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Concentrations and Loads of Mercury, PCBs and PBDEs in the Lower Guadalupe River, San Jose, California: Water Years 2003, 2004, and 2005

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CONCENTRATIONS AND LOADS OF MERCURY, PCBs, AND PBDEs IN THE LOWER GUADALUPE RIVER, SAN JOSE, CALIFORNIA:

WATER YEARS 2003, 2004, AND 2005.

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EXECUTIVE SUMMARY

This report summarizes and interprets mercury concentration data collected in Guadalupe River water during the winter seasons of Water Years 2003, 2004 and 2005. Our objective is to describe concentration variability between years and to estimate loads. Discharge during the three years was 111%, 96%, and 133% of the 1971 - 2000 average (55 Mm^3). Each year was marked by a differing number of storms and storm magnitudes. Water Year 2003 had fewer but higher magnitude storms of higher than Water Years 2004 and 2005. Water Year 2005 have the greatest number of storms but these were mostly in response to smaller low intensity rainfall events. Total mercury concentrations ranged between 178-18,673 ng/L in Water Year 2003, the detection limit and 1,419 ng/L in Water Year 2004, and 4-1,916 ng/L in Water Year 2005. Flow-weighted-mean-concentrations for suspended sediment were 204 mg/L, 191 mg/L, and 79 mg/L in Water Year 2003, 2004, and 2005 respectively. Similarly total mercury concentrations also decreased during the three years from 2,190 ng/L in the first year to 140 ng/L in Water Year 2005.Variation between years was a function of climatic forcing – we have no evidence there is a downward trend in the system. In WY 2005 dissolved mercury concentrations on average accounted for 3% of total mercury or conversely, particulate mercury on average accounted for 97% of total mercury transported in the water column. Total methylmercury concentrations measured in discrete samples during WY 2005 varied from 0.06 - 1.89 ng/L and exhibited a FWMC of 0.49 ng/L. Mercury concentrations in the bedload sediments of Guadalupe River ranged between 0.03 and 1.8 mg/kg (median of eight samples) and increased with decreasing grainsize. Water-column total mercury load varied between years in relation to climatic forcing. Loads were 116 ± 36 kg, 15 ± 4.5 kg, and 8 ± 2.5 kg in Water Years 2003, 2004, and 2005 respectively. Methylmercury load was 0.04 kg (0.5% of the total mercury load) in Water year 2005 and total mercury transported along the bed (bedload mercury) accounted for an additional 0.08 kg (1%). Our data support the hypotheses that methylmercury is sourced from in-channel production during low flow periods and that the majority of total mercury transported in the system is derived from out of channel sources in the historic New Almaden Mining District when rainfall intensity exceeds 30 mm in a 6-hour period. Other mercury sources such as runoff and channel erosion in the urban areas, atmospheric deposition, and channel erosion in tributaries adjacent to the historic mines appear to be subordinate. The development of a calibrated hydrological model would improve our interpretation of the existing data and would help to prioritize for implementation actions aimed at reducing particulate mercury concentrations and mercury loads.

Over the three years of study, total polychlorinated biphenyl (tPCB) concentrations ranged from 0.7 to 122.7 ng/l, with the maximum concentration measured on October 19, 2004. In all samples hexa-, hepta-, and octa-chlorobiphenyls comprised approximately 39 to 76% of tPCB concentrations. WY 2005 marked the beginning of polybrominated diphenyl ether (PBDE) measurements in Guadalupe River water samples. Total PBDE concentrations varied from 15.3 to 370.3 ng/l, with the maximum concentration measured on December 7, 2004. In all samples, BDE 209 comprised 31 to 65% of tPBDE concentrations. Elevated contaminant concentrations were generally associated with high discharge and suspended sediment concentrations. However, WY 2005 was characterized by a breakdown in this relationship. The complexities of the

Guadalupe River system exerted themselves during WY 2005 causing an increased separation of rising and falling stage tPCB concentrations compared to previous years. Likewise, tPBDE concentrations exhibited a considerable separation between rising and falling stage samples. Separate rising and falling stage regressions were therefore used in developing WY 2005 tPCB and tPBDE load estimates. Loads of tPCBs were 1.2 ± 0.3 kg, 0.7 ± 0.2 kg, and 0.7 ± 0.2 kg in Water Years 2003, 2004, and 2005 respectively. A total load of 2.3 ± 0.8 kg tPBDEs was estimated for WY 2005 (approximately 3x the PCB loads).

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SECTION ONE

CONCENTRATIONS AND LOADS OF MERCURY IN THE LOWER GUADALUPE RIVER: WATER YEARS 2003, 2004, AND 2005

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INTRODUCTION

Fluvial systems including rivers and engineered urban stormwater conveyance systems transmit mercury from watersheds to coastal waters. There, the mercury can bioaccumulate in the food web and cause direct harm to biota (Davis et al. 2003) and harm to humans through seafood consumption (Ratcliffe et al., 1996). Estuaries are particularly susceptible to enhanced mercury bioaccumulation because of they often have long flushing times, sediment and associated mercury deposition, and high biological productivity. Sources of mercury to watersheds and estuaries are well documented and include a wide variety of commercial and industrial uses (DTSC, 2000), atmospheric sources (Steding et al., 2002), and mining sources (Tetra Tech, 2003; Domagalski et al., 2004). In America, and in many other developed counties, the largest historic uses of mercury (batteries, paint, and lighting) have been banned or reduced substantially and mining has largely ceased (DTSC, 2000). Although mercury use in the urban environment is decreasing, mercury associated with legacy use is stored in urban soils and riverine and estuarine sediments. In some cases, legacy stores of mercury are permanently buried or in some other way confined. However, ongoing development of the coastal zone and its watersheds can disturb soils or alter the hydrology and geomorphology of riverine and estuarine systems and release this mercury to the biosphere. The source, process and rate of release, and form (dissolved, particulate, inorganic or organic [methyl]) can influence biological and human impacts.

Engineering channels by hardening (bed and bank stabilization), straightening, widening, or introducing biological elements can have a variety of impacts on mercury release and transport in the biosphere. Channel hardening and straightening (can include vegetation removal) reduces complexity, changes channel gradient, and improves transmission of water and sediment. These changes could conceptually reduce mercury storage and increase transport through a river reach. There could also be a reduction in mercury methylation if areas where methylation formerly took place are engineered out of the system (slow, wet, vegetated, anoxic areas with organic carbon and sulfate or biogenic sulfate production). In contrast, channel widening and the introduction of biological elements may increase the storage of mercury if a new floodplain forms inside the channel as the river trends towards a new geomorphic equilibrium. This could potentially create an environment suitable for mercury methylation. In addition to local effects on mercury processes, channel engineering could potentially impact the magnitude and timing of mercury load and forms of mercury entering an estuary or coastal water body downstream. In addition, continuing developments in the watershed might change future water and sediment supply and channel function with a concomitant change in mercury processes. Overall, the net change to mercury in a river reach in response to channel engineering projects is location specific and difficult to predict.

Dissolved, particulate, inorganic and methyl forms of mercury transport in the water column of various types of river systems is well documented (urban: Mason and Sullivan, 1998; mining: Ganguli et al., 2000; agricultural: Balogh et al., 2003; forested: Grigal, 2002). However, we are not aware of a single study on the transport of mercury in bedload. The influence of human modifications to river channel systems on mercury

release and transformation is not well documented. Although there have been some of studies on the influences of reservoirs on river systems (Schetagne et al., 2000; Waldron et al., 2000), we are not aware of any studies that have documented the influence of channel engineering on mercury transport. Channel modifications are likely to influence bedload transport of sediment and mercury and could also influence the magnitude and forms of mercury transport on a site specific basis. In addition, the maintenance of the new channel design might involve sediment removal and also influence sediment and mercury transport processes.

San Francisco Bay is an urbanized estuary contaminated with mercury derived from legacy mining sources and legacy and ongoing urban sources (Johnson and Looker, 2003). Water and sediment transport in its tributary river systems has been altered substantially by land use and channel engineering and floodplains have been drained and channelized with efficient networks of pipes and ditches. The Guadalupe River, a tributary entering the southern part of San Francisco Bay transmits water, sediment and mercury from the largest city in the Bay Area (San Jose) and mercury associated with releases historic and ongoing from the historic New Almaden Mining District. The flood control channel through San Jose was built in the 1960s and roughly follows the former Guadalupe River channel. The Santa Clara Valley Water District and the U.S. Army Corps on Engineers are modifying the channel through downtown San Jose in phases to meet modern drainage and aesthetic needs. There are concerns that changes to the channel during each phase of the project might induce changes in mercury bioavailability and transport.

The objective of this study is to provide baseline data on the concentrations, forms, and transport of mercury in water and suspended and bedload sediments. This data set can be used in the future to determine system response as the new channel matures and responds to future project phases that include changes to channel configuration in other upstream reaches. The data set can also be used to determine changes in suspended and bed sediment mercury loads in response to land use and management outside the main channels. The study also provides a new and unique data set on mercury and methylmercury transport in a system impacted by both mining and urban mercury sources.

METHODS

Sampling and Analysis of Suspended Sediments

Water sampling was carried out over the winter months of Water Years 2003, 2004, and 2005 (Note that a Water Year (WY) in the United States begins October 1st and ends September 30th and is designated by the end date). All sampling was carried out at the United States Geological Survey (USGS) flow gauge, Guadalupe River at Highway (Hwy) 101 (gauge number 11169025) (Figure 1-1). The gauge is approximately 100 m upstream from Hwy 101 and is located under the San Jose International Airport rental car return bridge. The area upstream from the gauge is 414 km^2. The sum of the areas upstream from the Calero, Almaden, Guadalupe, and Vasona Reservoirs amounts to 178 km^2, leaving a 236 km^2 watershed available for production of flood runoff and supply of

sediment and mercury to the channel. At the USGS gauge, the river channel has a modified trapezoidal form to accommodate the maximum probable flood. The channel is approximately 36 m wide at water level and 64 m wide at the top of the 8 m banks (Figure 1-2). The low flow channel occupied a 10 m width on the right bank side of a central bridge pillar for the whole period. The location is ideal for water sampling; there is airport security, streetlight, and the bridge has a wide footpath and railing that provides a safe area to sample and make observations from.

Our hypothesis going into the study was that SSC and mercury would correlate with turbidity. This would provide a less expensive method for estimating water column mercury concentrations rather than collecting and analyzing 100s of samples for mercury analysis each year. As such, during the three WYs, a Forest Technology Systems Limited (FTS) model DTS-12 turbidity sensor equipped with an optical wiper was installed in the thalweg using a depth-proportional boom (Eads & Thomas, 1983) (Figure 1-3). The boom and sensor were anchored to the streambed and protected from impacts by a pre-existing block of concrete immediately upstream from the boom. Between WYs, the sensor was returned to the factory for a 6-point calibration in formazin standards and a firmware update. This combination of deployment methodology and maintenance helped to ensure high quality data and >99.99% data return. A Design Analyses Assoc. Inc. data logger and pressure transducer (model H350-XL) in the gauge house at the top of the left (west) bank of the river communicates with the turbidity sensor every 15 minutes via wiring housed inside a 1 inch galvanized pipe that runs down the left bank and across the low in-channel floodplain. The 15-minute turbidity data along with water stage height data are posted on the Internet real-time via the USGS web site (USGS, 2005) so that study participants can determine the best sampling strategy for suspended sediments and mercury. During site visits, field crews removed larger organic debris that occasionally lodged on the floats, cleaned the sensor optics with a mild detergent and toothbrush, and periodically compared the sensor measurements to grab samples taken near the sensor and measured for turbidity with a Hach 2100P portable turbidimeter (widely considered a standard device for field measurements).

Water sampling for analysis of suspended sediment concentration (SSC) and grain size was accomplished by the USGS using methods outlined in Guy (1969), Knott (1993), and Edwards and Glysson (1999). Briefly a cable winch or “b-reel” and a permanently attached D-74 depth-integrating sampler was deployed from the bridge railing during river stages beyond a safe level for wading and used to collect a single vertical in the thalweg. In addition, the variability of SSC in the cross-section was determined by deployment of a D-74 at multiple points from the bridge footpath using a four-wheel boom truck and a cable-and-reel system. These methods ensure samples represent the average SSC in the cross section even during periods of rapid flow. During wading stages, a US DH-48 hand-held depth-integrating sampler was used in the low flow cross-section under the bridge. Analysis of SSC and grain size was carried out at the USGS laboratory in Marina, California. During WY 2003, a total of 238 water samples were analyzed for SSC (gravimetrically after filtration through 0.45 micron filter) and four samples were analyzed for grain size distribution (sieve-pipette method) (for method

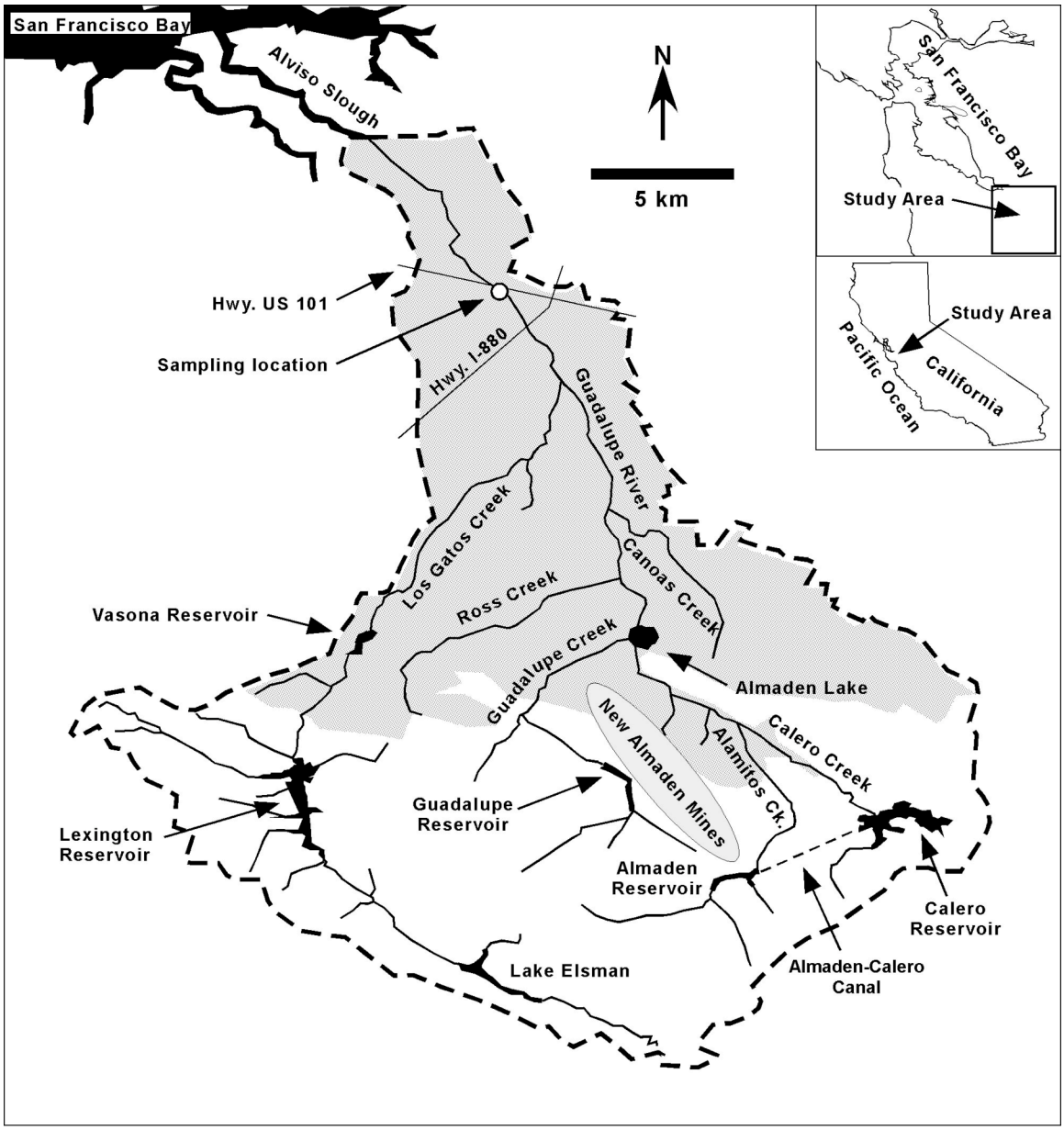

Figure 1-1. Study location map. Grey area indicate urbanized lower watershed.

details see Guy, 1969). During WY 2004, a total of 226 water samples were analyzed for SSC and six samples were analyzed for grain size distribution. During WY 2005, a total of 121 water samples were analyzed for SSC and 12 samples were analyzed for grain size distribution. The SSC data were combined with the turbidity data using LOESS fit (Cleveland, 1979) to estimate a continuous 15-minute SSC record. The continuous record was then adjusted for variation in the cross-section by the USGS using standard protocols. The USGS published the daily record for WY 2003 (Smithson, et al., 2004) and for WY 2004 (Webster et al., 2005).

