CONCENTRATIONS AND LOADS OF PCBs, OC PESTICIDES, AND MERCURY ASSOCIATED WITH SUSPENDED PARTICLES IN THE LOWER GUADALUPE RIVER, SAN JOSE, CALIFORNIA.

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SFEI Contribution #86
January 2004

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

EXECUTIVE SUMMARY

Polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and mercury are of current environmental concern in San Francisco Bay due to their lengthy persistence in the environment and their potential adverse effects on wildlife and human health. The use of PCBs and OC pesticides has been restricted or banned for decades, yet their concentrations are high enough in Bay sport fish to warrant the issuance of an interim consumption advisory for fish caught in the Bay. Similarly, mercury in the Bay is largely associated with legacy sources and pathways but due to its persistence in sediments, remains at concentrations of a sufficient magnitude to contribute to the health advisory. Consistent with these advisories, the Bay is listed as impaired for PCBs and mercury (high priority), and OC pesticides (lower priority). PCBs, OC pesticides, and mercury are derived from a range of pathways including the Sacramento and San Joaquin Rivers, small tributaries in the nine-county Bay Area, atmospheric deposition, industrial and municipal wastewater, and resuspension of contaminated Bay sediment. Knowledge of the relative magnitude of each of these pathways assists local environmental managers to develop and prioritize ways to reduce the health hazard and impairment of the Bay. The magnitude of loads emanating from small tributaries remains a large uncertainty in mass balance models of the Bay, yet knowing the magnitude of this pathway is of paramount importance for determining solutions for resolving impairment. This study assesses the influence of water and sediment runoff processes on concentrations and loads of PCBs, OC pesticides and mercury in the Guadalupe River, one of the larger local basins, and a known source of mercury loads associated with historic mining and likely source of trace organic contaminants loads associated with legacy urban and agricultural applications.

Rainfall in San Jose during the 2003 climatic year was 382 mm (15.02 inches) or 100% of the 30-year normal (1971-2000) and had an estimated return period of ~3 years. Runoff during the WY 2003 study year was ~52 Mm^3 (59 cfs) or ~95% of the 1971-2000 normal. During the study, 95% of the annual rainfall at San Jose and 97% of the rainfall at Loma Prieta (an example of an upper watershed location) occurred during the months November to April (the period normally described as the wet season in the Bay Area). Runoff at the sampling site followed a similar pattern with ~85% of the runoff occurring during November to April. During the period November 1st 2002 - June 30th 2003, there were a total of 73 rain days, 50% of the rainfall fell in just 8 days and 90% of the rainfall occurred in just 30 days. In terms of runoff, ~50% and 90% of the runoff occurred in just 12 and 120 days respectively. The largest flood peak occurred at 9:00 am on December 16th 2002 with an estimated return period of ~5 years.

Turbidity was measured every 15 minutes from November 1st 2002-May 31st 2003 (23,327 data points). Turbidity varied mainly in response to discharge from 3-819 NTU. A total of 238 water samples were collected and analyzed by the USGS for suspended sediment concentration (SSC). Measured SSC ranged from 5-1,012 mg L^{-1}. A relationship was developed between turbidity and SSC using a loess fit and used to estimate time continuous SSC at a 15-minute interval. SSC estimated in this manner ranged from 10-1,366 mg/L and had a flow-weighted mean concentration (FWMC) of 193 mg/L. A comparison of 15-minute SSC to 15-minute discharge revealed a complex series of hysteresis loops that enabled an accurate estimation of suspended sediment loads. During the period October 1st to May 31st a total of 10,328 t of suspended sediment was transported past the study location. A maximum daily sediment load of 2,823 t (27% of the total) occurred on December 16th 2002. Fifty percent of the suspended sediment was transported in just 3 days and 90% of the suspended sediment load occurred in just 14 days. A total of 7,027 t or 68% of the total annual load was transported in response to the series of floods that occurred during December.

