

*San Francisco Estuary Institute Regional Watershed Program*

# **Concentrations and Loads of Mercury, PCBs, and OC Pesticides in the Lower Guadalupe River, San Jose, California: Water Years 2003 and 2004.**

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Jon Leatherbarrow  
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SFEI Contribution 409  
July 2005

San Francisco Estuary Institute



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This report can be cited as:

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.

## EXECUTIVE SUMMARY

*This report summarizes and interprets mercury, trace elements, PCBs and OC pesticides concentration data collected in Guadalupe River water during the winter seasons of water years 2003 and 2004. Our objective is to describe concentration variability between years and to determine loads. We will present some hypotheses on the processes of mercury source, release, and transport and the source, release, and transport processes of other trace elements and the organic contaminants. We estimate total mercury loads, loads of other total trace elements, loads of PCBs and OC pesticides entering San Francisco Bay under the range of climatic conditions encountered. In addition, we use a simple rating curve method to estimate a five-year average mercury loads and a probable maximum mercury load based upon observed rainfall intensity and runoff data from water year 1975 – 2004.*

*All sampling was carried out at the United State Geological Survey flow gauge, on Guadalupe River at U.S. Highway 101. The area upstream from the gauge is 414 km<sup>2</sup>. At this location data was logged automatically from a turbidity sensor installed in the thalweg of the low flow channel. Water samples for analysis of total mercury, total silver, total arsenic, total cadmium, total chromium, total copper, total nickel, total lead, total zinc, PCBs OC pesticides, suspended sediment concentration, dissolved organic carbon, and particulate organic carbon were collected in the thalweg within 1 m of the turbidity probe using clean-hands protocols where appropriate.*

*Discharge during water year 2003 was 111% of the 1971 - 2000 normal (55 Mm<sup>3</sup>). The majority of runoff occurred during December 2002 when flow peaked at 171.9 m<sup>3</sup>/s on December 16<sup>th</sup>. A first flush effect was evident for suspended sediment concentration. Suspended sediment concentration peaked during the first storm series of the season on November 7<sup>th</sup> at 1,366 mg/L and reached only 1,152 mg/L on December 16<sup>th</sup> (a larger storm peak). Discharge during our second year of study (water year 2004) was 96% of normal. Compared to water year 2003, the year was typified by a greater number of smaller storms. Discharge peaked at 124.3 m<sup>3</sup>/s on January 1<sup>st</sup> with a suspended sediment peak 1 hour later of 905 mg/L. The first flush effect was also evident in the second year of study. Suspended sediment concentration reached a peak of 1,117 mg/L on November 9<sup>th</sup> during the first flood of the season.*

*During water year 2003 total mercury concentrations varied from 0.18 – 18.67 µg/L. In our second year of study, total mercury concentrations varied from 0.01 – 1.42 µg/L. The variation of total mercury concentration relative to suspended sediment concentration was distinctive when compared to the other trace elements; mercury did not exhibit first flush characteristics, and the highest mercury concentrations were uniquely associated with the first year of observations. Our observations during water year 2003 fall within the range of concentrations that might be expected in watershed impacted by mercury mining (1-1,000 µg/L). Our observations during water year 2004, although still falling in the range that might be expected in mining areas, are perhaps more typical of the upper range of what might be expected in urbanized areas (200-2,000 µg/L). The other trace elements displayed concentrations that are typical of urban areas with the exception of copper, chromium and nickel which appeared to fall in the high range of observations elsewhere. We propose that elevated concentrations of chromium and nickel might be associated with the geology of the region.*

*Total PCB concentrations in water year 2003 ranged between 3.4 - 90 ng L<sup>-1</sup> and in water year 2004 ranged from 0.73 - 66 ng L<sup>-1</sup>. The maximum t-PCB concentrations were associated with high discharge and suspended sediment concentrations. In all samples, hexa-, hepta-, and octa-chlorobiphenyls comprised approximately 45 to 64% of t-PCB concentrations. Total DDT*

concentrations in water year 2004 ranged between 0.55 - 55 ng L<sup>-1</sup>. Total DDT concentrations were comprised primarily of p,p'-DDE (22 to 53%), p,p'-DDD (12-38%), and p,p'-DDT (10-45%). Total chlordane concentrations in water year 2004 ranged from 0.63 - 53 ng L<sup>-1</sup>. Total chlordane concentrations were comprised primarily of alpha-chlordane (27-36%), gamma-chlordane (24-31%), and trans-nonachlor (19-30%). Dieldrin concentrations in water year 2004 ranged from 0.19 to 3.8 ng L<sup>-1</sup>. Pesticide concentration ranges measured in WY 2004 were similar to ranges measured in WY 2003 for t-DDT (1.7 to 71 ng L<sup>-1</sup>), t-chlordane (1.6 to 64 ng L<sup>-1</sup>), and dieldrin (0.3 to 6.0 ng L<sup>-1</sup>). Similar to PCBs, high concentration of the pesticides were associated with high discharge and suspended sediment concentration.

Daily water discharge in the Guadalupe River watershed varied over 2 orders of magnitude. Daily loads of suspended sediment varied from 0.37 - 3,269 t (almost 4 orders of magnitude). The daily loads of mercury, trace elements, and trace organics followed similar patterns. Monthly discharge varied by 16x during the wet season of WY 2003 and by 5x during WY 2004. Monthly suspended sediment loads in the first year varied by ~400x and were greatest in the months of November and December. During WY 2004, monthly loads varied less in response to a drier year (~70x) and were more evenly distributed across the four months of November to February. The intra-annual variability was also high for loads of total chromium, nickel, lead, and mercury (~100 - ~370x). Monthly loads of PCBs and DDT varied by ~40x in the first year and by 11-12x in the second year. For chlordane the variation was ~60x and ~16x and for dieldrin the variation was ~70x and 100x for water year 2003 and 2004 respectively. Although we have not measured dissolved fractions, our observations suggest that the particulate forms are the dominant forms during floods and overall in total loads.

Guadalupe River wet season loads varied inter-annually in response to climatic forcing. In water years 2003 and 2004, the loads of mercury were estimated to be 116 ± 37 kilograms and 14.8 ± 4.7 kilograms. In water year 2003 the loads of PCBs, DDT, chlordane, and dieldrin were 1200 ± 210 grams, 1100 ± 270 grams, 790 ± 13 grams, 82 ± 17 grams respectively. In the second year the loads were 700 ± 200 grams, 700 ± 210 grams, 550 ± 140 grams, 54 ± 13 grams respectively. Runoff in the wet season of WY 2004 was 85% of WY 2003. Suspended sediment loads in WY 2004 were 79% of those in WY 2003, and total silver, arsenic, cadmium, chromium, copper, nickel, lead, and zinc all followed the same pattern (79 - 83%). Trace organic contaminant loads in WY 2004 were approximately 58 to 70% of loads estimated in WY 2003. In contrast, POC and mercury were much more variable than either discharge or suspended sediment suggesting that processes in addition to sediment erosion were contributing to the loads.

The data gathered so far in the Guadalupe River watershed covers only a small portion of the historic climatic variability. Given only two years of data and the added complexity of mercury source, release, and transport, it is challenging to make long-term mercury loads estimates. Given the data limitations, long-term estimates were made using regression relationships between monthly discharge and monthly mercury load. The data were stratified into months when mercury concentrations were less than or greater than 2 µg/L. Monthly discharge and rainfall intensity data were retrieved from the USGS and the Santa Clara Valley Water District. Loads for each water year were estimated using the discharge-load regression relationships. During months when rainfall intensity was >50.8 mm (2 inches) in a 6-hour period, the regression equation corresponding to the hypothesized new mercury-release conditions was applied for that and the subsequent one month. For all other months, the regression equation corresponding to no release was applied. The annual average load estimated was 157 kilograms. Annual loads would be expected to range from 26 grams in a water year like 1977 to 1,070 kilograms in a water year like 1983. Water year 1977 was one of the driest on record in the Bay Area and water year 1983 was one of the wettest. Extreme climate variability poses a problem to

*City and County managers who may be asked to manage urban runoff to achieve loading goals. To help deal with this problem, it has been proposed that loads could be averaged over a sufficiently long period to reduce the impact of one extremely wet year on failing to meet a goal. Even if a 7-year averaging period is chosen, average loads over each 7-year period would be expected to vary from 23 - 330 kilograms or about 15 - 200% of the estimated annual average load (157 kilograms).*

*In this study so far, we have made hypotheses about the possible physical processes of release and transport of total mercury in the watershed in both space and time – important issues for the design of programs to reduce loads. Capture of further samples for mercury analysis during subsequent years with high rainfall intensity will help to strengthen our present hypotheses however, sampling further upstream near the historic New Almaden Mining District would provide a better understanding of source, release, and transport processes. At present we have little understanding of what percentage of this estimated mercury load is biologically available or how these loading rates compare with the rate of methylation and demethylation. Future years of sampling will provide further information on source, release, and transport processes of mercury and the organic trace contaminants (including PBDEs), particulate and methyl mercury concentrations and of relevance to biological endpoints.*

## **ACKNOWLEDGEMENTS**

*The authors are sincerely grateful the SFEI field-staff: Nicole David, Ben Greenfield, Donald Yee, Jennifer Hunt, Sarah Pearce, and Chuck Striplen, and the USGS field staff: Kris Nilsen and John Budlong. Laboratory analyses were completed by AXYS Analytical Services LTD (PCBs and OC pesticides), Moss Landing Marine Laboratories (mercury, silver, arsenic, cadmium, chromium, copper, nickel, lead, and zinc), USGS (suspended sediment and grainsize), and Applied Marine Sciences, Inc., Texas (organic carbon). We acknowledge the Sources Pathways and Loadings Workgroup (SPLWG) of the Regional Monitoring Program for Trace Substances (RMP) in all project stages from concept development through to review of the final draft and the CEP Technical Committee for oversight during project implementation. We were pleased to have received manuscript reviews from David Drury (SCVWD), Todd Fisher (Axys Analytical Services Limited), Neil Ganju (USGS), Larry Bahr (FSSD), Carrie Austin (and Region 2 RWQCB), Aaron Slowey (Stanford University), Jon Konnan (BASMAA), and James Downing (CSJ). Funding for the project during, this, the second year of study was provided by the Clean Estuary Partnership (\$75,000) and the Regional Monitoring Program for Trace Substances (\$50,000).*

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**SECTION ONE**

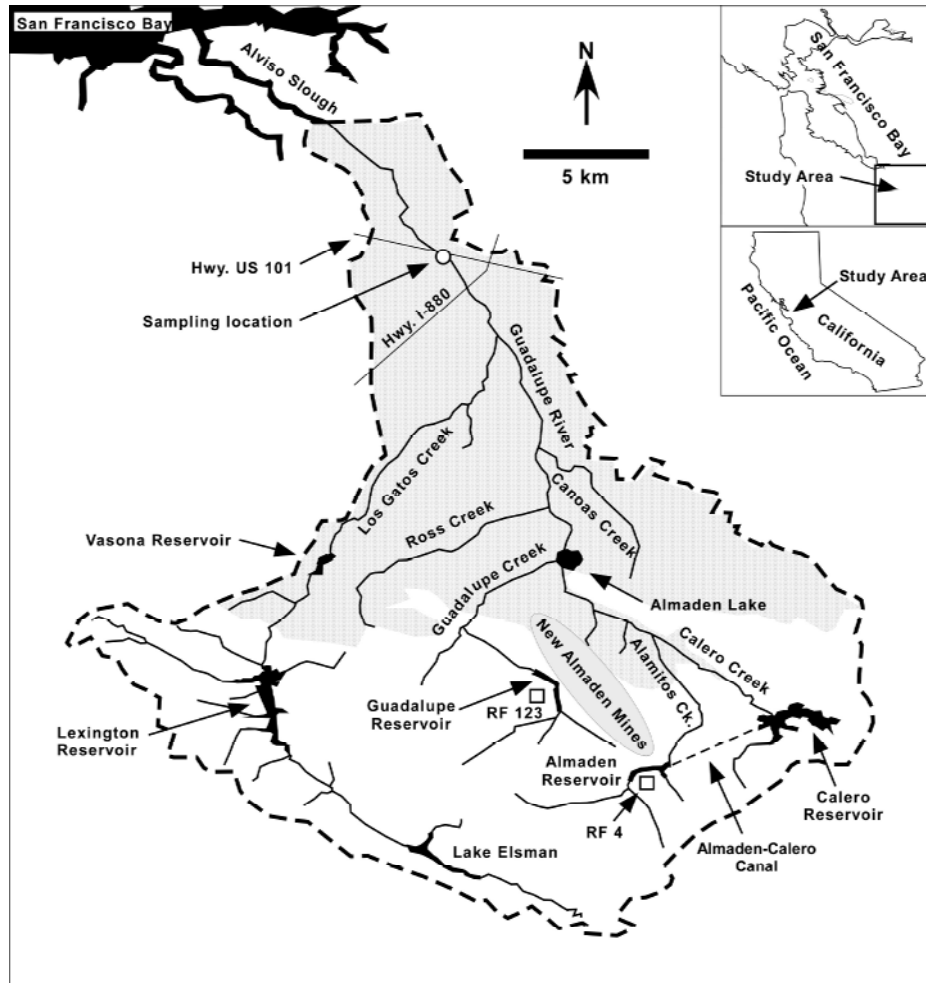
**MERCURY TRANSPORT PROCESSES  
IN THE GUADALUPE RIVER:  
WATER YEARS 2003 AND 2004**

## INTRODUCTION

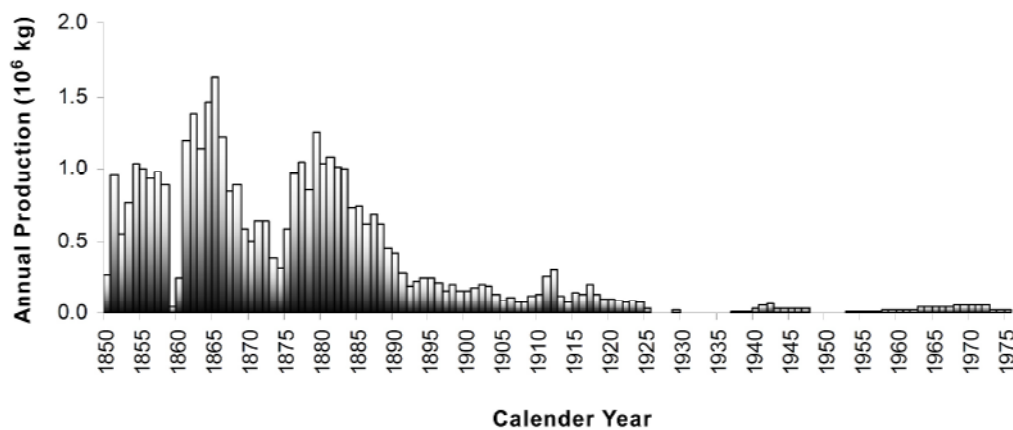
San Francisco Bay, the largest estuarine embayment on the west coast of the Americas, is contaminated with mercury. Studies provide evidence that mercury derived from the consumption of contaminated fish can cause neurological disorders in humans (Ratcliffe et al., 1996). The most sensitive section of the population is likely to be the unborn child or fetus exposed to methyl mercury *in utero*. Fishing advisories for San Francisco Bay were first issued in 1994 and then updated in 1999 (COEHHA 1999). A San Francisco Bay fish consumption study provided valuable data on fishing, cooking and consumption habits of recreational and subsistence fishers (CDHS and SFEI 2000). Although there are historic accounts of chronic mercury poisoning of mercury retort workers in the historic New Almaden Mining District (Meagher, 1869), that we know of, there are no statistics on modern mercury poisoning in the Bay Area or on subtle issues such as the association of mercury with child learning difficulties. But it seems likely that children in families that rely on the Bay as a source of fish protein are at risk. There is however, growing evidence that mercury is the cause of hatching failures in some native rare and endangered species (Schwarzbach et al. 1996; Schwarzbach et al. 2000; CDFG 2002; Davis et al. 2003). Clearly mercury contamination is a major problem.

Mercury is persistent and fluxes out of the Bay are small compared to the mass stored in the Bay. A simple model predicts it will take >200 years for water quality in the Bay to reach standards suitable for unrestricted human use if no intervention of the mercury cycle occurs and 120 years if current total mercury loads are reduced by 50% over the next 20 years (Johnson and Looker, 2003). The control measures presently in place are largely prescribed in the absence of any local information that unequivocally links total mercury loads to methylation and the uptake by estuarine biota (the base of exposure routes to wild life and humans). These are areas that require immediate research but are not addressed in the work presented here. Estimates of recovery time will likely be modified over the next several decades as the system is monitored for response to total mercury load control measures and as the processes that govern the conversion of total mercury to organic forms are better understood.

Mercury in San Francisco Bay is mostly derived from legacy sources either directly from runoff at historic mercury mines or indirectly from runoff in watersheds where mercury amalgamation was used for processing gold during the 1860's gold rush (Alpers and Hunerlach). Other minor sources include runoff from rural and upland areas, urban stormwater, wastewater, and atmospheric deposition (McKee et al., 2003). The Guadalupe River watershed (Figure 1-1), the focus of this study, includes a large urban area and the historic New Almaden Mining District, the source of ~30% of the North American mercury production to-date and ~6% of the world production since 1850 (Cargill et al., 1980; Hylander and Meili, 2003). Mercury production in the historic Almaden Mining District peaked at 47,194 flasks (~1.6 million kilograms) in 1865 and total production had exceeded 1,163,000 flasks (40 million kilograms) when mine closure occurred in 1975 (Figure 1-2). Although most mercury mass probably entered the Bay 50 - 150 years ago, mercury derived from this legacy source is still entering the Bay today. Loads from urban areas and adjacent historic mines need to be better understood to help problem definition and to provide data to evaluate the effectiveness of clean-up activities.



**Figure 1-1.** The location of the Guadalupe River watershed. River gauges (○); Rain gauges (□); Densely urbanized lower watershed (⊙).



**Figure 1-2.** Mineral mercury production in the historic New Almaden Mining District (Bailey and Everhart, 1964; Cargill et al., 1980).

Guadalupe River watershed is an ideal study area for improving our knowledge on contemporary allochthonous mercury loading to the Bay. Contaminated areas in the historic New Almaden Mining District include calcines piles (crushed and roasted ore rock), waste-rock piles, road segments that were paved with cemented calcines, furnace and processing areas, landslide debris, and the bank, bar, and terrace deposits of intermittent and perennial first order creeks or “gulches” (Dames and Moore, 1989). Off-site, most of the contamination was deposited during extreme storms over the past 150 years in Almaden Reservoir, Guadalupe Reservoir, Calero Reservoir and bank, bar, and terrace deposits in Guadalupe Creek, Alamitos Creek, Almaden Lake, and Guadalupe River. There is mounting evidence that much of this on- and off-site material is still part of the active hydrological cycle - most especially during intense rainstorms (McKee and Leatherbarrow, 2005). In addition to fishing advisories for San Francisco Bay, there are fishing advisories for water bodies within and adjacent to the historic New Almaden Mining District including: Calero, Almaden and Guadalupe Reservoirs, Alamitos and Guadalupe Creeks, and the Guadalupe River. The densely urbanized portion of the watershed makes up ~44% of the area upstream from the sampling location and overall the watershed is about 46% urbanized. Mercury runoff from urban areas mainly influences water quality in the lower reaches of the Alamitos and Guadalupe creeks, other urban creeks such as Ross Creek, and the Guadalupe River. The diverse nature and complexity of mercury sources and hydrology make for an ideal study area but add challenges to data interpretation.

There have been several recent studies that describe aspects of mercury processes in the Guadalupe River Watershed. Leatherbarrow et al. (2002) collected samples on nine occasions in Alviso Slough during 1997, 1998, and 1999 when flow in the Guadalupe River ranged between 0.3 - 13.5 m<sup>3</sup>/s. They made estimates of total mercury load (29 kilograms) based on flow-weighted mean concentration and average annual flow. That same year, a study by Thomas et al. (2002) reported data on water column mercury concentrations collected throughout the watershed during October 2000 when flow conditions ranged between 0.4 - 4.2 m<sup>3</sup>/s. Thomas et al. (2002) made an estimate of total mercury load of 4 - 30 kilograms based on combining suspended particulate mercury concentrations (0.5 - 4 mg/kg) with the annual average sediment load (7,400 t) reported by Davis et. al. (2000). McKee and Leatherbarrow (2005) used data collected during large floods of WY 2003 to develop a hypothesis of mercury source-transport characteristics under a variety of climatic conditions but did not present loading estimates. The Guadalupe River is capable of discharges >300 m<sup>3</sup>/s and a flood flow of >75 m<sup>3</sup>/s has a return interval of 1:2 years. Neither Leatherbarrow et al. (2002) or Thomas et al. (2002) estimated total mercury loads during the annual range of flow conditions, let alone during large floods when high concentrations and loads would be expected. Previously there was no defensible estimate of the inter-annual variation of concentrations and loads or of annual average loads for the watershed.