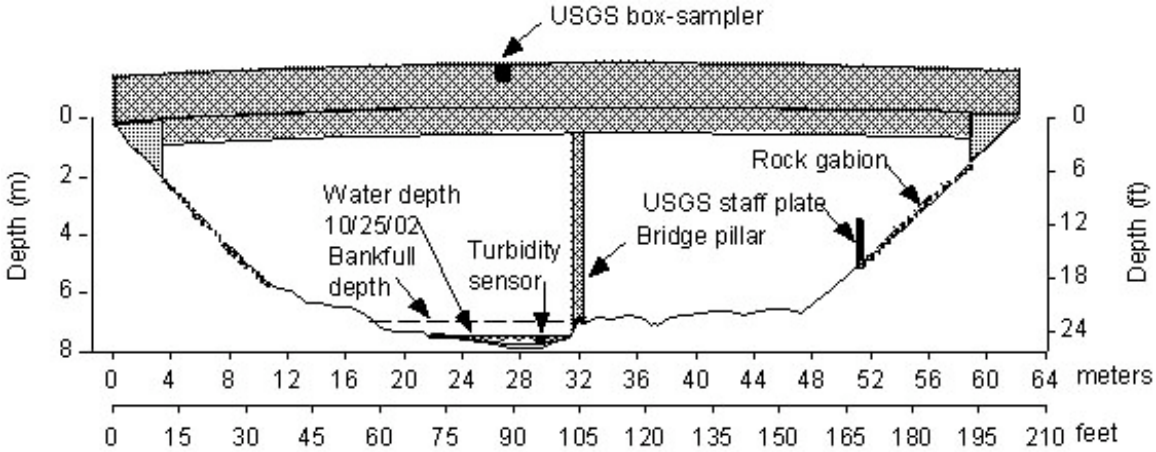

Figure 1-2. Channel form at the sampling location under the rental car return bridge at the San Jose International airport.

Figure 1-3. Forest Technology Systems Limited (FTS) model DTS-12 turbidity sensor equipped with an optical wiper installed in the thalweg using a depth-proportional boom.

Water Sampling for Mercury and Organic Carbon

Water samples for analysis of water chemistry were collected in the thalweg within 1 m of the turbidity probe using clean-hands protocols (Bloom, 1995). During WY 2003, samples were collected by a specially designed dip-sampler consisting of a sample-rinsed sample bottle cup attached to a 12 m long fiberglass pole. During non-wading stage, the dip-sampler loaded with a sampling bottle was passed into the water column near the turbidity sensor achieving a depth of 0.5 - 1.5 m below water surface depending on flow conditions (Note that the water column is about 1 m deep at low flow). This was done because the D-95 sampling equipment was held up at the manufacturer. Using turbidity as a surrogate, we tested the variation of SSC in both the vertical and the horizontal directions and found that the dip-sampling method was without bias and accurate within 2% of the turbidity measured from the D-74 depth-integrating sampler. Thus we concluded that the water samples during our first year of sampling were adequately representative of the entire water column near the probe. During WY 2004 and 2005 a trace element clean D-95 depth-integrating sampler (that utilizes laboratory trace element cleaned Teflon components) was deployed in a single vertical within 1 meter of the turbidity sensor using a b-reel from a four-wheel-boom-truck (Figure 1-4). At wading stages during both WYs, samples were taken by hand dipping at approximately mid-depth directly under the bridge in the deepest portion of the stream within 1 m of the turbidity probe. Unlike SSC, for mercury analysis, it was only necessary to get a representative sample from a single vertical; adjustment for variation across the channel was completed using SSC as a surrogate. All samples were discretely labeled, placed on ice, and transported to the laboratory for preservation and analysis.

Bed Sediment Sampling for Bed Sediment Loads and Mercury Analysis

Bed sediment samples were collected using a BL-84 bedload sampler (Figure 1-5). USGS protocols for total sediment daily loads were followed when collecting samples for analysis of bedload and grainsize distribution. Briefly, a sample was taken at even intervals across the active channel at a given stage height. The sampler was deployed by lowering to just above the water surface and then dropping it fast through the water column until it was resting on the bed. The time on the bottom was recorded as were the number of sampling stations to get the total time of deployment for each composite sample. Samples were taken in pairs (one pass across the river and one pass back). Laboratory analysis on five sample pairs was carried out the USGS laboratory in Marina, California. Daily bedloads were estimated using USGS standards protocols and provided to SFEI. Samples for bedload Hg analysis were taken in the same manner except the sampler was only deployed in the thalweg. To our knowledge, this methodology has never been used in any other river system. Therefore, in order to check the method for potential contamination associated with using a metallic sampler (lined only with sheet plastic taped in place), a single grab sample was taken during low flow. We found no differences between the grab sample and samples taken with the bedload sampler confirming our sampling methodology was robust.

Figure 1-4. D-95 depth-integrating sampler, b-reel, and four-wheel-boom-truck.

Figure 1-5. BL-84 bedload sampler with a sediment sample ready for retrieval.

Laboratory Analysis of Mercury and Organic Carbon

Water samples were analyzed for total mercury (HgT), dissolved mercury (HgD), total methylmercury (MeHgT) and dissolved methylmercury (MeHgD) by Moss Landing Marine Laboratory (MLML), Moss Landing, California. Particulate mercury (HgP) was calculated by difference (HgT – HgD = HgP). Particulate methylmercury was also calculated by difference (MeHgT – MeHgD = MeHgP). Total organic carbon (TOC) and dissolved organic carbon (DOC) were analyzed by Applied Marine Sciences Inc, League City, Texas. POC was calculated by difference (TOC-DOC = POC).

Upon receipt at the labs (commonly within 36 hours), mercury samples were preserved with a final concentration of 0.5% v/v bromine monochloride (BrCl) and MeHg samples with 0.5% v/v hydrochloric acid . During WY 2004 and 2005, prior to preservation, each sample was given a trace clean Teflon stir bar and placed on a magnetic stir plate. Aliquots were pipetted out of the homogenous sample for HgT and HgD. During WY 2005 samples were also aliquoted for MeHgT and MeHgD. Dissolved samples were filtered using acid-cleaned Nalgene 0.45 micron Filter Units. When samples were received after the 48 hour hold time, no dissolved fractions were aliquoted. Hg samples were analyzed with cold vapor atomic fluorescence following U.S. EPA method 1631e (U.S.E.P.A., 2002). A sample size of 30 mL was used and complete digestion of the Hg associated with sediment particles was ensured by colorimetric addition of BrCl. MeHg samples were analyzed with cold vapor atomic fluorescence following U.S. EPA method 1630 (U.S.E.P.A., 1998). A sample size of 80 mL was distilled. A volatile methyl-ethylmercury derivative was created, then purged with nitrogen and collected for thermal desorption and analysis.

Bed sediment samples were analyzed for total mercury on eight grainsize fractions. Samples were received at the laboratory in a refrigerated state and then were fractioned in the laboratory using polycarbonate sieves with nylon mesh and deionized rinse water. Each size class, with the exception of <63µm, was aliquoted immediately into digestion vials, then dried overnight at approximately 80°C. The smallest size class was allowed to settle for up to 2 days, then the sediment was pipetted into the digestion vial. This was again allowed to settle, the supernatant pipetted out, and any remaining liquid evaporated overnight at 80°C. Material obtained from this three step process was homogenized and prepared for analysis. Sediment Hg samples were analyzed by SOP-CALFED.D16. Samples were digested with aqua regia prior to analysis. Mercuric ions were reduced to Hg^0 with $SnCl_2$ and total mercury was quantified by atomic absorption using a Perkin-Elmer flow injection mercury analyzer. DOC and POC water samples were refrigerated at 4°C in the dark until analysis. DOC and POC were analyzed by catalytic combustion using U.S. EPA method 415.1 (USEPA., 1983).

Mercury Analysis Quality Assurance

The Hg and MeHg analysis methods were chosen to ensure the expected concentrations were beyond the method detection limits (MDL). Dissolved MeHg (collected only in WY 2005) concentrations were closest to the detection limit with 2% of the data below the detection limit (MDL) of 0.02 ng/L and 35% of the data <3x the MDL.

In the case of HgT, one sample taken during base flow was below MDL, however 87% of the samples collected over all WY recorded Hg concentrations >250x the MDL. Relative percent difference (RPD), calculated as the difference in concentration of a pair of analytical duplicates divided by the average of the duplicates was within the target range of ±25% with the exception of one batch for Hg that was marginally outside the desirable range (Table 1-1). Samples in this batch were flagged as potential outliers but did not appear anomalous when compared to other Hg or SSC data. The seven field replicates yielded RPDs for Hg of 7.0 – 21.5%. The percent recoveries for standard reference materials were within the target range (75 – 125% for Hg, 70 – 130% for MeHg). The percent recoveries for matrix spikes were within the target range (75 - 125% for Hg, 70 – 130% for MeHg) (Table 1-1). The quality assurance samples included three method blanks for each analytical batch of Hg and MeHg analyses. MeHg field blanks were <MDL, however Hg field blanks were 0.25 – 6.5 ng/L. This highest field blank went via a complex route to get to our lab and therefore likely represents a worst case scenario, whereas the others detected were less than 3x MDL.

The sediment Hg analysis method was chosen to ensure the expected concentrations were beyond the method detection limits (MDL). Eighty percent of sediment Hg concentrations were >10x the MDL (0.006 µg/g dry). Two samples were below MDL: one from the largest size class (>3.8 mm), the other from the second smallest class (>63 µm) which had low mass of material obtained for analysis. Relative percent difference was within the target range of ±25% with the exception of two batches. The analytical duplication for these two batches was performed on larger size class (>250 µm) samples which often vary widely in Hg concentration. The percent recoveries for standard reference materials for all batches were within the target range (75 - 125%), as were those for matrix spikes. The quality assurance samples included three method blanks for each analytical batch.

Table 1-1. Quality Control parameters for mercury and methylmercury analyzed in this study.

Water Year	Substances Analyzed	Detection Limit (MDL) (ng/L)	Relative Percent Difference (RPD) ±25% (±30% MeHg)	Percent Recovery of Standard Reference Material ±25% (±30% MeHg)	Percent Recovery of Matrix Spike ±25% (±30% MeHg)	Method Blank	Field Blank (µg/L)
2003	**Total Mercury**	0.2	2.0 – 21.5	85 – 110	79 - 119	<MDL	6.5
2004	**Total Mercury**	0.16	4.5 - 26.4	92 - 124	86 - 122	<MDL	-
2005	**Total & Dissolved Mercury**	0.16	1.9 - 18.5	80 - 108	90 - 108	<MDL	0.25 - 0.3
	Total & Dissolved Methylmercury	0.02	0.8 - 15.6	88 - 109	87 - 107	<MDL	<MDL
	Sediment Mercury	0.006 µg/g	1.3 - 182	105 - 118	84 - 111	<MDL	NA

Loads Calculations

Suspended Sediment

Loads of each analyte were calculated for the winter months of WY 2003, 2004, and 2005 using the concentration data collected during this study and 15-minute discharge data provided by the USGS. An ideal sampling protocol would characterize analyte concentrations at a time interval that approaches environmental variability especially during storm events when most of the load is transported. In reality however, this is cost prohibitive – samples only represent a snapshot in time. Concentrations between snapshots are estimated using surrogates such as discharge or turbidity or various methods of mathematical interpolation. In this study, suspended sediment loads were determined by combining the 15-minute SSC estimates derived from turbidity measurements with 15-minute discharge. The estimate of suspended sediment load is considered very accurate because the sampling regime was at a time interval sufficient to characterize almost all variability in concentrations. The method used to calculate loads of each mercury form differed depending largely on individual relationships with SSC and are less accurate than the estimate of suspended sediment load.

Total Mercury

The calculation of HgT load was challenging because of the complex patterns of source, release, and transport from contaminated areas in and adjacent to the historic New Almaden Mining District. The data were stratified based on the predominant source of runoff ("lower urban" versus "upper non-urban") and two regression relationships were developed. In fact, the upper non-urban part of the hydrograph rarely if ever consisted of solely upper watershed runoff but was a varying mixture of the waning stages of urban runoff and the rising and falling stages upper watershed runoff, but for the sake of distinction we have adopted this terminology. Loads were calculated by combining 15-minite discharge with concentrations determined using the *lower urban* regressions for the first 7 hours of each runoff event and combining 15-minute discharge with concentrations determined using the *upper non-urban* regressions for the remainder of each runoff event and during base flow. For some storm events the method was modified to take into account the variation in runoff source and routing when rainfall began sometimes 2-3 hours earlier in the upper watershed or when multiple rises in stage occurred in quick succession. Thus, the 7-hour period when the *lower urban* regression was applied was the default used for the 7-hour rise unless there was evidence to apply the *upper non-urban* regression. The evidence included rainfall distribution, intensity, and timing and sometimes very subtle changes in turbidity/SSC that indicated a new source of water had just arrived at our sampling location.

On the rising and falling stages of most storms, mercury showed a positive regression relationship with SSC. However, a third stratum was also identified that was associated with certain rainfall intensities and antecedent rainfall conditions (McKee et al., 2004; McKee et al., 2005). During periods when rainfall intensity in the historic New Almaden Mining District exceeded 40 - 60 mm in a 6-hour period and/or rainfall in a 24-hour period exceeded 100 mm, Hg concentrations were observed in excess of 2 µg/L and showed an inverse relationship with SSC on the falling stage of the flood hydrograph. As

the season progressed, the rainfall intensity required to cause high Hg concentrations at our sampling location decreased to 25 - 30 mm. During these periods, Hg concentrations were estimated between samples using a combination of regression and linear interpolation guided by changes in SSC relative to discharge, and knowledge of rainfall distribution and timing. These "hypothesized new mercury-release conditions" (explained in detail by McKee et al., 2004 and McKee et al., 2005) were met during WY 2003 but not during WYs 2004 or 2005 when rainfall intensity was always <60 mm in a 6-hour period.

In these ways rainfall distribution and timing in addition to subtle changes in turbidity/SSC relative to discharge were used to make confident decisions on the best method of interpolation that was superior and went beyond the simple application of mathematical interpolation methodologies. Mercury concentrations estimated in these ways were then combined with 15-minite discharges to calculate loads that were then summed for each month and each wet season of each WY. An example of the calculations for one of the complex storms is provided in appendix B of McKee et al. (2005).

Total Methylmercury

MeHgT data were available for WY 2005 only. The calculation of MeHgT loads completed by developing a relationship between SSC and MeHgT. The equation of this relationship was then used to estimate continuous MeHgT concentrations for the entire wet season. Concentrations during the first two floods did not conform to this relationship. Concentrations were estimated for these floods using linear interpolation between samples based upon MeHgT/SSC ratios.

Bedload Total mercury

Total mercury loads moving along the bed were estimated by combining sediment bedloads, sediment grainsize, and mercury concentrations on each grainsize. Three factors confounded the estimate: 1. The USGS does not report bedloads in each grainsize fraction so these had to be estimated by apportioning the total annual load into each grainsize based on the percentage of mass in each grainsize; 2. The USGS did not report grain sizes <0.5 mm yet we know there is HgT variation on small grain sizes; 3. We did not measure HgT concentrations on grain sizes >4 mm. Although these factors undoubtedly influence the HgT load estimate, we are certainly better off than if we had had no grainsize data for bed sediment loads and only measured HgT on bulk sediment. If we did not have grainsize data and only HgT on bulk sediment, we would have underestimated bed sediment Hg loads because the majority of Hg in transported in on fine sediment material; both factors would have caused an unpredictable low bias in load calculations.

Error Estimates

The total error was estimated using the reasonable maximum error associated with each source of uncertainty in our analyses and calculations. Errors accounted for during

loads estimation were discharge (±10%), suspended sediment (±2%), variation of HgT in the cross section (±10%), and interpolation / SSC-mercury regressions (±10%). The coefficient of variation (CV) of duplicate field samples ranged from 5-25% for HgT and from 3-15% for MeHgT. We chose to set the error associated with the determination of HgT and MeHgT concentrations at a given time to the maximum CV to remain on the conservative side. Total errors for loads calculations were SSC: ±15%; HgT: ±31%; MeHgT: ±24%.

Errors associated with daily sediment bedload provided by the USGS are not reported however, it seems reasonable that errors would be at least double those of suspended sediment (±30%). No duplicate analyses were completed for bed sediment concentrations in each grainsize. In the absence of better information, we will assume a CV of ±50%. Therefore, the total error associated with mercury bedloads is estimated at ±58%.