In 22 samples collected during varying stages of storm events, t-PCB concentrations ranged from 3.4-90 ng L^{-1} with a FWMC of 54 ng L^{-1}. In all samples, PCB congener distributions were indicative of predominant contributions of Aroclor 1254 and 1260 with hexa-, hepta-, and octa-chlorobiphenyls comprising ~50-75% of t-PCB concentrations. Total DDT concentrations ranged from 1.7-71 ng L^{-1} with a FWMC of 48 ng L^{-1}. Total chlordane concentrations ranged from 1.6-64 ng L^{-1} with a FWMC of 40 ng L^{-1}. Dieldrin concentrations ranged from 0.3-6.0 ng L^{-1} with a FWMC of 3.7 ng L^{-1}. Trace organic contaminants were positively correlated to instantaneous discharge and SSC with maximum concentrations occurring on December 16th during the largest flood peak. The positive correlations suggest that trace organic contaminant residues originate from diffuse sources of similar origin to suspended sediment. The relative abundance of individual PCB congeners and DDT compounds in Guadalupe River samples varied with discharge and were suggestive of different sources contributing to contaminant transport to the bottom of the watershed. As discharge increased, sources of Aroclor 1254-related PCBs increased in importance while contributions from sources of Aroclor 1260-related PCBs decreased. Of the individual DDT compounds, DDD (o,p' + p.p'-DDD) was the most predominant compound at low discharge, but decreased in importance at high flows. In contrast, contributions of DDT (o,p'- + p,p'-DDT) increased with discharge suggesting that relatively unweathered material was being transported from land surfaces in the watershed. A first flush effect was evident and indicated by unique contaminant patterns in the early storms of the season. Total loads during the study were 1.1± 0.3 kg t-PCBs, 0.91 ± 0.26 kg t-DDT, 0.69 ± 0.12 kg t-chlordane, and 0.075 ± 0.017 kg dieldrin. Most of the trace contaminant load (54-65%) occurred during December when the largest storms occurred. Loads of this magnitude will likely contribute to delayed recovery of Bay contamination by PCBs, DDT, and chlordane.

Using clean hands protocols, 26 samples were collected during varying stages of storm events. Concentrations of total mercury varied from 0.2-18.7 µg/L with a FWMC of 3.7 µg/L. Maximum total mercury concentrations did not coincide with flood peaks. Total mercury correlated for short periods with discharge and suspended sediment, but when all the data were grouped, total mercury did not correlate with any other parameter measured. In contrast, concentrations of suspended sediment, particulate organic carbon, and all other trace elements correlated with discharge, while trace elements correlated with each other. These results suggest that sources of mercury relative to suspended sediment vary from storm to storm and that the dominant sources of the other trace elements are separated from the dominant sources of total mercury. This is consistent with the knowledge that mercury is mainly sourced from creeks and reservoirs adjacent to the New Almaden Mining District. On December 16th 2002, a series of reservoir releases began from Calero, Almaden and Guadalupe Reservoirs. These releases influenced mercury concentration and load, defining two distinct periods. During the pre-reservoir release period, total mercury concentrations ranged from 0.2-4.7 µg/L and had a FWMC of 0.76 µg/L. During the post-reservoir release period, total mercury concentrations ranged from 1.3-18.7 µg/L and had a FWMC of 5.1 µg/L. The source of mercury is most likely sediments stored in Calero, Alamitos, and Guadalupe Creeks that are mobilized by relatively "clean" water with low concentrations of suspended sediment released from the reservoirs. Load estimates were generated for the period October to May. Daily loads varied by 7,000x from 4.6 g - 32 kg. In total, 312 ±82 kg of total mercury was transported into lower South San Francisco Bay. This estimate of total mercury load is ~10x greater than previously reported in studies on the Guadalupe River that did not capture such large floods or the effects of reservoir release. Climate during the study year was approximately average, however, it is presently unknown what influence relatively dry climate during 2001 and 2002 might have had on the magnitude of the loads, and it is presently not clear how inter-annual differences in reservoir operation might influence mercury loads. These questions are the primary focus of subsequent years of study.

ACKNOWLEDGEMENTS

The authors are sincerely grateful for the assistance that many people and groups have provided. Review, both written and verbal, has helped the authors make significant improvements during all stages of this project from initial concept, through sampling design, proposal development, fieldwork, laboratory analysis, data interpretation, and reporting. The fieldwork component of this project required dedication by SFEI field-staff during the winter months at any time in response to rainfall, 24 hours a day, 7 days a week. In particular we are indebted to Nicole David, Ben Greenfield, Donald Yee, Jennifer Hunt, Sarah Pearce, Chuck Striplen and Eric Wittner for their contributions to the SFEI high-flow-studies field-team and their dedication and concentration during rainstorms when working conditions were not always ideal. We would also like to thank Chris Neilson for his dedication to the USGS suspended sediment sampling component of the study and staff at the Marina USGS field office, in particular John Budlong. We acknowledge field contributions by Russ Flegal and staff at UCSC during the initial site reconnaissance and the November 2002 storm. 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, zinc, and suspended sediment), 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 received detailed technical reviews from xxxxxxxx, xxxxxxxxxx, xxxxxxxx that substantially improved the document. Finally, we are indebted to Shannah Anderson and Aleatsae Scibuola for their physical and emotional contributions and acceptance of the midnight and holidays hours spent on this project.