This study was funded by a consortium of city, county, and industry groups in the Bay Area that hold permits issued by the State to discharge stormwater runoff and wastewaters to the Bay. The study was specifically developed to contribute to information that will enhance the environmental management of mercury. It follows

some of the recommendations of previous studies (Leatherbarrow et al., 2002; Thomas et al., 2002). Our objective here is to use data gathered over water years (WYs) 2003 and 2004 to describe concentration variability between years and to determine loads. We will present some hypotheses on the processes of mercury source, release, and transport and the source, release, and transport processes of other trace elements. We estimate total mercury loads and loads of other total trace elements entering San Francisco Bay under a range of climatic conditions. In addition, we use a simple rating curve method to estimate a five-year average loads and a probable maximum load based upon observed rainfall intensity and runoff data from WY 1975 – 2004.

## **METHODS**

### **Sampling and Analysis of Suspended Sediments**

Water sampling was carried out over the winter months of WYs 2003 and 2004 (Note that a water year in the United States begins October 1<sup>st</sup> and ends September 30<sup>th</sup> 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). 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<sup>2</sup>. The sum of the areas upstream from the Calero, Almaden, Guadalupe, and Vasona Reservoirs amounts to 178 km<sup>2</sup>, leaving a 236 km<sup>2</sup> watershed available for production of flood runoff. The highest elevation in the watershed is 1,155 m however much of the valley floor is <200 m above sea level. 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. The low flow channel occupied a 15 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, mercury and the other trace element would closely correlate with turbidity. This would provide us with a less expensive method for estimating water column concentrations of trace contaminants than collecting and analyzing 100s of samples. As such, during both 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). 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 >99.9% 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 so

that study participants can determine the best sampling strategy for suspended sediments and contaminants. 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 x-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 (Note that here we do not present any analysis of grain size effects on mercury concentrations but this may be done during the reporting phase of a future year of data collection). 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). During WY 2004, a total of 226 water samples were analyzed for SSC and six samples were analyzed for grain size distribution (for method details see Guy, 1969). These sample concentrations were combined with the turbidity measurements at Redwood Sciences Laboratory, Arcata, California using LOESS fit (Cleveland, 1979) to estimate a continuous 15-minute SSC record. They were 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).

### **Sampling and Analysis of Mercury, Trace Elements, 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 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, 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. 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 these analytes, 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.

Water samples were analyzed for total mercury (Hg), and other trace elements: total silver (Ag), total arsenic (As), total cadmium (Cd), total chromium (Cr), total copper (Cu), total nickel (Ni), total lead (Pb), and total zinc (Zn) by Moss Landing Marine Laboratory (MLML), Moss Landing, California. Dissolved organic carbon (DOC) and particulate organic carbon (POC) were analyzed by Applied Marine Sciences Inc, League City, Texas. Upon receipt at the labs (commonly within 36 hours), water samples for Hg analysis were preserved with a final concentration of 0.5% v/v bromine monochloride (BrCl), water samples for other total trace element analysis were acidified to a final concentration of 1% v/v nitric acid (HNO<sub>3</sub>), and DOC and POC water samples were refrigerated at 4°C in the dark until analysis. All samples for Hg and trace elements analysis were mixed media in that they were water samples containing suspended sediment concentrations ranging from a few mg/L to over 1,000 mg/L. 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 40 mL was used and complete digestion of the Hg associated with sediment particles was ensured by colorimetric addition of BrCl. Other total trace element samples were analyzed using ICP-MS following U.S. EPA method 1638 (U.S.E.P.A., 1996). DOC and POC were analyzed by catalytic combustion using U.S. EPA method 415.1 (U.S.E.P.A., 1983).

## Quality Assurance

The Hg and other total trace element analysis methods were chosen to ensure the expected concentrations were beyond the method detection limits (MDL). Ag concentrations were closest to the detection limit with 36% of the data being below the detection limit (MDL) of 0.008 µg/L and 19% of the data <5x the MDL. On the other end of the spectrum, 95% of the Cu concentrations were 1,600x greater than the MDL. In the case of Hg, one sample taken during base flow at 10:30 on 01/22/04 in which SSC was 19 mg/L was below MDL but 95% of the samples 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. Three field replicates taken under stable flow conditions yielded RPDs for Hg of 7.6 – 18.5% and RPDs of 0.4 - 6.8% for other total trace elements. With the exception of one batch of Ag

analyses, the percent recoveries for standard reference materials were within the target range (75 - 125%). Silver concentrations in this batch were considered acceptable as the matrix spike and duplicate recoveries were within the data quality objectives. The percent recoveries for matrix spikes were within the target range (75 - 125%) except for one batch for chromium (145%) (Table 1-1). All other QA parameters, including duplicate and SRM data, were acceptable for chromium giving us reasonable confidence in the data. The quality assurance samples included one method blank for each analytical batch of other total trace elements and three method blanks for each batch of Hg analyses. Other total trace element concentrations in blank samples were generally not detected; therefore samples were not blank corrected with the exception of Cu for one batch and As for another batch (Table 1-1). A field blank was <MDL for trace elements with the exception of Hg, which had a blank concentration of 0.0065 µg/L. This field blank went via a complex route to get to our lab and therefore likely represents a worst case scenario. We intend to collect more field blanks in the future to confirm our field quality control procedures.

**Table 1-1.** Quality control parameters of total mercury and other total trace elements analyzed in this study.

Substances Analyzed	Detection Limit (MDL) (µg/L)	Relative Percent Difference (RPD)	Percent Recovery of Standard Reference Material	Percent Recovery of Matrix Spike	Method Blank (µg/L)	Field Blank (µg/L)
Total Mercury	0.0002	2.0 – 26.4	85 – 124	80 – 122	<MDL	0.0065
Total Silver	0.008	1.5 – 6.4	61 – 102	80 – 103	<MDL	<MDL
Total Arsenic	0.1	0.3 – 9.3	89 – 99	96 – 122	<MDL – 1.00	<MDL
Total Cadmium	0.002	0.0 – 6.8	96 – 106	100 – 121	<MDL	<MDL
Total Chromium	0.03	0.5 – 14.0	95 – 100	97 – 145	<MDL	<MDL
Total Copper	0.003	0.2 – 5.3	99 – 105	94 – 99	<MDL – 0.03	<MDL
Total Nickel	0.006	0.4 – 9.7	96 – 100	94 – 98	<MDL	<MDL
Total Lead	0.002	0.0 – 0.9	98 – 106	92 – 107	<MDL	<MDL
Total Zinc	0.02	0.1 – 3.6	97 – 106	96 – 106	<MDL	<MDL

## Loads Calculation

### *Suspended Sediment, DOC and POC*

Loads of each analyte were calculated for the winter months of WY 2003 and 2004 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 their 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 our study on the Guadalupe River, suspended sediment loads were determined by combining the 15-minute SSC estimates derived from turbidity measurements with 15-minute discharge. The methods used to calculate loads of the other analytes differed depending largely on individual relationships with SSC. DOC and POC did not correlate with SSC or discharge. Loads



were determined by combining 15-minute discharge with concentrations estimated by extrapolating between samples using linear interpolation.

#### *Trace Elements other than Mercury*

Time continuous concentrations of total trace elements excluding Hg were determined by developing regression relationships between SSC and each trace element. The data were stratified based on the predominant source of runoff (“lower urban” versus “upper non-urban”) and two regression relationships were developed for each trace element. 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-minute 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. In this way 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*

The calculation of Hg load was more challenging because of the complex patterns of source, release, and transport from contaminated areas in and adjacent to the historic New Almaden Mining District. Data were stratified in a similar manner to the other trace elements and regression relationships were developed with SSC for *lower urban* and *upper non-urban* derived discharge. 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 and Leatherbarrow, 2005 and developed further below). 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 more detail later) were met during WY 2003 but not during WY 2004 when rainfall

intensity was always <60 mm in a 6-hour period. Mercury concentrations estimated in these ways were then combined with 15-minute discharges to calculate loads that were then summed for each month and each wet season of each water year. An example of the calculations for one of the complex storms is provided in appendix B.

There are other methods that could have been used to estimate concentrations between “snapshot samples” in order to estimate loads. For example, we could have calculated a flow-weighted mean concentration (FWMC) from our discrete samples for each year and multiplied this with wet season or annual discharge to estimate loads. However, our sampling regime was heavily biased to floods in both sampling years, thus the loads would have been over estimated. 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 our sampling design. We could have used linear interpolation to estimate concentrations between samples for generating loads; however, again, the flood-focused sampling design was not well suited to this method. We chose a flood-based sampling design 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 is cost prohibitive. The flood-focused sampling design we chose is well suited to the use of turbidity as a surrogate measure, is most accurate if loads generation is an end point because >90% of the annual loads occurs during floods, but prohibits the use of simple averaging or interpolative estimators during loads calculation.

#### *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 ( $\pm 10\%$ ), suspended sediment ( $\pm 2\%$ ), variation of Hg in the cross section ( $\pm 10\%$ ), and interpolation / SSC-mercury regressions ( $\pm 10\%$ ). The RPD of field duplicates was always less than the laboratory duplicates. In the case of Hg, the RPD exceeded 25% for one laboratory batch and averaged 11.9% across all 7 batches. We chose to set the laboratory error associated with the determination of mercury concentration at a given time to the maximum RPD ( $\pm 26.4\%$ ) to remain on the conservative side. The total error of the estimated Hg loads was estimated to be  $\pm 32\%$ . Errors were estimated for the other trace elements in a similar manner using the maximum RPDs (Table 1-1) and for DOC and POC based on QA data provided by our laboratory ( $0.00 \leq \text{RPD} \leq 9.95$ ). Total errors for the other trace elements ranged between 18 - 23% and for SSC, POC and DOC were 15%, 19%, 19% respectively.

## **RESULTS AND DISCUSSION**

### **Discharge and Suspended Sediment Concentrations**

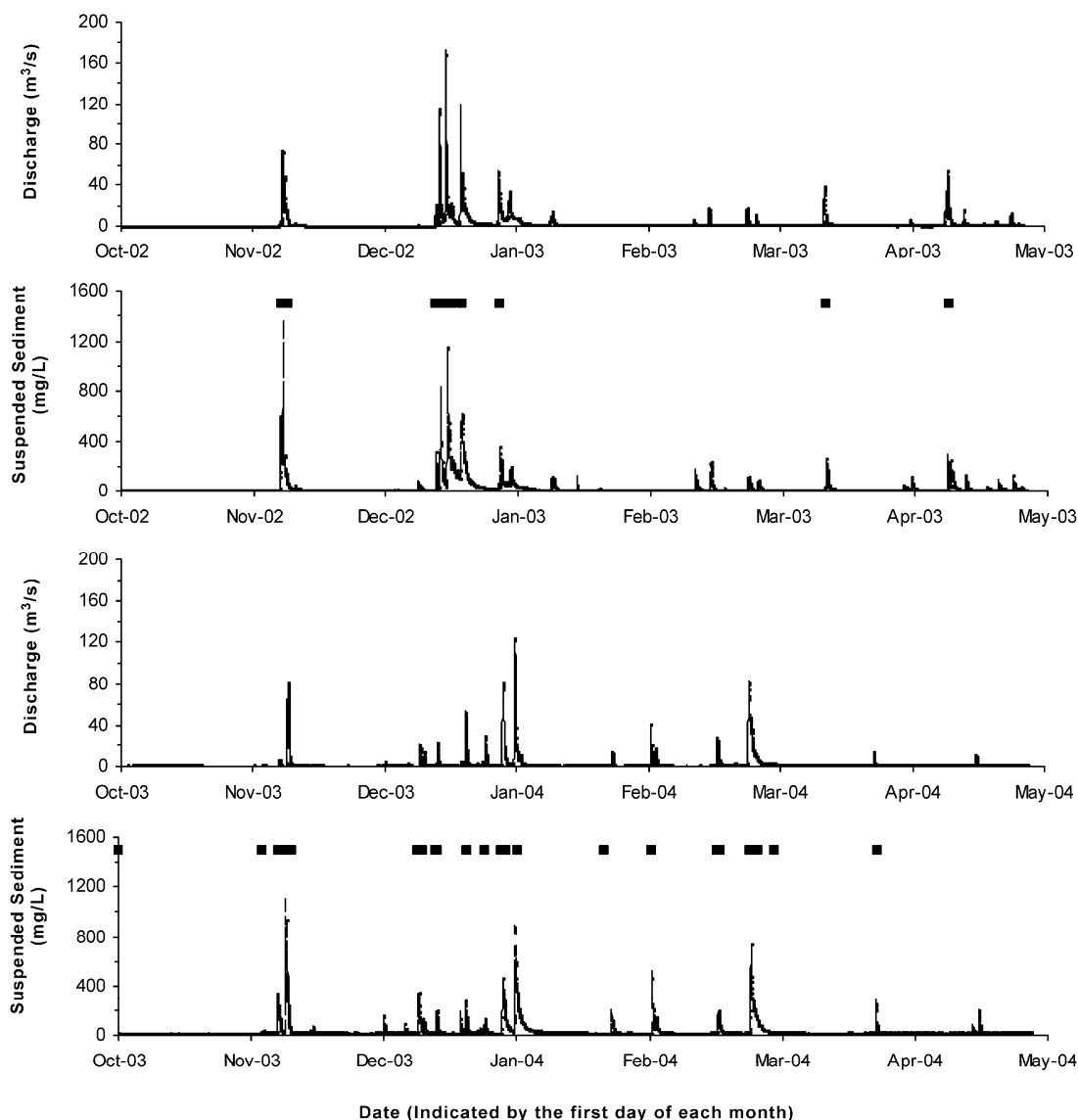
About 94% of the discharge in the Guadalupe River occurs on average during the winter months (November to April) in response to regional scale rain depressions that move southeast or eastward over California from the central and polar Pacific Ocean (McKee et al., 2003). Such depressions derived from the Pacific Ocean usually last 24 - 72 hours and pass over the watershed as a series of rain producing cloud bands.

Discharge at the sampling location begins to rise 30 minutes after rainfall begins in the lower urbanized watershed and 6 - 7 hours after rainfall begins in mountainous areas of the upper watershed. Rainfall is typically greater at higher elevations in the upper watershed but rainfall distribution is highly variable depending on the direction of the Pacific storm track during each specific storm. On occasions rainfall can be evenly distributed or greater in the lower urbanized portion at elevations of 0 - 60 m above sea level. This variable distribution of rainfall influences the volume and timing of discharge produced from the lower heavily urbanized areas and the upper non-urbanized areas. The first 6 - 7 hours of a storm hydrograph is assumed to be completely urban runoff for purposes of this study and analysis. Hydrographic response that occurs beyond 6 - 7 hours is a combination of urban and non-urban watershed runoff. In WY 2003, only ~45% of the basin water yield was derived from the watershed upstream from the urban area despite 54% being non-urban and greater upper watershed rainfall. In contrast, during WY 2004, 51% of the basin water yield was from the upper watershed (SCVWD, unpublished data). On occasions, the instantaneous contribution of Alamitos Creek upstream of Graystone Lane and Guadalupe Creek upstream from Shannon Road (a combined area of 62 km<sup>2</sup> excluding the areas upstream from the Calero (18 km<sup>2</sup>), Almaden (30 km<sup>2</sup>), and Guadalupe (15 km<sup>2</sup>) reservoirs) reached >50% of the flow at the sampling location assuming a 3 hour routing time and it was very often 20 - 50% of the flow during the falling stages of floods; these observations are of interest when considering contaminant sources, pathways, concentrations, and loads. For example, on December 16<sup>th</sup> 2002, 56% of the flow was likely derived from these sub-watersheds on the falling stages of the flood. A similar situation was observed on December 29<sup>th</sup> 2002, and January 1<sup>st</sup> 2003.

Discharge during WY 2003 was 111% of the 1971 - 2000 normal (55 Mm<sup>3</sup>). The majority of runoff occurred during December 2002 when flow for the largest storm of the year peaked at 171.9 m<sup>3</sup>/s at 9:00 on December 16<sup>th</sup> (Figure 1-3a). 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 7<sup>th</sup> at 22:15 at 1,366 mg/L and reached only 1,152 mg/L at 10 am on December 16<sup>th</sup> (Figure 1-3b). Discharge during our second year of study (WY 2004) was 96% of normal (Figure 1-3c). Compared to WY 2003, the year was typified by a greater number of smaller storms. Discharge peaked at 124.3 m<sup>3</sup>/s at 14:00 on January 1<sup>st</sup> with a suspended sediment peak 1 hour later of 905 mg/L (Figure 1-3d). The first flush effect was also evident in the second year of study. SSC reached a peak of 1,117 mg/L on November 9<sup>th</sup> at 0:15 during the first flood of the season.

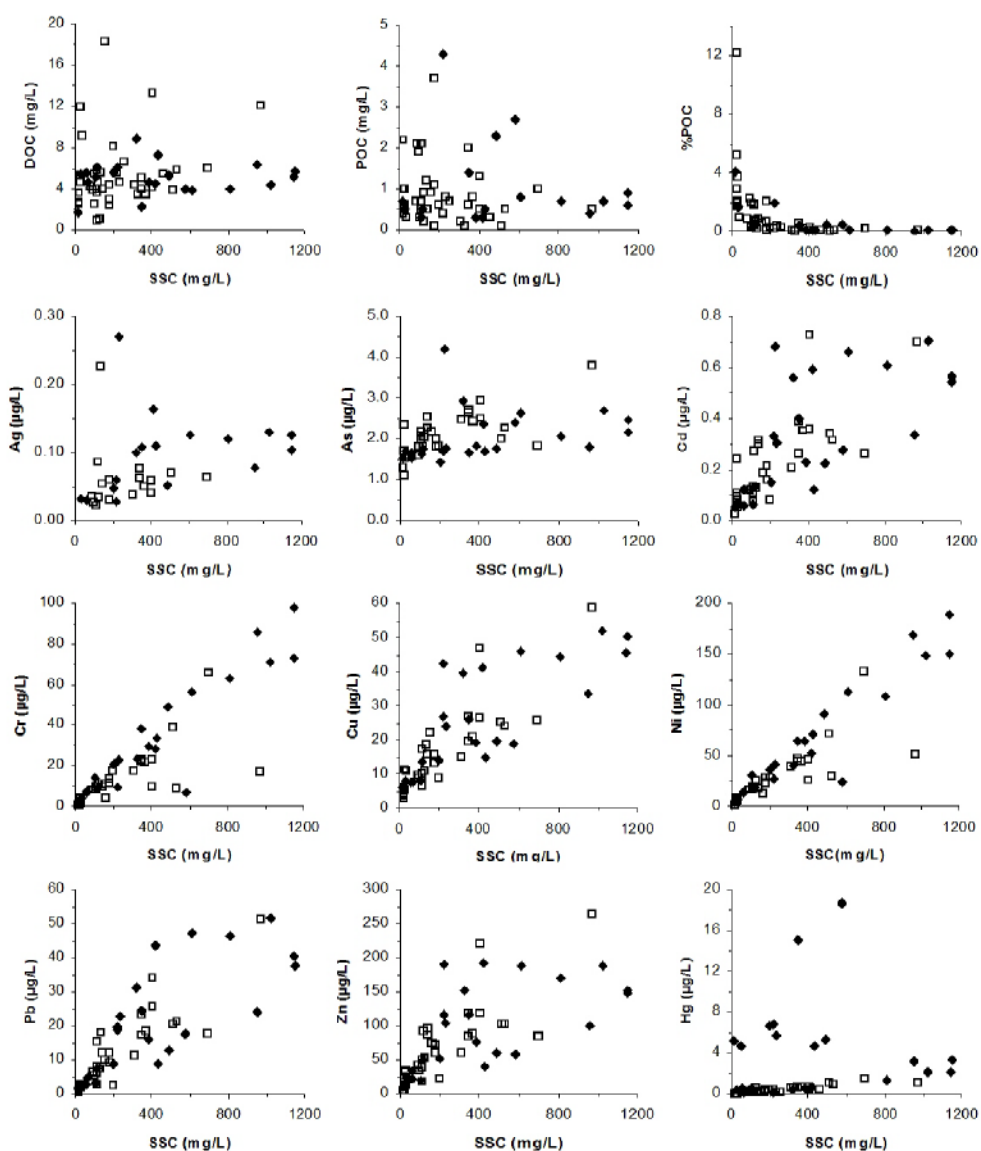
### **Organic Carbon Concentrations**

Sampling for organic carbon, other total trace elements, and Hg was focused on high flow events when concentrations are known to increase over base flow conditions and when the majority of load is transported in the River (Figure 1-3). DOC concentrations ranged between 0.9 - 18.3 mg/L and were similar between years if the data



**Figure 1-3.** Hydrology, SSC, and water sampling periods (■) during the winters of water years 2003 and 2004.

from the first flush (data only available during the second year) are excluded (Figure 1-4). During the first flush, concentrations ranged between 11.9 and 18.3 mg/L. DOC concentrations were variable with respect to SSC and discharge and did not correlate in a linear manner. The FWMC for DOC was 5.3 and 5.9 mg/L for WY 2003 and WY 2004 respectively (Table 1-2). Note that the FWMCs for all analytes were calculated by dividing total load by total discharge for the wet season (October – May) and NOT by using discrete samples only. POC concentrations ranged from 0.1 - 4.3 mg/L



**Figure 1-4.** Relationships between suspended sediment and dissolved organic carbon, particulate organic carbon, other total trace elements, and total mercury during water year 2003 (◆) and water year 2004 (□).