RESULTS AND DISCUSSION

Discharge during WY 2003 was 111% of the 1971 - 2000 average (55 Mm^3). The majority of runoff occurred during December 2002 when flow for the largest storm of the year peaked at 172 m^3/s at 9:00 on December 16th (Figure 1-6a). Patterns of SSC virtually mimicked discharge however a first flush effect was evident. The term "first flush" is used to describe a pattern of highest suspended sediment concentrations relative to discharge in the first large storm of the year compared to other storms with similar or even greater discharge. SSC peaked during the first storm series of the season on November 7th at 22:15 at 1,366 mg/L and reached only 1,152 mg/L at 10 am on December 16th despite a greater discharge (Figure 1-6b). Discharge during our second year of study (WY 2004) was 96% of average (Figure 1-6c). Compared to WY 2003, the WY 2004 was typified by a greater number of smaller storms. Discharge peaked at 124 m^3/s at 14:00 on January 1st with a suspended sediment peak 1 hour later of 905 mg/L (Figure 1-6d). The first flush effect was also evident in the second year of study. SSC reached a peak of 1,117 mg/L on November 9th at 0:15 during the first flood of the season. Discharge during WY 2005 was 133% of average. In a similar fashion to WY 2004, WY 2005 was also typified by many small storms (Figure 1-6e). Discharge peaked at 112 m^3/s at 15:30 on October 19th with a suspended sediment peak of 1,160 mg/L 3 hours earlier associated with the urban runoff peak (Figure 1-6f). The first flush effect was also evident in the third year of study. Despite annual discharge being greatest among the three WYs during WY 2005, peak flow was the least, and overall there were many storms but mostly of a lower magnitude than encountered in the other two WYs. Therefore overall, in WY 2005, there was less energy during any one storm to mobilize sediment, a fact that is reflected in a much lower suspended sediment flow-weighted-mean concentration (79 mg/L) (Table 1-2).

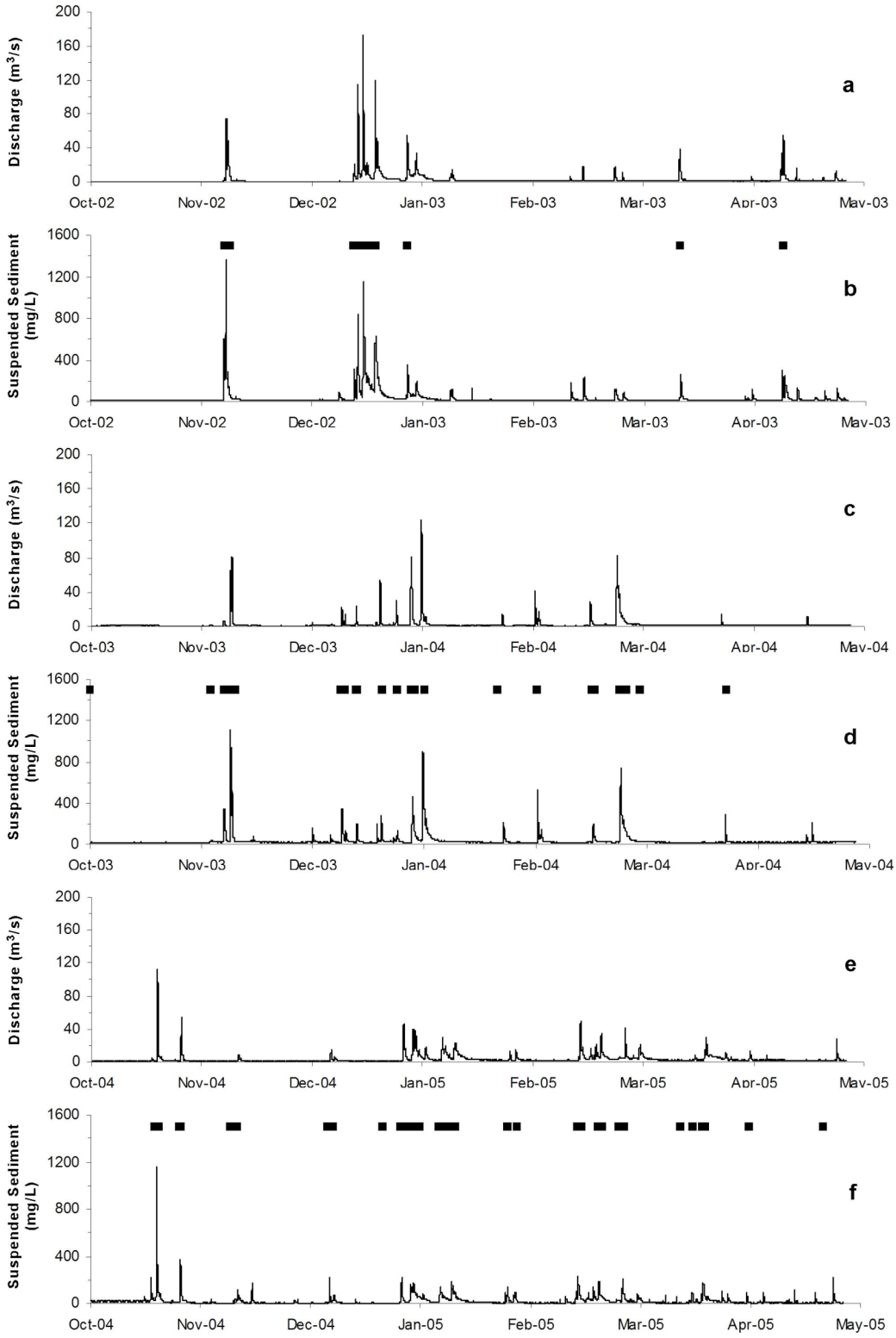

Figure 1-6. Discharge, suspended sediment concentration and total mercury sampling periods (black bars and dots) during Water Year 2003 (a, b), 2004 (c, d), and 2005 (e, f).

Table 1-2. Mercury and organic carbon concentrations during each Water Year.

	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)
WY 2003							
Minimum	17	MDL	1.8	178	-	-	-
Maximum	1,148	4.3	8.9	18,673	-	-	-
Mean	394	1.1	5.1	3,579	-	-	-
Median	321	0.7	5.3	2,116	-	-	-
FWMC	204	2.3	5.3	2,190	-	-	-
Number	25	16	20	25	-	-	-
WY 2004							
Minimum	18	0.1	0.9	MDL	-	-	-
Maximum	970	3.7	18.3	1,419	-	-	-
Mean	220	0.9	5.3	359	-	-	-
Median	150	0.7	4.4	251	-	-	-
FWMC	191	1.0	5.9	329	-	-	-
Number	40	40	40	37	-	-	-
WY 2005							
Minimum	6	0.1	1.0	4	0.93	0.06	0.04
Maximum	720	3.7	11.5	1,916	12.20	1.89	0.15
Mean	130	0.7	4.3	222	4.77	0.69	0.07
Median	96	0.4	4.0	128	4.39	0.58	0.08
FWMC	79	0.90	4.3	140	4.71	0.49	0.08
Number	52	43	44	52	44	42	42

Dissolved organic carbon (DOC) concentrations over the three WYs ranged from 0.9 – 18.3 mg/L (Table 1-2). DOC concentrations were greatest during the first flood of the year but similar between years if the data from the first flush (data only available during WY 2004 and 2005) are excluded. Particulate organic carbon (POC) concentrations ranged from 0.1 - 4.3 mg/L and were similar between years. POC concentrations did not appear to show any consistent relationship to discharge or SSC and peaked each WY during flood flow but were not greatest during the first flush. With the exception of the sample taken at 6:25 am on 12/14/03 and the sample taken on 12/07/04 at 2:20 am POC concentrations measured in discrete samples were always less than DOC concentrations. The percentage of suspended sediment that was organic (%POC) ranged between 0.02 - 12.22% and systematically decreased with increasing SSC. Overall, the organic carbon data suggest that the Guadalupe River watershed has low POC concentrations and typical DOC concentrations when compared to other mixed land use watersheds that are described in the literature on environmental mercury (e.g. Mason and Sullivan, 1998).

Total mercury concentration varied considerably depending on climatic differences between floods and between years. Peak concentrations occurred in WY

2003, when the largest floods occurred in response to higher rainfall during individual storms and higher rainfall intensity (Figure 1-7). Median HgT concentrations (based on discrete samples) also decreased from WY 2003 to WY 2005 in response to climatic forcing (Table 1-2). Despite annual and wet season discharge during WY 2005 being the greatest among the years sampled, median, mean, and flow-weighted mean HgT concentrations were least. This reflects lower energy for transport during smaller peak floods and the numerous small floods throughout the season that were responsible for most of the transport. These observations further support previous hypotheses that greater rainfall intensity is responsible for soil erosion and transport of mercury out of the historic mining areas (McKee et al., 2004, 2005). In WY 2005 when HgD was measured, dissolved concentrations on average accounted for 3% of HgT or conversely, HgP on average accounted for 97% of HgT. These observations are consistent with many other studies (e.g. Lawson et al., 2001) and reflect the strong affinity of mercury to organic and particulate matter, and the climatic mechanisms of release (soil, bed, and bank erosion associated with rainfall and runoff).

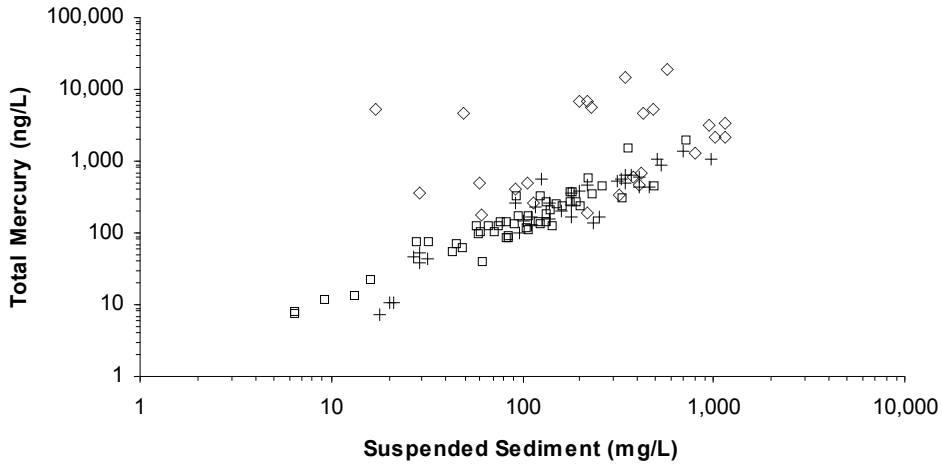

Figure 1-7. Total Hg concentrations in relation to suspended sediment concentrations in the Guadalupe River at Highway 101 during the wet seasons of Water Years 2003, 2004, and 2005. Water Year 2003 (◊); Water Year 2004 (+); Water Year 2005 ().

MeHgT concentrations measured in discrete samples during WY 2005 varied from 0.06 - 1.89 ng/L and exhibited a FWMC of 0.49 ng/L (calculated as total load divided by total discharge) (Table 1-2). MeHgT concentrations peaked during the first floods of the wet season in WY 2005 and followed clockwise hysteresis patterns in a similar manner to suspended sediment concentrations during the first two floods (Figure 1-8a). Particulate methylmercury concentrations were greater during lower discharge conditions (Figure 1-8b) and the percentage of HgT that is MeHgT decreases with

increasing HgT concentration supporting a hypothesis that methylmercury is mainly derived from within channels and is supply limited during winter storms. These observations are similar to those by Mason and Sullivan (1998) on the Anacostia River and by Lawson et al. (2001) for the Potomac River and Herring Run. Mason and Sullivan suggested that this is caused by more efficient MeHg production at low flow, flushing of MeHg enriched sediments in high flows and the supply of inorganic Hg to the river during storms without a concurrent supply of MeHg. Overall MeHgT concentrations accounted for 0.4% of the mercury transport in the Guadalupe River. This appears to be lesser than observed by other authors for mixed land use systems (e.g. 0.6-4.5% Lawson et al., 2001; 3.5-10.8 Balogh et al., 2003) and perhaps more typical of mining impacted systems where HgT concentrations are much greater (e.g. Ganguli et al., 2000; Rytuba 2003).

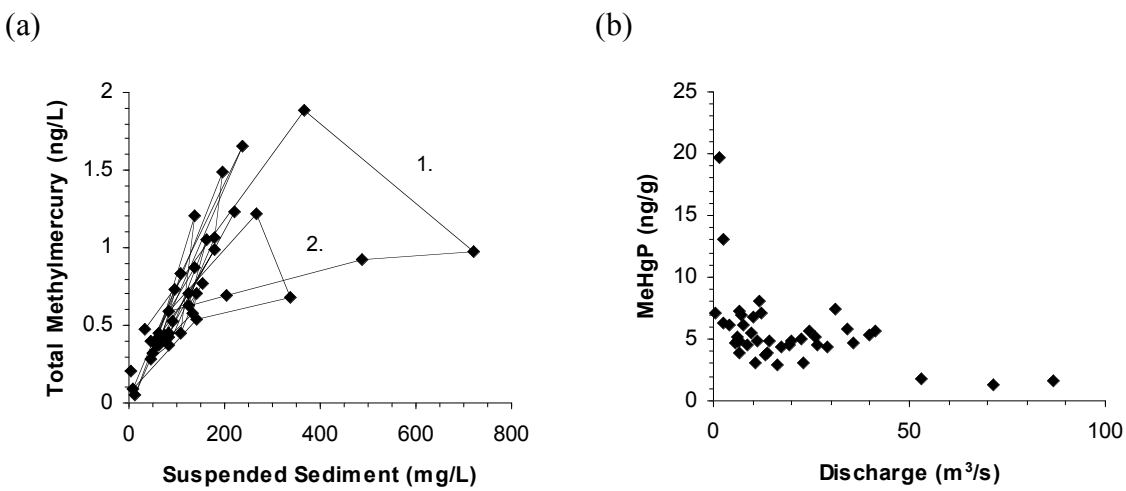

Figure 1-8. Methylmercury concentrations in the Guadalupe River at High 101 during Water Year 2005. Annotation: (a) 1. First flush; (a) 2. Second flood of the winter season.

A partition coefficient (K_d) is a measure of the affinity of a metal to sediment where greater log K_d indicates stronger affinity. Partition coefficients were estimated using equations (1) and (2) below (e.g. Ganguli et al., 2000; Lawson et al., 2001). Partition coefficients for total mercury ranged between 5.1 - 6.1 where the greatest affinity to suspended sediments occurred during low flow conditions (Figure 1-9). Partition coefficients for MeHgT were less than those for HgT and ranged between 4.2 - 5.4 (Figure 1-9). Methylmercury also appeared to have a stronger affinity to suspended

$$K_d\ (HgT) = HgP\ (mg/kg)\ /\ HgD\ (mg/L) \quad (1)$$

$$K_d\ (MeHgT) = MeHgP\ (mg/kg)\ /\ MeHgD\ (mg/L) \quad (2)$$

sediments during low flow. The range observed in the Guadalupe River at Hwy 101 falls within the range observed in other systems (Mason and Sullivan, 1998; Ganguli et al., 2000; Lawson et al., 2001; Lawson and Mason, 2001). Ganguli et al. (2000) also observed K_d (HgT) > K_d (MeHgT) in a mine impacted system whereas in other systems the distinction is less obvious or the reverse. However, it is uncommon for K_d to decrease in a single system in relation to increasing discharge, and the opposite has been observed (e.g. Hurley et al., 1998). We suggest that this happens in the Guadalupe River because of an increase in dissolved Hg entering 1st order tributary creeks during low flow periods from ground water or more likely mine adits in the historic Mining District. Once in the surface fluvial system, this dissolved mercury very quickly partitions onto fine grained sediment or colloidal materials and is transported in suspension downstream. With just a single year of data for particulate and dissolved mercury it is difficult to be sure of the upstream processes occurring.

