall in Hayward and suspended sediment loads in Zone 4 Line A.

(tributary to Guadalupe River) using clean hand protocols. Just seven grab samples (plus one duplicate) were collected from Coyote Creek at the USGS gauge (11172175) during wading stages, mid channel, mid-depth of five floods during WY 2005. In the case of San Pedro, just six samples were taken during three rain storms during WY 2006 from a manhole located at 37°20'37.64"N, 121°54'2.76"W using a depth integrating DH81 sampler that incorporates laboratory cleaned Teflon components. The manhole allows access to an approximate 2 m diameter storm drain, the bottom of which is approximately 3-4 meters under the land surface. The drain enters the Guadalupe River 143 m from the sampling location and under the flow conditions observed to-date, experiences no back up from the main river.

Samples were analyzed for total mercury, PCBs, SSC, and organic carbon using the same, labs as employed previously for the Guadalupe River study and most recently in the Z4LA study (Table 11 and Table 12). All samples have passed through the RMP data management process to ensure data quality). Comparisons between the data confirm regional trends and provide for some new hypotheses. Concentrations of all the trace elements except HgT are similar between the Guadalupe River and Z4LA (Table 11). Concentrations of HgT in Z4LA are similar to those observed in Coyote Creek and fall within the range observed in the San Pedro Road storm drain in San Jose, but are much greater in the Guadalupe River due to historic mining influence. In contrast, MeHgT concentrations are similar between the three systems for which MeHgT has been measured (Z4LA, Coyote Creek and Guadalupe River) (Table 11). The urban systems have a greater ratio of MeHgT:HgT than the mining-impacted Guadalupe River. Given that WY 2007, the year that Z4LA was sampled, was a dry year (70% mean annual rainfall), these data suggest that MeHg production is not related to the availability of HgT. During drier years, even during the winter months the watershed is likely going through periods of wetting and drying due to rainfall events being smaller and more spaced out and perhaps also because urban irrigation overflow plays a role in wetting parts of the stormwater system. Wetting and drying is proposed as a key factor in

Table 11. Concentrations of suspended sediment, mercury and other trace elements in Bay Area watersheds. MDL = method detection limit.

	SSC (mg/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)	MeHgT (%)	Ag (ug/L)	Al (ug/L)	As (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Mn (ug/L)	Ni (ug/L)	Pb (ug/L)	Se (ug/L)	Zn (ug/L)
Z4LA WY 07 Min.	1.42	1.85	0.83	0.08	<MDL	-	<MDL	82.5	0.66	0.04	0.98	3.24	11.1	3.26	0.56	<MDL	7.45
Max.	2,740	55.4	7.61	1.3	0.27	-	0.08	4,490	2.38	0.42	39.2	27.6	192	49	22.2	1.17	181
FWMC	212	48.1	-	1.4	-	2.8	0.07	3,740	1.10	0.36	12.1	21.5	172	15.1	14.9	0.20	175
Guadalupe WY 03 Min.	17	178	-	-	-	-	MDL	-	1.4	0.05	2.1	6.1	-	3.7	1.5	-	9.4
Max.	1,150	18,700	-	-	-	-	0.27	-	4.2	0.7	98	52	-	189	52	-	193
FWMC	214	2,190	-	-	-	-	0.06	-	2	0.21	15	16	-	30	12	-	67
Guadalupe WY 04 Min.	18	MDL	-	-	-	-	MDL	-	1.1	0.03	0.8	2.7	-	1.8	0.2	-	4.6
Max.	970	1,420	-	-	-	-	0.23	-	3.8	0.72	66	59	-	133	51	-	265
FWMC	201	329	-	-	-	-	0.06	-	2	0.21	15	15	-	28	11	-	63
Guadalupe WY 05 Min.	6	4	0.93	0.06	0.04	-	MDL	-	1.1	0.03	2	3.1	-	3.4	0.43	-	4.9
Max.	720	1,920	12.2	1.89	0.15	-	0.35	-	5.2	1.3	52	91	-	105	81	-	350
FWMC	85	140	4.71	0.49	0.08	0.4	0.05	-	1.5	0.1	5.3	8.1	-	11	6.3	-	32
Guadalupe WY 06 Min.	13	6	0.59	0.05	0.02	-	-	-	-	-	-	-	-	-	-	-	-
Max.	652	891	15.3	2.22	0.16	-	-	-	-	-	-	-	-	-	-	-	-
FWMC	109	237	-	0.59	-	0.2	-	-	-	-	-	-	-	-	-	-	-
Guadalupe (Estimated long-term mean)	240	2,210	-	0.56	-	-	.061	-	1.8	0.21	29	15	-	55	17	-	64
Coyote Creek WY 05 Min.	51.8	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Max.	338	59	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FWMC	215	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
San Pedro Stormdrain, San Jose WY 06 Low flow	3	2.1	1.38	0.02	0.02	1.0	-	-	-	-	-	-	-	-	-	-	-
High flow	858	499	6.66	0.815	0.07	0.2	-	-	-	-	-	-	-	-	-	-	-
FWMC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 12. Concentrations of suspended sediment, dissolved and particulate organic carbon and trace organic compounds in Bay Area watersheds. MDL = method detection limit.

	SSC (mg/L)	DOC (mg/L)	POC (mg/L)	t-PCBs (ng/L)	t-PBDEs (ng/L)	PAHs (ng/L)	DDTs (ng/L)	Chlordanes (ng/L)	Dieldrin (ng/L)
Z4LA WY 2007									
Min.	1.42	3.2	0.1	0.4	2.8	1.4	7.4	3.5	0.7
Max.	2,740	11.6	4.7	46.0	141	19.7	59.5	16.4	4.6
FWMC	212	5.5	1.2	27.3	76.9	10.2	31.5	11.3	2.5
Guadalupe WY 2003									
Min.	17	1.8	MDL	3.4	-	-	1.7	1.6	0.3
Max.	1,150	8.9	4.3	90.0	-	-	71	64	6
FWMC	204	5.3	2.3	55.0	-	-	45	40	3.8
Guadalupe WY 2004									
Min.	18	0.9	0.1	0.7	-	-	0.6	0.6	0.2
Max.	970	18.3	3.7	66.0	-	-	55	53	3.8
FWMC	191	5.9	1.0	26.0	-	-	28	25	2
Guadalupe WY 2005									
Min.	6	1.0	0.1	7.4	15.3	-	-	-	-
Max.	720	11.5	3.7	123	370	-	-	-	-
FWMC	79	4.3	0.9	44.7	95.4	-	-	-	-
Guadalupe WY 2006									
Min.	13	3.5	0.1	3.6	4.1	-	-	-	-
Max.	652	9.2	1.2	167	212	-	-	-	-
FWMC	109	-	-	12.0	39.8	-	-	-	-
Guadalupe (Estimated long-term average)	240	-	-	15.4	39.5	-	28.7	26.6	2.1
Coyote Creek WY 2005									
Min.	51.8	6.1	0.4	2.6	7.1	-	-	-	-
Max.	338	6.5	0.9	10.3	36.6	-	-	-	-
FWMC	215	-	-	9.3	30.0	-	-	-	-

methylmercury production in wetland systems of the Bay Area (e.g. Slotten 2008; Yee et al., in review). We hypothesize that MeHgT is more likely related to the proportional area or number of environments in a watershed conducive to methylation and the wet and drying of these environments. This is somewhat further supported by a relationship between SSC and MeHg (Figure 34). Since SSC is a proxy for flow (low SSC occurs at low flow), the inverse relationship between SSC (mg/L) and MeHg (ug/kg) is likely due to a combination of dilution during high flows and more production of MeHg during low flows when wetting and drying is a possible process enhancing methylation. Also of interest is the observation that during low flow, MeHg particle concentrations in the freshwater Guadalupe River system and Z4LA are in excess of 10 ug/kg, a magnitude similar to or even greater than observed in salt water marshes of the North Bay (e.g., Heim et al., 2007).

PCB concentrations have been measured in Z4LA, Guadalupe River, and Coyote Creek (Table 12). Similar to the trace elements (excluding Hg), concentrations observed in flowing stormwater are similar between Z4LA and Guadalupe River. Although these data suggest that Coyote has lower concentrations, the lower concentrations observed more likely are an artifact of the sampling (just seven samples from two small floods) rather than a reflection of a real difference. A similar trend is seen in the PBDE data across the systems and as a general rule, PBDE concentrations are about 2 to 3 times greater in magnitude than PCB concentrations. DDT, chlordane and dieldrin concentrations also are similar between systems.

Concentrations on particles

When observing trends in stormwater, another method of comparing watershed systems is to develop graphical relationships between suspended sediment and trace element concentrations in water. The slope of the relationships thus developed provides an estimate of the average particle concentrations for each trace contaminant (mass of contaminant per unit mass of suspended sediment). The slope is actually a measure of the average ratio of SSC to the contaminant concentration being considered and not a true measure of the average particle concentration because a small portion of each contaminant is in dissolved form (perhaps indicated by positive intercepts on the scatter plots). But for comparative purposes at the regional scale, these graphical representations are very instructive (Figure 35). In the case of Hg (Figure 35a), the 100% urbanized Z4LA watershed has the lowest particle concentration of any system we have yet observed in the Bay Area. In contrast, the mining impacted and urbanized Guadalupe River watershed has the highest particle concentration. The old urban San Pedro Road Storm drain (watershed area approximately 1 km^2) is intermediate between the two extremes and allows the generation of a hypotheses that "old urban" systems like San Pedro may be more contaminated with Hg than "middle ages urban" systems like Z4LA.