Funding for the project during, this, the first year of study was provided by the Clean Estuary Partnership.

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INTRODUCTION

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PROBLEM STATEMENT

The magnitude of storm water loads is a significant uncertainty that needs to be resolved for contaminants of concern (mercury, PCBs, PAHs, and OC pesticides) (Davis et al 1999, Davis 2001; Johnson and Looker, 2003). Approaches for assessment of loads have been limited by available data and has used either runoff coefficients and land use analysis, or sediment concentrations and sediment load estimates to derive planning level estimates of contaminant loads (Davis et al., 2000; Gunther et al., 2001; KLI 2001, 2002). These approaches negate many accepted hydrological principles such as seasonal antecedent moisture conditions and runoff, the influence of slope, soils types and vegetation on runoff and the temporally complex relationships between sediment and contaminant concentrations and runoff. As such, present estimates have inherent uncertainty that limits the accuracy of mass balance models and the ability to quantify potential benefits that can result from management actions in the watershed, wetlands, and Bay. It is hypothesized that present loads estimates lack precision and accuracy and are biased low. Discussions of the Bay Area Stormwater Management Agencies Association (BASMAA) Monitoring Committee, the Clean Estuary Partnership (CEP) and recommendations over the past three years from the Regional Monitoring Program's Sources Pathways and Loadings Workgroup (SPLWG) have identified the need for a more rigorous approach to assessing loads of sediment and contaminants from watersheds.

AIM

The main aim of this project was to improve knowledge on the magnitude of contaminant loads entering the Bay from local tributaries and in doing so improve our understanding of contaminant process in the Bay (such as described by the PCB single box mass balance model (Davis, 2002) and thereby assist in the development of TMDLs and the management of the Bay (e.g. Johnson and Looker, 2003). The project also has a number of secondary aims. These include a) the demonstration of an integrated methodology for accurately determining loads of PCBs and other trace contaminants in a key contaminated watershed, b) an analysis of the performance of the method in order to make recommendations on how best to sample other watersheds in the future, and c) a comparison of the results with the SIMPLE MODEL (Davis et at. 2000) in order to accept or reject its use as a tool for estimating loads for management purposes.

CHOOSING A WATERSHED TO STUDY

The Estuary Interface Pilot Study (Leatherbarrow et al., 2002) and the recently released San Francisco Bay mercury TMDL report (Johnson and Looker, 2003) have highlighted the Guadalupe River watershed as a source of mercury to the Bay associated with the history of mercury mining in the New Almaden mining district. RMP sampling over the past decade has shown high concentrations of Hg and PCBs on the estuary margin near the outlet of the Guadalupe River (e.g. RMP, 2003). Studies on bed sediment contaminant concentration have found that some urban drainages in the Guadalupe River watershed have high concentrations of mercury and PCBs relative to other watersheds around the Bay (Gunther et al., 2001; KLI 2001, 2002). Although the Guadalupe River watershed is somewhat unique in terms of mercury sources, there are a number of other

areas around the Bay that may be contaminated with respect to PCBs (e.g. Some watersheds in Richmond, Oakland, and the adjacent Coyote Creek watershed). These issues in addition to sampling logistics and potential collaborations were discussed by the Sources Pathways and Loadings Workgroup. After deliberation, the SPLWG recommended that a "Small Tributaries Loading Study" be carried out on Guadalupe River watershed for a period of 4 years. This report represents the final deliverable of the first year of data collection and analysis.

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SECTION TWO

METHODS

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LOCATION AND PHYSIOGRAPHY

The Guadalupe River watershed is located in the Santa Clara Valley basin and drains to Lower South San Francisco Bay (south of Dumbarton Bridge) (Figure 2-1a). The Guadalupe River watershed is bordered on the west by the San Tomas Creek watershed, on the east by the Coyote Creek watershed and to the south by coastal watersheds. Guadalupe Creek flows from its headwaters in the eastern Santa Cruz Mountains to its confluence with Alamitos Creek at Coleman Road in the city of San Jose where it becomes Guadalupe River and continues its journey through the city, past the San Jose International Airport and beyond Highway 101. The influence from the ocean tides begins between the Montague Expressway and Highway 237 before the River ultimately discharges to the South Bay via Alviso Slough.