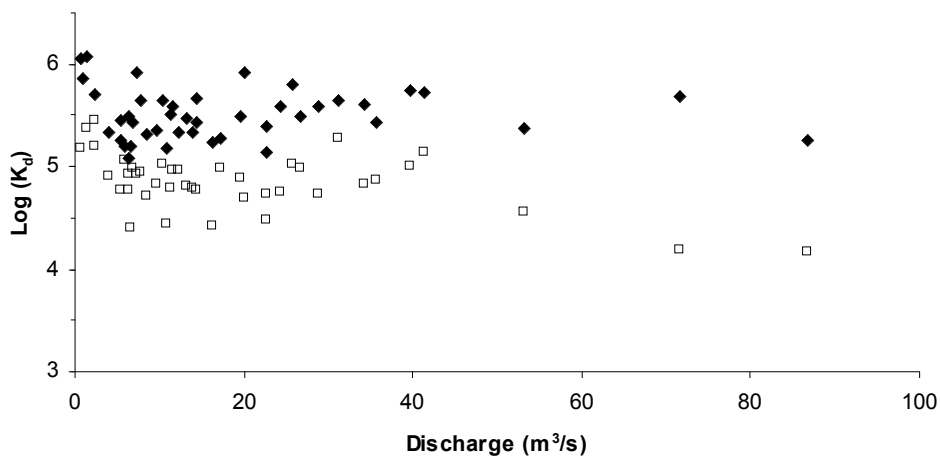

Figure 1-9. Partition coefficients for total mercury and methylmercury calculated with data gathered during Water Year 2005. Total mercury (♦); Total methylmercury (□).

During WY 2005, bed sediment was mobilized when flow exceeded 24 m^3/s (approximately 1 m above base flow). Mercury concentrations in the bedload sediments of Guadalupe River ranged between 0.03 and 1.8 mg/kg (median of eight samples) (Figure 1-10). Median concentrations generally increased with decreasing grainsize however, there was much variation in the data for a given grainsize. For example, concentrations in the >0.25 mm fraction ranged between 0.26 - 0.51 mg/kg with the exception of one sample that had a concentration of 13.2 mg/kg. Concentrations in the <0.625 mm fraction ranged between 0.8 - 2.9 mg/kg. We propose the variability is associated with the transport of grains of enriched sediment derived from bed and bank

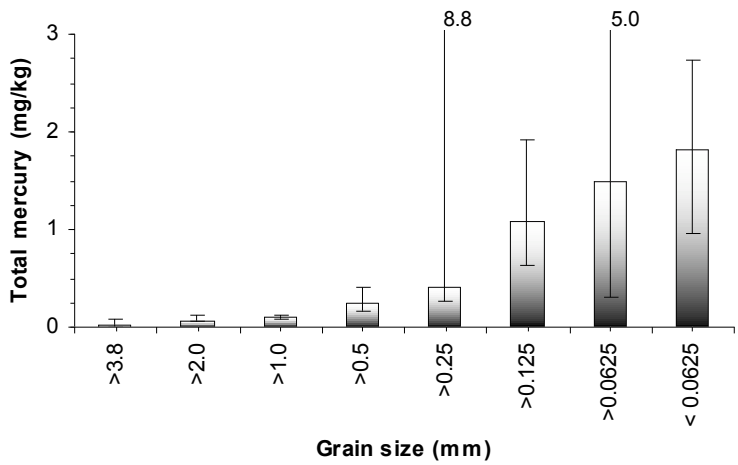

Figure 1-10. Median, 5 percentile, and 95 percentile total mercury concentrations in bedload sediment in relation to grainsize estimated from 8 samples.

erosion of calcrete calcine deposits in the Alamitos Creek tributary or other mine related debris (perhaps even grains of cinnabar that are heterogeneously mixed with sediment derived from other less contaminated sources. Mercury concentrations in the fine fraction of bedload sediments (<0.0625 mm) most closely matched water-column HgP concentrations normalized to suspended sediment concentrations that ranged between 0.6 - 4.1 mg/kg during WY 2005. This is consistent with the fact that >90% of the suspended sediment in Guadalupe River during floods has a grainsize <0.0625 mm.

Water-column total mercury load varied between years in relation to climatic forcing (Figure 1-11). The highest annual load of the study period occurred during WY 2003 when peak discharge was the greatest and when peak rainfall intensity was the greatest. Loads were lowest during WY 2005 due to storm events with relatively low discharge and rainfall intensity despite a large number of storms. Total methylmercury load was 0.04 kg during WY 2005 (the only year it was measured). Overall, about 0.08 kg or 1% of the total mercury load was transported along the bed during WY 2005 (Table 1-3). Normalized to the area below the reservoirs, these water column HgT loads are equivalent to 492, 64, and 34 $\mu g/m^2/yr$ respectively and the MeHgT load is equivalent to 0.17 $\mu g/m^2/yr$ (Table 1-4).

The export of HgT from the Guadalupe River exceeds all the watersheds reviewed (Table 1-4). Generally the watershed exports of Hg range between 0.3 - 8.5 $\mu g/m^2/yr$, a conclusion not dissimilar to that made in a previous review (Grigal, 2002); 75% of the observations in Grigal's review range between 1 - 3 $\mu g/m^2yr$. The high export from the Anacostia River was likely due to a history of industrialization in addition to atmospheric deposition (Mason and Sullivan, 1998; Lawson et al., 2001). The high export associated with Changchum is likely a result of the combustion of oil and coal in urban areas for heating, and inputs from industrial and medical facilities (Fang et al., 2004). The study of

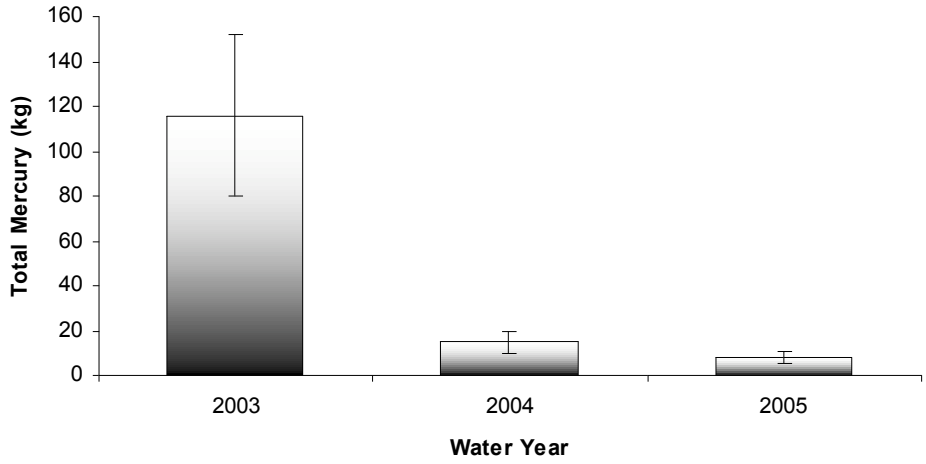

Figure 1-11. Total water column mercury loads in the Guadalupe River at Highway 101.

Table 1-3. Total bedload concentrations and load estimates for the Guadalupe River during Water Year 2005.

	Grainsize (mm)								Total
	<0.5	<1	<2	<4	<8	<16	<32	<64	
Percent Finer Than (%)	1.0	6.0	15	30.5	50.5	74.5	98	100	
Bedload Sediment Transport (t)	15	75	136	234	302	362	355	30	1,509
Mercury (mg/kg)	0.42	0.24	0.094	0.058	0.029	0.029	0.029	0.029	
Bedload Mercury Transport (g)	6	18	13	14	9	10	10	1	80±46

Cache Creek (Domagalski et al., 2004), a historic Hg mining area in the Coast Range of California occurred during two dry years. WY 2000 sustained a flow of just 55% of the mean annual runoff for that basin. The Hg export from Cache Creek for a year of average flow would likely be much greater than double the export reported by Domagalski et al. (2004) for WY 2000. Even so, perhaps the Guadalupe River exhibits one of the highest river exports of HgT in the world to our knowledge and certainly higher than most other watersheds with mixed land uses of open space, urban, and agricultural land uses. Note that this conclusion would remain true even if we normalized the loads to the entire watershed area upstream of our sampling locations (rather than removing the area upstream from the reservoirs from the calculation). The export of MeHgT in the Guadalupe River at Hwy 101 also appears to fall at the higher end of observations in other watersheds (Table 1-4). We presently have no explanation for this observation but speculate it might also be the result of the mining influence.

Table 1-4. Mercury exports in selected watersheds of other parts of the world. Note that the estimates for the Guadalupe were made by normalizing with the area downstream of the reservoirs (236 km^2) rather than the whole watershed area upstream from our sampling location (414 km^2). It is not clear if the effects of reservoirs have been accounted for in the other studies.

Reference	Watershed	Land Use	Drainage Area (km^2)	Total Mercury ($\mu g/m^2/yr$)	Methylmercury ($\mu g/m^2/yr$)
This study	Guadalupe WY 2003	Hg mining, urban	236	492	
This study	Guadalupe WY 2004		236	64	
This study	Guadalupe WY 2004		236	34	0.17
Domagalski et al. (2004)	Cache, USA WY 2000	Hg mining	2,893	4.3	
	Cache, USA WY 2001		2,893	1.6	
		Urban, agriculture, open			0.06
Lawson et al. (2001)	Potomac, USA		72,000	8.50	
		Agriculture, open, urban			0.03
	Susquehanna, USA		29,900	1.35	
		Open, agriculture, urban			0.15
	Rappahannock, USA		4,130	3.35	
	Anacostia, USA	?	340	22.21	0.16
		Agriculture, open, urban			0.12
	Choptank, USA		292	3.35	
	Blacklick Run, USA	?	6	6.94	0.04
	Herring Run, USA	100% urban	6	4.77	0.08
	Herrington Cr., USA	?	3	3.96	0.08
Fang et al. (2004)	Changchum NE China	Industrial urban	158	24.05	-
Balogh et al. (1998)	Minnesota 1995	Agriculture, open, urban	44,000	1.4	-
	Minnesota 1996		44,000	0.97	-
		Open, agriculture, urban			-
	Headwater Mississippi, USA 1995		51,500	0.51	
	Headwater Mississippi, USA 1996		51,500	0.46	-
		Open, agriculture, urban			-
	St Croix, USA 1995		20,000	0.43	
	St Croix, USA 1996		20,000	0.52	-
Balogh et al. (2005)	St Peter, USA 2000	Mixed	40,145	0.61	-
	St Peter, USA 2001		40,145	2.2	0.041
	Judson, USA 2000	Mixed	29,526	0.26	-
	Judson, USA 2001		29,526	1.2	0.036
	Blue Earth, USA 2000	Mixed	6,294	0.87	-
	Blue Earth, USA 2001		6,294	5.4	0.071
	Le Sueur 2000	Mixed	2,849	3.4	-
	Le Sueur 2001		2,849	6.4	0.09
	Anoka, USA 2002	Mixed	45,440	0.64	0.069
	Anoka, USA 2003		45,440	0.35	0.033
	Rum, USA 2003	Mixed	3,522	0.58	0.066

Sampling during the Guadalupe River study presented here was specifically tailored to provide data for the use of the turbidity surrogate interpolation method for loads estimation. It is extremely important to match sampling design with loads calculation methodology. There are other sampling designs and interpolation methods that could have been used to estimate concentrations between "snapshot samples" in order to estimate loads. For example, a flow-weighted mean concentration (FWMC) could have been calculated from our discrete samples for each year and multiplied with wet season or annual discharge to estimate loads. However, the sampling regime was heavily biased to floods during all sampling years, thus loads would be over estimated using the FWMC interpolation methodology. This situation would have been slightly improved by grouping the data and applying several FWMCs to several flow periods however, the estimated loads would still have been biased high because of the sampling design. Linear interpolation could have been use to estimate concentrations between samples for generating loads; however, again, the flood-focused sampling design was not well suited to this method because during some floods, only a single concentration data point was available and often a base flow sample before and after a flood was not taken. A flood-focused sampling design was chosen because our interest was primarily loads calculations and because traveling to the sampling site each day for the several days after a flood in addition to routine sampling during dry periods was cost prohibitive. The flood-focused sampling design is well suited to the use of turbidity as a surrogate measure and is most accurate if loads generation is the primary end point because >90% of the annual loads occurs during floods. However, such a sampling design prohibits the use of simple averaging or interpolative estimators during loads calculation.

Mercury is a known bio-toxin and as such there are various EPA criterions that may be applicable for helping to assess the overall health of the Guadalupe River at Hwy 101. Mercury concentrations in the Guadalupe River watershed are elevated with regard to U.S. EPA drinking water standards (2 µg/L: USEPA, 2002) and near continuously (during the entire wet season October 1st to April 30th) exceed the U.S. EPA chronic aquatic life water standard (12 ng/L; USEPA 1999). In addition, the EPA also suggests a 4-day average criterion of 770 for ng/L and a 1-hour criterion of 1,400 ng/L. In WY 2003, the 1-hour criteria was equaled or exceeded 582 times and the 4-day criteria was equaled or exceeded 57 times. In WY 2004, the 1-hour criteria was equaled or exceeded once and the 4-day criteria was never equaled or exceeded. In WY 2005, the 1-hour criteria was equaled or exceeded 4 times and the 4-day criteria was never equaled or exceeded. It is interesting to note that the majority of the load is particulate and inorganic and only 0.4% is methylmercury. Inorganic mercury is not immediately bioavailable and must go through bacterially mediated transformation processes before becoming bioavailable to higher level trophic organisms. Therefore, upon entering San Francisco Bay, the majority of mercury derived from the Guadalupe River watershed may not be immediately bioavailable to wildlife of concern and humans. Overall the Guadalupe River watershed provides about 18% of the annual mercury load to San Francisco Bay and is an area of management focus. A total maximum daily load (TMDL) report is presently being completed by the Santa Clara Valley Water District (SCVWD), the San Francisco Bay Regional Water Quality Control Board, (RWQCB), and other local

partners. When completed, the report will contain the rationale for biological and human linkages and recommendations for reducing loads and improving water quality.

Conceptually, mercury transported past the Hwy 101 sampling location is derived from a variety of sources. Sources include rainout from the atmosphere, erosion and transport of mining wastes from the 1st and 2nd order tributaries in the historic New Almaden Mining District, release from reservoirs, erosion and transport of bed and bank sediments in Guadalupe Creek and Alamitos Creek, and in Guadalupe River, and transport of mercury used in urban areas in urban runoff. In previous reports (McKee et al., 2004; McKee et al., 2005), we presented evidence that largely discounted mercury release from reservoirs as a large source to the lower Guadalupe River. It was also recognized that mercury concentrations on a particle basis were greater on falling stages of floods when the majority of runoff is derived from the upper watershed. This helped to support the hypothesis that urban runoff, although an important and perhaps a more constant annual supply of mercury to the River, is a subordinate source during moderate and higher rainfall years and over the longer term. In addition, erosion from in-channel bed and bank sediments although undoubtedly occurring, was also ruled out as the dominant source due to our observations of elevated mercury concentrations late on the falling stages. During falling stages of floods, channel re-deposition would be occurring rather than bed and bank erosion. These same arguments are valid for the subordinate role of channel modifications in the downtown area as a supply of mercury to the lower River during floods. However, it is possible that excavations during base flow may have caused small increases in turbidity with related small releases of mercury and it is possible that as new channel configurations mature, environments suitable for methylation may form. Overall, it appears that sources of mercury in the upper watershed are supplying the majority of mercury transported past our sampling location at Hwy 101.

Release of mercury in the upper watershed from the historic Mining District could occur via landslides directly into tributaries, soil erosion carried in sheet flow, and soluble or micro-colloidal phases transported in interflow and ground water. McKee et al. (2004; 2005) proposed intense rainfall as the dominant mechanism for release of mercury during floods from sources in and adjacent to the Mining District. Intense rainfall could conceivably influence landslide instigation, sheet flow erosion, interflow and ground water flow. Intense rainfall as a driver for release is supported by our most recent observations in WY 2005 (Figure 1-12). Particle concentrations of >8 mg/kg are only associated with rainfall in the Mining District of >30 mm in a 6-hour period. The data also appear to support a conclusion that earlier in the wet season, slightly elevated particle concentrations (3-5 mg/kg) can occur at lower rainfall intensities during the first floods of a wet season. These are associated with urban runoff and might include in-channel bed and back erosion of mercury sourced from the upper watershed but temporarily stored in the channel of the lower Guadalupe River. It could also include erosion of sediment and soils from reaches where channel modifications have recently occurred. Mostly we observe concentrations from 1-2 mg/kg in response to low intensity rainfall (Figure 1-12). The analysis presently here is confounded by the lack of

knowledge on sources of water at the time of each discrete sample. Each sample represents the

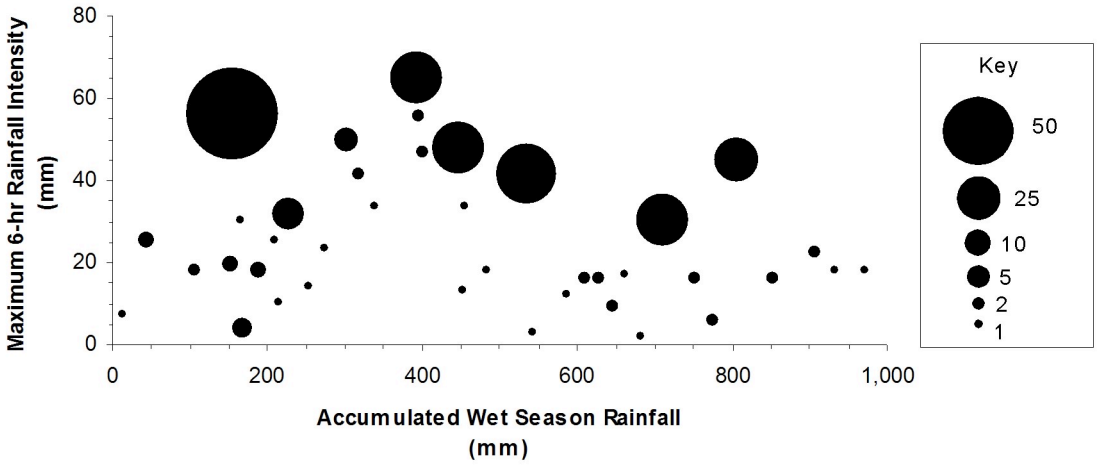

Figure 1-12. The ratio of total mercury to suspended sediment concentration (mg HgT: kg SSC) in relation to accumulated wet season rainfall and rainfall intensity in the historic New Almaden Mining District. Rainfall data from the Almaden RF-4 gauge were provided by the Santa Clara Valley Water District.

integration of water, suspended sediment, and mercury released from multiple source locations in the watershed. A fully-calibrated hydrological model if available would improve our ability to determine sources, estimate loads, and help prioritize management techniques aimed at reducing sediment concentrations, net methylmercury production, and mercury loads in support of the Bay and Guadalupe River mercury TMDLs.