In contrast, Z4LA shows the greatest estimated average particle concentration of PCBs relative to Guadalupe River and Coyote Creek although the differences are not statistically significant (Figure 35b). All three watersheds have an industrial land use legacy that precedes the PCB ban (1978). The only data yet collected on non-urban Bay
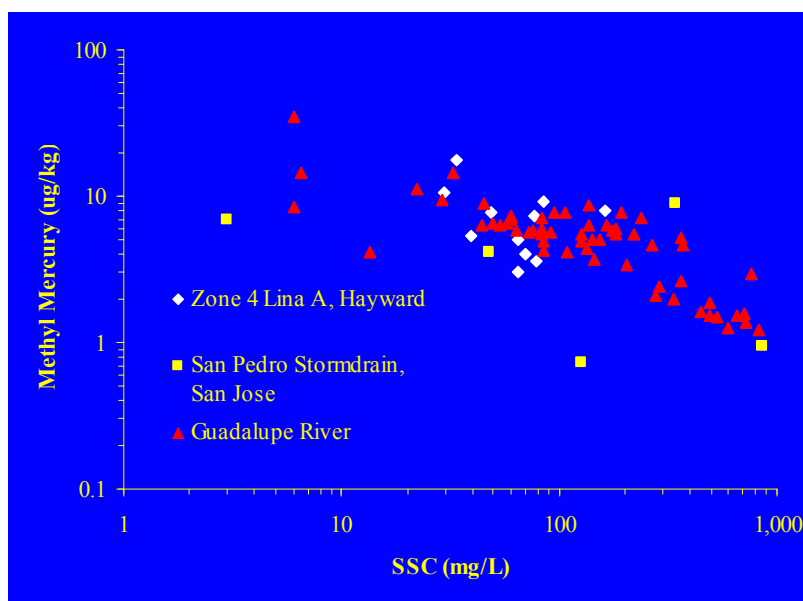
Figure 34. Concentration of methyl mercury associated with particles. Note inverse relationship between methyl mercury and suspended sediment concentrations and that maximum methylmercury concentrations are similar to those observed in wetland sediments of the North Bay (e.g., Heim 2007).

Area stormwater are those samples collected on the falling stages of floods in Guadalupe River and Coyote Creek when runoff was derived from the upper rural areas of these systems. These data are consistent with our hypothesis that PCB sources mainly are from urban areas; particle concentrations are lower in the non-urban runoff (Figure 35b).

In the case of PBDEs, regional trends are similar to those for PCBs; there is no significant difference between estimates of average particle concentrations in Z4LA, Guadalupe River and Coyote Creek. These are much greater than concentrations found in flow derived from upper, more rural areas of the Guadalupe and Coyote Creek watersheds. Given that some PBDEs are still in current use (penta- and octa- formulations were banned in 2006), it is unknown why the regional PCB and PBDE trends are similar. Potential reasons are that the sources are similar, or because atmospheric deposition and wind or vehicular redistribution vectors coupled with runoff from impervious land use are the main drivers. These possibilities remain uninvestigated.

Yields (Area-normalized loads)
Larger watersheds can have orders of magnitude more runoff due to their size and this combined with similar or lower concentrations typically generates greater suspended
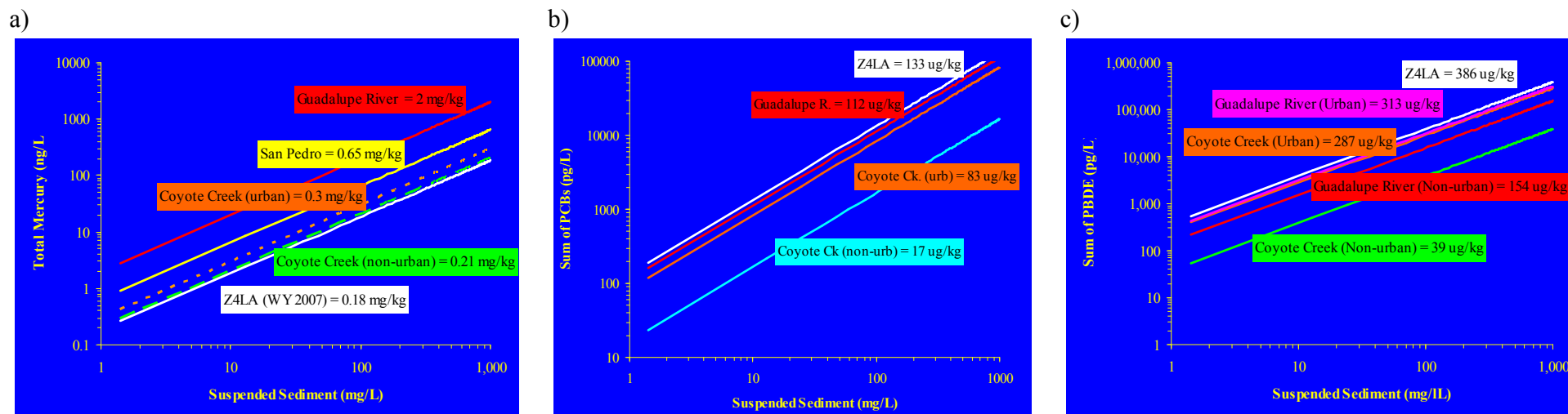
Figure 35. Estimated particle concentrations (represented by the gradients of the regression lines) for watershed systems in the Bay Area based on ratios between suspended sediment concentrations and contaminant concentrations. a) Mercury, b) PCBs, and c) PBDEs. Note, for Guadalupe River not all years showed a contrast between urban runoff and non-urban runoff because of climatic factors and perhaps because only 20% of the watershed is in non-urban land uses downstream from the reservoirs.

sediment and contaminant loads on an annual basis. In order to better compare pollutant loads between watersheds of differing size, loads can be normalized by watershed area. Even then, climatic influences confound comparisons unless years with similar climatic characteristics are available. Since Z4LA received about 70% mean annual rainfall (MAR) in WY 2007, yields were compared to loads in the Guadalupe River that occurred during WY 2004 (also a 70% MAR for that system) (Table 13). In the case of Guadalupe River, yields were computed for the area downstream of the reservoirs. Keeping in mind that the errors associated with our load measurements are about plus or minus 35%, this comparison shows some very interesting results.

During a 70% MAR WY, the Guadalupe River had greater yields of suspended sediment, mercury, arsenic, chromium, and nickel, likely due to mining and natural sources in the rocks and soils of this watershed and the steep erodible peaks of Loma Prieta and Mt. Umunhum in the Santa Cruz Mountains. Ag, Cd, Cu, Pb, PCBs, PBDEs, DDT, and dieldrin (organochlorine historic use pesticides) loads were similar in the two watersheds. For zinc, and perhaps methylmercury, data to-date indicate that the Hayward watershed has greater yields discharged to the Bay. Arsenic, although naturally occurring in minerals and soils, occurs in greater concentrations in urban environments due to use in pigments, weed and insect control, timber treatment, and as a byproduct of industrial processes and fossil fuel combustion emissions (Smedley and Kinniburgh, 2002). We currently have no explanation as to why arsenic is greater in the Guadalupe River than in Z4LA. Zinc has a variety of urban uses including galvanizing and plating, tires, and batteries but we do not know why Hayward would differ so greatly from San Jose in the use of zinc. It is perhaps surprising that methylmercury yield may be greater in Hayward than in the Guadalupe River given that there is no shortage of inorganic mercury load from the historic mining areas in the upper Guadalupe River. In contrast, the Guadalupe River has greater yields of chlordane (an organochlorine historic use pesticide). The reason is not known but perhaps it is because there is a significant legacy source in the Guadalupe associated with agricultural and landscape usage between 1948-1983, more so that Hayward. The patterns are not inconsistent with those in Bay water which do seem to suggest higher concentrations in the South Bay, however, higher concentrations of DDT and Dieldrin are also seen in the South Bay (e.g. Figure 2-10, Connor et al., 2004). As more data in collected in watersheds in the coming years, perhaps explanations for these patterns will begin to emerge.

Implications for Regional-Scale Loads to San Francisco Bay

Data collected to-date in Guadalupe River, Coyote Creek, San Pedro storm drain and most recently Z4LA can be manipulated in a variety of ways to make regional estimates of average contaminant loads entering the Bay. Essentially the simple methods fall into two categories:

Method A: Combine estimates of regionally relevant flow-weighted mean concentrations (FWMC) with estimates of regional-scale runoff.

Method B: Combine estimates of regionally relevant mean particle concentrations with estimates of regional-scale suspended sediment loads.

Table 13. Loads of pollutants entering the Bay from Z4LA in Hayward during water year 2007 in comparison to loads entering the Bay from the Guadalupe River watershed in San Jose during water year 2004. All loads are in kilograms with the exception of suspended sediments. For the purposes of the comparison, the load estimates were converted to yields (by normalizing by watershed area) for two years of similar rainfall (both about 70% mean annual rainfall). The shaded cells in the table indicate when a difference in yield between two watersheds is statistically significant.

	Area (sqkm)	Suspended Sediment (t)	Total Mercury	Total Methyl-mercury	Total Silver	Total Arsenic	Total Cadmium	Total Chromium	Total Copper	Total Nickel	Total Lead	Total Zinc	Sum of PCBs	Sum of PBDEs	DDT	Chlordane	Dieldrin
Mass Loads																	
Hayward Urban watershed (Z4LA WY 2007)	4.5	110	0.025	0.00072	0.036	0.58	0.19	6.4	11	8.0	7.9	92	0.014	0.041	0.017	0.0060	0.0013
Guadalupe River (WY 2004)	236	8500	15	0.021	3.0	104	10	640	710.0	1200	520	3000	0.77	1.6	0.77	0.59	0.060
		Suspended Sediment (t/km^2)	Total Mercury (ug/m^2)	Total MethylMercury (ug/m^2)	Total Silver (ug/m^2)	Total Arsenic (ug/m^2)	Total Cadmium (ug/m^2)	Total Chromium (ug/m^2)	Total Copper (ug/m^2)	Total Nickel (ug/m^2)	Total Lead (ug/m^2)	Total Zinc (ug/m^2)	Sum of PCBs (ug/m^2)	Sum of PBDEs (ug/m^2)	DDT (ug/m^2)	Chlordane (ug/m^2)	Dieldrin (ug/m^2)
Yields (Area-Scaled Loads)																	
Hayward Urban watershed (Z4LA WY 2007)	4.5	25	5.7	0.16	8.0	129	43	1,410	2,520	1,770	1,750	20,600	3.2	9.0	3.7	1.3	0.30
Guadalupe River (WY 2004)	236	36	64	0.088	12.6	440	41	2,712	3,008	5,085	2,203	12,712	3.3	6.7	3.3	2.5	0.26
Statistically different?		Yes	Yes	Maybe	No	Yes	No	Yes	No	Yes	No	Yes	No	No	No	Maybe	No

These can be thought of as methods in the "tool box" for loads calculation and both are fundamentally flawed as they simplify complex hydrological source-release-transport processes. In all methods of load calculation, when the data can be justifiably stratified or categorized, the resulting estimate of loads is likely to be more accurate. For example, rather than assuming all land uses have the same contaminant and runoff characteristics it is better to stratify the data into at least urban and non-urban categories. As discussed in the previous sections, there is some evidence that old urban and old industrial areas have higher concentrations of Hg and PCBs than areas that have been more recently urbanized or industrialized. If this is the case, then the estimates that follow that are based on a simple urban/ non-urban stratification should be bias low. In any case, the draft Small Tributaries Loading Strategy describes the need to use more sophisticated modeling to estimate regional loads. For example, an advanced spreadsheet model (Ha and Stenstrom, 2008) has been proposed as has extending the use of the HSPF model being tested in the Guadalupe River watershed by the RMP (Lent et al., 2009).