**Table 1-2.** Flow-weighted mean concentrations (FWMC) for parameters measured parameters. Note that the FWMCs were calculated by dividing total load by total discharge for the wet season (October – May) and NOT by using discrete samples only.

	SSC (mg/L)	DOC (mg/L)	POC (mg/L)	Ag (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)	Hg (µg/L)
WY 2003	204	5.3	2.3	0.06	2.0	0.21	14.7	15.5	28.3	11.8	65.4	2.19
WY 2004	191	5.9	1.0	0.06	2.0	0.20	13.9	14.8	26.7	11.0	62.0	0.329

and were similar between years. The FWMC for POC was 2.3 and 1.0 mg/L for WY 2003 and WY 2004 respectively. With the exception of the sample taken at 6:25 am on 12/14/03, 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).

When POC concentrations were compared to DOC concentrations we observed a complex relationship. Low DOC concentrations coincided with both low and high POC concentrations. At intermediate POC concentrations (0.3 - 1.3 mg/L), high DOC concentrations were observed. The pattern POC/DOC variability in the Guadalupe River reflects the combination of samples taken during the first flush of WY 2004, late falling stage samples, and base flow samples taken during periods of stable flow and is most associated with periodic enrichment of DOC. Apparently, an abundance DOC that has built up in the channels or perhaps Almaden Lake is washed out of the watershed during the first flush. It is counterintuitive that a similar phenomenon is not seen for POC. Instead, peak concentrations of POC almost invariably occurred once water from the upper watershed had arrived at our sampling location during a particular storm. The POC observations might be a result of sources from leaf matter associated with riparian vegetation, the transport of dislodged periphyton, or the transport of precipitates and flocculates associated with mine drainage. A full interpretation of POC/DOC processes is not possible at this time but would be relevant to pursue in the context of mercury-release and transport processes in and adjacent to the historic New Almaden Mining District.

### **Total Trace Elements, Total Mercury, and SSC**

Total concentrations of other trace elements showed a variety of patterns with regard to SSC but in general increased in relation to SSC with the exception of a few outliers (Figure 1-4). The patterns of total trace elements relative to SSC appear to be similar for Ag and As, for Cd, Cu, Pb, and Zn, and for Cr, and Ni. Hg varies with SSC in a unique manner relative to the other trace elements. The patterns included first flush phenomenon (when concentrations are highest in the first storms of the year regardless of the discharge magnitude) and hysteresis (when concentrations of Hg and trace elements relative to SSC or discharge are different on the rising stage relative to the falling stage).

During WY 2003, Ag concentrations varied from 0.03 - 0.27  $\mu\text{g/L}$ . In the second year of study, Ag concentrations varied from 0.02 - 0.23  $\mu\text{g/L}$ . In both years the FWMC of 0.06  $\mu\text{g/L}$ . There were three outliers with respect of SSC and no explanation could be found by looking for comparisons with the concentrations of DOC and POC or %POC but they were associated with the falling stage and were not associated with the first storms of the year (first flush).

During WY 2003, As concentrations varied from 1.4 - 4.2  $\mu\text{g/L}$  and exhibited a FWMC of 2.0  $\mu\text{g/L}$ . In the second year of study, As concentrations varied from 1.1 - 3.8  $\mu\text{g/L}$  and exhibited a FWMC of 2.0  $\mu\text{g/L}$ . The two outlier samples with respect of SSC with As concentrations in excess of 3.5  $\mu\text{g/L}$  were associated with the first flush of each season. The concentrations of arsenic that we observed are unremarkable and similar to those observed in Arcade Creek, Sacramento, California (Domagalski and Dileanis, 2000), and in urban areas of the Great Lakes watersheds of Canada (Marsalek and Schroeter, 1988). Our observations support an earlier conclusion (Anderson, 1998) and do not suggest high natural levels of As in the Guadalupe River watershed.

The total cadmium concentrations we observed in the Guadalupe appear typical of other urbanized systems – take for example, the Herring Run watershed tributary to Chesapeake Bay, USA (Lawson et al., 2001). During WY 2003 Cd concentrations varied from 0.05 - 0.70  $\mu\text{g/L}$  and exhibited a FWMC of 0.21  $\mu\text{g/L}$ . In the second year of study, Cd concentrations varied from 0.03 - 0.72  $\mu\text{g/L}$  and exhibited a FWMC of 0.20  $\mu\text{g/L}$ . Cd also exhibited a first flush character; highest concentrations relative to SSC were observed during the November 2002 storm and first storm series of December 2002 and the November 2003 storm.

Copper is commonly found in urban runoff and is known to be found in break pad wear debris (TDC, 2004). During WY 2003 Cu concentrations varied from 6.1 - 52  $\mu\text{g/L}$  and exhibited a FWMC of 15.5  $\mu\text{g/L}$ . In the second year of study, Cu concentrations varied from 2.7 - 59  $\mu\text{g/L}$  and exhibited a FWMC of 14.8  $\mu\text{g/L}$ . Cu also exhibited a first flush character; highest concentrations relative to SSC were observed during the November 2002 storm and first storm series of December 2002 and the November 2003 storm. The copper concentrations we observed appear to be greater than observed in other urban areas. For example, total copper concentrations were only  $6.8 \pm 2.1 \mu\text{g/L}$  ( $106.5 \pm 33.7 \mu\text{M}$ ) in the Herring Run urban area (Lawson et al., 2001) and Domagalski and Dileanis (2000) observed concentrations  $<6 \mu\text{g/L}$  in Arcade Creek. Our observations appear to be more similar to those expected for smaller source areas within the residential, commercial, and industrial urban landscape such as streets, lawns, parking lots and outfalls (Bannerman et al., 1993). The concentrations observed in the Guadalupe also appear to be typical of observations in other Bay Area watersheds - for example, Alameda and Coyote Creeks (Duke et al., 1999), and San Francisquito and Los Trancos Creeks (Owens et al., 2004).

During WY 2003 Pb concentrations varied from 1.5 - 52  $\mu\text{g/L}$  and exhibited a FWMC of 11.8  $\mu\text{g/L}$ . In the second year of study, Pb concentrations varied from 0.2 - 51  $\mu\text{g/L}$  and exhibited a FWMC of 11.0  $\mu\text{g/L}$ . The relationship between SSC and Pb shows a very close similarity to that displayed by SSC and Cu. This observation supports several hypotheses; either Cu and Pb are derived from the same source, or the processes that control the runoff of Cu and Pb are similar. The first hypothesis weakens the notion that copper is mainly associated with break pad wear debris and lead is largely a legacy of gasoline additives. The observations made here might be explained if the reservoir mass of both trace elements are large in the urban environment; under excess reservoir mass conditions, the erosion and transport of suspended sediment might be the limiting

factor that influences concentration and loading patterns in urban runoff rather than source characteristics. Concentrations of Pb in watersheds draining urban areas appear to vary widely; our observations fit within the bounds of observations elsewhere (e.g. Marsalek and Schroeter, 1988; Granier et al., 1990; Duke et al., 1999; Lawson et al., 2001).

During WY 2003 Zn concentrations varied from 9.4 - 193  $\mu\text{g/L}$  and exhibited a FWMC of 65.4  $\mu\text{g/L}$ . In the second year of study, Zn concentrations varied from 4.6 - 265  $\mu\text{g/L}$  and exhibited a FWMC of 62.0  $\mu\text{g/L}$ . In a similar manner to Cd, Cu, and Pb, Zn also exhibited first flush characteristics; concentrations relative to SSC were greater during the first floods of each water year. Our observations of Zn appear to be similar to other observations made in the Bay Area (Duke et al, 1999; Owens et al., 2004) and fall within the lower range of observations made in other parts of the world (e.g. Marsalek and Schroeter, 1988; Granier et al., 1990).

Chromium showed a strong positive relationship with SSC with the exception of four outliers. During WY 2003 Cr concentrations varied from 2.1 - 98  $\mu\text{g/L}$  and exhibited a FWMC of 14.7  $\mu\text{g/L}$ . In the second year of study, Cr concentrations varied from 0.80 - 66  $\mu\text{g/L}$  and exhibited a FWMC of 13.9  $\mu\text{g/L}$ . The four outliers are indicative of the rainfall distribution and timing causing a dominance of runoff from urban areas in relation to when these samples were gathered. During WY 2003 Ni concentrations varied from 3.7 - 189  $\mu\text{g/L}$  and exhibited a FWMC of 28.3  $\mu\text{g/L}$ . In the second year of study, Ni concentrations varied from 1.8 - 133  $\mu\text{g/L}$  and exhibited a FWMC of 26.7  $\mu\text{g/L}$ . The relationship between SSC and Ni is very similar to that of SSC and Cr and includes the same outliers probably caused by the same processes. Our observations of Cr and Ni concentrations fall in the high range of those reported in the literature (chromium and nickel – Granier et al., 1990; nickel - Marsalek and Schroeter, 1988) and appear to be greater in general to observations in some other urban areas (Domagalski and Dileanis, 2000; Lawson et al., 2001). Cr and Ni are known to be associated with the silica-carbonate source rocks of the historic New Almaden Mining District (Bailey and Everhart, 1964). We propose that the watershed geology and historic mining activities have led to additional release of Cr and Ni beyond what might normally be expected from urban runoff alone. A hypothesis that there are naturally high Ni concentrations in the watersheds of the Bay Area (Anderson, 1998) is supported by our observations in the Guadalupe River watershed.

Mercury contamination in California is known to be associated with industrial areas such as electric utilities and geothermal power generation, cement manufacturers, chlor-alkali plants, battery manufacturers, and waste incineration (DTSC, 2002). There are literally thousands uses of mercury in the urban environment – perhaps the most well known being in electrical components such as fluorescent light tubes, dentistry and cosmetic ointments (DTSC, 2002). In addition there are trace amounts of mercury in gasoline and other petrochemicals (0.22 – 3.2  $\mu\text{g/L}$ ) (Conaway et al., 2005). Although urban and industrial uses of mercury are 5x less than the peak consumption of the mid to late 70s, the consumption of gasoline and diesel fuel in the Bay Area has been increasing by about 223 million liters per year over the last decade (CALTRANS, 2002).



Background Hg concentrations in Californian soils range from 0.1 - 0.9 mg/kg (Bradford et al., 1996). Soils in urban areas can range between 0.06-16.7 mg/kg (Kot et al., 2001; Kot et al., 2002; Tijhuis et al., 2002; Münch, 1993; Ordóñez et al., 2003; Fang et al., 2004). Cinnabar mines are the primary source of mercury and mercury concentrations in soils surrounding, downstream and downwind from mining areas can be >1,000 mg/kg but 100 mg/kg is quite typical (e.g. Rytuba, 2002). Gaseous (Gustin, 2003) and aqueous (Lowry et al., 2004; Slowey et al., 2005) discharges as well as soil erosion contaminate water bodies downstream and downwind from urban, industrial and mining areas.

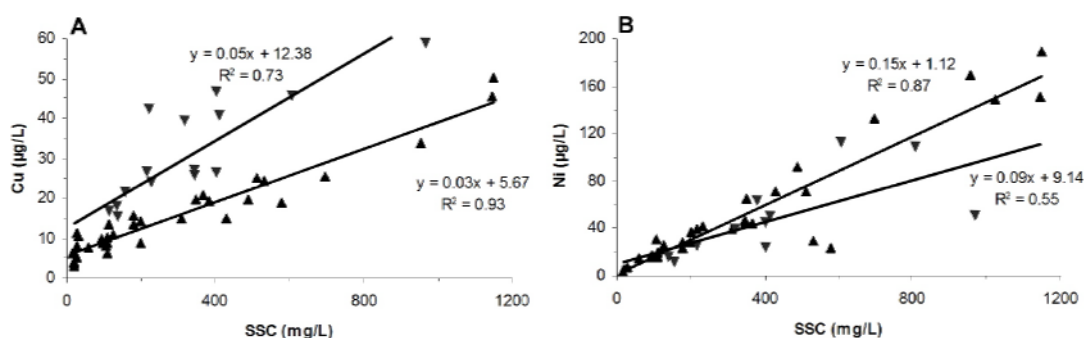
During WY 2003 Hg concentrations in the Guadalupe River varied from 0.18 - 18.67 µg/L and exhibited a FWMC of 2.19 µg/L. In our second year of study (WY 2004), Hg concentrations varied from 0.01 - 1.42 µg/L and exhibited a FWMC of 0.33 µg/L. The variation of Hg relative to SSC was distinctive when compared to the other trace elements, Hg did not exhibit first flush characteristics, and the outliers were uniquely associated with the first year of observations. Our observations during WY 2003 fall within the range of concentrations that might be expected in watershed impacted by mercury mining (McKee and Leatherbarrow, 2005). For example concentrations of total mercury in the surface waters of individual mercury mining areas of California have been reported in the range of 0.001 - 3.070 µg/L (Cache Creek: Domagalski et al., 2004), 0.004 - 12.4 µg/L (New Idria: Ganguli et al., 2000), and 0.485-1,040 µg/L (Gambonini: Whyte and Kirchner, 2000). Rytuba (2000) summarized mercury mine drainage processes across multiple mining areas in the California Coast Range mercury mineral belt citing total mercury concentrations ranging from 0.002 – 450 µg/L. It might be no surprise that the range and magnitude of mercury contamination observed in California has also been observed in the Almadén mines of Spain, the namesake of the historic New Almaden Mining District in the Guadalupe River watershed (0.002 to 20.3 µg/L: Nevado et al., 2003; Gray et al., 2004). Our observations during WY 2004 (and indeed for the rising stages of floods during WY 2003), although still falling in the range that might be expected in mining areas, are perhaps more typical of the upper range of what might be expected in urbanized areas (EPA 1983; Soller et al., 2003; Fang et al., 2004). This provides us with a hypothesis of what might be observed in urban stormwater outfalls if these were systematically sampled during storm runoff. In contrast, other urban areas show creek and outfall concentrations substantially below our FWMC for WY 2004 ranging between 0.001 - 0.210 µg/L (Marsalek and Schroeter, 1988; Domagalski and Dileanis, 2000; Lawson et al., 2001; Owens et al., 2004).

Without regard to source, Hg 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 exceed the U.S. EPA chronic aquatic life water standard (0.012 µg/L; USEPA 1999). In addition, the EPA also suggests a 4-day average criterion of 0.77 µg/L and a 1-hour criterion of 1.4 µg/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 1 time and the 4-day criteria was equaled or exceeded 0 times.

## **The Influence of Urban and Non-urban Runoff on Trace Element Concentrations**

The similarities of the relationships between SSC, other total trace elements, and total mercury are further discovered by comparing concentrations relative to the origins of water. Conceptually, trace elements derived mostly from urban sources should display greater concentrations in urban runoff. Trace elements associated with non-urban sources should exhibit greater concentrations in runoff derived from the upper watershed. This general concept is confounded by trace elements with multiple sources, the timing and mixing of runoff from the upper (non-urban) and lower (urban) watershed, magnitude of runoff, and the first flush phenomenon. We know that runoff generated from rainfall on the high mountains of the upper Guadalupe watershed takes 6 - 7 hours to reach the sampling location. We reasonably expect that most runoff for the first 6 - 7 hours during storm events (excluding base flow) is derived from rainfall and runoff in the lower watershed. In some cases, the flood events were entirely associated with rainfall in the lower watershed (e.g. the flood peak of February 3<sup>rd</sup>, 2004 @ 15:45). In other cases storm runoff was entirely associated with rainfall in the upper watershed (e.g. the flood peak of December 28<sup>th</sup>, 2002 @ 9:00 or December 24<sup>th</sup>, 2003 @ 17:45). Samples were divided into two subsets in this manner. For illustrative purposes, we focused on copper and nickel to demonstrate different kinds of transport response in relation to dominant sources (Figure 1-5).

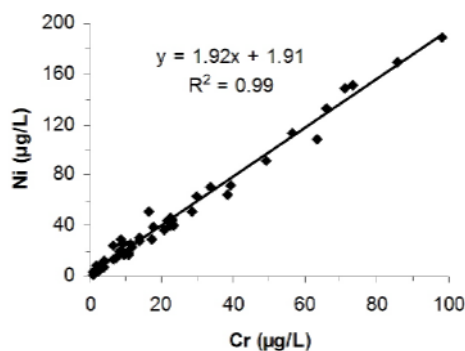
In most watersheds, copper is an urban contaminant. Copper concentration is low in the mineral deposits of the Quick Silver County Park (Bailey and Everhart, 1964). In response to the spatial source distribution across the watershed, Cu concentrations are greater with respect to SSC in water predominantly sourced from the urban lower watershed than in water sourced from the non-urban upper watershed (Figure 1-5A). The stronger relationship between Cu and SSC for upper watershed water relative to the relationship found for lower watershed water seems logical given the likely source of this copper is natural weathering of soils with trace amounts of copper (California average = 29 mg/kg: Bradford et al., 1996) and atmospheric deposition (Tsai et al., 2001; Tsai and Hoenicke, 2001; Nriagu, 1990). Both weathering and atmospheric deposition are processes that are likely to lead to a relatively homogeneous distribution across the upper watershed when compared to heterogeneous sources in the urban environment. In contrast, the relationship between Cu and SSC in the runoff predominantly associated with the urbanized portion of the watershed is less strong. This is suggestive of greater spatial and temporal variability in the release and transport of copper in the Guadalupe urban areas. There are multiple storm drain outfalls and urban creeks that combine to supply the mainstem Guadalupe River with water, sediment and copper loading from urban areas. In addition, the greater variability with respect to suspended sediment might result from a higher proportion of the urban-derived copper being in dissolved form; a suggestion supported by a greater y intercept in the graphical relation between SSC and Cu (Figure 1-5A). Similar patterns are observed for Cd, Pb, and Zn and a similar explanation may be valid.



**Figure 1-5.** The influence of the origin of runoff on concentrations of total copper and total nickel in relation to SSC. Discharge from the urbanized lower watershed (▼) and the non-urbanized upper watershed (▲).

Nickel, like Cu, is commonly monitored in urban runoff. In addition, Ni in the form of millerite (NiS) "...is nowhere abundant but is apparently widespread..." in the silica-carbonate rock of the historic New Almaden Mining District (Bailey and Everhart, 1964). Rytuba (2002) has observed highly elevated concentrations of Ni in mine drainage associated with silica-carbonate Hg mineralization. In the case of the Guadalupe, Ni concentrations with regard to SSC were greater in runoff derived from the non-urban upper watershed areas (Figure 1-5B). The concentrations we observed were much lower than those reported by Rytuba (2002) but in general our observations appear to suggest that the historic New Almaden Mining District and serpentine geology off the upper watershed is a richer source of Ni than the urban area. In a similar fashion to Cu, Ni showed a weaker correlation with SSC in discharge derived from urban runoff. Chromium is also present in the serpentine of the historic New Almaden Mining District (Bailey and Everhart, 1964). Cr shows a similar pattern to Ni in relation to SSC and indeed, Cr correlates strongly with Ni (Figure 1-6). So in summary, Cu, Cd, Pb, and Zn all show greater concentrations relative to suspended sediments in runoff derived mainly from urban areas of the watershed and Cr, Ni, and Hg (discussed in detail below) all show greater concentrations relative to suspended sediments in runoff dominantly derived from the upper watershed.

**Figure 1-6.** The relationship between total chromium and total nickel.



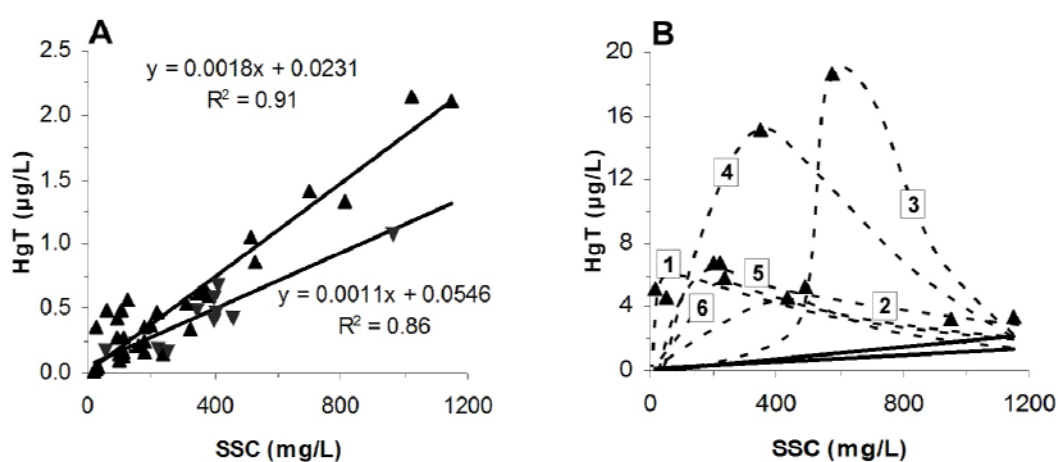
### Mercury Source, Release, and Transport Processes

The source, release and transport processes that influence Hg concentrations at our sampling location are unique with respect to all other parameters measured during this study. The complex patterns appear to be a result of temporally varying release and transport of mercury sourced from urban areas, the historic New Almaden Mining District, and probably temporary storage areas such as stream bank, bar, and terrace sediments (McKee and Leatherbarrow, 2005). The influence of rainfall, runoff and SSC on the pattern of Hg concentrations most closely resembles Cr and Ni; these trace elements all display greater particle concentrations in water sourced from the upper watershed (Note particle concentrations are estimated by dividing the trace element concentration by the SSC). Hg differs however, in that under certain rainfall conditions, concentrations increase beyond any concentration normally observed in runoff predominantly derived from the urban lower watershed ( $< 2.0 \mu\text{g/L}$ ) and may remain elevated during the waning stages of floods (McKee and Leatherbarrow, 2005). We hypothesize that rainfall intensity as well as soil moisture deficit in the historic New Almaden Mining District influences Hg concentrations observed downstream at our sampling location (Table 1-3).