The Guadalupe River watershed encompasses approximately 556 km^2 (200 mi^2). The watershed is the 4th largest in the Bay Area by area and the 5th largest in terms of annual discharge volume to the Bay. There are five main tributaries in the Guadalupe watershed: Los Gatos Creek, Ross Creek, Guadalupe Creek, Alamitos Creek, and Canaos Creek. The subwatersheds of Los Gatos Creek, Ross Creek, Guadalupe Creek, and Alamitos Creek gather runoff from the Santa Cruz Mountains, notable high points being Mt. Thayer (elevation 1,063 m [3,486 ft]) and Mt. Umunhum (elevation 1,063 m [3,486 ft]), and the summit of Loma Prieta (elevation 1,155 m [3,790 ft]).

All sampling during the study is carried out approximately 100 m (300 ft) upstream from where US Highway 101 passes over the Guadalupe River (Figure 2-1b). This location is on the northeast side of San Jose International Airport at the bridge that connects the main airport grounds to a rental car service center. This site was chosen to make use of the recently established USGS stream gage, Guadalupe River above Highway 101 at San Jose (11169025). This gage was established to replace the former USGS stream gage, Guadalupe River at San Jose (11169000) that was discontinued to make way for channel modifications and redevelopment. Sampling was carried out from this bridge during flood flow and directly under the bridge during wading stages (Figure 2-2a, b). The reach has been straightened and widened and the X-section geometry has been modified to a trapezoid to improve the transmission of flood discharge. The upper banks in the vicinity of the bridge have been secured from erosion by wire covered rock gabion. The main features of the channel at the sampling location include the low-flow channel, a low-flow channel partially submerged bar, a low-flow channel left bank, an in-channel floodplain that marks the height of the bankfull discharge (approximately 1.5 year return interval flood), and the upper (high flow) trapezoidal banks (Figure 2-3). The bed at the sampling location consists of poorly sorted gravels, sands and silts with a median grainsize (D_{50}) of 10 mm (visual estimate). The in-channel floodplain is vegetated with grasses, reeds and other soft-stemmed riparian plants and there are sparsely located larger trees both upstream and downstream of the bridge.

(a) (b)

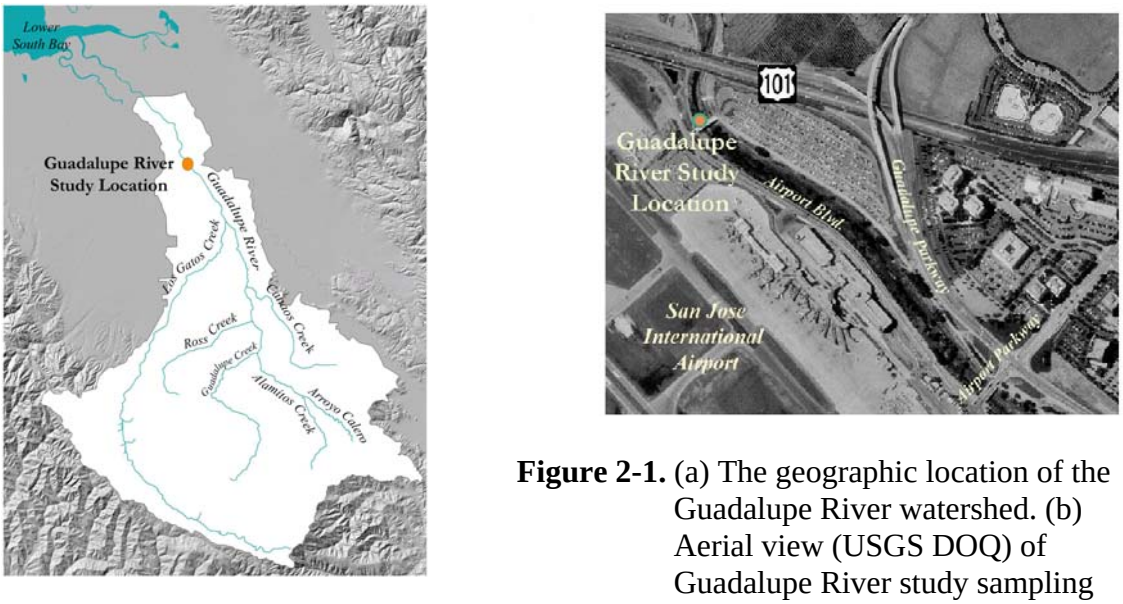

Figure 2-1. (a) The geographic location of the Guadalupe River watershed. (b) Aerial view (USGS DOQ) of Guadalupe River study sampling location.