REFERENCES

Balogh, S.J., Meyer, M.L., and Johnson, D.K., 1998. Transport of mercury in three contracting river basins. Environmental Science and Technology 32, 456-462.

Balogh, S.J., Huang, Y., Offerman, H.J., Meyer, M.L., and Johnson, D.K., 2003. Methylmercury in rivers draining cultivated watersheds. The Science of the Total Environment 303, 305-313.

Balogh, S.J., Nollet, Y.H., and Offerman, H.J., 2005. A comparison of total mercury and methylmercury export from various Minnesota watersheds. Science of the Total Environment 340, 261-270.

Bloom N.S., 1995. Mercury as a case study of ultra-clean sample handling and storage in aquatic trace-metal research. Environmental Lab March/April, 20-25.

Cleveland, R.B. (1979) Robust locally weighted regression and smoothing scatterplots. Journal of the American Statistical Association, 74, 829 - 836.

Davis, J., D. Yee, J. Collins, S. Schwarzbach, and S. Luoma, 2003. Potential for Increased Mercury Accumulation in the Estuary Food Web. San Francisco Estuary and Watershed Science, pp. 1 to 8.

Domagalski, J.L., Alpers, C.N., Slotton, D.G., Suchanek, T.H., and Ayers, S.M., 2004. Mercury and methyl mercury concentrations and loads in the Cache Creek watershed, California. Science of the Total Environment 327, 215-237.

DTSC, 2002. Mercury report. Final report of the Department of Toxic Substances Control, Hazardous Waste Management Program, State Regulatory Programs Division, Sacramento, August 2002. 125pp. http://www.dtsc.ca.gov/HazardousWaste/Mercury/HWM_REP_Mercury_Final.pdf

Eads, R. and Thomas, R.B. (1983) Evaluation of a depth proportional intake device for automatic pumping samplers. Water Resources Bulletin 19, 289 - 292.

Edwards, T. K. and Glysson, G. D., 1999. Field methods for measurement of fluvial sediment. Techniques for water-resources investigations of the United States Geological Survey; Book 3, Chapter C2, 89 p.

Fang, F., Wang, Q., and Li, J., 2004. Urban environmental mercury in Changchun, a metropolitan city in northeastern China: source, cycle and fate. Science of the Total Environment 330, 159 - 170.

Ganguli, P.M., Mason, R.P., Abu-Saba, K.E., Anderson, R.S., Flegal, A.R., 2000 Mercury speciation in drainage from the New Idria Mercury Mine, California. Environmental Science and Technology 34, 4773-4779.

Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environmental Reviews 10, 1-39.

Guy, H. P., 1969. Laboratory theory and methods for sediment analysis. Techniques of Water-Resources Investigations, Book 5, Chapter C1, 58pp.

Hurley, J.P., Cowell, S.E., Shafer, M.M., and Hughes, P.E., 1998. Partitioning and transport of total and methyl mercury in the lower Fox River, Wisconsin. Environment, Science and Technology 32, 1424-32.

Johnson W., and Looker R., 2003. Mercury in San Francisco Bay: Total Maximum Daily Loads Report. California Regional Water Quality Control Board San Francisco Bay Region. June 6th 2003.

Knott, J.M., 1993. Quality assurance plan for the collection and processing of sediment data by the U.S. Geological Survey, Water Resources Division. U.S. Geological Survey open-file report; 92 - 499, 18 pp.

Lawson, N.M., Mason, R.P., and Laporte, J-M., 2001. The fate and transport of mercury, methylmercury, and other trace metals in Chesapeake Bay tributaries. Water Research 35, 501 - 515.

Lawson and Mason, 2001. Concentration of mercury, methylmercury, cadmium, lead, arsenic, and selenium in the rain and stream water of two contrasting watersheds in western Maryland. Water Research 35, 4039-4052.

Mason, R.P., and Sullivan, K.A., 1998. Mercury and methyl mercury transport through an urban watershed. Water Resources 32, 321 - 330.

McKee, L., Leatherbarrow, J., Pearce, S., and Davis, J., 2003. A review of urban runoff processes in the Bay Area: Existing knowledge, conceptual models, and monitoring recommendations. A report prepared for the Sources, Pathways and Loading Workgroup of the Regional Monitoring Program for Trace Substances. SFEI Contribution 66. San Francisco Estuary Institute, Oakland, Ca. http://www.sfei.org/rmp/reports/splwg/Urban_runoff_literature~000.pdf

McKee, L., Leatherbarrow, J., Eads, R., and Freeman, L., 2004. Concentrations and loads of PCBs, OC pesticides, and mercury associated with suspended sediments in the lower Guadalupe River, San Jose, California. A Technical Report of the Regional Watershed Program: SFEI Contribution #86. San Francisco Estuary Institute, Oakland, CA. 79pp.

McKee, L., Leatherbarrow, J., and Oram, J., 2005. Concentrations and loads of mercury, PCBs, and OC pesticides in the lower Guadalupe River, San Jose, California: Water Years 2003 and 2004. A Technical Report of the Regional Watershed Program: SFEI Contribution #409. San Francisco Estuary Institute, Oakland, CA. 72pp.

Rattcliffe, H.E., Swanson, G.M., and Fischer, L.J., 1996. Human exposure to mercury: A critical assessment of the evidence of adverse health effects. Journal of Toxicology and Environmental Health 49, 221 - 270.

Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impact. Environmental Geology 43, 326-338.

Schetagne, R., Doyon, J-F., and Fournier, J-J., 2000. Export of mercury downstream from reservoirs. The Science of the Total Environment 260, 135-145.

SCVWD, 2005. Unpublished runoff data for the Guadalupe River. Santa Clara Valley Water District.

Smithson, J.R., Webster, M.D., Pope, G.L., Friebel, J.R., and Freeman, L.A., 2004. Water Resources Data, California, Water Year 2003, Volume 2. Pacific Slope Basins from Arroyo Grande to Oregon State Line except Central Valley. Water-Data Report CA-03-2. Prepared in cooperation with California Department of Water Resources and with other agencies. U.S. Geological Survey, Sacramento, California.

Steding, D. J. and Flegal, A. R., 2002. Mercury concentrations in coastal California precipitation: evidence of local and trans-Pacific fluxes of mercury to North America. Journal of Geophysical Research 107, 11-1 – 11-7.

Tetra Tech, 2003. Guadalupe River Watershed Mercury TMDL Project: Draft Conceptual Model Report, Technical Memorandum 4.1. Prepared for Santa Clara Valley Water District by Tetra Tech Inc., Lafayette, CA. October 2003.

USEPA, 1999. National recommended water quality criteria – Correction. U.S. Environmental Protection Agency, Office of Water, 822-Z-99-001.

USEPA, 2002. List of drinking water contaminants and there maximum contaminant levels. U.S. Environmental Protection Agency, EPA 816-F-02-013. July 2002.

USGS, 2005. Real-time California provisional water data, Guadalupe River at San Jose, Ca 11169025. http://waterdata.usgs.gov/ca/nwis/uv?dd_cd=01&dd_cd=02&dd_cd=13&format=gif&period=31&site_no=11169025

Waldron, M. C., Colman, J. A., and Breault, R. F., 2000. Distribution, hydrologic transport, and cycling of total mercury and methyl mercury in a contaminated river-reservoir-wetland system (Sudbury River, eastern Massachusetts). Canadian Journal of Fisheries and Aquatic Science 57, 1080-1091.

Webster, M.D., Pope, G.L., Friebel, Freeman, L.A., and Brockner, S.J., 2005. Water Resources Data, California, Water Year 2004, Volume 2. Pacific Slope Basins from Arroyo Grande to Oregon State Line except Central Valley. Water-Data Report CA-04-2. Prepared in cooperation with California Department of Water Resources and with other agencies. U.S. Geological Survey, Sacramento, California.

SECTION TWO

CONCENTRATIONS AND LOADS OF PCBS AND PBDES IN THE LOWER GUADALUPE RIVER: WATER YEARS 2003, 2004, AND 2005

John Oram, Jon Leatherbarrow, and Lester McKee

INTRODUCTION

Mass loading of persistent organic contaminants to San Francisco Bay through urban runoff and its impact on water quality is of key concern in developing long-term management plans aimed at attaining water quality standards in the Bay. Legacy contaminants of particular concern are polychlorinated biphenyls (PCBs) and several classes of organochlorine (OC) pesticides for which the Bay is listed as impaired by the Clean Water Act 303(d) list (SWRCB, 2003a). Additionally, much attention has been given to polybrominated diphenyl ethers (PBDEs), an emerging class of organic contaminants which, due to their widespread use, increasing environmental concentrations, and concerns about their potential bioaccumulation, are listed on the State Water Resource Control Board Section 303(d) monitoring list (SWRCB, 2003b).

McKee and Leatherbarrow (2005) estimated loads of PCBs and OC pesticides in the lower Guadalupe River for water years 2003 and 2004. This report builds upon previous work and presents the first analysis of a new PBDE data set.

METHODS

Sample and Data Collection

Thirteen water samples were collected from the sampling location on Guadalupe River at U.S. Highway 101 during water year (WY) 2005. Samples were collected during varying stages of storm events for analysis of PCBs and PBDEs (Figure 2-1C and 2-2C). Concentrations of 38 individual and co-eluting PCB congeners and 40 individual and co-eluting PBDE congeners were measured and summed to derive total PCB (tPCB) and total PBDE (tPBDE) concentrations in water samples (Table 2-1). Samples were also collected for analysis of particulate organic carbon (POC) and dissolved organic carbon (DOC). Additionally, suspended sediment concentrations (SSC) were measured by the U.S. Geological Survey and turbidity data were collected by Redwood Sciences Laboratory, U.S. Department of Agriculture. Methods of data collection for hydrology, POC, DOC, SSC, and contaminants are described in section one of this report.

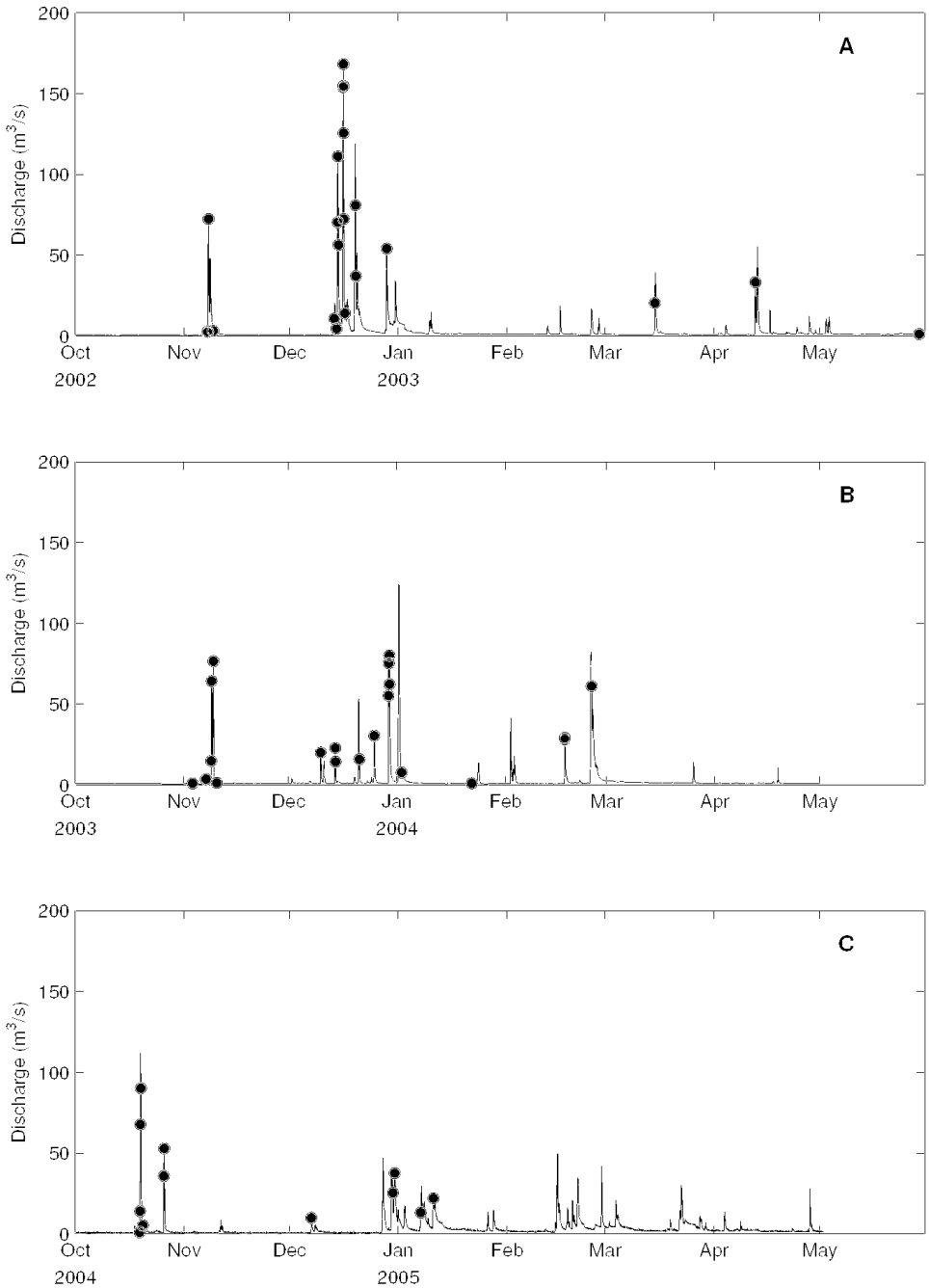

Figure 2-1 Guadalupe River discharge for water years 2003(A), 2004(B), and 2005(C). Data for water years 2003 and 2004 are from McKee and Leatherbarrow (2005).