**Table 1-3.** Rainfall intensities, season-to-date rainfall and total mercury concentrations during major floods.

Storm	Peak	Rainfall (mm)			Time of maximum 6-hour intensity	Maximum observed Hg ( $\mu\text{g/L}$ )
		6-hour	24-hour	Season-to-date		
<b>WY 2003</b>						
1	1	15	17	17	11/7/2002 5:00	-
	2	48	81	83	11/7/2002 22:00	0.5
	3	45	130	155	11/8/2002 10:00	4.7
2	1	27	67	226	12/13/2002 19:00	0.4
	2	47	72	283	12/14/2002 18:00	0.7
	3	63	81	373	12/16/2002 6:00	4.7
	4	6	20	392	12/17/2002 9:00	6.7
3	1	44	45	442	12/19/2002 16:00	18.7
4	1	40	55	546	12/28/2002 17:00	15.1
5	1	33	55	721	3/15/2003 5:00	6.8
6	1	25	85	846	4/13/2003 6:00	5.8
<b>WY 2004</b>						
1	1	7	7	13	11/7/2003 6:00	0.2
	2	39	70	83	11/8/2003 23:00	1.1
2	1	30	40	165	12/10/2003 5:00	0.5
	2	4	10	169	12/11/2003 3:00	0.6
3	1	18	18	188	12/14/2003 6:00	0.4
4	1	15	16	213	12/21/2003 0:00	0.1
5	1	14	19	253	12/25/2003 11:00	0.2
6	1	42	66	319	12/29/2003 15:00	0.6
7	1	55	75	394	1/1/2004 13:00	0.4
8	1	36	41	461	2/2/2004 14:00	0.4
9	1	45	60	543	2/17/2004 23:00	0.3
10	1	59	70	625	2/25/2004 12:00	1.4
11	1	11	12	659	3/25/2004 18:00	0.4

The data generated during WY 2004 supports small refinements in the hypothesis presented by McKee and Leatherbarrow (2005). Whereas McKee and Leatherbarrow (2005) placed some emphasis on rainfall for the season-to-date in their hypothesis for *new mercury-release conditions*, this has not endured the reanalysis allowed by a second year of data. For example, based on season-to-date rainfall and 6-hour rainfall intensity, the January 1<sup>st</sup> and the February 25<sup>th</sup> storms of WY 2004 might have been expected to have sufficient force to cause elevated Hg concentrations at our sampling location; this was not observed (Table 1-3). It appears season-to-date rainfall is subordinate compared to the temporal rapidity of successive storms and rainfall intensity which alleviate soil moisture. During 1<sup>st</sup> and 2<sup>nd</sup> peaks of the first two storms in WY 2003, and during all storms of WY 2004 Hg concentrations were slightly lower with respect to SSC on the predominantly urban portion of the hydrograph than on the falling stages of floods when the source of water includes runoff from the non-urban upper watershed (Figure 1-7A). During the 3<sup>rd</sup> peak of storm 1 and the 3<sup>rd</sup> and 4<sup>th</sup> peaks of storm 2 and all subsequent storms in WY 2003, Hg concentrations were  $>2 \mu\text{g/L}$  in the portion of the hydrograph that was dominated by non-urban upper watershed water (Figure 1-7B). The hysteresis pattern shown for storm 2 is constrained by multiple samples; the patterns suggested for the other storms are based on fewer data points and represent our emergent understanding from the two years of data.



**Figure 1-7.** The transport process of total mercury with respect to suspended sediment concentrations during storms with (A) Low intensity rainfall conditions, and (B) High intensity rainfall conditions (Note the storm numbers that are consistent with those in Table 1-3). Downward triangles are for samples in water derived from the lower urban watershed and upward triangles are for samples in water from the upper non-urban part of the hydrograph.

There are at least several alternate hypotheses for our observations other than release caused by intense rainfall. Perhaps the management of release water from the two most mercury contaminated reservoirs (Almaden and Guadalupe) had an influence on Hg in runoff derived from the upper non-urban areas. Concentrations in the reservoir water alone was ruled out (McKee and Leatherbarrow, 2005) but perhaps the releases wetted contaminated bank, bar, and terrace material below the reservoirs sufficiently to release mercury. During WY 2003, both the Guadalupe and Almaden reservoirs were released intermittently beginning December 13<sup>th</sup> and December 19<sup>th</sup> respectively. There were no reservoir releases in WY 2004 during our study period. The reservoir release hypothesis does not explain the high Hg concentration observed during the 3<sup>rd</sup> peak of the 1<sup>st</sup> flood in WY 2003 because this flood occurred before reservoir release began. Another other plausible hypothesis is: Concentrations of Hg exceeding 2 µg/L may be wholly associated with channel resuspension. Under this scenario, perhaps higher rainfall intensity causes increased stream velocities associated with fast rate of rise of the storm hydrograph, resulting in release of Hg associated with more rapid or severe stream bank and bar erosion. Concentrations found in channel bed sediment are known to vary considerably throughout the watershed and have been observed in concentrations >100 mg/kg in contaminated areas of Alamitos Creek and Guadalupe Creek. However, bed sediment as a major source during WY 2003 is largely ruled out by high concentrations during the falling stages of runoff events when channel re-deposition, not resuspension, would be occurring. The third hypotheses results from the observation that WY 2003 followed two years of less than average discharge (WY 2001 [65% Mean Annual Runoff {MAR}] and 2002 [40% MAR]). Perhaps there was a large mass of mercury stored in or near channels adjacent to or downstream of the historic New Almaden Mining District during drier years that was transported out of the system in WY 2003. However, under this scenario, questions arise: why were concentrations not elevated during the 2<sup>nd</sup> peak of the first flood of WY 2003 or the first and larger peak of the 2<sup>nd</sup> flood. Although it is possible that the cause of elevated Hg concentrations during the first year is a combination of both an antecedent mass available for transport and rainfall intensity, it is surprising that the January and February floods of WY 2004 did not cause a similar albeit more moderate release.

The fact that Cr and Ni did not correlate with Hg at Hg concentrations >2 µg/L implies that either Cr and Ni are not present in areas from where these greater concentrations of Hg are sourced or that the process that releases Hg from source areas is selective and does not leach or erode Cr and Ni. “Chromite (Cr<sub>2</sub>O<sub>4</sub>) occurs sparingly in small lenses and irregular stringers in the serpentine of the New Almaden mining district” (Bailey and Everhart, 1964). The Hg bearing silica-carbonate rock is chiefly composed of 35% silica, 60% magnesite (MgCO<sub>3</sub>), up to several percent chromite ((Fe<sup>2+</sup>, Mg) Cr<sub>2</sub>O<sub>4</sub>) or picotite ((Cr, Fe<sup>2+</sup>) Al<sub>2</sub>O<sub>4</sub>) and Ni is present in minor amounts (Bailey and Everhart, 1964). Ni and Cr are found in serpentine soils of the Coast Range of California at concentrations ranging from 1,590 - 4,760 mg/kg and in the case of Cr can be more enriched than the parent rock (Oze et al., 2004). Rytuba (2002) found that other trace elements such as Ni and Cr that are present in silica-carbonate mercury ores are also typically present in calcines in high concentrations (100 – 500 mg/kg).

During the ore roasting process when ore was typically heated to 600-700°C, a number of secondary mercury minerals are formed that are typically more soluble than cinnabar and these remain present in the waste products. Metacinnabar is the most common byproduct mineral in calcines of silica-carbonate deposits and is very fine grained (sub-micrometer) and forms on the surfaces of rock fragments and in the soot of the condensing systems (Rytuba 2003). It appears that these secondary mercury minerals may be subject to preferential mechanical weathering and become enriched in fine fractions. In addition, soluble phases may be subject to increased leaching in as grain size decreases (Kim et al., 2004).

In addition to mechanical weathering, Hg leaching may be associated with changes in pH, conductivity and dissolved oxygen. Acid mine drainage is not a dominant processes of Hg release in the historic New Almaden Mining District (Tetra Tech, 2003). Dolomite ((CaMg(CO<sub>3</sub>)<sub>2</sub>) is the most abundant carbonate in the District and magnesite is the most dominant replacement mineral in the silica-carbonate rocks of the district (Bailey and Everhart, 1964). Siderite (FeCO<sub>3</sub>) is only a minor mineral in the carbonates and pyrite is sometimes locally present (e.g. at the Senator Mine) but seldom associated with cinnabar across the historic New Almaden Mining District (with the exception of Senator Mine) (Bailey and Everhart, 1964). The lack of abundant acid forming minerals and the buffering capacity of the carbonates present, limits acid mine drainage and the release and transport of Hg via this process.

Regnell (1994) described the effect of pH and dissolved oxygen on the release of total and methyl Hg under laboratory conditions. They found that mercury enriched sediment in anaerobic freshwater systems with microbial activity stimulated by available nutrients released mercury. A recent paper by Lowry et al. (2004) and a forthcoming paper (Slowey et al., 2005b) discuss release of Hg colloids and dissolved Hg from mine tailings and waste rock caused by perturbations in ionic strength and organic acid. Their work demonstrates that substantial release of mercury can occur, particularly in the colloidal phase. They submit that similar processes are occurring in mining areas in response to seasonal shifts in ionic strength associated with rainfall and runoff. It possible that this kind of process occurs in the historic New Almaden Mining District but it is not known if these or other processes can achieve selective release of Hg without Cr or Ni. It is possible that the roasting process does not produce soluble or fine particulate forms of Cr or Ni. For example, the oxidation of Cr during the roasting process might lead to Cr<sup>3+</sup>, a less soluble form or Cr<sup>6+</sup> a more soluble form. Given the Hg-Cr-Ni relationships shown by our data, our present hypotheses are: Dissolved, fine grained or colloidal mercury is released from calcined ore stored outside the low flow channels through the physical and geochemical processes described above during high intensity rain events; Ni and Cr are released and transported through rainfall-runoff induced erosion processes more similar to the other trace elements.

As our study progresses we hope to incorporate the results of other ongoing studies in the New Almaden area and employ modeling techniques to better understand the hydrology of the watershed and to help us to accept or reject our current hypotheses on mercury source, release, and transport processes. It is important to resolve the question

of how mercury is released in to the fluvial system under high flow conditions so that watershed management efforts can focus on retarding the release and transport processes.

## **Loads in the Guadalupe River Watershed**

Concentrations of Hg, other total trace elements and our ancillary parameters (DOC, POC, and SSC) have provided useful insights into impacts of runoff from urban areas and the historic New Almaden Mining District on water quality in the Guadalupe River. However, the focus of this study was to determine the loads of mercury and trace elements that pass from the watershed into San Francisco Bay.

### *Maximum Daily Loads*

Daily water discharge in the Guadalupe River watershed varied over 2 orders of magnitude between low flow periods and floods. Daily loads of suspended sediment varied from 0.37 - 3,269 t (Table 1-4). The maximum daily load occurred on December 16<sup>th</sup> 2002 and accounted for 30% of the load during the wet season of WY 2003 (Table 1-4). Maximum daily loads of Cr and Ni also occurred on December 16<sup>th</sup> 2002 and accounted for almost a third of the wet season total during WY 2003. The maximum daily load for all other parameters measured account for 6 - 21% of the total wet season load for WY 2003. During the second and drier year of the study, the maximum daily loads of each trace element generally accounted for a slightly lower portion of the total wet season load, a phenomenon expected for substances that are derived from diffuse sources and adsorbed to particles. The exceptions were DOC, POC, and Hg. We propose that Hg differed from the other substances because in the first year new mercury was released into the system from the historic New Almaden Mining District. In this instance, the maximum daily load for Hg accounted for less of the total wet season load for that year because concentrations increased or remained elevated during the falling stages of floods. Whereas in the second year Hg concentrations more closely followed SSC and dropped rapidly after the peak in discharge; loads were more associated with peak discharge than lower flow periods. We presently offer no strong hypotheses for DOC and POC; perhaps limited supply during much higher flows played a role.

### *Monthly Loads*

Monthly discharge varied by 16x during the wet season of WY 2003 and by 5x during WY 2004 in response to fair weather conditions and Pacific maritime storms passing over the Bay Area (Table 1-5). In months when flooding occurred, suspended sediment was entrained from temporary storage areas and transported from the watershed past our sampling location. Monthly suspended sediment loads in the first year varied by ~400x and were greatest in the months of November and December when both SSC and discharge were the greatest. During these two months, ~46% of the annual water flow occurred and ~87% of the wet season suspended sediment load was transported. During WY 2004, monthly loads varied less in response to a drier year (~70x) and were more evenly distributed across the four months of November to February as a result of many storms that were more moderate in nature than those encountered in the first year. These four months accounted for ~63% of the discharge and ~96% of the suspended sediment load. This magnitude of intra-annual variation is typical of Bay Area watersheds and



**Table 1-4.** Variation of Guadalupe River daily loads of suspended sediments, dissolved and particulate organic carbon, other total trace elements, and total mercury during each water year.

	SS (t)	POC (kg)	DOC (kg)	Ag (kg)	As (kg)	Cd (kg)	Cr (kg)	Cu (kg)	Ni (kg)	Pb (kg)	Zn (kg)	Hg (kg)
<b>WY 2003</b>												
<b>Minimum daily</b>	0.4	20	331	0.002	0.08	0.004	0.03	0.3	0.08	0.2	2	0.002
<b>Maximum daily</b>	3,269	8,080	24,051	0.42	10	1.9	250	149	485	129	541	20
<b>Maximum (% total)</b>	30	7	9	13	10	17	32	18	32	21	16	17
<b>WY 2004</b>												
<b>Minimum daily</b>	0.9	18	64	0.0017	0.07	0.001	0.05	0.2	0.09	0.03	0.3	0.0004
<b>Maximum daily</b>	2,109	8,349	30,689	0.32	8.8	1.4	159	104	307	87	396	3.8
<b>Maximum (% total)</b>	25	19	13	13	10	16	26	16	26	18	15	26

**Table 1-5.** Monthly loads of suspended sediments, dissolved and particulate organic carbon, other total trace elements, and total mercury during each water year. See the methods section for a description of how errors were calculated. See methods section for the calculation of the error term.

	Discharge		SS	DOC		POC		Ag	As	Cd	Cr	Cu	Ni	Pb	Zn	Hg
	(Mm <sup>3</sup> )	(%)	(t)	(kg)	(% TOC)	(kg)	(% TOC)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)
<b>Oct 2002</b>	1.5	2.4	19	13,116	94.7	737	5.3	0.07	2.7	0.14	1.5	10	3.6	5.8	53	0.07
<b>Nov</b>	5.4	8.9	1,709	47,882	94.7	2,690	5.3	0.39	12	1.5	112	117	216	93	468	6.1
<b>Dec</b>	22.8	37.5	7,661	101,581	74.7	34,473	25.3	1.6	49	6.38	549	482	1,057	387	1,913	77
<b>Jan 2003</b>	5.5	9.0	149	15,960	60.2	10,573	39.8	0.26	10	0.60	13	42	26	26	215	4.0
<b>Feb</b>	3.9	6.4	193	18,499	59.0	12,840	41.0	0.19	7.5	0.53	17	36	31	23	174	5.6
<b>Mar</b>	4.0	6.6	245	24,410	58.7	17,191	41.3	0.20	7.9	0.57	20	40	38	26	190	8.5
<b>Apr</b>	6.5	10.7	610	39,771	58.7	28,035	41.3	0.34	12	0.90	48	64	94	45	302	11
<b>May</b>	3.5	5.7	219	21,241	58.7	14,973	41.3	0.17	6.6	0.44	18	31	35	20	150	3.4
<b>Jun</b>	2.3	3.8	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Jul</b>	1.9	3.1	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Aug</b>	1.8	2.9	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Sep</b>	1.8	3.0	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Total</b>	<u>60.8</u>	<u>100.0</u>	<u>10,806</u>	<u>282,460</u>	<u>69.9</u>	<u>121,512</u>	<u>30.1</u>	<u>3.2</u>	<u>108</u>	<u>11</u>	<u>779</u>	<u>820</u>	<u>1,501</u>	<u>626</u>	<u>3,465</u>	<u>116</u>
<b>Error (+/-)</b>			<u>1,635</u>	<u>53,144</u>		<u>22,862</u>		<u>0.6</u>	<u>22</u>	<u>2</u>	<u>179</u>	<u>155</u>	<u>309</u>	<u>114</u>	<u>641</u>	<u>37</u>
<b>Oct 2003</b>	2.0	3.8	36	5,007	53.2	4,406	46.8	0.06	2.6	0.05	1.9	7.1	3.5	0.9	10	0.015
<b>Nov</b>	5.4	10.1	1824	42,452	73.6	15,192	26.4	0.40	12	1.7	111	132	213	104	519	2.6
<b>Dec</b>	9.5	18.1	1591	36,338	79.2	9,526	20.8	0.54	19	1.9	122	135	231	99	578	2.8
<b>Jan 2004</b>	7.9	14.9	2419	52,306	90.8	5,292	9.2	0.51	16	1.9	184	140	355	112	566	4.4
<b>Feb</b>	10.5	19.9	2401	51,389	90.3	5,546	9.7	0.64	22	2.5	182	179	344	134	736	4.1
<b>Mar</b>	4.1	7.8	136	28,768	91.7	2,604	8.3	0.20	7.8	0.44	10	31	22	20	162	0.33
<b>Apr</b>	2.8	5.3	78	25,641	96.8	845	3.2	0.13	5.3	0.32	7.0	22	14	13	112	0.19
<b>May</b>	2.6	5.0	93	23,978	96.8	790	3.2	0.13	4.9	0.27	7.1	19	15	12	101	0.23
<b>Jun</b>	2.0	3.8	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Jul</b>	2.0	3.9	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Aug</b>	2.0	3.7	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Sep</b>	1.9	3.6	----	----	----	----	----	----	----	----	----	----	----	----	----	----
<b>Total</b>	<u>52.8</u>	<u>100.0</u>	<u>8,579</u>	<u>265,880</u>	<u>85.7</u>	<u>44,202</u>	<u>14.3</u>	<u>2.6</u>	<u>90</u>	<u>9.0</u>	<u>625</u>	<u>666</u>	<u>1,197</u>	<u>494</u>	<u>2,784</u>	<u>14.8</u>
<b>Error (+/-)</b>			<u>1,298</u>	<u>50,025</u>		<u>8,316</u>		<u>0.5</u>	<u>18</u>	<u>1.7</u>	<u>143</u>	<u>126</u>	<u>246</u>	<u>90</u>	<u>515</u>	<u>4.7</u>

watersheds in other parts of the world typified by wet-dry climatic regimes (McKee and Eyre, 2002; McKee et al., 2003). The intra-annual variability was also high (~100 - ~370x) for Cr, Ni, Pb, and Hg. This suggests that for this watershed, these substances are dominantly transported attached to particles or, in the case of Hg, as intrinsic Hg-bearing mineral colloids. In contrast, DOC was less episodic, a trait typical of dissolved substances that may be transported efficiently during low flow conditions (e.g. Webb and Walling, 1982).

#### *Wet Season Loads*

Guadalupe River wet season loads varied inter-annually in response to climatic forcing. Runoff in the wet season of WY 2004 was 85% of WY 2003. Suspended sediment loads in WY 2004 were 79% of those in WY 2003, and Ag, As, Cd, Cr, Cu, Ni, Pb, and Zn all followed the same pattern (79 - 83%). DOC was less inter-annually variable than discharge, suggesting that processes other than runoff, such as production in the system, influenced the load observed. In contrast, POC and Hg were much more variable than either discharge or suspended sediment. The processes of POC and Hg release appear to be more complex than runoff and sediment erosion associated with rainfall. In the case of POC, perhaps overland flow associated with the higher rainfall intensity experienced in the first year was responsible for delivering particulate organic matter from watershed surfaces, but delivery of riparian organic matter cannot be ruled out. As stated previously, we postulate that the greater inter-annual variability of Hg was associated with release of contaminated water and / or sediment from within the historic New Almaden Mining District.