Estimates of regional storm water loads using these simple methods vary greatly (Table 14 and Table 15). We cannot presume to suggest that one method is better than the other, nor can we know if one method or the other is better for some POC than others. For example, regional estimates of Hg range between 32 and 91 kg for urban stormwater. Both of these estimates are lower than those published in the San Francisco Bay TMDL but there is no way of knowing the accuracy of any of these estimates. Estimates of regional PCB loads vary from 9.2-26 kg. The estimate in the Bay TMDL is 20 kg. For PBDEs, the estimates range from 28-79 kg and are much greater than previous regional estimates for BDE 47 and 209 (20 kg), two of the most abundant congeners in the Bay (Oram et al., 2008). Perhaps surprising, the loads of PCBs (a substance banned from use in 1978) still are greater than the estimate for PAHs, a substance that has ongoing contemporary sources. Perhaps even more surprising, the Bay receives an estimated average mass of trace elements of 159,000 kg each year. Some fraction of this is probably natural or derived from atmospheric deposition from sources outside the Bay Area, but the majority is estimated to be associated with the human influence on trace element cycles in the biosphere.

Recommendations

1. Given that Zone 4 Line A experienced a relatively dry year during this first year of sampling, it is recommended that additional samples be collected during years of greater rainfall and runoff to improve confidence on inter-annual variation, allow for the development of long-term average loads, and to provide a baseline for future comparisons. Reconstruction of the channel began in the summer of 2007 and influenced the success of sampling in the following year and may have influenced the load of suspended sediment and perhaps contaminants. This will be discussed in a subsequent report.

2. Given that current regional loads estimates are crude at best, effort should be put to:

Table 14. Estimates of regional loads based on small tributaries loads studies data collected from water year 2003 – 2007 in Guadalupe River at Hwy 101 in San Jose, Coyote Creek at Hwy 237 in San Jose, San Pedro Road Storm Drain in San Jose, and Zone 4 Line A at Cabot Blvd in Hayward. Here loads estimates were made by combining estimates of average urban stormwater concentrations (mass of contaminant per unit water volume) with an estimate of average annual long-term stormwater volume (750,703,000 m^3) based on the SIMPLE model (Davis et al., 2000).

	SSC	HgT	MeHgT	Ag	As	Cd	Cr	Cu	Ni	Pb	Se	Zn	t-PCBs	t-PBDEs	PAHs	DDTs	Chlor-danes	Dieldrin
	(mg/L)	(ng/L)	(ng/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Z4LA WY 2007 FWMC	212	48.1	1.4	0.07	1.1	0.36	12.1	21.5	15.1	14.9	0.2	175	27.3	76.9	10.2	31.5	11.3	2.5
Guadalupe (Estimated long-term average)		-	-	0.06	1.8	0.21	28.6	15.2	55.0	17.2	-	64.0	15.4	39.5	-	28.7	26.6	2.1
Coyote Creek WY 2005 (average of High and low flow)		35	-															
Coyote Creek WY 2005 FWMC		-	-	-	-	-	-	-	-	-	-	-	9.3	30	-	-	-	-
San Pedro Stormdrain, San Jose WY 2006 (average of High and low flow)	430	251	0.42	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Regional average	321	111	0.9	0.07	1.5	0.28	20	18	35	16	0.2	120	17	49	10.2	30	19	2
	Metric t/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y	kg/y
Estimated average urban stormwater load	240,976	84	0.7	49	1,089	213	15,280	13,790	26,312	12,030	150	89,709	13	37	8	23	14	2

Table 15. Estimates of regional loads based on small tributaries loads studies data collected from water year 2003 – 2007 in Guadalupe River at Hwy 101 in San Jose, Coyote Creek at Hwy 237 in San Jose, San Pedro Road Storm Drain in San Jose, and Zone 4 Line A at Cabot Blvd in Hayward. Here estimates were made by combining estimates of average urban stormwater concentrations (mass of contaminant per unit suspended sediment mass) with an estimate of average stormwater suspended sediment load (240,976 metric t) based on the estimate in Table 14 above. Note this is greater by a factor of 2.9x than the estimate by Davis et al. (2000) (83,700 metric t) generated using the SIMPLE model.

	HgT (mg/kg)	PCBs (ug/kg)	PBDEs (ug/kg)
Z4LA WY 2007	0.18	133	386
Guadalupe (Urban)	-	112	313
Coyote Creek WY 2005 (Urban)	0.30	83	287
San Pedro Stormdrain, San Jose WY 2006	0.65		
Regional average	0.38	109	329
	kg/y	kg/y	kg/y
Estimated average urban stormwater load (kg/year) based on suspended sediment estimate from Table 14.	91	26	79
Estimated average urban stormwater load (kg/year) based on suspended sediment estimate from Davis et al. (2000)	32	9.2	28

a) Gathering data in watersheds with contrasting land-use types (newer urban, older urban, mixed land use, and agricultural/open space land use).

b) Developing better methods of regional extrapolation of data using models such as HSPF.

3. Given that methylated or potentially methylated forms of mercury are of most concern, continued effort should be made to improve our regional data set for MeHgT and reactive mercury (Hg-R).

4. Given the somewhat unexpected similarity between watersheds in relation to particle concentrations of PCBs and PBDEs, a hypothesis emerges that imperviousness plays a strong role in the transport of these substances. It is possible that directly connected imperviousness in combination with land use types is controlling loads at the regional scale. More data is needed during wetter years to test these hypotheses.

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APPENDICES

Appendix A. Mercury, Trace Elements, SSC and Organic Carbon Quality Assurance

Samples were received in good condition between November 15, 2006 and April 20, 2007. Two of the coolers containing waters for metals, mercury and methylmercury were received outside the optimal temperature range of 4±2C. Two SSC coolers arrived at 15.3°C and 20.7°C. The samples were believed to have been unaffected by the slight temperature differences.

Three field duplicates were collected and analyzed for HgT, while two of the three were each also analyzed for HgD, MeHgT, MeHgD, and other trace elements. Relative percent difference (RPD) is calculated as the difference in concentration of a pair of analytical duplicates divided by the average of the duplicates, and the target RPD range is ±25%. This target range was exceeded in at least one duplicate set of Hg and MeHg samples, as well as two of the other trace elements (Appendix Table A1). The average RPD of all the analytes achieved the target with the exception of Cr (mean = 29%).

The laboratory analyzed 11 Hg sample duplicates, 7 methylmercury duplicates, and 3 duplicates of all other trace elements. RPDs of all lab duplicates were within the target range of ±25% with the exception of one batch for selenium that was marginally outside the desirable range (Appendix Table A1). The percent recoveries for standard reference materials were within the target range (75 – 125%, 70 – 130% for MeHg) without exception. The percent recoveries for matrix spikes were within the target range (75 - 125%, 70 – 130% for MeHg) for all samples except one batch of aluminum. The quality assurance samples included three method blanks for each analytical batch of Hg and MeHg analyses, one or two method blanks for other trace elements, and two to five method blanks for SSC. Trace element concentrations in the method blanks were not detected. All lab blank concentrations for all analytes were below the method detection limit (MDL). In cases where minor SSC were detected in the method blanks, samples were corrected using the average blank concentration for the batch.

Table A1. Quality control results for mercury, methylmercury, and trace elements analyzed in this study. RPD = Relative Percent Difference; SRM = Standard Reference Material; NC = Not Calculable due to one or more values <MDL; ND = No Data

Parameter	Detection Limit (MDL)	Reporting Limit (RL)	RPD of Lab Duplicates (% range; % mean)	RPD of Field Duplicates (% range; % mean)	Percent Recovery of SRM	Percent Recovery of Matrix Spike
Total & Dissolved Mercury	0.20 ngL⁻¹	0.20 ngL⁻¹	1.7 – 12; 7.2	4 – 54; 24	75.5 – 121	81.7 - 122
Total & Dissolved Methylmercury	0.020 ngL⁻¹	0.02 ngL⁻¹	0 – 19; 7.1	3 – 29; 12	97.2 – 120	86.7 - 126
Ag	0.01 µgL⁻¹	0.05 µgL⁻¹	0.9 - 3.2; 2.0	0 – 40; 20	90.6 – 95.4	77.3 – 84
Al	0.10 µgL⁻¹	0.50 µgL⁻¹	0.3 - 1.9; .9	2 – 7; 4.3	103 – 106	103 – 151
As	0.10 µgL⁻¹	0.50 µgL⁻¹	0.4 - 6.0; 3.9	5 – 11; 8	97.1 – 104	100 – 125
Cd	0.01 µgL⁻¹	0.03 µgL⁻¹	0.5 – 1.7; 1.1	0 – 7; 3.5	100 – 103	110 – 124
Cr	0.03 µgL⁻¹	0.10 µgL⁻¹	1.0 – 2.0; 1.5	5 – 54; 29	100-102	98.8 – 117
Cu	0.01 µgL⁻¹	0.03 µgL⁻¹	1.5 - 2.3; 1.9	0 – 3; 1.3	97.8 – 101	87.6 – 111
Mn	0.01 µgL⁻¹	0.03 µgL⁻¹	1.1 - 1.6; 1.3	0 – 3; 1.8	98.8 – 100	107 – 116
Ni	0.01 µgL⁻¹	0.05 µgL⁻¹	0.1 - 2.3; 1.3	1 – 33; 17	97.5 – 99.3	91.6 – 110
Pb	0.01 µgL⁻¹	0.03 µgL⁻¹	0.4 - 1.6; .9	0 – 1; 0.4	97.5 – 98.8	92.4 – 104
Se	0.10 µgL⁻¹	0.50 µgL⁻¹	NC – 30; 30	ND	98 – 107	99.1 – 110
Zn	0.10 µgL⁻¹	0.30 µgL⁻¹	0.3 - 2.1; 1.0	3 – 4; 3.3	101 – 102	97.8 - 111

Appendix B. PCBs, PBDEs, PAHs, and Pesticides Analysis Quality Assurance

Quality assurance and quality control criteria were based on protocols outlined in the RMP Quality Assurance Program Plan (Lowe *et al.*, 1999) and in EPA Method 1668, Revision A (USEPA, 1999). Quality assurance samples included laboratory blanks, matrix spikes, $^{13}C_{12}$-labeled surrogates and duplicate field samples. Concentrations in samples with $^{13}C_{12}$-labeled surrogate recoveries outside of method specifications (25-150%) were estimated and qualified (q). Attempts to bring recoveries within the normal range by additional clean-up procedures and reanalysis were not possible for some samples due to complete consumption of the low sample volumes collected in the study. These data have greater uncertainty; however, sample concentrations reported with surrogate recoveries outside of the normal range were not rejected because concentrations fell within the range of reported concentrations. Concentrations not measured above limits of quantification were substituted with zero concentration for calculation of t-PCBs, t-DDT, and t-chlordane.