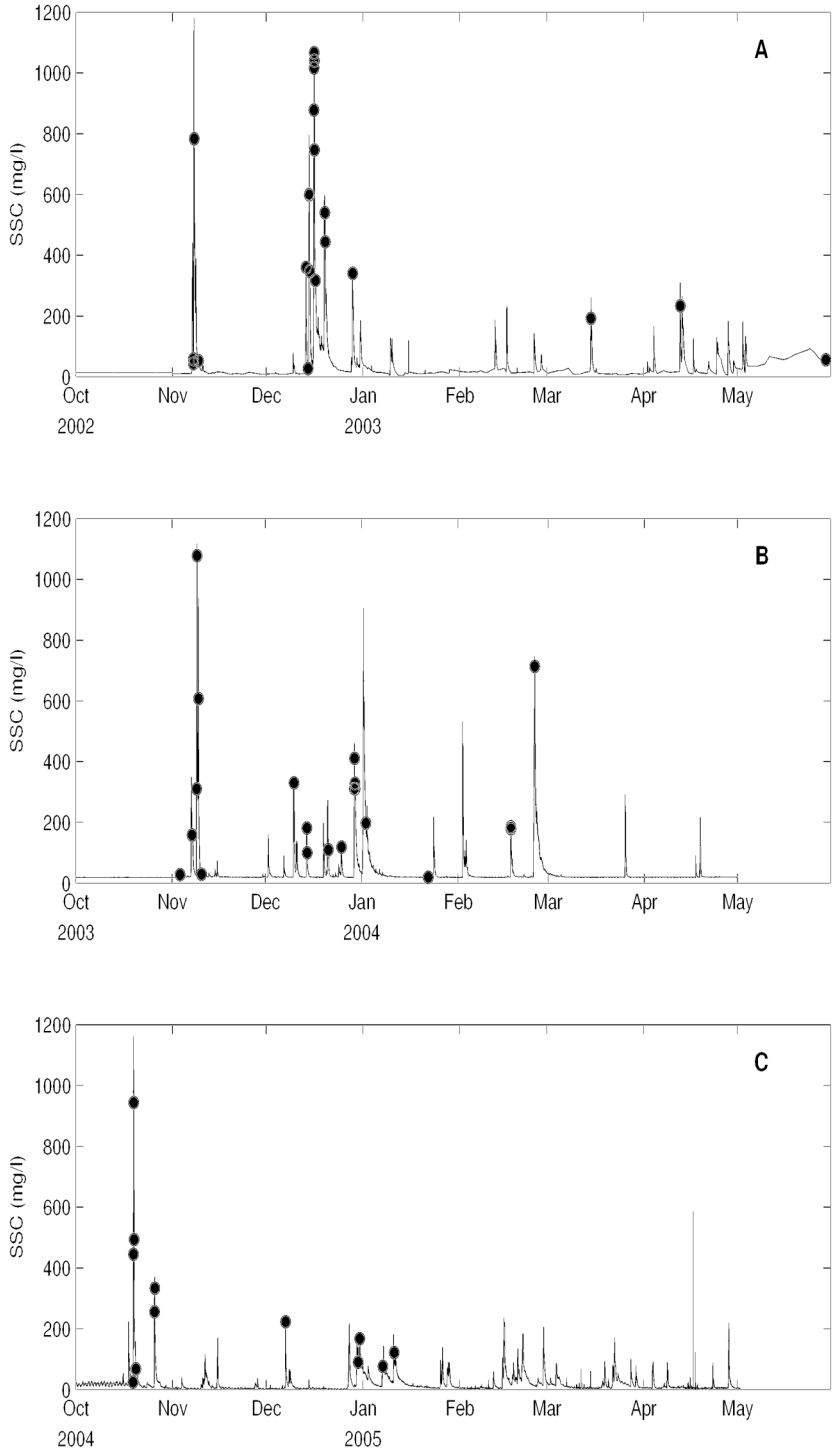

Figure 2-2 Suspended sediment concentration (SSC) in Guadalupe River for water years 2003(A), 2004(B), and 2005(C). Data for water years 2003 and 2004 are from McKee and Leatherbarrow (2005).

Table 2-1 Polychlorinated biphenyl (PCB) and polybrominated diphenyl ether (PBDE) congeners measured in Guadalupe River water samples during water year 2005.

PCBs		PBDEs	
PCB 008	PCB 132	BDE 007	BDE 099
PCB 018 / 030	PCB 138 / 129 / 160 / 163	BDE 008 / 011	BDE 100
PCB 028 / 020	PCB 141	BDE 010	BDE 105
PCB 031	PCB 149 / 147	BDE 012 / 013	BDE 116
PCB 033 / 021	PCB 151 / 135 / 154	BDE 015	BDE 119 / 120
PCB 044 / 047 / 065	PCB 153 / 168	BDE 017 / 025	BDE 126
PCB 049 / 069	PCB 156 / 157	BDE 028 / 033	BDE 128
PCB 052	PCB 158	BDE 030	BDE 138 / 166
PCB 056	PCB 170	BDE 032	BDE 140
PCB 060	PCB 174	BDE 035	BDE 153
PCB 066	PCB 177	BDE 037	BDE 154
PCB 070 / 061 / 074 / 076	PCB 180 / 193	BDE 047	BDE 155
PCB 087 / 086 / 097 / 108 / 119 / 125	PCB 183 / 185	BDE 049	BDE 181
PCB 095 / 093 / 098 / 100 / 102	PCB 187	BDE 051	BDE 183
PCB 099 / 083	PCB 194	BDE 066	BDE 190
PCB 101 / 090 / 113	PCB 195	BDE 071	BDE 203
PCB 105	PCB 201	BDE 075	BDE 206
PCB 110 / 115	PCB 203	BDE 077	BDE 207
PCB 118		BDE 079	BDE 208
PCB 128 / 166		BDE 085	BDE 209

Sample Preparation and Analysis

Trace organic contaminants were analyzed by AXYS Analytical Services Limited, Sidney, British Columbis, Canada. PCBs were analyzed using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS) following EPA method 1668 revision A (USEPA, 1999). PBDEs were analyzed using HRGC/HRMS following AXYS Analytical Services standard operating procedures (AXYS Analytical Services, 2002). Methods of sample preparation and analysis of SSC and organic carbon are described in section of this report.

Quality Assurance and Control

At the time of writing, trace organic water samples collected in water year 2005 have not yet been subject to standard quality assurance and quality control criteria. Quality assurance and quality control procedures will be performed in the near future and will be based on protocols outlined in the RMP Quality Assurance Program Plan (Lowe *et al.*, 1999). See McKee and Leatherbarrow (2005) for QA/QC procedures performed on samples from water years 2003 and 2004.

Load Estimation

Contaminant loads were calculated on 15-minute intervals by relating measured concentrations of PCBs and PBDEs to measurements of stream discharge, turbidity, and SSC. First, LOESS was used to fit SSC measurements and 15-minute turbidity measurements to construct a time series of SSC on a 15-minute time interval from October 1, 2004 to April 30, 2005. Detailed methods are described in McKee *et al.* (2004). USGS standard protocols were used to account for cross-sectional variation in SSC. Second, two linear regressions were established between contaminant concentrations and corresponding SSC; One regression for 'rising' stage samples when water was derived from urban runoff and another for 'falling' stage samples when water

was derived mainly from the upper watershed. The regressions were used to construct a record of contaminant concentrations on a 15-minute time interval over the duration of the study. Finally, contaminant concentrations were multiplied by 15-minute discharge to calculate 15-minute contaminant loads. Contaminant loads were then integrated to derive load estimates on daily, monthly, and seasonal time scales.

Errors in contaminant loads were estimated based on estimates of individual sources of error from data collection, laboratory analysis, and regression analysis. Estimated data collection errors include stream flow measurement (±10%), SSC measurement (±5%), regression of turbidity and SSC (±2%), and cross-sectional variability in SSC (±10%). Errors in laboratory measurements of contaminants were based on analytical accuracy: ±6% for tPCBs and ±6% for tPBDEs. Regression errors were based on the coefficients of determination (see Figure 2-4 and Figure 2-5). Total errors for contaminant loads were estimated by propagation of errors; ±23% for tPCBs; ±34% for tPBDEs.

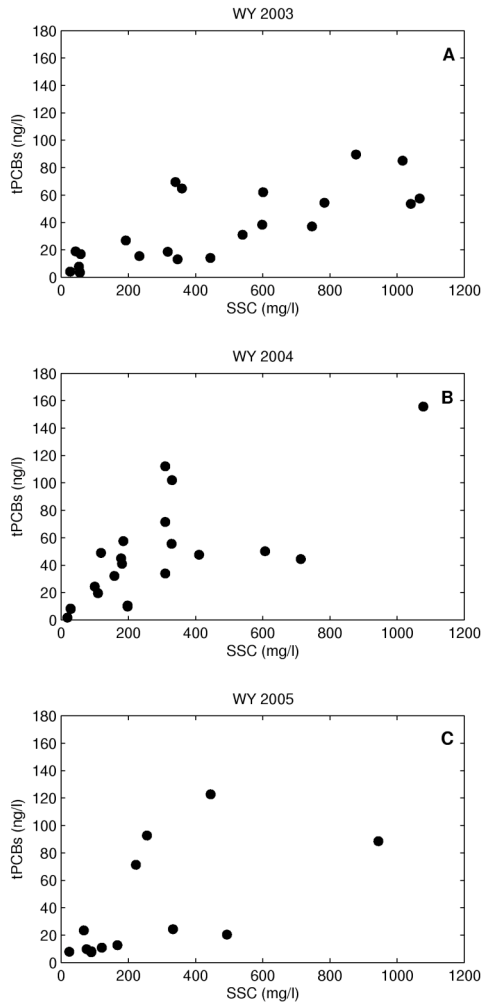

Figure 2-3 Scatter plots of total PCBs and SSC in Guadalupe River water samples taken in water years 2003(A), 2004(B), and 2005(C). Data for water years 2003 and 2004 are from McKee and Leatherbarrow (2005).

RESULTS

Polychlorinated Biphenyls (PCBs)

Total PCB concentrations in WY 2005 water samples ranged from 7.4 to 122.7 ng/l, with a flow-weighted mean concentration of 44.7 ng/l (Table 2-2). The maximum tPCB concentration was observed on October 19, 2004 at 11:05 AM. Discharge and SSC measurements at that time were 709 cfs and 365 mg/l, respectively. The maximum tPCB concentration of 122.7 ng/l was the highest measured in three years of monitoring. In all WY 2005 samples, hexa-, hepta-, and octa-chlorobiphenyls comprised 39 to 76% of tPCB concentrations.

Total PCB concentrations were positively correlated to SSC for both 'rising' and 'falling' stage samples (Figure 2-4). Daily loads of tPCBs ranged from 0.11 to 196.1 g, with the maximum load occurring on January 19, 2005 and comprising approximately 17% of the total WY 2005 load. Monthly loads of tPCBs ranged from 8 to 260 g, with the maximum monthly load occurring in October 2004 and comprising approximately 37% of the total load (Table 2-3). A total load of 712 ± 165 g tPCBs was estimated for WY 2005.

Table 2-2 Summary of hydrology, water quality, and PCB and PBDE concentrations in Guadalupe River water samples for water year 2005.

Site Code	Date	Discharge (cfs)	SSC (mg/l)	POC (mg/l)	DOC (mg/l)	TOC (mg/l)	tPCBs (ng/l)	tPBDEs (ng/l)
GR300	10/19/04 7:57	84	33	1.1	8.5	9.6	7.8	75.1
GR301	10/19/04 11:05	709	365	3.1	11.5	14.6	122.7	221.3
GR302	10/19/04 13:50	2,530	720	3.3	5.6	8.9	88.5	184.0
GR303	10/19/04 16:55	3,060	489	1.5	4.8	6.3	20.3	36.2
GR305	10/20/04 7:30	138	83	0.5	6.1	6.6	23.4	69.4
GR310	10/26/04 6:05	1,020	267	0.6	4.4	5.0	92.7	164.9
GR311	10/26/04 8:05	1,880	339	0.7	3.8	4.5	24.3	47.7
GR341	12/7/04 6:00	367	236	0.5	6.3	6.8	71.3	370.3
GR383	12/30/04 12:30	800	106	0.3	3.4	3.7	8.0	18.3
GR383	Duplicate	--	--	--	--	--	7.4	15.3
GR384	12/30/04 23:59	1,210	185	0.5	3.7	4.2	12.6	38.3
GR401	1/7/05 10:40	403	92	0.4	4.0	4.4	9.8	20.8
GR411	1/11/05 1:07	691	141	1.1	3.3	4.4	10.8	25.9
Range							7.4 - 122.7	15.3 - 370.3
FWMC*							44.7	95.4

* FWMC = flow-weighted mean concentration

Table 2-3 Monthly and seasonal loads of suspended sediment, PCBs, and PBDEs in Guadalupe River for water years 2003, 2004, and 2005. Loads for water years 2003 and 2004 are from McKee and Leatherbarrow (2005).

WY 2003	October	November	December	January	February	March	April	May	Total	Error
Discharge (Mm3)	1.5	5.4	22.8	5.5	3.9	4.0	6.5	3.5	53.1	--
Percent of total (%)	2.8	10.2	42.9	10.4	7.3	7.5	12.2	6.6	--	--
Susp. Sediment (t)	19	1,709	7,661	149	193	245	610	219	10,805	--
Percent of total (%)	0.2	15.8	70.9	1.4	1.8	2.3	5.6	2.0	--	--
tPCBs (g)	16	156	686	66	52	57	103	49	1,185	210 (18%)
Percent of total (%)	1.4	13.2	57.9	5.6	4.4	4.8	8.7	4.1	--	--

WY 2004	October	November	December	January	February	March	April	May	Total	Error
Discharge (Mm3)	2.0	5.4	9.5	7.9	11.0	4.1	2.8	2.6	45.3	--
Percent of total (%)	4.4	11.9	21.0	17.4	24.3	9.1	6.2	5.7	--	--
Susp. Sediment (t)	36	1,824	1,591	2,419	2,401	136	78	93	8,578	--
Percent of total (%)	0.4	21.3	18.5	28.2	28.0	1.6	0.9	1.1	--	--
tPCBs (g)	15	121	138	166	182	34	22	22	700	200 (29%)
Percent of total (%)	2.1	17.3	19.7	23.7	26.0	4.9	3.1	3.1	--	--

WY 2005	October	November	December	January	February	March	April	May	Total	Error
Discharge (Mm3)	6.2	2.2	8.4	12.8	11.4	11.1	5.7	--	58.0	--
Percent of total (%)	10.7	3.7	14.5	22.2	19.6	19.2	9.8	--	--	--
Susp. Sediment (t)	1,928	48	796	639	857	465	186	--	4,918	--
Percent of total (%)	41.3	0.8	15.6	13.3	18.1	8.0	3.0	--	--	--
tPCBs (g)	260	8	98	99	148	63	36	--	712	165 (23%)
Percent of total (%)	36.6	1.1	13.7	13.9	20.8	8.8	5.0	--	--	--
tPBDEs (g)	552	42	325	390	573	286	143	--	2,312	794 (34%)
Percent of total (%)	23.9	1.8	14.1	16.9	24.8	12.4	6.2	--	--	--

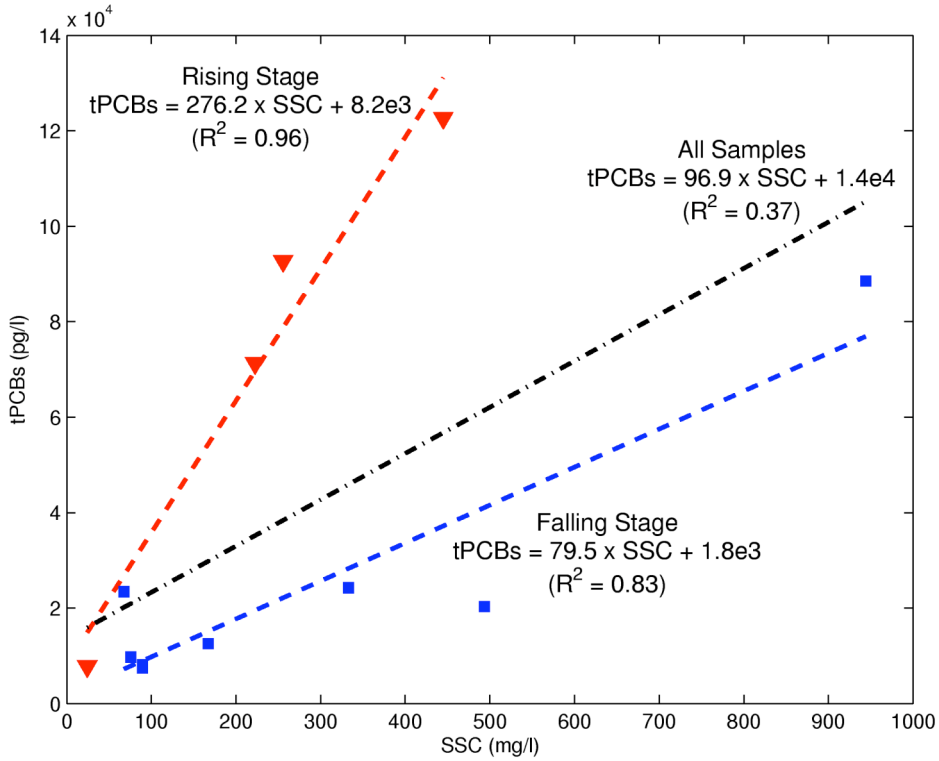

Figure 2-4 Linear regressions of total PCBs as a function of SSC for Guadalupe River water samples taken in water year 2005. Samples were separated according to river stage and spatial patterns of precipitation in order to identify contributions from lower (i.e., urban) and upper (i.e., non-urban) portions of the watershed.