Reconnaissance surveys of the District during floods suggests that only a few of the first and second order creeks would have sufficient flow and sediment load to impact the mainstem under the rainfall and runoff conditions during WY 2003 and 2004. This might imply that further remediation to reduce Hg loads is unnecessary in smaller contaminated tributaries, however it is also possible that these creeks are highly episodic and provide high Hg loads during just the wettest years. Detailed work on these small creeks including flood sampling and analysis for Hg and perhaps discharge measurement and loads estimation would help to accept or reject mercury-release hypotheses.

Loads have been estimated previously for the Guadalupe River for suspended sediment and other trace elements (Davis et al., 2000; Leatherbarrow et al., 2002), and Hg (KLI, 2002; Leatherbarrow et al., 2002; Thomas et al. 2002) (Table 1-6). Davis et al. (2000) used a simple model based on land use, rainfall, and runoff coefficients to estimate loads from locally derived land use specific stormwater concentration data. If we use the average of the loads for WY 2003 and WY 2004, the estimates provided by Davis et al. appear to have underestimated suspended sediment loads by ~0.64x and over estimated the trace element loads by 1.2 to 8.2x (Cd: 8.2x, Cr: 1.7x, Cu: 3x, Ni: 1.2x, Pb: 6.1x, and Zn: 3.6x). Estimates for Hg from previous authors are similar to, or 2x those we measured during WY 2004. The loads we measured during WY 2003 are greater than those estimated previously mainly because we observed Hg concentrations at a magnitude not encountered previously. This is important when we consider the San Francisco Bay system as a whole. Our loads analysis on the Guadalupe River and another

**Table 1-6.** Comparisons of WY 2003, and WY 2004 loads in the Guadalupe measured during this study with previous published estimates for the Guadalupe River. See the methods section for a description of how errors were calculated.

	SS (t)	DOC (kg)	POC (kg)	Ag (kg)	As (kg)	Cd (kg)	Cr (kg)	Cu (kg)	Ni (kg)	Pb (kg)	Zn (kg)	Hg (kg)
<b>WY 2003 (This study)</b>	10,806	282,460	121,512	3.2	108	11	779	820	1,501	626	3,465	116
<b>Error (+/-)</b>	1,635	53,144	22,862	0.6	22	2	179	155	309	114	641	37
<b>WY 2004 (This study)</b>	8,579	265,880	44,202	2.6	90	9.0	625	666	1,197	494	2,784	14.8
<b>Error (+/-)</b>	1,298	50,025	8,316	0.5	18	1.7	143	126	246	90	515	4.7
<b>Davis et al., 2000</b>	6,200	-	-	-	-	82.8	1,160	2,244	1,666	3,402	11,200	-
<b>KLI, 2002</b>		-	-	-	-	-	-	-	-	-	-	2.9 - 12.7
<b>Leatherbarrow et al., 2002</b>	11,000	-	-	3	230	9	1,400	700	2,000	500	3,100	29
<b>Thomas et al., 2002</b>	-	-	-	-	-	-	-	-	-	-	-	4 - 30

study of a similar nature carried on at Mallard Island on the Sacramento River (Leatherbarrow et al., 2004) has confirmed that the Guadalupe River is the second largest source of total mercury to the Bay and the largest source to the South Bay. Reduction of mercury loads in the Guadalupe River could help improve water quality of the Bay.

It is difficult to compare Guadalupe River loads with rivers in other parts of the world given different areas and water management. However, this can be achieved by normalizing river loads to watershed area to derive exports (unit mass/unit area/unit time). The estimates for the Guadalupe were made by normalizing with the area downstream of the reservoirs (236 km<sup>2</sup>) rather than the whole watershed area upstream from our sampling location (414 km<sup>2</sup>). This was done based on the hypotheses that the reservoirs capture virtually all Hg. We assumed this because it is most likely true for suspended sediment. Discounting area upstream from reservoir may or may not have been done in the other studies. It appears that the unit exports of Cd, Cr, Cu, Ni, Pd, and Zn are greater than found in the Potomac and Susquehanna (Lawson et al., 2001). However, this observation might be a function of watershed size (larger watersheds would likely have lower unit exports because of a greater potential for storage in sediments and biota or loss to the atmosphere). Here, we have not done an exhaustive review of exports of trace elements in other urban systems; but this should be done in the future to place the Guadalupe results in context.

The export of Hg from watersheds is related to land use and point source influences. Generally, the greater the human use of a watershed, the greater the mercury concentrations in river waters and the exports of mercury out of the system. The export of Hg from the Guadalupe River exceeds all the watersheds reviewed (Table 1-7). Generally the watershed exports of Hg range between 0.3 - 8.5 µg/m<sup>2</sup>/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 µg/m<sup>2</sup>/yr. 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 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). Even so, perhaps the Guadalupe River exhibits one of the highest river exports of Hg 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).

**Table 1-7.** 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<sup>2</sup>) rather than the whole watershed area upstream from our sampling location (414 km<sup>2</sup>). This may or may not have been the case in the other studies.

Reference	Watershed	Land Use	Drainage Area (km <sup>2</sup> )	Hg (µg/m <sup>2</sup> /yr)
<b>This study</b>	Guadalupe WY 2003	Hg mining, urban	236	493
<b>This study</b>	Guadalupe WY 2004		236	63
<b>Domagalski et al. (2004)</b>	Cache, USA WY 2000	Hg mining	2,893	4.3
	Cache, USA WY 2001		2,893	1.6
<b>Lawson et al. (2001)</b>	Potomac, USA	Urban, agriculture, open	72,000	8.50
	Susquehanna, USA	Agriculture, open, urban	29,900	1.35
	Rappahannock, USA	Open, agriculture, urban	4,130	3.35
	Anacostia, USA	?	340	22.21
	Choptank, USA	Agriculture, open, urban	292	3.35
	Blacklick Run, USA	?	6	6.94
	Herring Run, USA	100% urban	6	4.77
	Herrington Cr., USA	?	3	3.96
<b>Feng et al. (2004)</b>	Changchun NE China	Industrial urban	158	24.05
<b>Balogh et al. (1998)</b>	Minnesota 1995	Agriculture, open, urban	44,000	1.4
	Minnesota 1996		44,000	0.97
	Headwater Mississippi, USA 1995	Open, agriculture, urban	51,500	0.51
	Headwater Mississippi, USA 1996		51,500	0.46
	St Croix, USA 1995	Open, agriculture, urban	20,000	0.43
	St Croix, USA 1996		20,000	0.52
<b>Balogh et al., (in press)</b>	St Peter, USA 2000	Mixed	40,145	0.61
	St Peter, USA 2001		40,145	2.2
	Judson, USA 2000	Mixed	29,526	0.26
	Judson, USA 2001		29,526	1.2
	Blue Earth, USA 2000	Mixed	6,294	0.87
	Blue Earth, USA 2001		6,294	5.4
	Le Sueur 2000	Mixed	2,849	3.4
	Le Sueur 2001		2,849	6.4
	Anoka, USA 2002	Mixed	45,440	0.64
	Anoka, USA 2003		45,440	0.35
	Rum, USA 2003	Mixed	3,522	0.58

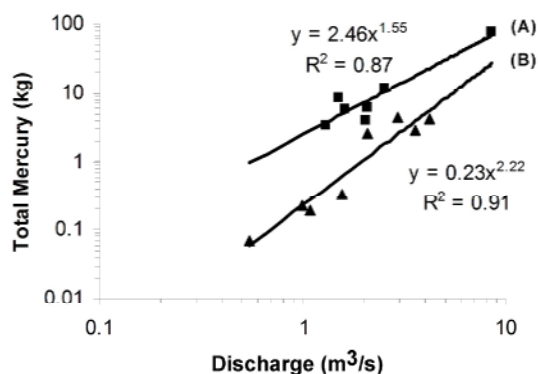
### Annual Mercury Loads, Probable Maximum Loads, and 5-year Averages

Managers interested in the types of data we have collected might ask: What are the 1. Annual loads, 2. Long-term annual average loads, 3. Maximum annual load, 4. What is the average load that might be experienced over 5-year periods of differing climatic forcing, and 5. What is the trend of the system? These questions are hard to answer given only two years of data and the uncertainty in the answers increase from

questions 1 thru 5. Here we present hypotheses for the answers to the first four of these questions and offer some commentary on the question of trends.

The data gathered so far in the Guadalupe River watershed cover only a small portion of the climatic variability described by historic rainfall and runoff records. For example, runoff measured at the San Jose (USGS gauge number 11169000) has varied from 2.9 - 251.8 Mm<sup>3</sup>. In comparison, rainfall and runoff during our study period was 367 and 271 mm and 60.8 and 52.9 Mm<sup>3</sup> for WY 2003 and 2004 respectively (Note WY 2004 is provisional data). Given only two years of data and the added complexity of mercury source, release, and transport, it is challenging to make long-term estimates without a surrogate measure such as a long-term SSC record. Given data limitations, long-term estimates were made using regression relationships between monthly discharge and monthly Hg load (Figure 1-8). The data from our study years were stratified into months when Hg concentrations exceeded 2 µg/L and those that did not exceed 2 µg/L. This stratification was essentially a division between years with the exception of October 2002 which also fell in the latter stratum. Monthly discharge data were retrieved from published USGS records for the previous 30-year period (WYs 1975 - 2004). Santa Clara Valley Water District has been collecting rainfall intensity data near the historic New Almaden Mining District since 1970. Gauge Almaden Watershed RF-4 (Alert I.D. 2080) data were retrieved for the 1975 - 2004 period also. This gauge is just outside the historic New Almaden Mining Area but is located nearby, northwest of Alamitos Road, approximately one half mile southwest of Hicks Road, at Twin Creeks resort. It represents the best indication of rainfall conditions at the southern extent of the historic New Almaden Mining District. Loads for each water year were estimated using the discharge-load regression relationships. During months when rainfall intensity was >50.8 mm (2 inches) in a 6-hour period the regression equation corresponding to the hypothesized *new mercury-release conditions* was applied for that and the subsequent one month. The additional one month Hg load was assumed to be *new mercury-release conditions* because our WY 2003 data suggests that even small amounts of rainfall following large rainfall events causes elevated Hg concentrations at our sampling location. For all other months, the regression equation corresponding to no release was applied.

**Figure 1-8.** Relationship between monthly average discharge and monthly mercury load for (A) Months when Hg concentrations exceeded 2 µg/L (hypothesized *new mercury-release conditions*), and (B) Those months that did not exceed 2 µg/L.



### *Annual Loads*

Annual loads for WYs 2003 and 2004 can be estimated with relative certainty. Most of the flow, suspended sediment load and therefore Hg load occurs in the Guadalupe River during the wet season (McKee et al., 2003). For months when we did not measure loads (June, July, August, and September) we estimated mercury loads using regression relationships (Figure 1-8). Mercury loads for WYs 2003 and 2004 were estimated at 116.4 kilograms and 15.4 kilograms. Thus, not measuring loads during the dry season underestimates annual loads in the Guadalupe River by approximately 0.5 kilograms.

### *Long-term Annual Average Mercury Loads*

The annual average mercury load was estimated by reasonably assuming that the climatic variability of the last 30 years is typical of the range of conditions that might be experienced in the watershed (McKee et al., 2003). The annual average load estimated using the method described above and the regressions (Figure 1-8) was 157 kilograms. If we did not extend the hypothesized *new mercury-release conditions* for an additional one month, the long term average would be 143 kilograms. Even if we use the regression equation generated using mercury concentrations  $<2 \mu\text{g/L}$  (Figure 1-8 (B)) we still arrive at an average annual estimate of 128 kilograms. This occurs because the numerical solutions of the regression equations converge at a discharge of  $34.9 \text{ m}^3/\text{s}$ . The maximum monthly discharge recorded in the Guadalupe River over the past 30 years was  $33 \text{ m}^3/\text{s}$ .

### *Maximum Probable Mercury Load*

Using the methodology described above, annual loads would be expected to range from 26 grams in a water year like 1977 to 1,070 kilograms in a water year like 1983. WY 1977 was one of the driest on record in the Bay Area (McKee et al, 2003). Again, given the convergence of the regression lines (Figure 1-8), the choice of regression line does not have a large influence on the maximum probable load. Using just regression line (B), we estimate the maximum probable load would be 910 kilograms.

### *5-year Average Mercury Loads*

Climate in the Bay Area varies greatly both intra-annually and inter-annually (McKee et al., 2003). In fact, climate in the Bay Area is one of the most variable in the world. This poses a very real problem to City and County managers in the Bay Area who may be asked to manage urban runoff to achieve a permitted stormwater load of mercury. To help deal with this problem, it has been proposed that loads should be averaged over a sufficiently long period reduce the impact of one extremely wet year on causing an exceedance. Although we provide no scientific assessment of what averaging period should be used, we present three possibly useful scenarios: 1. A 3-year averaging period, 2. A 5-year averaging period, and 3. A 7-year averaging period (Table 1-8). This analysis tells us that even if a 7-year averaging period is chosen, average loads over each 7-year period would be expected to vary from 23 - 330 kilograms or about 15 - 210% of the estimated annual average load (157 kilograms).



**Table 1-8.** The range of loads expected in the Guadalupe River on a 3-year, 5-year, and 7-year basis.

	3-year average load (kg)	5-year average load (kg)	7-year average load (kg)
<b>Minimum</b>	1.1	6.2	23
<b>Maximum</b>	519	443	330

*Trends in mercury loads*

To measure trends in either concentrations or loads of mercury in any river system is challenging but even more difficult in the Bay Area given climatic variation. One might reasonably ask what time period is needed to see trends? In general it is accepted that smaller watersheds tend to have lower ability to store sediment and thus lower buffering capacity and “memory” for anthropogenic or natural perturbations. Trends in chemical concentrations and loads are most often observed in watersheds when management initiatives cause a dramatic change, e.g., implementation of secondary or tertiary sewage treatment, or changes to fertilizer management, or animal effluent management. In other cases, water quality improvements have followed the banning of substances such as lead in gasoline. Conaway et al. (undated) showed that Hg concentrations in a south Bay core taken in triangle marsh had already increased by 5 fold over background by 1870 ( $\pm 10$  years). This suggests that watershed loads responded very quickly to the beginning of commercial mercury mining around 1850, an interesting result underscoring the influence of mine tailings transport on the river. But it is less clear how fast the watershed could respond if supply could be “turned off”. It would be useful to review relevant literature and develop a model to predict how long it would take to see reductions of Hg loads in the Guadalupe River under a variety of scenarios.

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**SECTION TWO**

**PCB AND OC PESTICIDE PROCESSES  
IN GUADALUPE RIVER:  
WATER YEARS 2003 AND 2004**

**Jon Leatherbarrow, Lester McKee and John Oram**



## INTRODUCTION

Mass loading of persistent organic contaminants to San Francisco Bay through urban runoff and its impact on water quality impairment is a key issue of concern in developing long-term management plans aimed at attaining water quality standards in the Bay. Organic 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 2004). In 1994, concentrations of these bioaccumulative contaminants measured in Bay sport fish contributed to the issuance of an interim fish consumption advisory, which has since remained in place (OEHHA 1994). In turn, the fish advisory has been the main driver of the development of a PCB TMDL for the Bay (Hetzel 2004).

The use and handling of PCBs and OC pesticides throughout much of the 20<sup>th</sup> century led to widespread distribution of contaminant residues in Bay Area watersheds (Law and Goerlitz 1974). PCBs were used in industrial applications as insulating fluids in transformers, capacitors, and electromagnets, and in various secondary applications (ATSDR 2000). OC pesticides were used as insecticides for agricultural purposes and in urban areas for pest control and mosquito abatement (Mischke et al. 1985; Nowell et al. 1999). Both contaminant classes have been restricted or banned for decades; however, contaminated soils and sediment stored in Bay watersheds serve as ongoing sources of contamination to local waterways and the Bay (KLI 2002; Salop et al. 2002; Leatherbarrow et al. 2002). KLI (2002) and Salop et al. (2002) showed a non-uniform distribution of these contaminants in bed sediment of Bay Area creeks and storm drains characterized by high concentrations in urban areas relative to non-urban areas. Accordingly, current conceptual models suggest that PCBs and chlordane are associated with urban sources, while DDT and dieldrin are linked to both urban and agricultural sources (Davis et al. 2004; Hetzel 2004; Connor et al. 2004).

Efforts to improve our understanding of processes governing the transport of PCBs and OC pesticides in urban runoff to the Bay has been limited mostly to literature review, conceptual models, and land-use-based watershed models (Davis et al. 2000; KLI 2002; Davis et al. 2001; McKee et al. 2003; Hetzel 2004; Davis et al. 2004; Connor et al. 2004). These studies have provided valuable information in highlighting the potentially significant magnitude of contaminant loads from urban runoff relative to other major contaminant transport pathways (e.g., atmospheric deposition). In addition, these studies have informed numerical contaminant fate models and TMDL-related studies that attempt to link contaminant loads from various pathways to the long-term impacts on the entire Bay system. In particular, the current PCB TMDL proposes 95% reduction in urban runoff PCB loads based on an order-of-magnitude estimate of 40 kg/yr from KLI (2002; 2005). In the context of contaminant fate models and TMDLs, the necessity of understanding potential impacts of contaminant loads from urban runoff and benefits of long-term load reductions is evident.

Perhaps the most important outcome of studies conducted thus far has been the identification of key uncertainties in our knowledge of contaminant loading in urban runoff for which further investigation would benefit scientific and management progress.

Current load estimates of PCBs and OC pesticides entering the Bay from urban runoff are only approximate due to the complexities in characterizing the spatial heterogeneity of sources in the watershed. Furthermore, the temporal dynamics of contaminant concentrations and loads has not been well-defined for Bay Area tributaries on varying time scales from hours to decades. Thus, it is difficult to estimate a realistic range of seasonal or annual contaminant loads entering the Bay and how those loads will change over a period of decades. Despite the uncertainties, contaminant fate models and the PCB TMDL use existing estimates for forecasting long-term recovery rates of water quality in the Bay and proposing reduction strategies for attaining water quality targets.

In consideration of these data gaps and uncertainties, this study was implemented in water year (WY) 2003 to improve our knowledge of the magnitude of contaminant loads entering the Bay from urban runoff and improve our understanding of temporal dynamics that influence contaminant loading. The study site is located in a lower reach of Guadalupe River, which drains a heavily urbanized mixed land-use watershed and enters Lower South San Francisco Bay near San Jose, California. This report summarizes the second year of monitoring data collected in WY 2004, which, combined with information collected in WY 2003, will assist in refining our ability to inform future modeling efforts and management strategies for the Bay and its watersheds.

## **METHODS**

### **Sample and Data Collection**

In WY 2004, 20 samples were collected from the sampling location on Guadalupe River at U.S. Highway 101 (See Section One of this report for details on the sampling location). Samples were collected during varying stages of storm events for analysis of PCBs and OC pesticides (Figure 2-1, Table 2-1). Combined with WY 2003 samples, 42 samples in total were collected for organic contaminant analyses. Concentrations of thirty-eight individual and co-eluting PCB congeners were measured and summed to derive total PCB (t-PCB) concentrations in water samples. This group of congeners comprised the 40 PCB congeners that are typically measured by the RMP. Total DDT (t-DDT) concentrations represented the sum of concentrations of o,p' and p,p'-isomers of DDD, DDE, and DDT. Total chlordane (t-chlordane) concentrations represented the sum of alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide. Dieldrin was measured directly. Samples were also collected for analysis of particulate organic carbon (POC) and dissolved organic carbon (DOC). In addition, stream flow and 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.

### **Sample Preparation and Analysis**

Trace organic contaminants were analyzed by AXYS Analytical Services Limited, Sidney, British Columbia, Canada. PCBs were analyzed using high resolution gas chromatography/ high resolution mass spectrometry (HRGC/ HRMS) following EPA method 1668 revision A (USEPA, 1999). Pesticides were analyzed using isotope dilution HRGC/ HRMS. Prior to analysis, two liters were sub-sampled from four-liter sample

bottles, spiked with  $^{13}\text{C}_{12}$ -labeled standards and filtered. The filtrate was liquid/liquid extracted with dichloromethane (DCM), and the particulate was soxhlet extracted with DCM. The two extracts from each sample were combined, reduced in volume and exchanged to hexane. Labeled PCB clean-up standards were spiked into the extract prior to chromatographic column clean up procedures. Clean-up procedures involved separating the extract into two fractions (fraction E1, containing the PCB congeners and less polar pesticides, and fraction E2, containing the more polar pesticides) using a Florisil chromatographic column. The E1 and E2 fractions were separately spiked with labeled recovery (internal) standards prior to instrumental analysis. Samples were analyzed using HRGC/HRMS with a VG 70 VSE HRMS equipped with an HP 5890 gas chromatograph, a CTC auto-sampler, and an Alpha data system running Micromass software. A DB-5 (60 m, 0.25 mm i.d., 0.1  $\mu\text{m}$  film thickness) chromatography column was coupled directly to the MS source. The MS was operated at 8000 (static) mass resolution in the electron impact mode using multiple ion detection, acquiring at least two ions for each target and surrogate compound. Methods of sample preparation and analysis of SSC and organic carbon are described in Section One.