No PCB measurements were below detection. RPDs of PCB congeners measured in the one field duplicate sample ranged from 3 to 37% (Appendix Table B1). Approximately one-half of the PBDE congeners were detected less than 100% of the time, and three were never detected. The RPDs of PBDE field duplicates ranged from 0 to 40%. All PAHs analyzed were detected in all samples and only the pesticide Aldrin was not detected in only one sample. The RPDs ranged between 0.21 and 21% for PAHs and between 0 and 57.6% for pesticides.

Table B1. Quality assurance and control summary. DF = detection frequency (%) of analytes in field samples. MDL = method detection limit. NA = not available. ND = not detected. RPD = relative percent difference of concentrations measured in field duplicate. Units in header.

Parameter	Lab Blank Conc. pgL^{-1}	Field Sample pgL^{-1}	MDL Range pgL^{-1}	DF %	RPD %
PCBs					
PCB 008	8.62 - 11.6	5.3 - 113	0.361 - 4.53	100	5.52
PCB 018/30	6.35 - 8.71	14.1 - 292	0.227 - 0.388	100	19.4
PCB 028/20	5.58 - 7.63	16.6 - 1320	0.246 - 0.61	100	31.4
PCB 031	4.32 - 5.3	6.27 - 635	0.246 - 0.58	100	36.5
PCB 033/21	3.01 - 3.73	2.19 - 337	0.246 - 0.579	100	37.4
PCB 044/47/65	3.82 - 4.96	22.3 - 1730	0.227 - 0.38	100	16.4
PCB 049/69	1.98 - 2.18	10.9 - 943	0.227 - 0.356	100	16.3
PCB 052	5.63 - 5.81	27 - 1820	0.227 - 0.406	100	16.4
PCB 056	0.848 - 0.989	2.7 - 739	0.248 - 1.57	100	13.6
PCB 060	0.63 - 0.74	2.54 - 292	0.248 - 1.6	100	16.5
PCB 066	1.75 - 2.74	11.1 - 1510	0.248 - 1.45	100	11.4
PCB 070/74/61/76	3.86 - 4.34	17.6 - 2170	0.248 - 1.46	100	13.7
PCB 087/97/86/108/119/125	1.15 - 1.54	12.1 - 1460	0.235 - 1.2	100	12.3
PCB 095/93/98/100/102	2.4 - 3.75	21.2 - 1650	0.248 - 1.42	100	13
PCB 099/83	1.31 - 1.46	7.46 - 996	0.263 - 1.47	100	13.6
PCB 101/90/113	1.92 - 2.4	16.9 - 1860	0.245 - 1.25	100	13.9

Table B1 continued; units in header.

Parameter	Lab Blank Conc. pgL⁻¹	Field Sample pgL⁻¹	MDL Range pgL⁻¹	DF %	RPD %
PCBs					
PCB 105	0.517 - 0.688	5.8 - 869	0.249 - 2.03	100	11.8
PCB 110/115	1.56 - 1.61	25.1 - 2650	0.231 - 1.04	100	12.9
PCB 118	1.2 - 1.77	13.5 - 1790	0.248 - 1.87	100	10.6
PCB 128/166	ND	5.04 - 550	0.248 - 2.17	100	16.3
PCB 132	ND - 0.324	9.86 - 1030	0.295 - 2.92	100	4.49
PCB 138/129/160/163	1.16 - 2.63	28.9 - 3130	0.248 - 2.34	100	9.23
PCB 141	ND	4.62 - 666	0.254 - 2.63	100	10.4
PCB 149/147	1.1 - 1.48	22.6 - 2360	0.265 - 2.45	100	5.41
PCB 151/135/154	ND - 0.557	10.1 - 1020	0.246 - 0.49	100	4
PCB 153/168	0.886 - 2.38	21.9 - 2530	0.248 - 2.05	100	8.52
PCB 156/157	ND	2.7 - 362	0.275 - 2.63	100	11.6
PCB 158	ND	2.8 - 314	0.248 - 1.82	100	10.2
PCB 170	ND - 0.295	7.39 - 1020	0.246 - 1.15	100	10.4
PCB 174	ND - 0.336	9.31 - 1350	0.246 - 0.972	100	5.82
PCB 177	ND	5.35 - 625	0.246 - 0.964	100	8.33
PCB 180/193	0.7 - 1.44	19.6 - 2990	0.245 - 0.871	100	10.2
PCB 183/185	ND - 0.302	7.46 - 941	0.246 - 0.944	100	7.58
PCB 187	0.516 - 0.634	15.7 - 1840	0.246 - 0.79	100	4.75
PCB 194	ND	6.83 - 1150	0.444 - 3.34	100	17.2
PCB 195	ND	2.27 - 339	0.452 - 3.64	100	9.35
PCB 201	ND	1.45 - 177	0.227 - 0.718	100	3.12
PCB 203	ND	7.97 - 1160	0.231 - 0.99	100	5.2
PBDEs					
BDE 007	ND	0.648 - 2.07	0.447 - 2.32	40	0
BDE 008/11	ND	0.734 - 4.5	0.447 - 1.77	80	13.8
BDE 010	ND	0 - 0	0.447 - 2.83	0	0
BDE 012/13	ND	0.582 - 4.16	0.447 - 1.53	95	11.5
BDE 015	ND	0.609 - 14.4	0.447 - 1.32	100	8.5
BDE 017/25	ND - 0.637	5.45 - 146	1.01 - 3.94	100	30.2
BDE 028/33	0.902 - 1.54	4.43 - 263	0.776 - 3.1	100	25.6
BDE 030	ND	1.5 - 1.5	1.16 - 4.4	5	0
BDE 032	ND	1.3 - 2.18	0.87 - 3.35	10	0
BDE 035	ND	0.673 - 55	0.653 - 2.96	100	4
BDE 037	ND - 0.868	1.61 - 14.9	0.604 - 2.99	100	19.4
BDE 047	22.8 - 34.8	128 - 10200	0.447 - 1.33	100	24.3
BDE 049	.654 - 1.62	10.6 - 536	0.447 - 1.83	100	19.1
BDE 051	ND	1.07 - 46.8	0.447 - 1.4	100	15.4
BDE 066	.895 - 1.18	5.06 - 476	0.447 - 2.27	100	19.5
BDE 071	ND - 0.512	1.81 - 72.9	0.447 - 2.02	100	11
BDE 075	ND	1.89 - 25.5	0.447 - 1.57	95	6.3
BDE 077	ND	0.516 - 6.38	0.447 - 1.23	90	8.5
BDE 079	ND	0.855 - 116	0.447 - 1.44	100	21.2
BDE 085	1.39 - 1.9	26.9 - 603	3.31 - 27.6	95	29.4
BDE 099	19.8 - 31.2	123 - 12400	2.35 - 15.2	100	24.9
BDE 100	3.68 - 6.48	28 - 2660	1.62 - 10.4	100	29.9

Table B1 continued; units in header.

Parameter	Lab Blank Conc. pgL^{-1}	Field Sample pgL^{-1}	MDL Range pgL^{-1}	DF %	RPD %
PBDEs					
BDE 105	ND	ND	4.56 - 38.5	0	0
BDE 116	ND	29 - 29	6.25 - 45.1	5	0
BDE 119/120	ND	8.02 - 93.8	3.63 - 24.4	80	17.8
BDE 126	ND	3.14 - 4.95	2.12 - 18.9	10	0
BDE 128	ND - 3.6	9.56 - 45.8	8.85 - 78.2	30	20.1
BDE 138/166	ND	14.5 - 178	0.465 - 28.8	95	27.9
BDE 140	ND	7.09 - 80.5	0.465 - 16.9	90	40
BDE 153	2.4 - 3.3	15.9 - 1310	0.465 - 13.5	100	26.9
BDE 154	1.65 - 3.33	12.8 - 1070	0.463 - 10.8	100	25.2
BDE 155	ND	1.32 - 87.8	0.463 - 9.36	90	40.3
BDE 181	ND	6.58 - 35.1	3.44 - 48.8	50	9
BDE 183	1.3 - 5.3	13.7 - 1190	1.85 - 27	100	24.5
BDE 190	ND	18.2 - 183	6.18 - 91.6	85	3.7
BDE 197/204	7.36	97.3 - 673	19.8 - 109	100	5.8
BDE 203	1.61 - 5.67	11.1 - 863	8.8 - 175	100	22.6
BDE 205	7.94	0 - 0	46.6 - 257	0	0
BDE 206	ND - 15.1	87.5 - 5080	7.85 - 118	100	16.5
BDE 207	ND - 30.3	127 - 8570	10.2 - 118	100	22
BDE 208	ND - 13.4	81.3 - 5160	10.7 - 118	100	22.3
BDE 209	ND - 481	1640 - 92900	60.5 - 1880	100	10
PAHs					
Acenaphthene	0.384	2.32 - 45.1	0.252 - 0.998	100	12.16
Acenaphthylene	0.07	2.35 - 16	0.0985 - 0.538	100	3.48
Anthracene	0.074	6.47 - 118	0.572 - 6.6	100	14.11
Benz(a)anthracene	ND	47.1 - 971	0.573 - 6.68	100	20.9
Benzo(a)pyrene	ND	89.3 - 1270	1.72 - 23.4	100	9.91
Benzo(b)fluoranthene	0.128	107 - 1480	1.28 - 19.3	100	5.49
Benzo(e)pyrene	0.171	122 - 1150	1.52 - 20.7	100	18.6
Benzo(g,h,i)perylene	0.078	116 - 1570	1.49 - 25.7	100	9.02
Benzo(k)fluoranthene	0.255	3.63 - 1500	1.46 - 18.9	100	18.8
Biphenyl	0.089	1.42 - 202	0.224 - 0.578	100	5.88
Chrysene	0.17	23.9 - 1910	0.644 - 7.16	100	13.2
Dibenz(a,h)anthracene	0.094	8.09 - 366	1.09 - 25.9	100	17.9
Dibenzothiophene	ND	3.68 - 87.1	0.158 - 1.11	100	5.65
Dimethylnaphthalene, 2,6-	0.116	2.16 - 230	0.264 - 151	86	0.212
Fluoranthene	0.071	7.5 - 949	0.575 - 7.17	100	8.62
Fluorene	0.126	1.94 - 1600	0.289 - 2.86	100	1.98
Indeno(1,2,3-c,d)pyrene	0.431	9.55 - 785	1.69 - 29	100	10.1
Methylnaphthalene, 1-	0.843	1.78 - 45.2	0.271 - 1.16	100	2.99
Methylnaphthalene, 2-	0.062	3.51 - 122	0.257 - 1.1	100	2.23
Methylphenanthrene, 1-	2.09	4.3 - 53.3	0.554 - 2.52	100	3.55
Naphthalene	ND	12.6 - 464	0.28 - 0.703	100	2.74
Perylene	0.254	33.3 - 1390	1.81 - 24.2	100	13
Phenanthrene	0.11	35.7 - 2640	0.526 - 3.05	100	9.05
Pyrene	0.194	10 - 814	0.577 - 7.19	100	9.66
Trimethylnaphthalene, 2,3,5-	985000	0.131 - 25.2	0.319 - 1.61	100	7.69