Polybrominated Diphenyl Ethers (PBDEs)

Total PBDE concentrations in WY 2005 water samples ranged from 15.3 to 370.3 ng/l, with a flow-weighted mean concentration of 95.4 ng/l (Table 2-2). The maximum tPBDE concentration was observed December 7, 2004 at 6:00 AM. Discharge and SSC measurements at that time were 367 cfs and 236 mg/l, respectively. In all WY 2005 samples, BDE 209 composed 31 to 65% of tPBDE concentrations.

Total PBDE concentrations were positively correlated to SSC for both 'rising' and 'falling' stage samples (Figure 2-5). Daily loads of tPBDEs ranged from 0.58 to 365.2 g, with the maximum load occurring on January 19, 2005 and comprising approximately 16% of the total WY 2005 load. Monthly loads of tPBDEs ranged from 42 to 552 g, with the maximum monthly load occurring in October 2004 and comprising approximately 24% of the total load (Table 2-3). A total load of 2,312 ± 794 g tPBDEs was estimated for WY 2005.

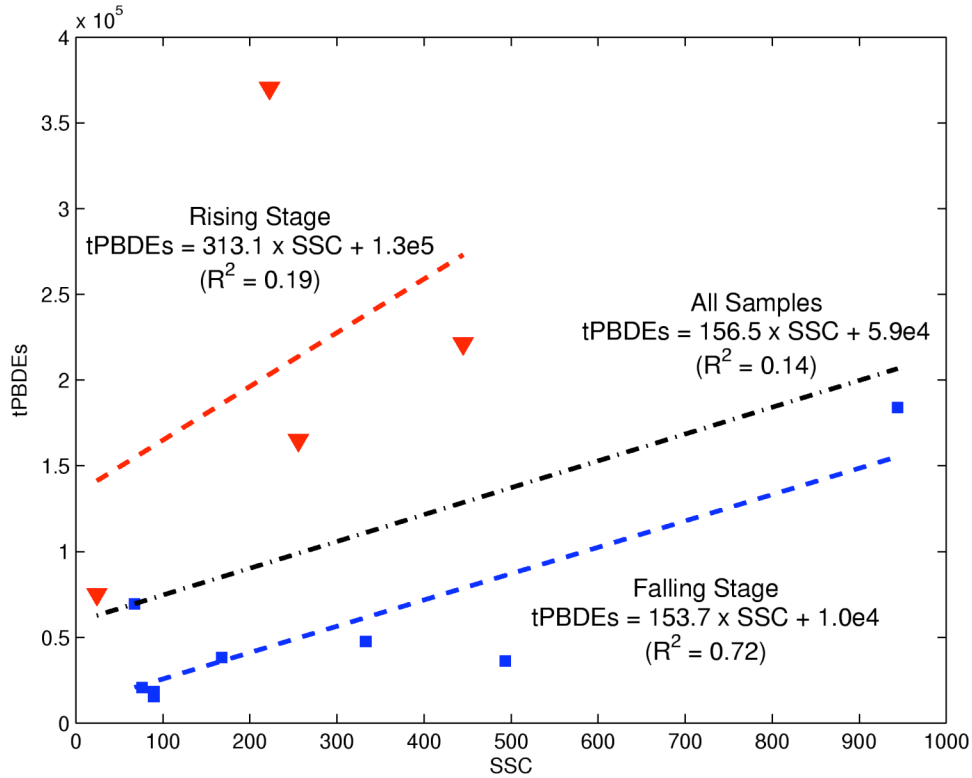

Figure 2-5 Linear regressions of total PBDEs as a function of SSC for Guadalupe River water samples taken in water year 2005. Samples were separated according to river stage and spatial patterns of precipitation in order to identify contributions from lower (i.e., urban) and upper (i.e., non-urban) portions of the watershed.

DISCUSSION

Comparison of Three Years of PCB Measurements

McKee and Leatherbarrow (2005) examined the inter-annual variability of PCB and OC pesticide loads in Guadalupe River in response to variable hydrology and sediment discharge. With the addition of the WY 2005 data presented here, three years of PCB load estimates exist for the Guadalupe River. Comparison of these three years of data provides even more insight into the inter-annual variability of the system.

Of the three years of monitoring, WY 2005 experienced the highest total discharge volume and lowest total sediment load (Table 2-3); Total discharge in WY 2005 was approximately 110% of the WY 2003 discharge and 128% of the WY 2004 discharge; WY 2005 sediment load was only 42% of the WY 2003 sediment load and 53% of the WY 2004 load. Despite the difference in respective discharge volumes and sediment loads, the tPCB load for WY 2005 was approximately equal to that of WY 2004. WY 2004 and WY 2005 tPCB loads were roughly two-thirds of WY 2003 loads. The relative timing of tPCB loads across the three water years was very different. Water years 2003 and 2005 were characterized by highly episodic loads with approximately 58% of the total WY 2003 tPCB load delivered during December 2002 and approximately 37% of

the total WY 2005 tPCB load delivered during October 2004. WY 2004 tPCB loads were not so episodic, with similar proportions of loads being spread out over two to three months.

Linear relationships between contaminants and SSC began to fail in WY 2005 (Figure 2-3). McKee and Leatherbarrow (2005) noted that contaminant concentrations varied appreciably on storm-event time scales, with higher concentrations measured during rising stages of storm events. WY 2005 data support this finding. In fact, WY 2005 results show an even more pronounced separation between rising and falling stage tPCB concentrations (Figure 2-3). The linear relationship between WY 2005 tPCB concentration and SSC improved appreciably when samples were separated according to stage. The decision was therefore made to use the split regressions to calculate contaminant loads for WY 2005. In past years (i.e., WY 2003 and 2004) regressions were not split according to stage.

It must be noted that the terms 'rising' and 'falling' stage as used here do not follow their strict hydrologic definitions. The classification involves combining information regarding river stage and spatial precipitation patterns with the authors' conceptual model of the watershed. As such, the classification is meant to distinguish urban from non-urban sources. The 'rising-falling' terminology arises from the thought that the rising stage represents contributions from the urban lower watershed while the falling stage represents contributions from the non-urban upper watershed. The breakdown of the linear relationship of tPCBs and SSC for all WY 2005 samples supports the conceptual model that runoff originating in the urbanized lower watershed has a greater level of contamination by PCBs than upper watershed runoff. Additionally, WY 2005 data point to the need for a more sophisticated analysis of the system's hydrology. A numerical watershed model would appreciably improve our understanding of the complexities of the Guadalupe River and allow for more accurate contaminant source identification and loads estimates.

The complex influence of watershed hydrology on PCB source activation is further evidenced by examining PCB congener patterns during high- and low-flow conditions (Figure 2-6). During low-flow, the hexa- and hepta-CB congeners contributed the greatest proportions of tPCBs. As flow increased the contribution of these congeners decreased and the contribution of lower molecular weight congeners (i.e., tri-, tetra-, and penta-CB congeners) increased. Foster *et al.* (2003) have attributed such phenomenon to varying sources of sediment originating from resuspended finer grain material at low-flow and erosion of watershed soils and sediments at high-flow. Additionally, Rostad (1997) found large proportions of high-molecular weight PCB congeners observed in low-flow may point to transport of more extensively weathered and degraded PCBs. It is likely that similar processes are occurring in the Guadalupe River. If so, various watershed sources could be distinguished by detailed analysis and interpretation of congener patterns.

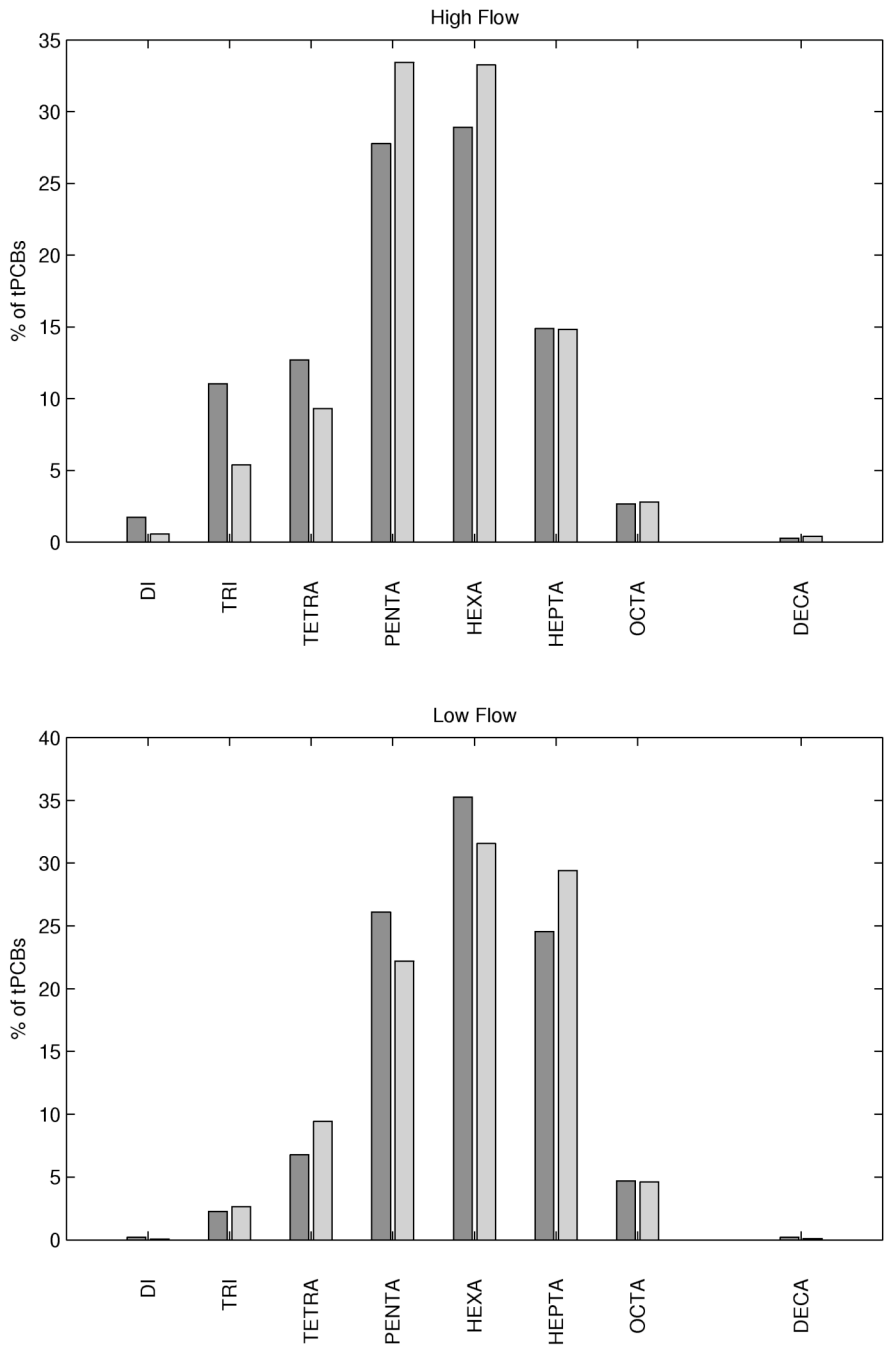

Figure 2-6 PCB congener patterns for selected high and low flow samples.

First Year of PBDE Measurements

PBDEs have been recently identified in San Francisco Bay water, sediment, wastewater effluent, bivalves, fish, wildlife, and humans (She *et al.*, 2002, 2004; Petreas *et al.*, 2003; Holden *et al.*, 2003; North, 2004; Oros and David, 2002; Oros *et al.*, 2005a). Total PBDE concentrations in RMP 2002 water samples ranged from 3 to 523 pg/l, with the highest concentrations found in Lower South Bay (SFEI, 2004; Oros *et al.*, 2005b). Total PBDE concentrations in Bay sediment samples ranged from below detection limits

to 212 ng/g, with the highest concentrations found in the South Bay (SFEI, 2004; Oros *et al.*, 2005b).

Information on sources of PBDEs to San Francisco Bay is limited (Oros *et al.*, 2005b). North (2004) estimated the tPBDE loading rate from a municipal wastewater effluent to be 0.9 kg/yr. Assuming that this loading rate applies to all wastewater treatment plants that discharge into the Bay, the total tPBDE load from discharged effluents would be approximately 23 kg/yr (roughly ten times the estimated tPCB wastewater load) (Oros *et al.*, 2005b). Applying the Guadalupe River tPBDE load of 2,312 g/yr estimated in this study to the urban proportion of the Bay Area - approximately 40% of the total 6,650 km^2 (McKee *et al.*, 2003) - an urban tPBDE load of approximately 15 kg/yr is estimated for Bay Area urban watersheds. This load does not include contributions from non-urban watersheds or non-point sources. Nor does the estimate account for inter-annual variability of tPBDE loads. Future PBDE monitoring at Guadalupe River will help refine the analysis.

CONCLUSIONS

Concentrations of tPCBs and tPBDEs varied by two orders of magnitude between base- and peak-flow conditions. Likewise, daily and monthly contaminant loads varied appreciably. Separation of tPCB concentrations of rising and falling stage water samples increased in WY 2005 compared to previous water years, prompting the development of two separate tPCB versus SSC regressions. Rising and falling stage regressions were developed for tPBDEs as well. Though the use of separate regressions is thought to better load analysis, a numerical watershed model would appreciably improve our understanding of the complexities of the Guadalupe River and allow for more accurate estimates. Even more, in understanding the impact of runoff from Guadalupe River and other tributaries on water quality in the Bay, it is important to consider how Bay waters and sediments assimilate contaminant load pulses of varying time duration (McKee and Leatherbarrow, 2005). A numerical watershed model will aid in this analysis by providing accurate sediment and contaminant load estimates on various time scales.

REFERENCES

AXYS Analytical Services (2002). Analytical method for the determination of Polybrominated Diphenyl Ethers by high resolution GC/MS. SOP MLA-025 Rev 02. AXYS Analytical Services Ltd, Sidney, BC, Canada.

Foster, G. D., Roberts, Jr, E. C., Gruessner, B., and Velinsky, D. J. (2003). Hydorgeochemistry and transport of organic contaminants in an urban watershed of Chesapeake Bay (USA). *Applied Geochemistry*, **15**, 901–915.

Holden, A., She, J., Tanner, M., Lunder, S., Sharp, R., and Hooper, K. (2003). PBDEs in the San Francisco Bay Area: measurement in fish. *Organohalogen Compounds*, **61**, 255–258.

Lowe, S., Hoenicke, R., and Davis, J. (1999). 1999 Quality Assurance Project Plan of the Regional Monitoring Program for Trace Substances. RMP Contribution 33, San Francisco Estuary Institute, Oakland, CA.

McKee, L. J. and Leatherbarrow, J. E. (2005). Concentrations and loads of mercury, PCBs, and OC pesticides in the lower Guadalupe River, San Jose, CA: Water Years 2003 and 2004. A Technical Report of the Regional Watershed Program: SFEI Contribution XX, San Francisco Estuary Institute, Oakland, CA.

McKee, L. J., Leatherbarrow, J. E., Pearce, S., and Davis, J. A. (2003). A review of urban runoff processes in the Bay Area: existing knowledge, conceptual models, and monitoring recommendations. RMP Technical Report. SFEI Contribution 66, San Francisco Estuary Institute, Oakland, CA.

McKee, L. J., Leatherbarrow, J. E., Eads, R., and Freeman, L. (2004). Concentrations and loads of PCBs, OC pesticides, and mercury associated with suspended sediments in the lower Guadalupe River, San Jose, California. A Technical Report of the Regional Watershed Program: SFEI Contribution 86, San Francisco Estuary Institute, Oakland, CA.

North, K. (2004). Tracking polybrominated diphenyl ether releases in a wastewater treatment plant effluent, Palo Alto, California. *Environmental Science and Technology*, **38**, 4484–4488.

Oros, D. R. and David, N. (2002). Identification and evaluation of unidentified organic contaminants in the San Francisco Estuary. RMP Technical Report: SFEI Contribution 45, San Francisco Estuary Institute, Oakland, CA.

Oros, D. R., Hoover, D., Rodigari, F., Crane, D., and Sericano, J. (2005a). Levels and distributions of polybrominated diphenyl ethers in water, surface sediments, and bivalves from the San Francisco Estuary. *Environmental Science and Technology*, **39**, 33–41.

Oros, D. R., Taberski, K., and McDonald, T. A. (2005b). Polybrominated Diphenyl Ether (PBDE) Flame Retardants in San Francisco Bay. In *The Pulse of the Estuary: Monitoring and Managing Water Quality in the San Francisco Estuary. SFEI Contribution 78*. San Francisco Estuary Institute, Oakland, CA.