### Quality Assurance and Control

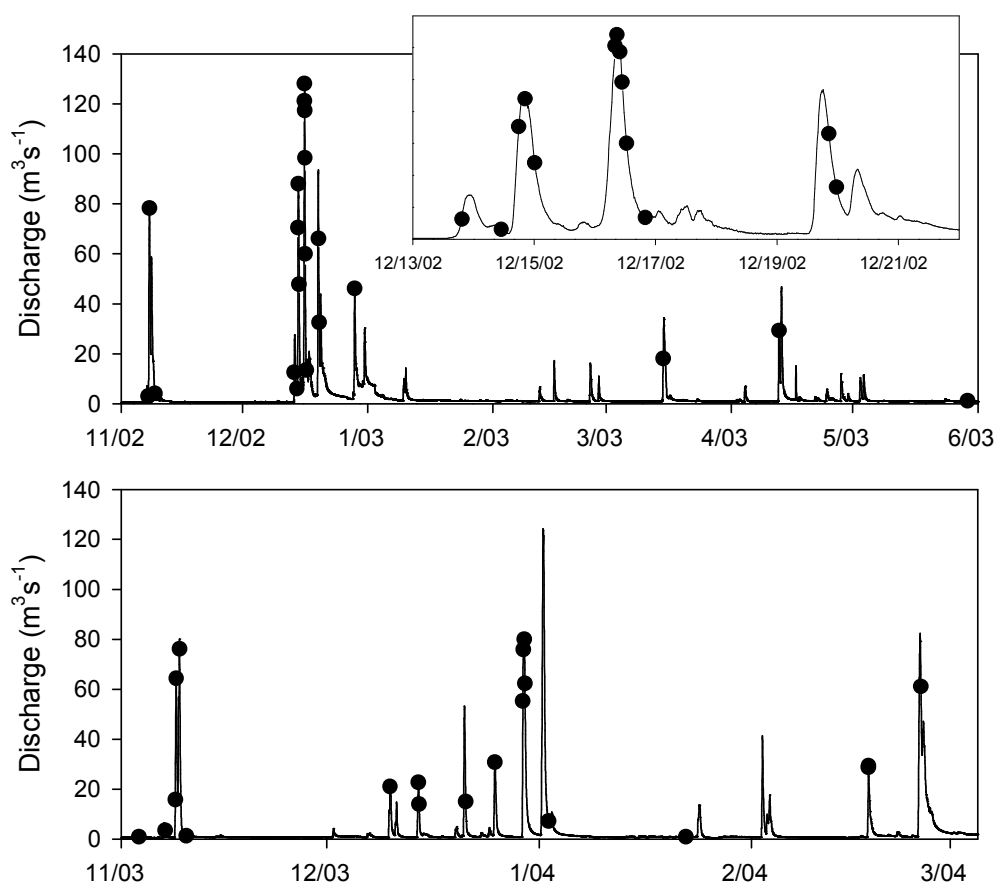
Quality assurance and quality control criteria were based on protocols outlined in the RMP Quality Assurance Program Plan (Lowe *et al.* 1999) and in EPA Method 1668, Revision A (USEPA 1999). Quality assurance samples included laboratory blanks, matrix spikes,  $^{13}\text{C}_{12}$ -labeled surrogate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

### Load Estimation

Contaminant loads were calculated on 15-minute time intervals by relating measured concentrations of PCBs and OC pesticides to measurements of stream flow, turbidity and SSC. The first step involved using LOESS fit between frequent SSC measurements and turbidity collected on 15-minute time intervals to construct a record of SSC on 15-minute time intervals from November 1, 2002 to May 31, 2003 and October 1, 2003 to April 30, 2004. Detailed methods are described in McKee *et al.* (2004). This was done with 238 SSC samples in WY 2003 and 226 SSC samples in WY 2004 and then modified to account for cross-sectional variation in SSC using USGS standard protocols. The second step involved using linear regression between contaminant concentrations and corresponding SSC collected in each sampling event to construct a record of contaminant concentrations on 15-minute time intervals over the duration of study. Finally, contaminant concentrations were multiplied by 15-minute flow volumes to

calculate 15-minute contaminant loads. Contaminant loads were then summed to derive load estimates of daily, monthly, and seasonal time scales.

Errors in contaminant loads were estimated based on estimates of individual sources of error from data collection, laboratory measurement, and regression analyses. The following individual estimated errors were taken into account for data collection: stream flow measurement ( $\pm 10\%$ ), SSC measurement ( $\pm 5\%$ ), regression of turbidity and SSC ( $\pm 2\%$ ), and cross-sectional variability in SSC ( $\pm 10\%$ ). Errors in laboratory measurements of contaminants were estimated based on analytical accuracy:  $\pm 6\%$  for t-PCBs,  $\pm 8\%$  for t-DDT,  $\pm 5\%$  for t-Chlordane, and  $\pm 8\%$  for dieldrin. Regression errors were based on coefficients of determination:  $\pm 24\%$  for t-PCBs,  $\pm 25\%$  for t-DDT,  $\pm 20\%$  for t-Chlordane, and  $\pm 18\%$  for dieldrin. Total errors were estimated by the propagation of errors. Total errors estimated for contaminant loads were  $\pm 30\%$  for t-PCBs,  $\pm 30\%$  for t-DDT,  $\pm 26\%$  for t-Chlordane, and  $\pm 24\%$  for dieldrin.



**Figure 2-1.** Sampling events in Guadalupe River in WY 2003 (upper panel) and WY 2004 (lower panel). Sampling events are depicted as filled circles on the hydrograph. Twenty-two samples were collected in WY 2003. Twenty samples were collected in WY 2004.

**Table 2-1.** Organic contaminants measured in Guadalupe River water samples.

t-PCBs			Pesticides
PCB 008	PCB 128/166		t-DDT
PCB 018/30	PCB 132		o,p'-DDD
PCB 028/20	PCB 138/129/160/163		o,p'-DDE
PCB 031	PCB 141		o,p'-DDT
PCB 033/21	PCB 149/147		p,p'-DDD
PCB 044/47/65	PCB 151/135/154		p,p'-DDE
PCB 049/69	PCB 153/168		p,p'-DDT
PCB 052	PCB 156/157		
PCB 056	PCB 158		t-chlordane
PCB 060	PCB 170		alpha-chlordane
PCB 066	PCB 174		gamma-chlordane
PCB 070/74/61/76	PCB 177		cis-nonachlor
PCB 087/97/86/108/119/125	PCB 180/193		trans-nonachlor
PCB 095/93/98/100/102	PCB 183/185		heptachlor
PCB 099/83	PCB 187		heptachlor epoxide
PCB 101/90/113	PCB 194		Oxychlordane
PCB 105	PCB 195		
PCB 110/115	PCB 201		Dieldrin
PCB 118	PCB 203		

## RESULTS

### Polychlorinated Biphenyls (PCBs)

Total PCB concentrations in WY 2004 ranged from 0.73 to 66 ng L<sup>-1</sup> and exhibited a flow-weighted mean concentration (FWMC) of 26 ng L<sup>-1</sup> (Table 2-2). The maximum t-PCB concentration measured on November 9<sup>th</sup>, 2003 at 12:07 AM coincided with a stream discharge of 64 m<sup>3</sup>s<sup>-1</sup> and a maximum SSC of 1,068 mg L<sup>-1</sup>. In all samples, hexa-, hepta-, and octa-chlorobiphenyls comprised approximately 45 to 64% of t-PCB concentrations. All PCB congener concentrations were above detection limits and reported (Table 2-3). Relative percent differences (RPDs) of PCB congener concentrations in duplicates were below QA limits of <35%.

Daily, monthly, and seasonal PCB loads were estimated for the wet season of WY 2004 using only the linear regression parameters derived from t-PCB concentrations and SSC measured in the second year of monitoring. Total PCB concentrations were positively correlated to SSC in WY 2004 samples (Figure 2-2). Daily loads of t-PCBs ranged from 0.56 to 126 g with the maximum occurring on January 1, 2004 and comprising approximately 18% of the seasonal load. Monthly loads ranged from 15 to 182 g t-PCBs (Table 2-4). Maximum monthly loads occurred in February (26% of seasonal load) and January (23%). A seasonal load of 0.70 kg of t-PCBs was estimated for WY 2004.

## Organochlorine Pesticides

Total DDT concentrations in WY 2004 ranged from 0.55 to 55 ng L<sup>-1</sup> and exhibited a FWMC of 28 ng L<sup>-1</sup> (Table 2-2). Total DDT concentrations were comprised primarily of p,p'-DDE (22 to 53%), p,p'-DDD (12-38%), and p,p'-DDT (10-45%). Total chlordane concentrations ranged from 0.63 to 53 ng L<sup>-1</sup> and exhibited a FWMC of 25 ng L<sup>-1</sup> (Table 2-2). Total chlordane concentrations were comprised primarily of alpha-chlordane (27-36%), gamma-chlordane (24-31%), and trans-nonachlor (19-30%). Dieldrin concentrations ranged from 0.19 to 3.8 ng L<sup>-1</sup> and exhibited a FWMC of 2.0 ng L<sup>-1</sup> (Table 2-2). Pesticide concentration ranges measured in WY 2004 were similar to ranges measured in WY 2003 for t-DDT (1.7 to 71 ng L<sup>-1</sup>), t-chlordane (1.6 to 64 ng L<sup>-1</sup>), and dieldrin (0.3 to 6.0 ng L<sup>-1</sup>). Similar to PCBs, maximum concentrations of dieldrin were measured on November 9th, 2003 at 12:07 AM when discharge was 64 m<sup>3</sup>s<sup>-1</sup> and maximum SSC was measured at 1,068 mg L<sup>-1</sup>. Maximum concentrations of t-DDT and t-chlordane were measured on December 29<sup>th</sup> at 5:10 PM when discharge was 76 m<sup>3</sup>s<sup>-1</sup> and SSC was 405 mg L<sup>-1</sup>. Of all pesticides measured, only one concentration of o,p'-DDD was below detection (Table 2-3). All RPDs in pesticide concentrations in field duplicates were within QA limits (<35%).

Daily, monthly, and seasonal pesticide loads were estimated based on 15-minute loads estimated using the regression between pesticides and SSC (Figure 2-2). Daily loads of pesticides ranged from 0.38 to 122 g t-DDT, 0.22 to 108 g t-Chlordane, and 0.033 to 8.9 g dieldrin. For all three pesticides, maximum daily loads occurred on January 1, 2004 and comprised approximately 16 to 20% of the seasonal pesticide loads. Monthly pesticide loads ranged from 16 to 181 g t-DDT, 9.4 to 146 g t-Chlordane, and 1.4 to 14 g dieldrin (Table 2-4). Maximum monthly loads occurred in January (23-25%) and February (26-27%). Estimated seasonal loads of pesticides were 0.70 kg t-DDT, 0.55 kg t-chlordane, and 0.054 kg dieldrin.

## DISCUSSION

### Comparison of Two Years of Monitoring

A comparison of contaminant loads between the two years of monitoring provides some initial insight into the inter-annual variability of contaminant transport in runoff in response to variable hydrology and sediment discharge. Contaminant loads were lower in WY 2004 compared to the previous year due to reduced runoff volumes and sediment loads. Runoff and sediment loads in WY 2004 were 87% and 81% of values measured in WY 2003. As a result, contaminant loads in WY 2004 were approximately 58 to 70% of loads estimated in WY 2003. Nevertheless, linear relationships between contaminants and SSC remained relatively consistent between the two years (Figure 2-2), indicating that sediment supplied to the lower watershed is relatively uniform with respect to contamination by PCBs and OC pesticides. Furthermore, variability in contaminant loads was mostly driven by variability in sediment loads.

Another difference between years is in the temporal distribution of contaminant loads. In WY 2003, approximately 57 to 61% of contaminant loads occurred in the month of December, whereas the same proportion of contaminant loading in WY 2004 was

**Table 2-2.** Summary of hydrology, water quality, and organic contaminant concentrations in Guadalupe River water samples. DDD, DDE, and DDT represent the sum of o,p' and p,p'-isomers of each compound. FWMC = flow-weighted mean concentration.

Date	Time	Q	SSC	POC	DOC	TOC	t-PCB	t-DDT	DDD	DDE	DDT	t-CHL	ACHL	GCHL	TNON	DIEL
			m3/s	mg/L	mg/L	mg/L	mg/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
WY2003	Range						3.4-90	1.7-71	0.9-17	0.4-31	0.3-26	1.6-64	0.5-19	0.4-19	0.4-18	0.3-6.0
	FWMC						55	45	10	19	17	40	11	11	12	3.8
WY2004	Range						0.7-66	0.6-55	0.3-12	0.1-25	0.09-19	0.6-53	0.2-16	0.2-16	0.1-15	0.2-3.8
	FWMC						26	28	6	12	10	25	7.3	7.2	6.7	2.0
9/30/2003	12:28	0.7*	18*	2.2	2.5	4.7	0.93	0.55	0.34	0.13	0.09	0.63	0.23	0.17	0.13	0.19
11/3/2003	13:30	1.0	28	0.6	11.9	12.5	3.5	1.7	0.68	0.63	0.38	2.0	0.62	0.57	0.49	0.28
11/7/2003	9:51	3.5	157	0.9	18.3	19.2	14	7.1	1.8	2.8	2.5	7.3	2.3	2.1	1.9	1.0
11/8/2003	21:25	16	310	1.3	13.3	14.6	47	32	12	12	8.0	20	5.8	6.2	5.1	2.1
11/9/2003	0:27	64	1068	0.5	12.1	12.6	66	49	12	22	14	52	16	15	14	3.8
11/9/2003	12:28	76	598	0.5	5.8	6.3	21	30	6	14	11	28	8.4	8.0	7.5	2.8
11/10/2003	11:57	1.3	29	0.5	5.3	5.8	3.4	2.4	0.85	0.89	0.69	2.5	0.82	0.69	0.58	0.52
12/10/2003	5:31	21	348	2.0	5.0	7.0	44	43	10	19	15	23	6.9	7.0	5.9	1.9
12/14/2003	9:13	23	179	1.1	2.4	3.5	17	19	3.4	9.4	6.1	15	4.6	4.5	3.9	1.5
12/14/2003	11:27	14	98	2.1	3.8	5.9	10	8.4	1.6	3.8	3.0	8.4	2.5	2.4	2.3	0.92
12/21/2003	7:05	15	107	0.7	4.0	4.7	8.3	9.4	1.8	4.5	3.0	7.9	2.4	2.2	2.1	1.1
12/25/2003	13:10	31	117	2.1	3.6	5.7	20	15	3.3	5.1	6.5	10.0	3.0	3.1	2.5	0.94
12/29/2003	15:00	55	310	0.5	4.1	4.6	30	26	6.9	9.4	10	22	6.3	6.5	6.0	1.6
12/29/2003	17:10	76	405	0.8	3.4	4.2	20	55	11	25	19	53	15	16	15	3.4
12/29/2003	20:10	80	329	0.6	4.0	4.6	24	25	6.8	9.2	9.2	18	5.3	5.2	4.9	1.5
12/29/2003	22:15	62	310	0.2	4.4	4.6	14	19	3.7	8.1	6.7	17	5.2	4.6	4.5	1.8
1/2/2004	8:46	7.3	198	0.6	8.1	8.7	4.4	7.1	1.0	3.8	2.3	4.4	1.2	1.0	1.1	0.71
1/2/2004	8:48	7.3	198	0.6	8.1	8.7	4.1	6.4	1.0	3.4	1.9	3.5	1.0	0.84	0.86	0.69
1/22/2004	10:35	1.0	19	1.0	2.5	3.5	0.73	0.61	0.27	0.18	0.15	0.81	0.28	0.21	0.15	0.22
2/18/2004	1:25	29	179	0.1	4.4	4.5	24	18	4.3	5.7	8.0	15	4.4	4.4	4.0	1.5
2/18/2004	1:40	29	179	0.1	4.4	4.5	19	16	3.5	5.6	6.9	14	3.7	4.1	3.7	1.4
2/25/2004	17:30	61	713	1.0	6.0	7.0	19	19	3.3	8.6	7.3	16	4.3	4.0	4.7	1.4

\* Reasonably assumed to be the same as 10/1/03

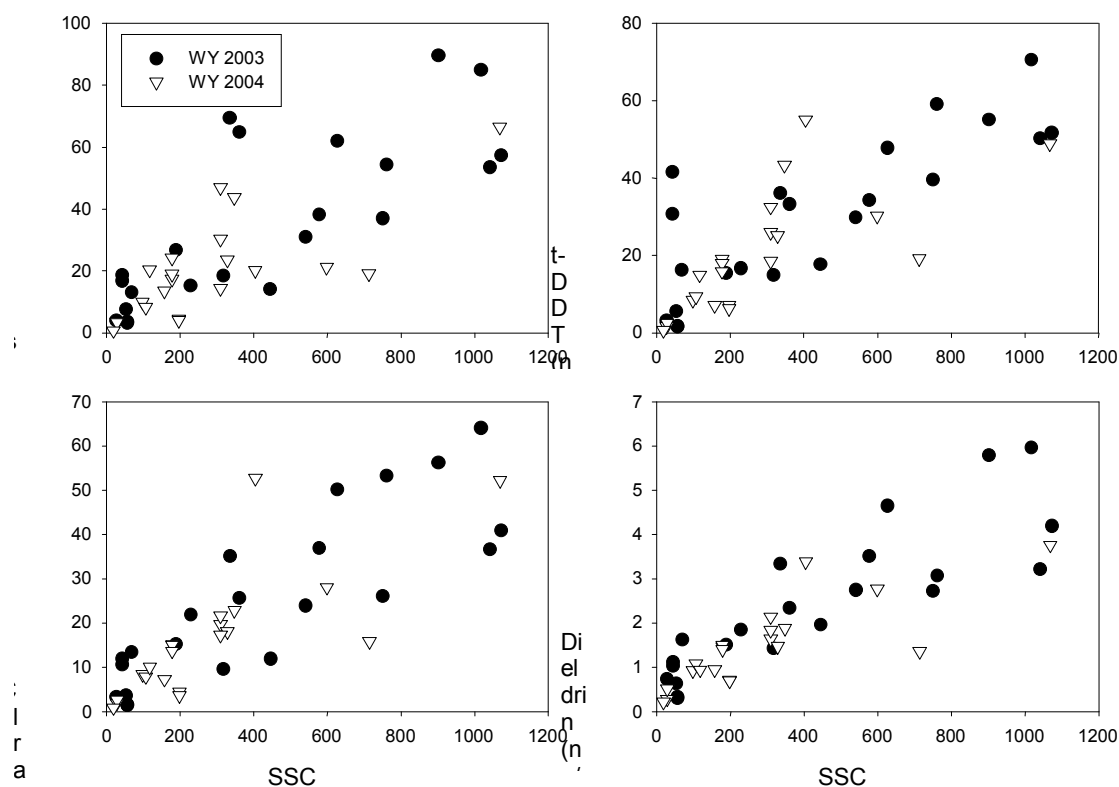
**Table 2-3.** Quality assurance and control summary. MDL = method detection limit. DF = detection frequency of contaminants in samples. RPD = relative percent difference of concentrations measured in two field duplicates. Accuracy is the range of matrix spike recoveries in three to five QA samples.