Table B1 continued; units in header.

Parameter	Lab Blank Conc. pgL^{-1}	Field Sample pgL^{-1}	MDL Range pgL^{-1}	DF %	RPD %
OC Pesticides					
Aldrin	14	12.1 - 32.4	3.6 - 8.99	86	NC
Chlordane, alpha-	5.87	1040 - 4730	6.36 - 32	100	0
Chlordane, gamma-	6.18	1090 - 5170	5.46 - 27.5	100	0.913
Dacthal	1.59	2000 - 7550	0.372 - 0.619	100	7.85
DDD(o,p')	ND	400 - 3780	9.08 - 27.3	100	8.79
DDD(p,p')	ND	1180 - 15700	15.2 - 45.5	100	10.6
DDE(o,p')	ND	198 - 1690	7.27 - 14.8	100	3.23
DDE(p,p')	ND	2350 - 18700	9.43 - 19	100	12.7
DDT(o,p')	ND	458 - 2710	11.7 - 35	100	4.72
DDT(p,p')	ND	2400 - 16900	16 - 49.1	100	5.13
Dieldrin	3.52	711 - 4590	3.85 - 11.6	100	8.74
Endosulfan I	63.7	170 - 480	12.6 - 36.7	100	9.11
Endosulfan II	112	235 - 1130	19.2 - 67.2	100	10.1
Endosulfan sulfate	ND	238 - 708	17.9 - 62.7	100	8.1
Endrin	8.67	72.2 - 378	5.15 - 15.4	100	21.2
HCH, alpha	5.03	126 - 299	3.57 - 5.88	100	0.917
HCH, beta	ND	51.7 - 267	5.38 - 9.06	100	5.31
HCH, delta	5.62	7.91 - 19.9	2.91 - 4.17	100	16
HCH, gamma	9.02	120 - 305	4.17 - 6.87	100	0.971
Heptachlor	5.97	25.4 - 105	2.94 - 6.35	100	2.33
Heptachlor epoxide	ND	73 - 249	2.37 - 4.33	100	13.8
Hexachlorobenzene	46.8	264 - 898	0.732 - 1.26	100	2.35
Mirex	2.43	12 - 70.2	1.45 - 6.43	100	57.6
Nonachlor, cis-	9.03	362 - 1960	14.8 - 51.7	100	5.64
Nonachlor, trans-	8.11	801 - 4050	6.94 - 33.5	100	2.59
Oxadiazon	ND	615 - 88200	3.25 - 8.01	100	33.5
Oxychlordane	ND	33.6 - 143	11.4 - 29.7	100	12
HCH, alpha	5.03	126 - 299	3.57 - 5.88	100	0.917
HCH, beta	ND	51.7 - 267	5.38 - 9.06	100	5.31
HCH, delta	5.62	7.91 - 19.9	2.91 - 4.17	100	16
HCH, gamma	9.02	120 - 305	4.17 - 6.87	100	0.971
Heptachlor	5.97	25.4 - 105	2.94 - 6.35	100	2.33
Heptachlor epoxide	ND	73 - 249	2.37 - 4.33	100	13.8
Hexachlorobenzene	46.8	264 - 898	0.732 - 1.26	100	2.35
Mirex	2.43	12 - 70.2	1.45 - 6.43	100	57.6
Nonachlor, cis-	9.03	362 - 1960	14.8 - 51.7	100	5.64
Nonachlor, trans-	8.11	801 - 4050	6.94 - 33.5	100	2.59
Oxadiazon	ND	615 - 88200	3.25 - 8.01	100	33.5
Oxychlordane	ND	33.6 - 143	11.4 - 29.7	100	12

Appendix C. Zone 4 Line A Year 1 Sample Data

Table C1. Mercury and organic carbon concentrations in Zone 4 Line A samples, WY 2007. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	SSC (mg/L)	DOC (mg/L)	POC (mg/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)
11/13/06	17:50	Z4LA-01	64.95	NS	NS	28	4.26	0.329	0.03
11/13/06	20:55	Z4LA-02	191.0	4.02	0.47	43	2.84	0.478	0.021
11/13/06	22:15	Z4LA-03	491.7	4.08	0.23	40	3.29	0.413	ND
11/13/06	23:25	Z4LA-04	39.78	3.89	0.06	16	3.89	0.213	0.030
11/26/06	15:25	Z4LA-10	48.18	11.56	0.50	19	5.11	0.373	0.110
11/26/06	16:40	Z4LA-11	362.8	6.19	0.26	52	2.45	0.081	0.028
11/26/06	18:25	Z4LA-12	29.40	5.31	0.07	17	3.86	0.315	0.054
12/9/06	17:35	Z4LA-20	86.90	7.98	2.29	10	NS	NS	NS
12/9/06	19:25	Z4LA-21	231.0	5.79	4.66	42	NS	NS	NS
12/12/06	15:20	Z4LA-22	65.22	6.38	0.88	18	4.24	0.200	0.033
1/4/07	9:15	Z4LA-30	76.82	NS	NS	30	4.38	0.562	0.083
2/7/07	5:30	Z4LA-40	1.415	3.21	0.13	2	NS	NS	NS
2/8/07	14:50	Z4LA-41	142.1	10.54	3.97	42	NS	NS	NS
2/8/07	18:35	Z4LA-42	65.82	7.55	2.27	29	NS	NS	NS
2/9/07	6:15	Z4LA-43	13.21	7.59	0.60	17	NS	NS	NS
2/9/07	7:35	Z4LA-44	127.4	4.87	0.64	23	NS	NS	NS
2/9/07	8:00	Z4LA-45	230	5.71	1.00	47	NS	NS	NS
2/9/07	9:35	Z4LA-46	55.34	NS	NS	18	NS	NS	NS
2/9/07	9:35	Z4LA-46 (Duplicate)	47.56	NS	NS	14	NS	NS	NS
2/9/07	11:25	Z4LA-47	108.0	NS	NS	32	NS	NS	NS
2/10/07	9:15	Z4LA-48	65.05	NS	NS	25	NS	NS	NS
2/10/07	10:20	Z4LA-48x	NS	NS	NS	14	NS	NS	NS
2/10/07	17:40	Z4LA-49	NS	NS	NS	20	NS	NS	NS
2/10/07	18:30	Z4LA-50	NS	NS	NS	13	NS	NS	NS
2/10/07	19:55	Z4LA-51	NS	NS	NS	12	NS	NS	NS
2/11/07	11:40	Z4LA-52	NS	4.82	0.27	8	NS	NS	NS
2/12/07	19:10	Z4LA-53	NS	NS	NS	23	NS	NS	NS
2/22/07	4:00	Z4LA-60	124.5	NS	NS	10	0.829	0.186	ND
2/22/07	4:55	Z4LA-61	188.6	NS	NS	55	3.19	0.483	0.08
2/22/07	5:45	Z4LA-62	71.36	NS	NS	14	3.15	0.237	0.113
2/22/07	5:45	Z4LA-62 (Duplicate)	67.68	NS	NS	16	3.02	0.318	0.101
2/22/07	6:00	Z4LA-63	79.08	NS	NS	24	3.5	0.286	0.097
4/11/07	6:40	Z4LA-70	161.3	NS	NS	30.2	2.31	1.30	0.27
4/11/07	7:00	Z4LA-71	78.75	NS	NS	39.0	7.12	0.782	0.270
4/11/07	7:05	Z4LA-71 (Duplicate)	90.23	NS	NS	30.9	4.1	0.757	0.262
4/11/07	7:50	Z4LA-72	33.57	NS	NS	24.0	5.4	0.592	0.224
4/11/07	9:25	Z4LA-73	NS	NS	NS	18.9	6.78	0.477	0.152
4/11/07	10:00	Z4LA-74	NS	NS	NS	31.3	NS	NS	NS
4/11/07	11:00	Z4LA-75	NS	NS	NS	21.3	7.61	0.473	0.21