Petreas, M., She, J., Brown, F. R., Winkler, J., Windham, G., Rogers, E., Zao, G., Bhatia, R., and Charles, M. J. (2003). High body burdens of 2,2'4,4'-tetrabromodiphenyl ether (BDE-47) in California women. *Environmental Health Perspectives*, **111**, 1175=1179.

Rostad, C. E. (1997). From the 1988 drought to the 1993 flood: transport of halogenated organic compounds with the Mississippi River suspended sediment at Thebes, Illinois. *Environmental Science and Technology*, **31**, 1308–1312.

SFEI (2004). 2002 Annual Monitoring Results. San Francisco Estuary Regional Monitoring Program for Trace Substances (RMP). San Francisco Estuary Institute, Oakland, CA.

She, J., Petreas, M., Winkler, J., Visita, P., McKinney, M., and Kopec, D. (2002). PBDEs in the San Francisco Bay Area: measurements in harbor seal blubber and human breast adipose tissue. *Chemosphere*, **46**, 697–707.

She, J., Holden, A., Tanner, M., Sharp, M., Adelsbach, T., and Hooper, K. (2004). Highest PBDE levels (max 64 ppm) yet found in biota measured in seabird eggs from San Francisco Bay. *Organohalogen Compounds*, **66**, 3939–3944.

SWRCB (2003a). 2002 Clean Water Act 303(d) list of water quality limited segments. State Water Resources Control Board, Sacramento, CA. Available online at: http://www.swrcb.ca.gov/tmdl/docs/2002reg2303dlist.pdf.

SWRCB (2003b). 2002 Clean Water Act 303(d) monitoring list. State Water Resources Control Board, Sacramento, CA. Available online at: http://www.swrcb. ca.gov/tmdl/docs/2002_mon_list_020403.pdf.

USEPA (1999). Method 1668, Revision A: Chlorinated biphenyl congeners in water, air, soil, sediment and tissue by HRGC/HRMS. U.S. Environmental Protection Agency. EPA No. EPA-821-R-00-002. Available online at: http://www.epa.gov/Region8/water/wastewater/biohome/biosolidsdown/methods/1668a5.pdf.

APPENDIX A: RAW MERCURY, TRACE ELEMENT, AND ANCILLARY DATA.

Sample No	Date	Time	Discharge (cfs)	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	Ag (ug/L)	As (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	Hg (ng/L)
GR 01	11/7/2002	16:30	84	221			0.03	4.2	0.7	9	43	27	19	191	191
GR 02	11/7/2002	18:00	206	411											471
GR 03AB	11/8/2002	17:00	717	91											420
GR 04	11/9/2002	7:30	117	49											4,657
GR 10	12/13/2002	19:18	382	321		8.9	0.10	2.9	0.6	23	40	41	31	152	337
GR 11	12/14/2002	0:46	549	115	0.50	6.1		1.8	0.1	9	14	19	8	50	269
GR 12	12/14/2002	11:15	148	29	0.50	5.4	0.03	1.7	0.1	4	8	7	3	24	361
GR 13	12/14/2002	17:30	1991	416	0.30	4.5	0.16	2.4	0.6	28	41	52	44	193	702
GR 14	12/14/2002	20:30	3917	610	0.80	3.9	0.13	2.6	0.7	57	46	113	47	188	
GR 15	12/15/2002	0:00	2137	382	0.30	4.6		1.9	0.2	30	19	64	16	77	596
GR 16	12/15/2002	11:00	280	106	0.30	5.1		1.7	0.1	14	8	31	3	21	494
GR 17	12/15/2002	16:30	214	60		5.5	0.03	1.7	0.1	8	8	15	3	22	483
GR 18	12/16/2002	3:00	491	61		4.6		1.5	0.1	6	8	13	5	33	178
GR 19	12/16/2002	7:45	5148	810	0.70	4.0	0.12	2.1	0.6	63	45	109	46	171	1,328
GR 20	12/16/2002	8:45	5937	1024	0.70	4.4	0.13	2.7	0.7	71	52	149	52	188	2,149
GR 21	12/16/2002	10:00	5385	1146	0.60	5.2	0.13	2.5	0.6	73	46	151	41	152	2,116
GR 22	12/16/2002	10:45	4431	1148	0.90	5.7	0.10	2.2	0.5	98	50	189	38	148	3,382
GR 23	12/16/2002	12:30	2567	955	0.40	6.3	0.08	1.8	0.3	86	34	169	24	100	3,177
GR 24	12/16/2002	19:45	494	430	0.50	7.3	0.11	1.7	0.1	34	15	71	9	40	4,653
GR 25	12/17/2002	10:00	695	200		5.5	0.05	1.4	0.1	21	14	36	9	53	6,699
GR 30	12/19/2002	20:30	2855	578	2.70	4.0		2.4	0.3	7	19	24	18	59	18,673
GR 31	12/19/2002	23:30	1308	487	2.30	5.3	0.05	1.8	0.2	49	20	92	13	60	5,293
GR 40	12/28/2002	18:25	1920	349	1.40	2.2	0.11	1.7	0.4	38	26	65	25	116	15,112
GR 50	3/15/2003	3:45	923	218	4.30	6.1	0.06	1.7	0.3	22	27	40	20	117	6,814
GR 51	4/12/2003	18:30	1197	231			0.27	1.8	0.3	23	24	42	23	105	5,767
GR 60AB	5/29/2003	10:15	39	17	0.70	1.8		1.5	0.1	2	6	4	2	9	5,155
GR100	9/30/2003	12:22	26	18	2.20	2.5		1.3	0.0	1	4	2	0	5	7
GR110 AB	11/3/2003	13:46	34	29	0.60	11.9		1.5	0.1	4	11	7	3	32	39
GR120	11/7/2003	9:47	125	159	0.90	18.3		2.2	0.2	4	22	13	10	74	203
GR130	11/8/2003	21:45	720	405	1.30	13.3	0.04	2.9	0.7	9	47	25	34	221	426
GR131	11/9/2003	0:43	2185	970	0.50	12.1		3.8	0.7	17	59	51	51	265	1,090
GR132	11/9/2003	12:42	2567	530	0.50	5.8		2.3	0.3	9	24	30	21	103	867

Appendix A (continued): Raw mercury, trace element, and ancillary data.

Sample No	Date	Time	Discharge (cfs)	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	Ag (ug/L)	As (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	Hg (ng/L)
GR133	11/10/2003	12:02	47	29	0.50	5.3		1.5	0.1	1	5	5	2	12	53
GR 140	12/9/2003	23:15	24	20	0.40	3.6		1.7	0.1	1	4	4	1	9	10
GR 141	12/10/2003	2:37	393	138	1.20	5.6	0.23	2.3	0.3	11	18	18	18	96	156
GR 142	12/10/2003	5:42	743	348	2.00	5.0	0.06	2.7	0.4	23	27	44	23	118	503
GR 143	12/10/2003	9:24	485	179	3.70	2.9	0.03	2.0	0.2	12	13	23	9	60	165
GR 144	12/10/2003	12:04	180	96	1.90	2.5	0.03	1.8	0.1	8	9	17	5	35	101
GR 145	12/11/2003	5:45	422	126	0.20	1.1	0.04	2.0	0.1	11	11	26	7	51	569
GR-150	12/14/2003	6:25	473	117	2.10	0.9	0.09	1.8	0.3	11	17	18	15	91	228
GR-151	12/14/2003	9:32	785	179	1.10	2.4	0.06	1.8	0.2	14	16	28	12	73	364
GR-152	12/14/2003	11:45	462	92	2.10	3.8	0.04	1.6	0.1	8	10	16	7	43	268
GR 160	12/21/2003	6:55	578	111	0.70	4.0		2.0	0.1	10	9	17	6	38	127
GR 170 AB	12/25/2003	13:31	1073	111	2.10	3.6	0.02	2.1	0.1	8	10	16	8	51	167
GR 180	12/29/2003	12:05	61	21	0.60	2.7		2.4	0.2	2	6	8	1	18	11
GR 181	12/29/2003	13:25	442	140	0.50	4.0	0.06	2.6	0.3	10	16	18	12	86	258
GR 182	12/29/2003	15:25	2311	405	0.50	4.1	0.06	2.5	0.4	23	27	45	26	119	603
GR 183	12/29/2003	17:30	2721	367	0.80	3.4	0.05	2.4	0.4	22	21	44	19	89	649
GR 184	12/29/2003	20:35	2736	348	0.60	4.0	0.08	2.6	0.3	22	20	47	17	84	619
GR 185	12/29/2003	22:35	2090	310	0.20	4.4	0.04	2.5	0.2	18	15	39	11	60	542
GR 186	12/30/2003	9:55	243	111	0.50	5.8		2.2	0.1	8	6	19	3	18	128
GR190	1/2/2004	8:54	257	198	0.60	8.1		1.8	0.1	17	9	29	2	22	372
GR200	1/22/2004	10:27	36	19	1.00	2.5		1.1	0.1	1	3	4	0	5	
GR210	2/2/2004	12:15	479	254	0.70	6.6									169
GR211	2/2/2004	14:15	1462	459	0.30	5.4									444
GR212	2/2/2004	16:55	706	235	0.80	4.6									140
GR 220	2/17/2004	23:53	417	122	0.90	4.7									
GR 221	2/18/2004	1:55	1019	179	0.10	4.4									251
GR 222	2/18/2004	10:40	270	79	0.70	4.2									
GR-231	2/25/2004	11:35	2185	329	0.10	3.5									568
GR-232	2/25/2004	15:05	2863	513	0.10	3.9	0.07	2.0	0.3	39	25	72	20	102	1,053
GR-233 AB	2/25/2004	17:47	2090	697	1.00	6.0	0.07	1.8	0.3	66	26	133	18	85	1,419
GR-234	2/26/2004	9:20	852	217	0.40	5.6									463
GR 235	2/27/2004	7:35	370	100	0.30	5.4									149
GR 236	3/2/2004	7:35	94	27	1.00	4.6									47
GR-240	3/26/2004	7:35	64	32	0.30	9.1		1.5	0.1	3	11	8	3	34	44

Appendix A (continued): Raw mercury, trace element, and ancillary data.

Sample No	Date/ Time	Discharge (cfs)	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	Ag (ug/L)	As (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)
300AB	10/19/04 7:57	84	33	1.1	8.5	0.03	1.7	0.27	5.4	22	11	6	79	73	4.2	0.5	0.05
301	10/19/04 11:05	709	365	3.1	11.5	0.02	5.2	1.26	52.0	91	105	81	350	1,496	5.0	1.9	0.10
302	10/19/04 13:50	2,530	720	3.3	5.6	0.17	3.3	0.75	45.5	61	102	54	236	1,916	5.4	1.0	0.08
303	10/19/04 16:55	3,060	489	1.5	4.8	0.05	2.2	0.29	18.2	23	41	18	83	446	4.9	0.9	0.11
304	10/19/04 20:45	572	203	1.1	5.4	0.03	2.0	0.14	11.4	14	26	9	44	226	6.3	0.7	0.11
305	10/20/04 7:30	138	83	0.5	6.1	0.03	1.9	0.17	7.9	14	15	8	63	83	4.4	0.6	0.08
310	10/26/04 6:05	1,020	267	0.6	4.4	0.35	2.9	0.44	28.6	48	52	33	189	443	4.3	1.2	0.08
311	10/26/04 8:05	1,880	339	0.7	3.8	0.03	1.7	0.25	15.7	20	33	16	87	306	3.8	0.7	0.05
312	10/26/04 12:00	804	143	0.4	3.9	0.01	1.7	0.10	8.2	11	18	6	38	122	6.0	0.5	0.10
320	11/9/04 7:40	23	6	0.6	1.0		1.4	0.04	2.0	3	3	0	5	8	0.9	0.1	0.05
330	11/11/04 11:54	257	95	0.6	6.5		1.6	0.12	9.4	14	18	7	49	308	3.9	0.7	0.08
340	12/7/04 2:20	37	13	3.7	1.9		1.5	0.07	4.4	5	6	1	10	13	1.2	0.1	
341	12/7/04 6:00	367	236	0.5	6.3		2.8	0.43	14.4	32	29	22	118	330	3.2	1.7	0.06
342	12/7/04 10:05	436	107	0.4	6.8		1.5	0.12	5.9	12	13	7	45	105	4.4	0.8	0.08
350	12/8/04 9:42	212	63	0.4	4.7		1.6	0.11	5.0	10	7	5	43	39	3.6	0.4	0.04
360	12/22/04 7:32	31	6		1.2		1.4	0.03	2.6	3	3	0	5	7			
370	12/27/04 11:21	87	60	0.3	4.6		1.9	0.15	5.8	12	9	4	45	4	2.0	0.4	0.04
371	12/27/04 21:56	608	85	0.2	3.4		1.3	0.10	5.6	10	12	5	38	89	5.3	0.4	0.05
380	12/30/04 2:10	1,210	164	0.1	3.8	0.05	1.6	0.18	11.8	17	26	11	66	235	3.5	1.1	0.09
381	12/30/04 5:18	944	127	0.3	3.0		1.5	0.16	8.2	12	19	7	48	128	3.2	0.6	0.05
382	12/30/04 8:30	1,260	153	0.3	3.0		1.6	0.14	10.3	12	22	9	51	239	5.6	0.8	0.06
383	12/30/04 12:30	800	106	0.3	3.4		1.5	0.10	6.1	8	15	5	34	113			
384	12/30/04 23:59	1,210	185	0.5	3.7		1.7	0.17	11.1	13	28	10	54	364			
385	12/31/04 14:10	345	96	0.5	5.8		1.6	0.05	6.3	7	18	3	20	167			
390	1/2/05 21:27	509	76	0.2	3.6		1.3	0.12	4.6	8	11	6	36	120	5.6	0.4	0.08
400	1/7/05 7:34	223	73	0.3	3.6		1.8	0.15	7.3	11	14	7	46	103	4.4	0.4	0.06
401AB	1/7/05 10:40	403	92	0.4	4.0	0.11	1.6	0.18	6.3	11	13	7	50	129	4.2	0.5	0.08
402	1/7/05 17:45	816	124	0.4	3.4		1.7	0.15	5.6	13	13	9	58	138			
403	1/9/05 11:06	227	49	0.3	4.7		1.5	0.07	4.3	6	8	3	21	59	8.6	0.3	0.08
410	1/10/05 22:30	494	134	0.6	3.3		1.7	0.23	3.8	15	8	19	80	137	4.7	0.6	0.06
411	1/11/05 1:07	691	141	1.1	3.3		1.5	0.16	5.8	13	14	10	60	198	4.4	0.7	0.06
412	1/11/05 18:05	380	109	0.2	4.7		1.9	0.07	7.6	7	13	3	23	171	10.0	0.4	0.11
420	1/26/05 14:04	406	137	0.4	4.5	0.07	1.5	0.21	15.8	20	30	13	75	263	5.0	1.2	0.09
430AB	1/28/05 8:26	272	60	0.8	2.6	0.02	1.1	0.08	5.9	7	11	4	32	98	3.6	0.4	0.07

Appendix A (continued): Raw mercury, trace element, and ancillary data.

Sample No	Date/ Time	Discharge (cfs)	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	Ag (ug/L)	As (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Ni (ug/L)	Pb (ug/L)	Zn (ug/L)	HgT (ng/L)	HgD (ng/L)	MeHgT (ng/L)	MeHgD (ng/L)
440	2/15/2005 7:44	1,100	195	0.7	2.9									261	2.9	1.5	0.04
441	2/15/2005 11:54	1,460	181	0.4	2.5									261	2.7	1.1	0.04
442	2/15/2005 16:38	470	85	0.4	2.9									83	3.1	0.4	0.06
443	2/16/2005 13:00	190	44	0.2	4.6									52	5.8	0.3	0.08
450	2/20/2005 22:30	345	59	0.8	4.4									95	6.7	0.4	0.08
451	2/21/2005 3:00	910	127											317	4.0	0.7	0.05
452	2/21/2005 9:06	800	181	0.8	4.4									353	7.7	1.0	0.09
453	2/22/2005 10:15	233	58	0.6	4.8									121	12.2	0.4	0.15
460	2/26/2005 19:35	192	29	0.4	4.0									74	8.0		
470	2/27/2005 23:21	1,400	222	0.4	3.6									553	4.5	1.2	0.05
471	2/28/2005 8:15	298	83	0.4	3.5									137	7.5	0.5	0.09
480	3/16/2005 8:45	56	9											11			
490	3/19/2005 16:20	237	67											123			
500	3/22/2005 8:15	506	77											136	3.8		0.08
510	3/22/2005 18:52	860	137											174	3.3	0.9	0.10
511	3/23/2005 7:45	239	45											68	5.2	0.4	0.08
520	4/4/2005 13:54	114	16											22			
530	4/25/2005 14:35	53	6											11	1.4	0.2	0.09