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(a) (b)

Figure 2-2. A view of the "Rental Car Return Bridge" (the study sampling location) looking from (a) the top of the left bank of the Guadalupe River and (b) looking upstream.

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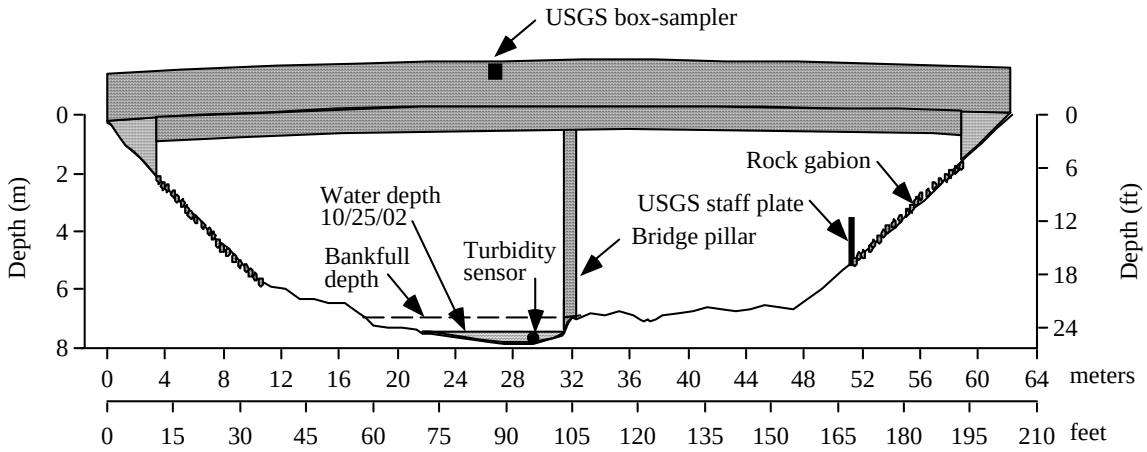

Figure 2-3. Surveyed scale X-section (v/h = 2) of the sampling location indicating the main channel features.

STUDY COMPONENTS AND TEAMS

The study incorporated three semi-separate sampling components that together formed a comprehensive integrated sampling methodology for estimating the concentrations and loads of suspended sediments, PCBs, OC pesticides, and mercury in a river system. The three components were:

1. Real time continuous turbidity measurement.
2. Manual sampling for suspended sediment concentration and grainsize using protocol developed by the USGS for sampling and computing suspended sediment daily loads.
3. Manual sampling for trace contaminant concentration using “clean hands” techniques for trace metals and mercury.

Each component was lead by a different member of the Study Team with ongoing communication that intensified during flood sampling periods.

REAL TIME CONTINUOUS TURBIDITY MEASUREMENT

Rand Eads of the USDA Forest Service, Redwood Sciences Laboratory, led this component of the study. A DTS-12 turbidity sensor, manufactured by Forest Technology Systems Limited (FTS), was purchased and installed at the Guadalupe site (Figure 2-4). The sensor was deployed using a depth-proportional boom (Eads & Thomas, 1983) that is anchored to the streambed and protected from impacts by a pre-existing block of concrete immediately upstream of the boom. In addition to the anchor, a stainless steel safety cable attaches the boom to the concrete block. The boom is constructed of aluminum and two high-density foam floats provide flotation. At about 3.3 m (11 ft) of stage, velocity and depth overcome flotation and the 4 m (13 ft) boom is fully submerged placing the sensor at a maximum distance of about 1 meter (3 feet) above the bed. The DTS-12 has a wiper that is activated before each measurement to removed small contaminates from the

optical sensor. Field crews removed larger organic debris lodged on the floats and near the sensor during site visits. The median turbidity value from each 15-minute wakeup is stored in the Design Analyses data logger and these values, in addition to water stage, are made available on the USGS web site so that study participants can determine the best sampling strategy for suspended sediments and contaminants. The DTS-12 records turbidity in nephelometric turbidity units (NTU) and is auto-scaling from 0-200 and 0-1600 (the new scaling is now 0-1600; the two ranges have eliminated). The DTS-12 measurements are periodically compared to grab samples taken near the sensor and are measured with a Hach 2100P portable turbidimeter (widely considered a standard device for field measurements). This provides assurance that the sensor is operating correctly. At the end of the season, the DTS-12 was returned to the factory for a 6-point calibration in formazin standards and a firmware update.