Table C2. Trace element concentrations in Zone 4 Line A samples, WY 2007. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Zn (µg/L)
11/13/06	17:50	Z4LA-01	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
11/13/06	20:55	Z4LA-02	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
11/13/06	22:15	Z4LA-03	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
11/13/06	23:25	Z4LA-04	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
11/26/06	15:25	Z4LA-10	0.03	1143	1.15	0.18	11.4	17.9	67.0	49.0	7.25	ND	84.9
11/26/06	16:40	Z4LA-11	0.07	3435	1.49	0.41	16.6	27.1	159	22.3	22.2	ND	148
11/26/06	18:25	Z4LA-12	0.02	940	0.94	0.13	23.5	11.1	45.8	30.0	5.66	ND	63.8
12/9/06	17:35	Z4LA-20	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
12/9/06	19:25	Z4LA-21	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
12/12/06	15:20	Z4LA-22	0.02	1206	1.95	0.13	4.61	12.6	54.4	5.10	7.26	0.27	72.1
1/4/07	9:15	Z4LA-30	0.02	1096	1.65	0.320	3.97	20.1	96.6	5.87	11.8	0.30	147
2/7/07	5:30	Z4LA-40	ND	82.5	1.56	0.04	0.98	3.24	11.1	3.92	0.56	0.95	7.45
2/8/07	14:50	Z4LA-41	0.07	4491	1.34	0.42	11.9	27.6	192	15.8	19.3	ND	181
2/8/07	18:35	Z4LA-42	0.04	2647	1.15	0.25	7.40	18.5	94.0	9.36	11.4	ND	111
2/9/07	6:15	Z4LA-43	0.02	982	0.99	0.11	3.29	10.4	33.4	4.30	4.62	0.11	62.1
2/9/07	7:35	Z4LA-44	0.05	1837	0.68	0.21	4.98	11.6	72.5	6.79	7.96	0.11	127
2/9/07	8:00	Z4LA-45	0.08	4110	1.11	0.41	10.7	24.4	187	13.8	19.1	0.11	167
2/9/07	9:35	Z4LA-46	0.02	1702	0.86	0.16	4.76	11.7	63.5	6.10	7.58	ND	80.7
2/9/07	9:35	Z4LA-46 (Duplicate)	0.03	1825	0.82	0.16	4.99	12.0	65.7	6.19	7.55	ND	83.9
2/9/07	11:25	Z4LA-47	0.03	2586	0.91	0.2	6.75	14.8	95.2	8.35	10.4	0.12	95.8
2/10/07	9:15	Z4LA-48	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/10/07	10:20	Z4LA-48x	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/10/07	17:40	Z4LA-49	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/10/07	18:30	Z4LA-50	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/10/07	19:55	Z4LA-51	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/11/07	11:40	Z4LA-52	0.02	908	1.56	0.09	2.74	5.43	22.4	3.26	2.63	0.25	50.0
2/12/07	19:10	Z4LA-53	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
2/22/07	4:00	Z4LA-60	0.02	1273	2.38	0.11	39.2	6.87	136	23.1	4.50	1.17	38.5
2/22/07	4:55	Z4LA-61	0.06	2874	0.88	0.31	30.4	20.8	117	26.7	12.8	0.13	141
2/22/07	5:45	Z4LA-62	0.02	1253	0.74	0.15	8.89	10.5	51.5	8.71	5.15	ND	71.7
2/22/07	5:45	Z4LA-62 (Duplicate)	0.02	1273	0.66	0.140	5.12	10.5	51.6	6.22	5.21	ND	73.6
2/22/07	6:00	Z4LA-63	0.03	1494	0.76	0.18	4.38	12.3	58.2	6.02	5.88	ND	90.3
4/11/07	6:40	Z4LA-70	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	7:00	Z4LA-71	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	7:05	Z4LA-71 (Duplicate)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	7:50	Z4LA-72	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	9:25	Z4LA-73	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	10:00	Z4LA-74	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
4/11/07	11:00	Z4LA-75	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

Table C3. PCB concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PCBs	PCB 008	PCB 018/30	PCB 028/20	PCB 031	PCB 033/21	PCB 044/47/65	PCB 049/69	PCB 052	PCB 056	PCB 060	PCB 066
Range of MDLs				0.36-4.5	0.23-0.39	0.25-0.61	0.25-0.58	0.25-0.58	0.23-0.38	0.23-0.36	0.23-0.41	0.25-1.6	0.25-1.6	0.25-1.5
11/13/06	17:43	Z4LA-01	7471	32	79	233	158	109	219	113	224	67	40	134
11/13/06	20:54	Z4LA-02	17285	R	123	328	199	83	406	222	525	131	62	257
11/13/06	22:08	Z4LA-03	17980	28	105	409	202	94	432	239	473	164	78	309
11/13/06	23:25	Z4LA-04	3983	R	20	86	31	10	108	58	121	34	15	64
11/26/06	18:21	Z4LA-12	5471	R	28	121	42	14	193	101	208	68	31	127
12/12/06	15:14	Z4LA-22	5611	R	28	94	29	R	138	73	170	47	22	87
1/4/07	9:17	Z4LA-30	11741	43	114	356	204	127	360	200	382	138	74	262
2/7/07	5:34	Z4LA-40	388	R	R	R	R	R	22	11	27	3	3	11
2/8/07	14:56	Z4LA-41	25866	78	176	465	336	227	468	249	558	197	108	417
2/8/07	18:42	Z4LA-42	11010	R	105	246	168	98	275	145	300	93	53	193
2/9/07	6:18	Z4LA-43	4533	R	40	116	56	13	127	66	138	41	23	87
2/9/07	7:36	Z4LA-44	13827	28	104	314	177	88	362	203	404	139	73	267
2/9/07	8:00	Z4LA-45	38663	113	292	806	536	337	932	513	1050	367	195	692
2/9/07	11:17	Z4LA-47	17046	40	116	285	208	120	333	175	402	119	64	234
2/11/07	12:04	Z4LA-52	2290	R	27	65	28	R	86	48	91	25	11	52
2/22/07	4:05	Z4LA-60	11678	42	72	253	129	75	289	158	346	107	49	213
2/22/07	4:37	Z4LA-61	46027	104	268	1320	635	309	1730	943	1820	739	292	1510
2/22/07	5:32	Z4LA-62	8995	R	57	199	125	81	185	98	198	62	32	130
2/22/07	5:34	Z4LA-62	8063	R	47	145	86	56	157	83	168	54	27	116
2/22/07	6:03	Z4LA-63	9688	R	62	214	123	70	240	132	263	99	48	189

Table C3 (continued). PCB concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PCBs	PCB 070/61/74/76	PCB 087/86/97/108/119/125	PCB 095/93/98/100/102	PCB 099/83	PCB 101/90/113	PCB 105	PCB 110/115	PCB 118	PCB 128/166	PCB 132	PCB 138/129/160/163
Range of MDLs				0.25-1.5	0.24-1.2	0.25-1.4	0.26-1.5	0.25-1.3	0.25-2	0.23-1	0.25-1.9	0.25-2.2	0.30-2.9	0.25-2.34
11/13/06	17:43	Z4LA-01	7471	270	227	234	143	288	147	421	314	86	186	594
11/13/06	20:54	Z4LA-02	17285	537	575	770	381	788	345	1160	706	256	571	1540
11/13/06	22:08	Z4LA-03	17980	527	474	683	324	635	307	1100	626	285	541	1560
11/13/06	23:25	Z4LA-04	3983	110	121	139	75	154	78	248	163	63	115	359
11/26/06	18:21	Z4LA-12	5471	208	181	195	111	222	118	339	240	83	137	447
12/12/06	15:14	Z4LA-22	5611	148	185	207	123	245	119	360	254	84	155	506
1/4/07	9:17	Z4LA-30	11741	460	346	391	223	455	204	648	426	122	280	882
2/7/07	5:34	Z4LA-40	388	18	12	21	7	17	6	25	14	5	10	29
2/8/07	14:56	Z4LA-41	25866	893	700	744	451	962	432	1250	893	306	573	1910
2/8/07	18:42	Z4LA-42	11010	405	324	339	196	426	206	581	424	137	249	811
2/9/07	6:18	Z4LA-43	4533	159	151	158	90	185	83	273	179	62	110	345
2/9/07	7:36	Z4LA-44	13827	464	457	523	294	584	271	896	560	163	401	1190
2/9/07	8:00	Z4LA-45	38663	1280	1170	1340	748	1580	655	2140	1400	389	1030	3100
2/9/07	11:17	Z4LA-47	17046	502	529	568	335	732	320	977	700	195	478	1490
2/11/07	12:04	Z4LA-52	2290	81	66	86	48	90	39	130	83	26	56	188
2/22/07	4:05	Z4LA-60	11678	386	395	442	257	501	251	780	543	193	330	1060
2/22/07	4:37	Z4LA-61	46027	2170	1460	1650	996	1860	869	2650	1790	550	1010	3130
2/22/07	5:32	Z4LA-62	8995	265	225	229	141	293	144	405	287	111	182	635
2/22/07	5:34	Z4LA-62	8063	231	199	201	123	255	128	356	258	94	174	579
2/22/07	6:03	Z4LA-63	9688	330	272	298	171	353	165	509	339	99	227	732

Table C3 (continued). PCB concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PCBs	PCB 141	PCB 149/147	PCB 151/135/154	PCB 153/168	PCB 156/157	PCB 158	PCB 170	PCB 174	PCB 177	PCB 180/193	PCB 183/185
Range of MDLs				0.25-2.6	0.27-2.5	0.25-0.49	0.25-2.1	0.28-2.6	0.25-1.8	0.25-1.2	0.25-0.97	0.25-0.96	0.25-0.87	0.25-0.94
11/13/06	17:43	Z4LA-01	7471	117	382	164	442	69	59	188	217	109	539	153
11/13/06	20:54	Z4LA-02	17285	284	1160	428	1100	162	153	376	482	218	1000	372
11/13/06	22:08	Z4LA-03	17980	279	1170	429	1060	160	155	446	589	234	1290	465
11/13/06	23:25	Z4LA-04	3983	67	246	91	260	39	34	105	126	59	285	94
11/26/06	18:21	Z4LA-12	5471	80	283	105	304	53	44	126	157	69	360	117
12/12/06	15:14	Z4LA-22	5611	97	337	124	381	59	50	148	168	75	392	129
1/4/07	9:17	Z4LA-30	11741	179	621	265	686	92	89	288	362	170	863	254
2/7/07	5:34	Z4LA-40	388	5	23	10	22	3	3	7	9	5	20	7
2/8/07	14:56	Z4LA-41	25866	420	1500	622	1690	203	188	759	1010	470	2360	731
2/8/07	18:42	Z4LA-42	11010	164	607	241	668	93	82	279	362	171	871	278
2/9/07	6:18	Z4LA-43	4533	67	260	102	272	40	36	103	130	64	321	102
2/9/07	7:36	Z4LA-44	13827	227	835	353	871	126	119	298	423	193	886	280
2/9/07	8:00	Z4LA-45	38663	666	2360	1020	2530	304	300	963	1350	625	2990	941
2/9/07	11:17	Z4LA-47	17046	318	1060	443	1190	151	145	469	607	282	1330	405
2/11/07	12:04	Z4LA-52	2290	35	126	51	144	19	18	59	65	34	157	49
2/22/07	4:05	Z4LA-60	11678	183	721	254	744	130	107	268	289	149	714	220
2/22/07	4:37	Z4LA-61	46027	600	2280	876	2380	362	314	1020	1240	592	2970	922
2/22/07	5:32	Z4LA-62	8995	142	494	204	563	66	63	272	389	175	911	274
2/22/07	5:34	Z4LA-62	8063	128	468	196	517	59	57	245	367	161	823	254
2/22/07	6:03	Z4LA-63	9688	161	544	239	608	73	71	267	382	171	856	257