	MDL	Blanks	Samples	DF	RPD	Accuracy
PARAMETER	(pg/L)	(pg/L)	(pg/L)	(%)	(%)	(%)
PCB 001	-	-	-	-	-	94-122
PCB 003	-	-	-	-	-	93-123
PCB 004	-	-	-	-	-	95-115
PCB 008	0.25-3.53	2.15-3.37	1.23-102	100	22-23	-
PCB 015	-	-	-	-	-	91-109
PCB 018/30	0.08-2.05	2.57-5.84	11.4-546	100	15-29	-
PCB 019	-	-	-	-	-	103-117
PCB 028/20	0.16-1.58	2.99-6.27	4.11-1810	100	15-16	-
PCB 031	0.16-1.55	3.06-4.78	2.18-1200	100	15-25	-
PCB 033/21	0.16-1.54	1.99-2.26	0.94-620	100	15-22	-
PCB 037	-	-	-	-	-	86-106
PCB 044/47/65	0.03-0.99	2.4-6.51	17.3-2020	100	12-13	-
PCB 049/69	0.02-0.94	1.06-3.94	11.4-1290	100	14-19	-
PCB 052	0.03-1.04	3.64-9.21	37.2-2320	100	11-12	-
PCB 054	-	-	-	-	-	105-124
PCB 056	0.2-7.44	ND-5.26	1.2-1190	100	5-11	-
PCB 060	0.2-7.25	ND-2.65	1.67-708	100	4-9	-
PCB 066	0.18-6.85	1.96-10.2	7.53-2190	100	8-8	-
PCB 070/74/61/76	0.18-6.9	3.17-36.9	11.9-3930	100	7-9	-
PCB 077	-	-	-	-	-	90-103
PCB 081	-	-	-	-	-	88-105
PCB 087/97/86/108/119/125	0.3-4.83	0.76-29.3	28.4-2300	100	8-22	-
PCB 095/93/98/100/102	0.33-5.39	ND-18.7	54.7-2790	100	13-16	-
PCB 099/83	0.35-5.49	0.84-24.7	26.1-1760	100	2-21	-
PCB 101/90/113	0.3-4.85	2.08-49.9	49.5-3290	100	1-23	-
PCB 104	-	-	-	-	-	97-112
PCB 105	0.33-9.7	0.48-5.15	9.32-1290	100	8-28	90-100
PCB 110/115	0.26-4.14	1.77-40.6	61-4290	100	2-21	-
PCB 114	-	-	-	-	-	90-106
PCB 118	0.31-8.82	1.25-16	24-2710	100	6-29	90-101
PCB 123	-	-	-	-	-	90-106
PCB 126	-	-	-	-	-	87-109
PCB 128/166	0.1-8.74	0.35-2.76	8.05-840	100	14-34	-
PCB 132	0.12-10.3	0.58-6.61	21.6-1780	100	6-32	-
PCB 138/129/160/163	0.1-8.52	1.2-17.6	54.5-5230	100	16-30	-
PCB 141	0.11-9.72	0.25-3	10.1-937	100	24-32	-
PCB 149/147	0.11-9.12	0.71-16.6	58.1-3920	100	13-27	-
PCB 151/135/154	0.03-1.06	ND-6.58	30.5-1950	100	2-28	-
PCB 153/168	0.09-7.63	1.49-17.6	47.7-3820	100	21-31	-



**Table 2-3 (continued).** Quality assurance and control summary. MDL = method detection limit. DF = detection frequency of contaminants in samples. RPD = relative percent difference of concentrations measured in two field duplicates. Accuracy is the range of matrix spike recoveries in three to five QA samples.

PARAMETER	MDL (pg/L)	Blanks (pg/L)	Samples (pg/L)	DF (%)	RPD (%)	Accuracy (%)
PCB 155	-	-	-	-	-	99-111
PCB 156	-	-	-	-	-	103-108
PCB 156/157	0.1-9.5	0.3-0.93	4.71-569	100	Jul-34	-
PCB 158	0.08-7	0.21-1.85	5.07-527	100	Sep-33	-
PCB 167	-	-	-	-	-	101-107
PCB 169	-	-	-	-	-	101-111
PCB 170	0.04-1.62	0.55-3.5	13.1-1290	100	17-21	-
PCB 174	0.04-1.49	0.24-4.51	16.2-1680	100	13-28	-
PCB 177	0.04-1.6	0.14-2.6	11.3-1040	100	17-30	-
PCB 180/193	0.03-1.28	0.75-8.4	31.9-3190	100	14-20	-
PCB 183/185	0.03-1.44	0.23-3.17	11.1-1040	100	19-29	-
PCB 187	0.03-1.36	0.44-6.09	22.8-2190	100	14-29	-
PCB 188	-	-	-	-	-	103-110
PCB 189	-	-	-	-	-	88-108
PCB 194	0.03-1.31	0.16-1.29	7.65-721	100	16-30	-
PCB 195	0.04-1.4	0.18-0.36	3.27-277	100	18-21	-
PCB 201	0.02-0.32	ND-0.28	1.2-116	100	4-27	-
PCB 202	-	-	-	-	-	98-104
PCB 203	0.03-0.39	0.12-1.01	5.59-965	100	15-21	-
PCB 205	-	-	-	-	-	97-106
PCB 206	-	-	-	-	-	101-112
PCB 208	-	-	-	-	-	100-106
PCB 209	-	-	-	-	-	94-104
Pesticides						
o,p'-DDD	1.95-77	ND	70-2990	95	2-18	87-101
o,p'-DDE	ND-79.7	ND	ND-3090	100	18-28	72-93
o,p'-DDT	2.69-94.3	ND	21.6-2990	100	16-16	85-99
p,p'-DDD	2.39-89.9	ND	203-9610	100	5-24	83-110
p,p'-DDE	0.77-133	ND	120-24200	100	1-8	91-106
p,p'-DDT	3.49-124	ND	63.5-16000	100	15-20	96-109
alpha-Chlordane	1.13-61.2	ND-0.7	226-15700	100	18-19	91-106
gamma-Chlordane	0.99-50.9	2.17-4.26	165-15500	100	8-22	93-103
cis-Nonachlor	4.02-164	ND-4.39	50-5860	100	7-33	95-106
trans-Nonachlor	1.27-73.1	ND-5.63	133-14600	100	7-26	94-101
Heptachlor	0.05-8.09	1.43-5.86	2.76-432	100	11-14	98-103
Heptachlor Epoxide	0.05-22.4	ND-ND	31.2-900	100	5-8	96-106
Oxychlordane	0.27-488	ND-1.29	21.5-902	100	4-33	88-117
Dieldrin	0.07-20.5	ND-2.91	192-3760	100	2-6	89-111



**Figure 2-2.** Scatter plots of organic contaminants and SSC in samples from WY 2003 and WY 2004. WY 2003 samples appear as filled circles. WY 2004 samples appear as open triangles.

spread out over 2 to 3 months. 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. It is reasonable to hypothesize that short-duration pulses of a certain magnitude of contaminant load entering the South and Lower South Bays will create greater localized storage of contaminated sediment compared to longer-duration loads of an equal magnitude that allow more time for in-Bay processes of dilution, deposition, burial, and/or advection to mitigate the impacts of the contaminant load. The differences that may occur due to this phenomenon, along with added complexities of transport of constituents from freshwater to tidal waters, highlight a need for greater understanding of the fate of runoff-derived contaminant loads entering the Bay.

Given that two years of monitoring at Guadalupe River has captured storm flows in years of near-average runoff volumes, a key uncertainty in understanding long-term variability in contaminant loads is the nature of contaminant-SSC relationships during extreme wet years. Annual runoff volumes during WYs 2003 (61 Mm<sup>3</sup>) and 2004 (53 Mm<sup>3</sup>) were lower than the 30-year maximum (252 Mm<sup>3</sup>) by a factor of four. If linear

responses to increased flows were realized in contaminant loads, then loads during wettest years would be higher by similar proportions; however, it is possible that the covariance of SSC with contaminants will change at higher flows in response to catastrophic events, such as debris flows, or from greater variety of sediment- and contaminant-source activation within the watershed. Thus, efforts to understand the long-term fate of contaminant loads entering the Bay must consider the potential impacts on contaminant storage and residence times from “new” contaminant loads transported during extreme events or seasons.

**Table 2-4.** Monthly and seasonal loads of SSC, PCBs, and OC pesticides in Guadalupe River for WYs 2003 and 2004.

WY 2003	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Annual
Discharge (Mm <sup>3</sup> )	1.5	5.4	22.8	5.5	3.9	4.0	6.5	3.5	2.3	1.9	1.8	1.8	60.8
Percent annual (%)	2.4	8.9	38	9.0	6.4	6.6	11	5.7	3.8	3.1	2.9	3.0	
SSC (t)	19	1,709	7,661	149	193	245	610	219	----	----	----	----	10,800
Percent annual (%)	0.18	16	71	1.4	1.8	2.3	5.6	2.0	----	----	----	----	
PCB (g)	16	156	686	66	52	57	103	49	----	----	----	----	1200 ± 210
DDT (g)	13	137	599	67	51	56	99	48	----	----	----	----	1100 ± 270
CHLOR (g)	8.1	108	477	39	32	36	66	30	----	----	----	----	790 ± 130
DIEL (g)	1.1	11	48	4.8	3.8	4.1	7.4	3.5	----	----	----	----	82 ± 17
Percent annual (%)	1	13-14	57-61	5-6	4-5	5	8-9	4-5					

WY 2004	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Annual
Discharge (Mm <sup>3</sup> )	2.0	5.4	9.5	7.9	11	4.1	2.8	2.6	2.0	2.0	2.0	1.9	52.8
Percent annual (%)	3.8	10	18	15	20	7.8	5.3	5.0	3.8	3.9	3.7	3.6	100
SSC (t)	36	1824	1591	2419	2401	136	78	93	----	----	----	----	8,600
Percent annual (%)	0.42	21	19	28	28	1.6	0.91	1.1	----	----	----	----	100
PCB (g)	15	121	138	166	182	34	22	22	----	----	----	----	700 ± 200
DDT (g)	16	119	139	163	181	36	24	23	----	----	----	----	700 ± 210
CHLOR (g)	9.4	101	107	137	146	22	14	14	----	----	----	----	550 ± 140
DIEL (g)	1.4	8.8	11	12	14	3.1	2.0	2.0	----	----	----	----	54 ± 13
Percent annual (%)	2-3	16-18	19-20	23-25	26-27	4-6	3-4	3-4					

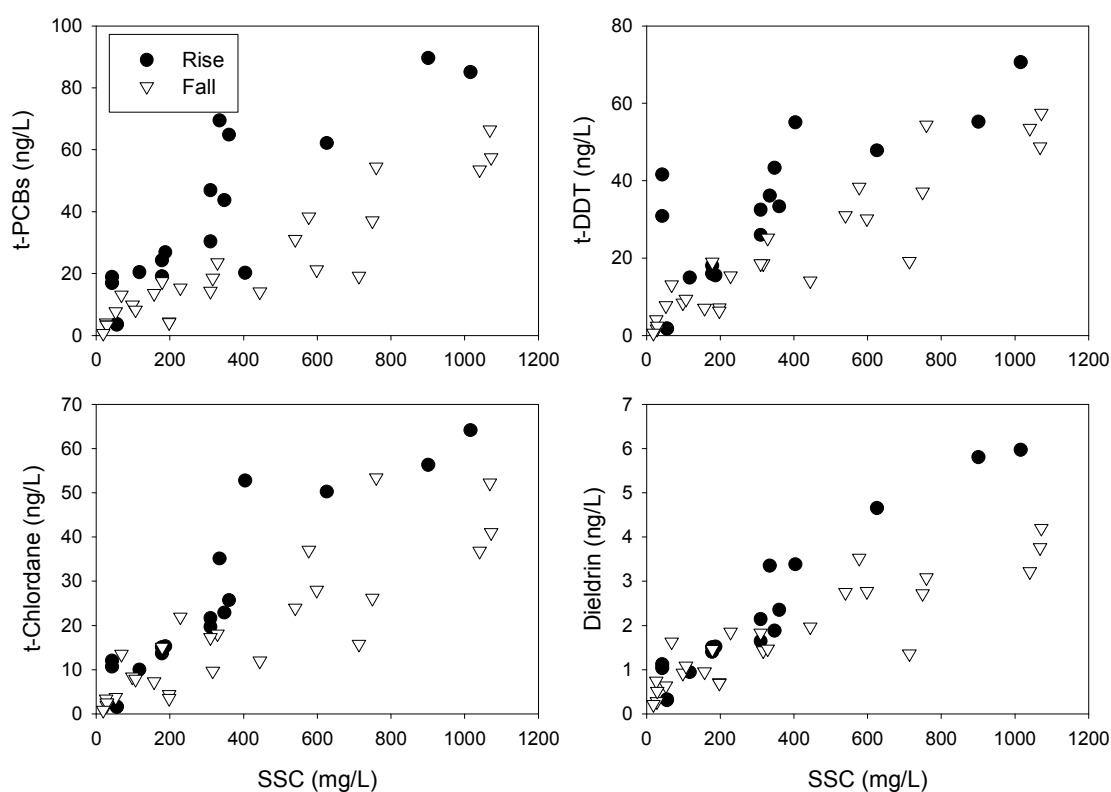
## Urban and Non-urban Runoff

Although contaminant concentrations on suspended sediment were relatively consistent between monitoring years, concentrations varied appreciably on storm-event time scales due to varying sources of runoff. Linear regressions of contaminant concentrations and SSC indicate that sediments sampled during rising stages of storm events were more contaminated than falling stage samples (Figure 2-3). In other words, for a given measurement of SSC, contaminant concentrations were generally higher in samples collected on the rising stage of a storm event compared to falling stage samples. This pattern was consistent over numerous storm events in both years of study and further supports the hypothesis stated in Leatherbarrow and McKee (2005) that runoff originating from the predominately urbanized lower watershed has a greater level of contamination by PCBs and OC pesticides than upper watershed runoff. Thus, the observed variations in rising and falling stage data sets could be used to differentiate between contaminant loads originating from both urban and non-urban runoff. To accomplish this task, it is necessary to use this information in conjunction with an appropriate hydrologic model that can generate information on the source of runoff.

Contaminant loads in Guadalupe River were compared to loads estimated for other river systems to evaluate potential influences of land use (Table 2-4). Loads were compared between watersheds by normalizing to watershed area to gain a general understanding of how different land uses differ in their contribution to tributary loading. For Guadalupe River loads, an effective drainage area was estimated to be 236 km<sup>2</sup> by subtracting the areas upstream of the major reservoirs (178 km<sup>2</sup>) from the total watershed area upstream from the study location (414 km<sup>2</sup>). Watershed yields of PCBs and chlordane from the densely urbanized watersheds of Guadalupe River and Anacostia River were an order of magnitude higher than yields from other predominately agricultural or open space watersheds, except for Susquehanna River. This is consistent with the current conceptual models that link these contaminants to historic usage and applications primarily in urban areas (Davis et al. 2004, Connor et al. 2004). Less distinct differences were observed in watershed yield estimates of DDT and dieldrin; this is likely a result of the historical application of these pesticides for both agricultural and urban purposes over a wide area of the watershed (Connor et al. 2004).

Watershed contaminant yields can provide crude estimates of contaminant loading for watersheds in which data are not available for more accurate means of estimating loads. For example, the two watersheds of predominantly urban land use (Guadalupe River and Anacostia River) had PCB yields ranging from 2.8 to 10 g/km<sup>2</sup>/yr, while the non-urbanized watershed yields ranged from 0.57 to 2.7 g/km<sup>2</sup>/yr. Thus, applying the urbanized watershed yields to the urban proportion of the Bay Area – approximately 40% of 6,650 km<sup>2</sup> (McKee et al. 2003, Davis et al. 2000) – an urban PCB load of 7 to 27 kg/yr would be estimated for Bay Area watersheds. By the same rationale, the non-urban watershed yield range would result in a non-urban PCB load ranging from 2 to 11 kg/yr. Similar application of watershed yields to pesticide loads would result in ranges in annual urban runoff loads of 2 to 12 kg DDT and 6 to 36 kg chlordane compared to non-urban runoff loads of 0.7 to 6 kg DDT and ~1 kg chlordane. These estimated urban runoff loads are similar in magnitude to the estimated loads reported by

KLI (2002; 2005) using a rational-method based model: 40 kg PCBs, 10 kg DDT and 38 kg chlordane. As with previous estimates, however, application of watershed yields for broader estimates of contaminant loading does not account for spatial heterogeneity of sources and loads between watersheds or inter-annual variability in hydrology or sediment transport processes. Thus, as noted previously, these watershed yields serve as crude tools of extrapolation to watersheds with limited or no data. Ideally, contaminant loads monitoring in several Bay Area watersheds with varying degrees of urbanization would provide realistic ranges of land-use based contaminant yields and temporal variability on seasonal and inter-annual scales for our system.



**Figure 2-3.** Scatter plots of organic contaminants and SSC in samples from WY 2003 and WY 2004. Rising stage samples appear as filled circles. Falling stage samples appear as open triangles. Guadalupe River (03)<sup>1</sup>

**Table 2-4.** Watershed yields of PCBs and OC pesticides in selected river systems.

Site	Area (km <sup>2</sup> )	%Urban (%)	PCBs		DDT		Chlordanes		Dieldrin	
			(kg/yr)	(g/yr/km <sup>2</sup> )	(kg/yr)	(g/yr/km <sup>2</sup> )	(kg/yr)	(g/yr/km <sup>2</sup> )	(kg/yr)	(g/yr/km <sup>2</sup> )
Guadalupe River (04)	246	44	0.7	2.8	0.7	2.8	0.55	2.2	0.052	0.21
Guadalupe River (03) <sup>1</sup>	246	44	1.2	4.9	1.1	4.5	0.79	3.2	0.082	0.33
Chesterville Branch <sup>2</sup>	15.8	0.1	0.009	0.57	0.0027	0.17	0.0031	~0.19	-	-
Nanticoke River <sup>2</sup>	195	5	0.12	0.62	0.303	1.55	~0.052	~0.26	-	-
Susquehanna River <sup>3</sup>	70160	5	76	1.1	-	-	-	-	-	-
Susquehanna River <sup>4</sup>	70160	5	160 - 190	2.3 - 2.7	41	0.58	31	0.44	12	0.17
Anacostia River – NE <sup>5</sup>	204	60	1.9	9.3	0.18	0.87	0.85	4.2	0.049	0.24
Anacostia River – NW <sup>5</sup>	138	60	1.4	10	0.28	2	1.9	13.6	0.059	0.43

<sup>1</sup>Leatherbarrow and McKee (2005)

<sup>2</sup>Foster et al. (2003); DDT comprised of p,p'-isomers of DDD, DDE, and DDT; Chlordanes comprised of alpha-, gamma-, and oxy-Chlordane, trans-Nonachlor, and heptachlor epoxide

<sup>3</sup>Ko and Baker (2004)

<sup>4</sup>Foster et al. (2000a); DDT comprised of p,p'-isomers of DDD, DDE, and DDT; Chlordanes comprised of alpha- and gamma-Chlordane, and trans-Nonachlor

<sup>5</sup>Foster et al. (2000b); DDT comprised of p,p'-isomers of DDD, DDE, and DDT and o,p'-DDD; Chlordanes comprised of alpha-, gamma-, and oxy-Chlordane, trans-Nonachlor, heptachlor, and heptachlor epoxide

## Impact of Urban Runoff on Water Quality in the Bay

To understand how ongoing contaminant loads from urban runoff influence water quality in the Bay, urban runoff must be evaluated in a larger context that considers the impacts of contaminant loading from other major transport pathways and the cycling of contaminants already in the Bay. This type of evaluation has been the focus of recent mass-budget model development for PCBs and OC pesticides conducted through the RMP (Davis 2004, Leatherbarrow et al. 2003, Leatherbarrow et al. 2005). A one-box model approach followed by Davis (2004) and Leatherbarrow et al. (2003) suggested that continued loads of PCBs and OC pesticides on the order of 10 kg per year were sufficient to delay recovery of water quality by decades. The one-box model approach did not differentiate between contaminant load pathways; however, based on the region wide loads estimates presented above and estimates provided by KLI (2002), it is probable that urban runoff transports PCB, DDT, and chlordane loads of this magnitude or greater to the Bay on an annual basis.

The understanding of PCB processes in the Bay was refined by Leatherbarrow et al. (2005) by using a multi-box model of San Francisco Bay that achieved greater spatial resolution within Bay segments and differentiation of contaminant loads from the major transport pathways. Preliminary model results indicate that reduction in PCB loads from urban runoff led to discernable reductions in sediment PCB concentrations in South and Lower South Bays compared to scenarios of no reduction in loading; other Bay segments were not significantly impacted. For example, a 95% reduction in the KLI (2002; 2005) estimate of 40 kg/yr, consistent with the proposed reduction allocated in the PCB TMDL (Hetzel, 2004), resulted in achieving Lower South Bay shallow sediment concentrations of 2 ng/g within approximately 65 years compared to 82 years with no reduction in loads.

In contrast, preliminary model results indicate that proportional reductions in PCB loads from the Sacramento/San Joaquin River Delta, wastewater effluent, and atmospheric deposition had negligible effects on sediment PCB concentrations. This was an important result from the model that indicates that continued PCB loading from urban runoff potentially contributes to delay in water quality recovery in the Bay.

The modeling effort by Leatherbarrow et al. (2005) provides additional insight into key uncertainties associated with contaminant loads from urban runoff that require further investigation for improving long-term forecasts of recovery times. As noted previously, the magnitude of loads from urban runoff were influential on recovery times in the South and Lower South Bays; however, uncertainties in current load estimates translate into uncertainties in initial conditions of the model, and consequently into model output. In addition, there are even greater uncertainties associated with how contaminant loads vary between years. This was reflected in the uncertainties surrounding a highly influential, yet poorly understood, parameter that describes the rate at which PCB loads naturally attenuate or diminish over time. Thus, in order to refine environmental fate models to integrate existing information to estimate recovery rates of the Bay, further investigation is necessary for understanding the spatial and temporal variability in magnitudes of contaminant loads and the long-term changes in loading over time.

## CONCLUSIONS

In this study, concentrations of PCBs and OC pesticides varied by one to two orders-of-magnitude between base- and peak-flow conditions in storm water samples collected from Guadalupe River over a two-year period. In addition, the variation in runoff and sediment transport led to daily and monthly contaminant loads that varied by orders of magnitude. Study results inform on the magnitudes of contaminant loads from an urbanized Bay Area watershed, as well as provide an initial step for extrapolating loads on spatial and temporal scales. Placed in a Bay-wide context, contaminant loads estimated in Guadalupe River potentially translate into regional urban runoff loads that contribute to measurable delays in water quality recovery.