(a) (b)

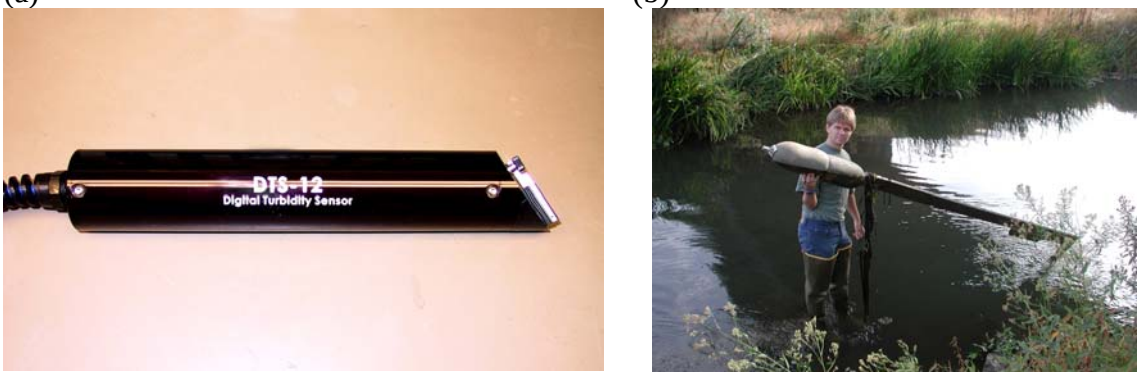

Figure 2-4. The DTS-12 turbidity sensor. a) The DTS-12 Turbidity Sensor. Note the wiper on the right side of the instrument. b) Photo of the installed sensor and bed-mounted boom at the Guadalupe River sampling location.

MANUAL SAMPLING FOR SUSPENDED SEDIMENT CONCENTRATION AND GRAINSIZE

Lawrence Freeman of the U.S. Geological Survey in Marina, California took the lead on this component of the study. The sampling equipment used to collect samples for suspended sediment analysis varied depending on stage. A USGS “box sampler” was mounted on the bridge railing at the Guadalupe site. The box sampler consisted of a cable winch or “b reel” and a permanently attached D-74 depth-integrating sampler (Figure 2-5a). The box sampler was used to collect samples during non-wading flows in a single vertical in the thalweg (the deepest point in the channel X-section). In addition, the variability of suspended sediment concentration in the X-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-real system (Figure 2-5b). During wading stages, a US DH-48 hand-held depth-integrating sampler (Figure 2-5c) was used in the low flow X-section under the bridge.

(a) (b) (c)

Figure 2-5. The suspended sediment samplers employed by the USGS at the Guadalupe River sampling location. (a) US D-74 depth-integrating sampler, (b) USGS Type A Crane with Type A Four-Wheel Truck and (c) US DH-48 hand-held depth-integrating sampler.

MANUAL SAMPLING FOR TRACE CONTAMINANT CONCENTRATION

SFEI staff took the lead on this component of the project. Sampling was carried out using two protocols. Both protocols involved the use of two persons (one designated "clean hands" and the other designated "dirty hands"). Double-bagged (Ziploc™) sample bottles prepared for mercury and trace metals were supplied by Moss Landing Marine Laboratory. During high flow, samples were taken by inserting a sample bottle into a specially designed dip-sampler that consisted of a sample rinsed sample bottle cup attached to a 12 m long fiberglass pole. The 'dirty hands' person did not touch the trace-metal clean bottles, but opened the Ziploc™ bags so that the "clean hands" person could remove them from the bags. The "clean hands" person, wearing a pair of trace metal clean polyethylene gloves, did not touch anything with her/his hands except the inner Ziploc™ bag and trace metal clean sampling components. The "clean hands" person loaded the bottle into the dip-sampler. The "dirty hands" person then passed the dip-sampler into the water column filling the bottle. Once the sample was returned to the level of the bridge railing, the "clean hands" person retrieved and capped the sample. The "dirty hands" person then secured the dip-sampler before assisting the "clean hands" person to re-double-bagging the sample. This procedure was completed twice (once for mercury and once for trace metals). After operations needing "clean hands" were completed, the trace metal sampling cup was removed and a 4L sample bottle for trace organics (PCBs and OC pesticides) was attached the 12 m pole and passed into the water column. A dip sample was also taken for suspended sediment and organic carbon analysis by passing a 500 ml sample bottle into the water column. During wading stages the same procedures were followed with respect to "clean hands" and "dirty hands" however, samples were taken by hand dipping at approximately mid-depth directly under the bridge in the deepest portion of the stream near the turbidity probe.