Table C3 (continued). PCB concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PCBs	PCB 187	PCB 194	PCB 195	PCB 201	PCB 203
Range of MDLs				0.25-0.79	0.44-3.3	0.45-3.6	0.23-0.72	0.23-0.99
11/13/06	17:43	Z4LA-01	7471	276	185	57	27	170
11/13/06	20:54	Z4LA-02	17285	643	363	122	71	386
11/13/06	22:08	Z4LA-03	17980	871	497	164	100	475
11/13/06	23:25	Z4LA-04	3983	177	93	33	17	87
11/26/06	18:21	Z4LA-12	5471	223	134	44	24	137
12/12/06	15:14	Z4LA-22	5611	233	135	46	24	140
1/4/07	9:17	Z4LA-30	11741	461	295	88	50	281
2/7/07	5:34	Z4LA-40	388	16	7	2	1	8
2/8/07	14:56	Z4LA-41	25866	1450	858	273	130	809
2/8/07	18:42	Z4LA-42	11010	545	352	106	56	362
2/9/07	6:18	Z4LA-43	4533	206	138	41	22	127
2/9/07	7:36	Z4LA-44	13827	514	297	96	58	289
2/9/07	8:00	Z4LA-45	38663	1580	930	321	176	942
2/9/07	11:17	Z4LA-47	17046	697	404	138	73	412
2/11/07	12:04	Z4LA-52	2290	84	48	14	8	52
2/22/07	4:05	Z4LA-60	11678	431	242	74	38	243
2/22/07	4:37	Z4LA-61	46027	1840	1150	339	177	1160
2/22/07	5:32	Z4LA-62	8995	560	341	112	49	296
2/22/07	5:34	Z4LA-62	8063	534	287	102	47	281
2/22/07	6:03	Z4LA-63	9688	466	272	96	48	242

Table C4. BDE concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PBDEs	PBDE 007	PBDE 008/11	PBDE 010	PBDE 012/13	PBDE 015	PBDE 017/25	PBDE 028/33	PBDE 030	PBDE 032	PBDE 035	PBDE 037	PBDE 047	PBDE 049
Range of MDLs				0.45-2.3	0.45-1.8	0.45-2.8	0.45-1.5	0.45-1.3	1-3.9	0.78-3.1	1.2-4.4	0.87-3.4	0.65-3	0.6-3	0.45-1.3	0.45-1.8
11/13/06	17:43	Z4LA-01	14,649	ND	2	ND	2	4	38	65	ND	ND	11	6	1,860	121
11/13/06	20:54	Z4LA-02	34,294	ND	2	ND	2	6	62	101	ND	ND	19	6	3,360	218
11/13/06	22:08	Z4LA-03	58,135	2	3	ND	3	10	79	98	ND	ND	15	9	3,390	229
11/13/06	23:25	Z4LA-04	9,376	ND	ND	ND	1	2	11	32	ND	ND	5	R	1,150	65
11/26/06	18:21	Z4LA-12	11,852	ND	ND	ND	1	2	11	33	ND	1	7	3	1,370	75
12/12/06	15:14	Z4LA-22	18,298	1	2	ND	2	2	13	28	ND	ND	8	3	1,070	61
1/4/07	9:17	Z4LA-30	28,459	ND	2	ND	2	6	50	85	ND	ND	16	6	2,680	171
2/7/07	5:34	Z4LA-40	2,824	ND	ND	ND	1	1	5	4	ND	ND	1	R	128	11
2/8/07	14:56	Z4LA-41	51,835	1	3	ND	2	7	94	161	ND	ND	40	10	5,540	291
2/8/07	18:42	Z4LA-42	24,890	1	1	ND	1	4	46	73	ND	ND	41	6	2,510	131
2/9/07	6:18	Z4LA-43	10,891	ND	ND	ND	1	2	20	37	ND	ND	16	5	1,190	65
2/9/07	7:36	Z4LA-44	47,376	ND	2	ND	3	6	60	105	ND	ND	23	6	3,420	212
2/9/07	8:00	Z4LA-45	141,218	2	5	ND	4	13	135	263	ND	ND	55	14	8,760	496
2/9/07	11:17	Z4LA-47	40,289	ND	2	ND	2	6	61	111	ND	ND	38	8	3,860	239
2/11/07	12:04	Z4LA-52	3,538	ND	1	ND	ND	2	7	13	ND	ND	3	R	491	28
2/22/07	4:05	Z4LA-60	44,588	1	2	ND	2	7	94	97	ND	2	10	9	3,620	241
2/22/07	4:37	Z4LA-61	120,115	2	4	ND	3	14	146	234	ND	ND	41	15	10,200	536
2/22/07	5:32	Z4LA-62	20,402	1	1	ND	1	3	29	61	ND	ND	7	4	2,120	126
2/22/07	5:34	Z4LA-62	17,336	ND	1	ND	1	3	21	47	2	ND	7	3	1,660	104
2/22/07	6:03	Z4LA-63	54,912	ND	2	ND	2	4	35	58	ND	ND	9	4	1,990	118

Table C4 (continued). BDE concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PBDEs	PBDE 051	PBDE 066	PBDE 071	PBDE 075	PBDE 077	PBDE 079	PBDE 085	PBDE 099	PBDE 100	PBDE 105	PBDE 116	PBDE 119/120	PBDE 126	PBDE 128
Range of MDLs				0.45-1.4	0.45-2.3	0.45-2	0.45-1.6	0.45-1.2	0.45-1.4	3.3-27	2.3-15	1.6-10	4.6-39	6.3-45	3.6-24	2.1-19	8.9-78
11/13/06	17:43	Z4LA-01	14,649	13	109	12	6	2	4	88	2,150	455	ND	ND	10	ND	ND
11/13/06	20:54	Z4LA-02	34,294	19	193	24	11	3	9	224	4,550	994	ND	ND	26	ND	15
11/13/06	22:08	Z4LA-03	58,135	23	192	24	10	4	7	180	4,250	981	ND	ND	30	ND	ND
11/13/06	23:25	Z4LA-04	9,376	5	53	5	3	1	4	59	1,320	292	ND	ND	ND	ND	ND
11/26/06	18:21	Z4LA-12	11,852	7	64	7	4	1	3	64	1,580	348	ND	ND	10	ND	ND
12/12/06	15:14	Z4LA-22	18,298	7	49	7	3	2	4	48	1,130	248	ND	ND	9	ND	ND
1/4/07	9:17	Z4LA-30	28,459	18	138	22	8	3	8	142	3,180	713	ND	ND	17	ND	ND
2/7/07	5:34	Z4LA-40	2,824	1	5	2	ND	ND	1	R	123	28	ND	ND	ND	ND	ND
2/8/07	14:56	Z4LA-41	51,835	26	257	43	18	3	61	284	6,270	1,390	ND	ND	34	ND	R
2/8/07	18:42	Z4LA-42	24,890	13	116	19	7	2	37	123	2,660	601	ND	ND	ND	ND	R
2/9/07	6:18	Z4LA-43	10,891	7	49	9	3	1	3	52	1,170	271	ND	ND	8	ND	18
2/9/07	7:36	Z4LA-44	47,376	21	180	26	12	3	11	176	4,170	929	ND	ND	30	ND	ND
2/9/07	8:00	Z4LA-45	141,218	44	475	46	24	6	15	532	11,100	2,460	ND	ND	70	ND	46
2/9/07	11:17	Z4LA-47	40,289	24	215	25	11	4	13	231	4,840	1,060	ND	ND	34	ND	ND
2/11/07	12:04	Z4LA-52	3,538	3	23	3	2	ND	2	27	554	126	ND	ND	ND	ND	ND
2/22/07	4:05	Z4LA-60	44,588	24	185	65	13	4	48	219	4,760	995	ND	29	27	ND	39
2/22/07	4:37	Z4LA-61	120,115	47	476	73	26	6	116	603	12,400	2,660	ND	ND	94	ND	R
2/22/07	5:32	Z4LA-62	20,402	12	112	16	7	1	32	115	2,530	572	ND	ND	14	3	12
2/22/07	5:34	Z4LA-62	17,336	10	92	15	6	1	26	86	1,970	423	ND	ND	12	ND	R
2/22/07	6:03	Z4LA-63	54,912	14	102	10	7	2	6	123	2,590	578	ND	ND	16	5	ND