Refinements of contaminant fate models currently used to estimate recovery times of water quality in the Bay require more accurate input pertaining to contaminant loads from Bay Area watersheds. Necessary input includes better estimates of the magnitude of loads, their spatial distribution in Bay Area watersheds, and their long-term temporal fluctuations and attenuation. Accordingly, further study to refine contaminant loads from Bay Area watersheds should incorporate loads monitoring programs in other observational watersheds for comparison and confirmation of patterns observed in Guadalupe River. Furthermore, long-term monitoring in one or several watersheds should be considered to refine our understanding on long-term changes in loading resulting from either natural attenuation or successful management activities. As long-term management strategies are developed to reduce contaminant loads from Bay Area watersheds, data collected from several observation watersheds, combined with physical-based watershed models, will improve our ability to discern impacts or benefits from these efforts.

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## 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 B: Example of calculations done to estimate mass loads.**

Date/Time	Almaden RF4 6h intensity	CSJ RF131	Alamitos RF1	Almaden RF4	Guadalupe WS RF123	Mt Umunhum RF69	Loma Prieta RF44	Discharge (cfs)	Turbidity (FNU)	SSC (mg/L)	Hg (ug/L)	Hg (kg)	Comments
2/2/04 0:00	0	0	0	0	0	0	0	28	4.4	19	0.06	0.000041	"Upper non-urban" regression equation applied because most base flow comes from the upper watershed
2/2/04 0:15								30	4.3	19	0.06	0.000044	
2/2/04 0:30								28	4.4	19	0.06	0.000041	
2/2/04 0:45								28	4.5	19	0.06	0.000041	
2/2/04 1:00	0	0	0	0	0	0	0	26	4.5	19	0.06	0.000039	
2/2/04 1:15								26	4.5	19	0.06	0.000038	
2/2/04 1:30								28	4.4	19	0.06	0.000040	
2/2/04 1:45								29	4.4	19	0.06	0.000043	
2/2/04 2:00	0	0	0	0	0	0	0	26	4.4	19	0.06	0.000038	
2/2/04 2:15								28	4.4	19	0.06	0.000040	
2/2/04 2:30								28	4.7	19	0.06	0.000041	
2/2/04 2:45								29	4.5	19	0.06	0.000042	
2/2/04 3:00	0	0	0	0	0	0	0.04	27	5.0	19	0.06	0.000040	
2/2/04 3:15								29	4.8	19	0.06	0.000043	
2/2/04 3:30								31	4.9	19	0.06	0.000045	
2/2/04 3:45								28	4.8	19	0.06	0.000041	
2/2/04 4:00	0	0	0	0	0	0	0	29	4.7	19	0.06	0.000042	

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2/2/04 4:15								25	4.5	19	0.06	0.000036
2/2/04 4:30								29	4.7	19	0.06	0.000043
2/2/04 4:45								27	4.6	19	0.06	0.000040
2/2/04 5:00	0	0	0	0	0	0	0.04	28	5.5	19	0.06	0.000042
2/2/04 5:15								26	4.5	19	0.06	0.000039
2/2/04 5:30								29	5.0	19	0.06	0.000042
2/2/04 5:45								26	4.6	19	0.06	0.000039
2/2/04 6:00	0	0	0	0	0	0.12	0.04	26	4.7	19	0.06	0.000038
2/2/04 6:15								31	5.0	19	0.06	0.000045
2/2/04 6:30								29	4.8	19	0.06	0.000043
2/2/04 6:45								26	4.9	19	0.06	0.000038
2/2/04 7:00	0.08	0	0	0.08	0.08	0.24	0.12	28	4.8	19	0.06	0.000041
2/2/04 7:15								28	4.7	19	0.06	0.000041
2/2/04 7:30								29	4.5	19	0.06	0.000042
2/2/04 7:45								28	4.3	19	0.06	0.000040
2/2/04 8:00	0.08	0	0	0	0	0.04	0	28	4.2	19	0.06	0.000041
2/2/04 8:15								29	3.8	19	0.06	0.000042
2/2/04 8:30								31	3.7	19	0.06	0.000044
2/2/04 8:45								29	3.8	19	0.06	0.000043
2/2/04 9:00	0.12	0	0	0.04	0.04	0	0.12	32	3.7	19	0.06	0.000046
2/2/04 9:15								29	3.8	19	0.06	0.000042
2/2/04 9:30								31	3.8	19	0.06	0.000045
2/2/04								29	3.7	19	0.06	0.000043

9:45													
2/2/04 10:00	0.43	0	0.12	0.31	0.28	0.55	0.35	29	3.8	19	0.06	0.000043	
2/2/04 10:15								32	4.5	19	0.06	0.000047	
2/2/04 10:30								68	25.0	29	0.09	0.000150	"Lower urban" regression equation applied as stage and turbidity begin to rise in response to rainfall in the urban areas
2/2/04 10:45								149	40.0	44	0.10	0.000394	
2/2/04 11:00	1.02	0.39	0.39	0.59	0.51	0.47	0.59	168	300.0	530	0.64	0.002736	
2/2/04 11:15								159	180.0	310	0.40	0.001600	
2/2/04 11:30								214	130.0	217	0.29	0.001596	
2/2/04 11:45								328	190.0	329	0.42	0.003478	
2/2/04 12:00	1.33	0.12	0.12	0.31	0.35	0.24	0.12	401	170.0	291	0.37	0.003828	
2/2/04 12:15								479	150.0	254	0.17	0.002063	
2/2/04 12:30								575	140.0	235	0.31	0.004593	
2/2/04 12:45								699	150.0	254	0.33	0.005946	
2/2/04 13:00	1.37	0	0	0.12	0.04	0.24	0.2	828	170.0	291	0.37	0.007908	
2/2/04 13:15								992	190.0	329	0.42	0.010519	
2/2/04 13:30								1158	210.0	367	0.46	0.013522	
2/2/04 13:45								1308	240.0	423	0.52	0.017325	
2/2/04 14:00	1.41	0	0	0.04	0.08	0	0.08	1418	260.0	459	0.56	0.020241	
2/2/04 14:15								1462	260.0	459	0.44	0.016543	In this case the "lower urban"

													regression was applied for 4 hours only because rainfall began 3 hours earlier in the middle and upper watershed than in the lower watershed.
2/2/04 14:30								1435	260.0	459	0.85	0.031079	"Upper non-urban" regression equation applied as middle and upper watershed runoff becomes the dominant source of water
2/2/04 14:45								1386	250.0	441	0.82	0.028879	
2/2/04 15:00	1.37	0.04	0	0	0.04	0	0	1292	230.0	405	0.75	0.024738	
2/2/04 15:15								1163	210.0	367	0.68	0.020255	
2/2/04 15:30								1106	190.0	329	0.61	0.017323	
2/2/04 15:45								996	180.0	310	0.58	0.014749	
2/2/04 16:00	1.06	0	0	0	0	0	0.04	940	170.0	291	0.55	0.013100	
2/2/04 16:15								852	160.0	273	0.51	0.011153	
2/2/04 16:30								808	150.0	254	0.48	0.009892	
2/2/04 16:45								743	150.0	254	0.48	0.009092	
2/2/04 17:00	0.47	0	0	0	0	0	0	706	140.0	235	0.14	0.002518	
2/2/04 17:15								649	140.0	235	0.45	0.007388	

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2/2/04 17:30								615	130.0	217	0.41	0.006470
2/2/04 17:45								559	130.0	217	0.41	0.005882
2/2/04 18:00	0.16	0.03	0	0	0	0	0	518	130.0	217	0.41	0.005454
2/2/04 18:15								494	120.0	198	0.38	0.004771
2/2/04 18:30								459	120.0	198	0.38	0.004432
2/2/04 18:45								436	110.0	179	0.34	0.003832
2/2/04 19:00	0.12	0.06	0	0.08	0	0.08	0.08	425	100.0	159	0.31	0.003358
2/2/04 19:15								395	98.0	156	0.30	0.003054
2/2/04 19:30								367	94.0	148	0.29	0.002702
2/2/04 19:45								338	91.0	142	0.28	0.002391
2/2/04 20:00	0.12	0	0	0.04	0.04	0	0.04	333	88.0	136	0.27	0.002265
2/2/04 20:15								305	85.0	130	0.26	0.001991
2/2/04 20:30								291	83.0	126	0.25	0.001850
2/2/04 20:45								265	79.0	117	0.23	0.001585
2/2/04 21:00	0.12	0.01	0	0	0	0	0.08	243	75.0	109	0.22	0.001356
2/2/04 21:15								225	72.0	103	0.21	0.001191
2/2/04 21:30								210	69.0	96	0.20	0.001049
2/2/04 21:45								199	66.0	90	0.18	0.000936
2/2/04 22:00	0.12	0	0	0	0	0	0	189	64.0	85	0.18	0.000850
2/2/04 22:15								180	62.0	81	0.17	0.000777
2/2/04 22:30								175	60.0	77	0.16	0.000723
2/2/04 22:45								164	58.0	73	0.15	0.000645
2/2/04	0.12	0	0	0	0	0	0	148	57.0	71	0.15	0.000571



23:00													
2/2/04 23:15								149	55.0	68	0.14	0.000551	
2/2/04 23:30								140	54.0	66	0.14	0.000506	
2/2/04 23:45								123	54.0	66	0.14	0.000445	
2/3/04 0:00	0.12	0	0	0	0	0	0	122	53.0	64	0.14	0.000429	
2/3/04 0:15								119	52.0	62	0.13	0.000410	
2/3/04 0:30								109	56.0	69	0.15	0.000411	
2/3/04 0:45								104	54.0	66	0.14	0.000374	
2/3/04 1:00	0.04	0	0	0	0	0	0	99	53.0	64	0.14	0.000348	
2/3/04 1:15								98	53.0	64	0.14	0.000344	
2/3/04 1:30								125	52.0	62	0.13	0.000429	
2/3/04 1:45								90	52.0	62	0.13	0.000308	
2/3/04 2:00	0.08	0	0.08	0.08	0.08	0.04	0.04	85	51.0	60	0.13	0.000286	
2/3/04 2:15								84	49.0	57	0.13	0.000269	
2/3/04 2:30								82	49.0	57	0.13	0.000262	
2/3/04 2:45								80	49.0	57	0.13	0.000255	
2/3/04 3:00	0.16	0.02	0.04	0.08	0.08	0.04	0.08	76	48.0	56	0.12	0.000240	
2/3/04 3:15								76	47.0	54	0.12	0.000234	
2/3/04 3:30								75	47.0	54	0.11	0.000219	
2/3/04 3:45								94	47.0	54	0.11	0.000273	"Lower urban" regression equation applied as stage and turbidity begin to rise in response to

													rainfall in the urban areas
2/3/04 4:00	0.16	0.06	0.04	0	0	0	0	109	47.0	54	0.11	0.000316	
2/3/04 4:15								114	51.0	60	0.12	0.000352	
2/3/04 4:30								121	48.0	56	0.12	0.000356	
2/3/04 4:45								154	51.0	60	0.12	0.000475	
2/3/04 5:00	0.16	0.02	0.04	0	0.04	0.08	0.04	190	58.0	73	0.14	0.000655	
2/3/04 5:15								239	64.0	85	0.15	0.000904	
2/3/04 5:30								270	65.0	88	0.15	0.001036	
2/3/04 5:45								278	64.0	85	0.15	0.001053	
2/3/04 6:00	0.16	0	0	0	0	0	0	296	62.0	81	0.14	0.001085	
2/3/04 6:15								319	62.0	81	0.14	0.001169	
2/3/04 6:30								328	63.0	83	0.15	0.001222	
2/3/04 6:45								335	63.0	83	0.15	0.001249	
2/3/04 7:00	0.2	0.02	0	0.04	0.04	0	0	355	62.0	81	0.14	0.001302	
2/3/04 7:15								340	60.0	77	0.14	0.001209	
2/3/04 7:30								342	60.0	77	0.14	0.001217	
2/3/04 7:45								312	58.0	73	0.14	0.001073	
2/3/04 8:00	0.16	0	0	0.04	0	0	0	321	57.0	71	0.13	0.001088	
2/3/04 8:15								298	55.0	68	0.13	0.000978	
2/3/04 8:30								278	53.0	64	0.12	0.000884	
2/3/04 8:45								272	51.0	60	0.12	0.000838	
2/3/04 9:00	0.08	0.01	0.04	0	0	0	0	259	50.0	59	0.12	0.000787	
2/3/04								253	50.0	59	0.12	0.000768	

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9:15													
2/3/04 9:30								251	48.0	56	0.12	0.000739	
2/3/04 9:45								243	49.0	57	0.12	0.000726	
2/3/04 10:00	0.08	0	0.04	0	0	0	0.04	239	49.0	57	0.12	0.000714	
2/3/04 10:15								233	50.0	59	0.12	0.000707	
2/3/04 10:30								229	49.0	57	0.12	0.000684	
2/3/04 10:45								237	48.0	56	0.12	0.000698	
2/3/04 11:00	0.08	0.05	0	0	0.08	0.08	0	231	49.0	57	0.12	0.000690	
2/3/04 11:15								221	49.0	57	0.12	0.000662	
2/3/04 11:30								233	50.0	59	0.12	0.000707	
2/3/04 11:45								253	50.0	59	0.12	0.000768	
2/3/04 12:00	0.08	0.13	0.04	0	0	0	0	267	50.0	59	0.12	0.000812	
2/3/04 12:15								282	51.0	60	0.12	0.000871	
2/3/04 12:30								282	53.0	64	0.12	0.000898	
2/3/04 12:45								298	56.0	69	0.13	0.000994	
2/3/04 13:00	0.12	0.05	0.08	0.08	0	0	0	298	57.0	71	0.13	0.001010	
2/3/04 13:15								314	62.0	81	0.14	0.001152	
2/3/04 13:30								338	68.0	94	0.16	0.001358	
2/3/04 13:45								377	68.0	94	0.16	0.001518	
2/3/04 14:00	0.08	0.07	0	0	0.04	0	0.08	398	70.0	98	0.16	0.001650	
2/3/04 14:15								470	73.0	105	0.17	0.002033	
2/3/04 14:30								491	79.0	117	0.18	0.002298	
2/3/04 14:45								512	83.0	126	0.19	0.002514	

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2/3/04 15:00	0.12	0.09	0.04	0.04	0	0	0	537	86.0	132	0.20	0.002726
2/3/04 15:15								581	88.0	136	0.20	0.003019
2/3/04 15:30								611	88.0	136	0.20	0.003174
2/3/04 15:45								625	91.0	142	0.21	0.003349
2/3/04 16:00	0.12	0.02	0	0	0	0	0.04	625	91.0	142	0.21	0.003349
2/3/04 16:15								618	91.0	142	0.21	0.003313
2/3/04 16:30								555	87.0	134	0.20	0.002853
2/3/04 16:45								549	83.0	126	0.19	0.002698
2/3/04 17:00	0.12	0	0.04	0	0	0	0	503	78.0	115	0.18	0.002325
2/3/04 17:15								491	77.0	113	0.18	0.002240
2/3/04 17:30								459	78.0	115	0.18	0.002121
2/3/04 17:45								411	78.0	115	0.18	0.001903
2/3/04 18:00	0.12	0	0	0	0	0	0	385	77.0	113	0.18	0.001758
2/3/04 18:15								357	74.0	107	0.17	0.001566
2/3/04 18:30								335	70.0	98	0.16	0.001389
2/3/04 18:45								316	67.0	92	0.16	0.001254
2/3/04 19:00	0.04	0	0	0	0	0	0.04	305	64.0	85	0.15	0.001154
2/3/04 19:15								291	62.0	81	0.14	0.001069
2/3/04 19:30								282	60.0	77	0.14	0.001004
2/3/04 19:45								274	57.0	71	0.13	0.000928
2/3/04 20:00	0.04	0	0	0	0	0	0	267	55.0	68	0.13	0.000878
2/3/04 20:15								255	53.0	64	0.12	0.000811
2/3/04								253	53.0	64	0.12	0.000804

20:30													
2/3/04 20:45								245	52.0	62	0.12	0.000767	
2/3/04 21:00	0	0	0	0	0	0	0	243	51.0	60	0.12	0.000749	
2/3/04 21:15								241	51.0	60	0.12	0.000743	
2/3/04 21:30								235	50.0	59	0.12	0.000713	
2/3/04 21:45								221	49.0	57	0.12	0.000662	
2/3/04 22:00	0	0	0	0	0	0	0	208	48.0	56	0.12	0.000614	
2/3/04 22:15								196	47.0	54	0.11	0.000568	
2/3/04 22:30								185	46.0	53	0.11	0.000530	
2/3/04 22:45								180	45.0	51	0.11	0.000508	
2/3/04 23:00	0	0	0	0	0	0	0	170	44.0	50	0.11	0.000473	
2/3/04 23:15								159	44.0	50	0.11	0.000442	
2/3/04 23:30								146	43.0	48	0.11	0.000402	
2/3/04 23:45								145	42.0	47	0.11	0.000393	In this case the "lower urban" regression was applied for 8 hours only because there was very low rainfall intensity in the upper watershed and low upper watershed runoff.
2/4/04 0:00	0.04	0	0.04	0.04	0	0	0.04	148	43.0	48	0.11	0.000415	"Upper non-urban" regression equation applied in response of a

													subtle increase in turbidity indicating mible and upper watershed runoff arrives at our sampling location
2/4/04 0:15								132	43.0	48	0.11	0.000370	
2/4/04 0:30								119	44.0	50	0.11	0.000342	
2/4/04 0:45								117	42.0	47	0.11	0.000320	
2/4/04 1:00	0.04	0	0	0	0	0	0	113	41.0	46	0.11	0.000303	
2/4/04 1:15								111	41.0	46	0.11	0.000299	
2/4/04 1:30								106	42.0	47	0.11	0.000292	
2/4/04 1:45								100	40.0	44	0.10	0.000263	
2/4/04 2:00	0.04	0	0	0	0.04	0	0	97	39.0	43	0.10	0.000248	
2/4/04 2:15								93	45.0	51	0.11	0.000272	
2/4/04 2:30								93	38.0	42	0.10	0.000234	
2/4/04 2:45								87	38.0	42	0.10	0.000219	
2/4/04 3:00	0.04	0	0	0	0	0	0.04	86	37.0	41	0.10	0.000212	
2/4/04 3:15								85	36.0	40	0.09	0.000205	
2/4/04 3:30								81	35.0	39	0.09	0.000190	
2/4/04 3:45								80	34.0	37	0.09	0.000183	
2/4/04 4:00	0.04	0	0	0	0	0	0	81	34.0	37	0.09	0.000186	
2/4/04 4:15								79	34.0	37	0.09	0.000181	
2/4/04								76	33.0	36	0.09	0.000172	

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4:30													
2/4/04 4:45								74	32.0	35	0.09	0.000164	
2/4/04 5:00	0.04	0	0	0	0	0	0	70	32.0	35	0.09	0.000155	
2/4/04 5:15								67	32.0	35	0.09	0.000149	
2/4/04 5:30								65	31.0	34	0.08	0.000141	
2/4/04 5:45								65	30.0	33	0.08	0.000138	
2/4/04 6:00	0	0	0	0	0	0	0	65	30.0	33	0.08	0.000138	
2/4/04 6:15								64	29.0	32	0.08	0.000133	
2/4/04 6:30								63	29.0	32	0.08	0.000130	
2/4/04 6:45								61	29.0	32	0.08	0.000126	
2/4/04 7:00	0	0	0	0	0	0	0	61	28.0	31	0.08	0.000123	
2/4/04 7:15								60	28.0	31	0.08	0.000121	
2/4/04 7:30								60	28.0	31	0.08	0.000121	
2/4/04 7:45								56	26.0	30	0.08	0.000110	
2/4/04 8:00	0	0	0	0	0	0	0	57	25.0	29	0.07	0.000109	
2/4/04 8:15								56	25.0	29	0.07	0.000107	
2/4/04 8:30								60	24.0	28	0.07	0.000112	
2/4/04 8:45								58	24.0	28	0.07	0.000109	
2/4/04 9:00	0	0	0	0	0	0	0	58	23.0	27	0.07	0.000107	
2/4/04 9:15								58	23.0	27	0.07	0.000107	
2/4/04 9:30								58	23.0	27	0.07	0.000106	
2/4/04 9:45								57	23.0	27	0.07	0.000106	
2/4/04 10:00	0	0	0	0	0	0	0	57	22.0	27	0.07	0.000103	

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2/4/04 10:15								52	21.0	26	0.07	0.000092	
2/4/04 10:30								49	21.0	26	0.07	0.000086	
2/4/04 10:45								49	21.0	26	0.07	0.000088	
2/4/04 11:00	0	0	0	0	0	0	0	49	21.0	26	0.07	0.000086	
2/4/04 11:15								50	20.0	25	0.07	0.000088	
2/4/04 11:30								51	19.0	25	0.07	0.000088	
2/4/04 11:45								50	19.0	25	0.07	0.000086	
2/4/04 12:00	0	0	0	0	0	0	0	49	19.0	25	0.07	0.000083	