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515 **SECTION THREE**

HYDROLOGICAL PROCESSES IN GUADALUPE RIVER, WY 2003

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Lester McKee

INTRODUCTION

Rainfall and runoff are the primary sources of energy in the Guadalupe watershed that transmit loads of sediments and contaminants from non-point sources into waterways and past the sampling location at USGS gage 11169025. Watershed loads will be described using the temporal scales of annual, monthly, daily, and instantaneous. In addition, the loads will be described for specific storm events to better understand the process of transport relating to runoff generation in the sub-watershed and urban areas. The following sections place the 2003 water year (WY) (the year beginning October 1st 2002 and ending September 31st 2003) and the 2003 climatic year (CY) (the rainfall year beginning July 1st 2003 and ending June 30th 2003) into the context of the period of record using the range of temporal scales listed above.

ANNUAL RAINFALL AND RUNOFF

Rainfall in San Jose has been recorded continuously from 1875 to present (a total of 129 years) (data collated and provided by Jan Null, Golden Gate Weather Services). The average rainfall for the period of record is 364 mm (14.33 inches). The greatest annual rainfall on record occurred in CY 1890 and was 770 mm (30.30 inches). The driest year on record was CY 1877 when only 123 mm (4.83 inches) was recorded. Rainfall in San Jose during the 2003 climatic year was 382 mm (15.02 inches) or 100% of the 30-year normal (1971-2000). An annual rainfall of this magnitude has a return period of about 3 years (Figure 3-1). Annual average rainfall varies spatially across the watershed mainly in response to elevation (Figure 3-2). Annual average rainfall varies from 350-400 mm (14-16 inches) in the more heavily urbanized areas of the watershed to 710 – 1,120 (28-44 inches) in the upper non-urban and mountainous areas. Rainfall at a given location in the Bay Area usually varies from about 40-200% of normal (McKee et al., 2003). On this basis we therefore predict the upper watershed to have a maximum annual precipitation of approximately 2,230 mm (88 inches).

Runoff in the Guadalupe River has been measured by the USGS continuously since WY 1930 at the Guadalupe River at San Jose stream gage (11169000) located at St John Street in the City of San Jose. The average annual runoff for the period WY 1930 - 2003 was 41 Mm^3 (or 45.9 cfs). There are four main reservoirs in the watershed that have been built during the period of discharge record, the last and largest of which was the Lexington Reservoir on Los Gatos Creek build in 1952 with a design capacity of 24.5 Mm^3 (19,834 acre-ft). A more realistic idea of the annual average discharge character is gained by analyzing the period WY 1971-2000 (consistent with the analysis of rainfall). Annual runoff for the WY 1971-2000 period varied from 2.9-252 Mm^3 (3.21-282 cfs) and averaged ~55 Mm^3 (61.8 cfs). Runoff during the WY 2003 study year was approximately ~52 Mm^3 (59 cfs) or about 95% of the 1971-2000 normal.

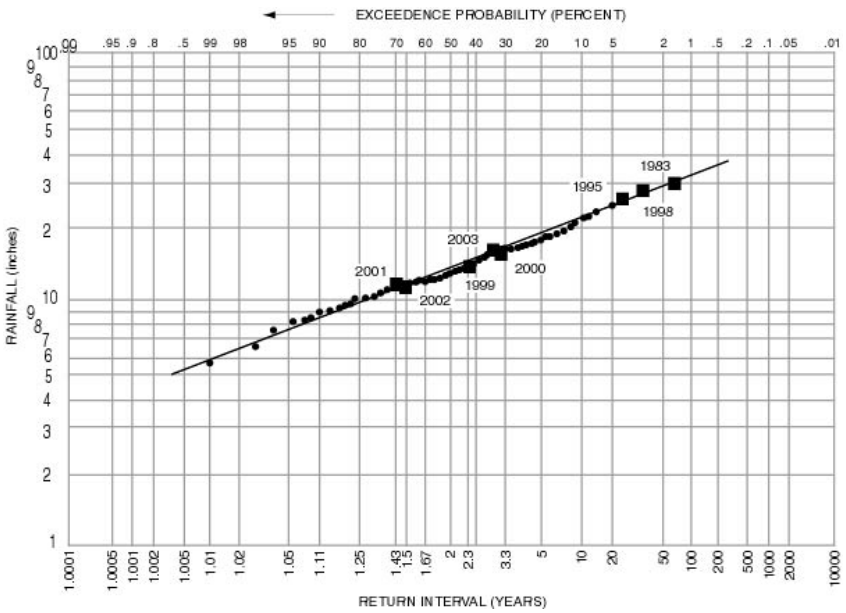

Figure 3-1. Return interval of annual rainfall based on data for the period 1931-2003 (Data downloaded from the Western Region Climate Center web site, WRCC, 2003).