Table C4 (continued). BDE concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PBDEs	PBDE 138/166	PBDE 140	PBDE 153	PBDE 154	PBDE 155	PBDE 181	PBDE 183	PBDE 190	PBDE 197/204	PBDE 203	PBDE 205	PBDE 206	PBDE 207	PBDE 208	PBDE 209
Range of MDLs				0.47-29	0.5-17	0.47-14	0.46-11	0.46-9.4	3.4-49	1.9-27	6.2-92	20-110	8.9-180	47-260	7.9-120	10-120	11-120	61-1900
11/13/06	17:43	Z4LA-01	14,649	26	10	232	180	13	ND	153	36	NR	126	NR	331	517	288	7,780
11/13/06	20:54	Z4LA-02	34,294	78	35	552	416	28	14	374	64	NR	288	NR	1,010	2,070	1,320	18,200
11/13/06	22:08	Z4LA-03	58,135	69	27	507	404	25	14	378	57	NR	220	NR	1,050	1,260	884	43,700
11/13/06	23:25	Z4LA-04	9,376	27	7	175	128	8	ND	151	24	NR	53	NR	264	317	183	5,030
11/26/06	18:21	Z4LA-12	11,852	28	8	177	139	9	7	70	24	NR	76	NR	376	480	338	6,530
12/12/06	15:14	Z4LA-22	18,298	21	9	159	104	8	ND	143	36	NR	133	NR	766	1,110	613	12,500
1/4/07	9:17	Z4LA-30	28,459	54	20	369	292	21	16	335	66	NR	169	NR	702	986	664	17,500
2/7/07	5:34	Z4LA-40	2,824	ND	ND	16	13	ND	ND	14	ND	NR	11	NR	88	127	86	2,160
2/8/07	14:56	Z4LA-41	51,835	98	44	717	514	48	ND	641	ND	517	501	R	1,980	2,990	2,050	27,200
2/8/07	18:42	Z4LA-42	24,890	48	22	326	246	20	ND	270	44	233	261	R	909	1,380	1,140	13,600
2/9/07	6:18	Z4LA-43	10,891	23	7	121	102	8	ND	117	18	97	112	R	370	599	461	5,930
2/9/07	7:36	Z4LA-44	47,376	60	28	529	410	28	23	596	85	NR	433	NR	1,840	3,390	2,060	28,500
2/9/07	8:00	Z4LA-45	141,218	152	61	1,310	1,070	78	35	1,190	183	NR	863	NR	5,080	8,570	5,160	92,900
2/9/07	11:17	Z4LA-47	40,289	72	30	587	424	29	17	378	62	NR	286	NR	1,110	1,530	1,080	23,900
2/11/07	12:04	Z4LA-52	3,538	15	ND	88	53	ND	ND	94	ND	NR	30	NR	103	149	81	1,640
2/22/07	4:05	Z4LA-60	44,588	83	43	664	454	1	ND	890	160	673	508	R	1,720	2,600	2,200	24,100
2/22/07	4:37	Z4LA-61	120,115	178	81	1,210	1,020	88	ND	658	154	614	718	R	3,430	4,680	3,290	76,300
2/22/07	5:32	Z4LA-62	20,402	36	15	283	219	16	7	151	30	125	182	R	779	1,310	872	10,600
2/22/07	5:34	Z4LA-62	17,336	27	10	216	170	11	7	118	29	118	145	R	660	1,050	697	9,590
2/22/07	6:03	Z4LA-63	54,912	47	16	304	232	17	15	169	38	NR	221	NR	1,670	1,890	1,420	43,200

Table C5. PAH concentrations in Zone 4 Line A samples, WY 2007. All units are in ng/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PAHs	t-LPAHs	Acenaphthene	Acenaphthylene	Anthracene	Biphenyl	Dimethylnaphthalene, 2,6-	Fluorene	Methylnaphthalene, 1-	Methylnaphthalene, 2-	Methylphenanthrene, 1-	Naphthalene
Range of MDLs					0.25-1.0	0.1-0.54	0.57-6.6	0.22-0.58	0.26-151	0.29-2.86	0.27-1.16	0.26-1.1	0.55-2.52	0.28-0.7
2/8/07	14:56	Z4LA-41	8015.46	508.46	9.01	6.07	28.6	7.05	13.4	11.6	8.23	13.9	43.4	22.7
2/8/07	18:42	Z4LA-42	3355.7	214.4	5.56	5.29	16	3.58	6.28	6.45	4.95	7.91	16.3	12.6
2/9/07	6:18	Z4LA-43	1373.31	68.61	2.32	2.35	6.47	1.42	2.16	1.94	1.78	3.51	4.3	R
2/22/07	4:05	Z4LA-60	2030.35	218.25	6	4.89	13.6	3.77	6.25	7.68	4.88	7.48	17.1	13.4
2/22/07	4:37	Z4LA-61	19667.6	2036.6	45.1	16	118	15.5	ND	54.5	36.7	45.2	122	53.3
2/22/07	5:32	Z4LA-62	1605.89	230.49	4.48	3.22	12.9	3.63	9.43	7.5	9.84	13.6	16.6	14.4
2/22/07	5:34	Z4LA-62	1788.63	240.73	5.06	3.11	11.2	3.85	9.45	7.65	9.55	13.3	17.2	14.8

Table C5 (continued). PAH concentrations in Zone 4 Line A samples, WY 2007. All units are in ng/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PAHs	t-LPAHs	Trimethyl lnaphthalene, 2,3,5-	Phenanthrene	Dibenzothiophene	t-HPAHs	Benz(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(e)pyrene	Benzo(g,h,i)perylene
Range of MDLs					0.32-1.61	0.53-3.05	0.16-1.11		0.57-6.68	1.72-23.4	1.28-19.3	1.52-20.7	1.49-25.7
2/8/07	14:56	Z4LA-41	8015.46	508.46	25.2	297	22.3	7507	275	480	881	665	750
2/8/07	18:42	Z4LA-42	3355.7	214.4	8.88	112	8.6	3141.3	122	220	334	272	312
2/9/07	6:18	Z4LA-43	1373.31	68.61	2.98	35.7	3.68	1304.7	47.1	89.3	147	122	139
2/22/07	4:05	Z4LA-60	2030.35	218.25	7.69	117	8.51	1812.1	80	145	173	155	181
2/22/07	4:37	Z4LA-61	19667.6	2036.6	53.2	1390	87.1	17631	971	1270	1480	1150	1570
2/22/07	5:32	Z4LA-62	1605.89	230.49	10.8	116	8.09	1375.4	55.2	96.9	124	107	127
2/22/07	5:34	Z4LA-62	1788.63	240.73	10	127	8.56	1547.9	68.1	107	131	129	139

Table C5 (continued). PAH concentrations in Zone 4 Line A samples, WY 2007. All units are in ng/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-PAHs	t-HPAHs	Benzo(k)fluoranthene	Chrysene	Dibenz(a,h)anthracene	Fluoranthene	Perylene	Pyrene	Indeno(1,2,3-c,d)pyrene
Range of MDLs					1.46-18.9	0.64-7.16	1.09-25.9	0.58-7.17	1.81-24.2	0.58-7.19	1.69-29
2/8/07	14:56	Z4LA-41	8015.46	7507	596	997	131	949	184	814	785
2/8/07	18:42	Z4LA-42	3355.7	3141.3	263	423	56.4	376	76.9	424	262
2/9/07	6:18	Z4LA-43	1373.31	1304.7	107	167	28	133	33.3	175	117
2/22/07	4:05	Z4LA-60	2030.35	1812.1	144	220	32.7	238	47.4	254	142
2/22/07	4:37	Z4LA-61	19667.6	17631	1500	1910	366	2710	464	2640	1600
2/22/07	5:32	Z4LA-62	1605.89	1375.4	116	177	23.9	211	27.4	207	103
2/22/07	5:34	Z4LA-62	1788.63	1547.9	140	202	28.6	230	31.2	228	114

Table C6. Pesticide concentrations in Zone 4 Line A samples, WY 2007. All units are in pg/L. ND – concentration was below detection limit. R = data was rejected. NS = analyte not analyzed in this sample.

Date	Time	Sample	t-DDTs	DDD(o,p')	DDE(o,p')	DDT(o,p')	DDD(p,p')	DDE(p,p')	DDT(p,p')	t-Chlordanes	Chlordane, alpha-	Chlordane, gamma-	Nonachlor, cis-	Nonachlor, trans-	Heptachlor	Heptachlor epoxide	Oxychlordane
				9.1-27	7.3-15	12-35	15-45	9.4-19	16-49		6.4-32	5.5-28	15-52	6.9-34	2.9-6.4	2.4-4.3	11-30
2/8/07	14:56	Z4LA-41	21,571	990	571	1,480	3,020	7,590	7,920	12,247	3,670	4,140	1,310	2,790	105	156	76
2/8/07	18:42	Z4LA-42	10,223	445	257	811	1,250	3,670	3,790	13,320	4,110	4,660	1,400	2,910	82	109	49
2/9/07	6:18	Z4LA-43	7,420	400	241	569	1,180	2,630	2,400	6,351	1,980	2,180	669	1,370	41	73	38
2/22/07	4:05	Z4LA-60	10,694	798	198	458	3,440	2,350	3,450	3,787	1,110	1,160	437	932	28	77	43
2/22/07	4:37	Z4LA-61	59,480	3,780	1,690	2,710	15,700	18,700	16,900	16,400	4,730	5,170	1,960	4,050	98	249	143
2/22/07	5:32	Z4LA-62	8,750	475	220	585	1,690	2,930	2,850	3,471	1,040	1,090	383	801	25	94	38
2/22/07	5:34	Z4LA-62	8,306	435	213	558	1,520	2,580	3,000	3,466	1,040	1,100	362	822	26	82	34

Date	Time	Sample	t-HCHs	HCH, alpha	HCH, beta	HCH, delta	HCH, gamma		Aldrin	Dacthal	Dieldrin	Endosulfan I	Endosulfan II	Endosulfan sulfate	Endrin	Hexachlorobenzene	Mirex	Oxadiazon
				3.6-5.9	5.4-9.1	2.9-4.2	4.2-6.9		3.6-9	0.4-0.6	3.9-12	16-37	44-67	18-63	5.2-15	0.7-1.3	1.5-6.4	3.3-8
2/8/07	14:56	Z4LA-41	543	180	76	R	287		R	7,550	1,760	370	653	505	152	898	44	81,400
2/8/07	18:42	Z4LA-42	486	162	58	R	266		R	4,920	1,280	234	352	365	80	583	28	88,200
2/9/07	6:18	Z4LA-43	405	126	58	R	221		R	4,570	845	R	R	314	72	264	13	61,400
2/22/07	4:05	Z4LA-60	300	128	52	R	120		R	2,000	824	215	R	279	104	292	25	615
2/22/07	4:37	Z4LA-61	891	299	267	20	305		R	6,690	4,590	480	1,130	708	378	774	70	57,700
2/22/07	5:32	Z4LA-62	510	217	86	R	207		R	5,030	776	199	R	258	96	295	22	23,100
2/22/07	5:34	Z4LA-62	515	219	91	R	205		R	4,650	711	218	R	238	78	302	12	32,400