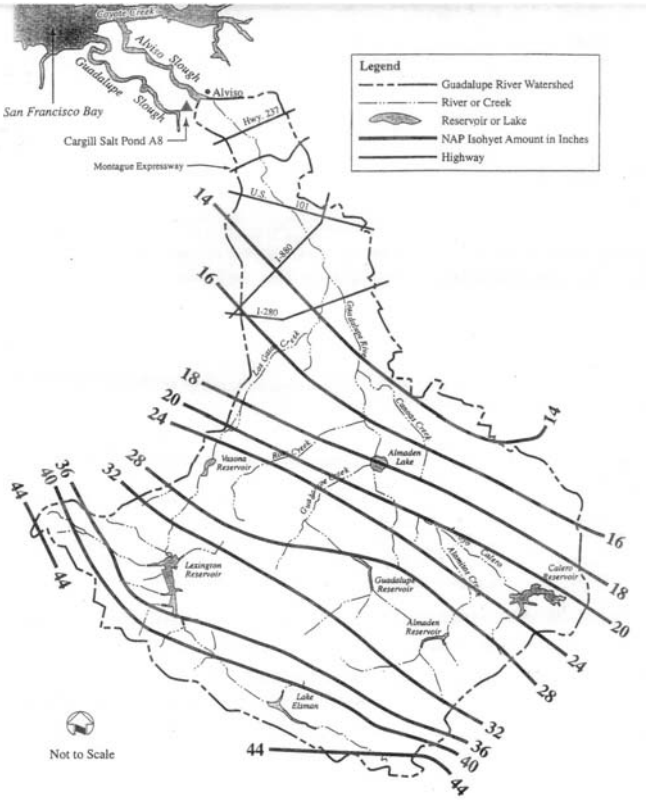

Figure 3-2. Variation of annual average rainfall across the Guadalupe River Watershed (Source: USACE, 2001).

MONTHLY RAINFALL AND RUNOFF

The majority of rainfall (89-91%) and runoff (87-99%) in Bay Area watersheds occurs on average during the wet season months of November to April inclusive (McKee et al., 2003). Guadalupe River is not an exception. In San Jose, on average during the period 1971-2000, 89% of rainfall and 91% of runoff occurred during the wet season months. During the CY 2003 study year, 95% of the annual rainfall at San Jose and 97% of the rainfall at Loma Prieta (an example of an upper watershed location) occurred during the months November to April (Table 3-1). Runoff at the sampling site followed a similar pattern with about 85% occurring during November to April (Table 3-1).

Table 3-1. Monthly rainfall and runoff in the Guadalupe River watershed during the study compared to long term averages (Rainfall data supplied by the Western Region Climate Center and the Santa Clara Valley Water District). USGS runoff data for WY 2003 are preliminary subject to review and publication).

	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Annual
San Jose Rainfall (mm)													
1971-2000	1.4	1.7	5.7	20.2	48.8	53.9	77.0	72.1	63.7	25.9	11.3	2.4	384
%Annual	0.4	0.4	1.5	5.3	12.7	14.0	20.0	18.8	16.6	6.7	2.9	0.6	100
Jul 1st 2002-Jun 30th 2003	0	0	0	0	43.2	144.5	14.0	36.3	17.0	105.4	21.1	0	382
%Annual	0	0	0	0	11.3	37.9	3.7	9.5	4.5	27.6	5.5	0	100
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Annual
Guadalupe runoff at San Jose (Mm^3)													
1971-2000	0.81	2.2	3.2	10.4	14.6	14.9	5.1	1.8	0.73	0.61	0.57	0.58	55.5
%Annual	1.5	4.0	5.8	18.8	26.2	26.8	9.2	3.2	1.3	1.1	1.0	1.1	100
Oct 1st 2002-Sep 30th 2003	0.30	4.3	23.4	5.0	3.4	3.2	5.4	2.8	1.5	1.0	0.90	1.1	52.3
%Annual	0.6	8.2	44.8	9.5	6.5	6.2	10.2	5.4	2.9	2.0	1.7	2.1	100

DAILY RAINFALL AND RUNOFF

The accumulation of rainfall and runoff in the Guadalupe River watershed during the study period was punctuated by a number of maritime storm systems that traveled across the watershed periodically. As a result, the majority of the rainfall and runoff occurred over relative short periods of time with rather longer periods in between (Figure 3-3). During the period November 1st 2002 – June 30th 2003, there were a total of 73 rain days (defined as a rainfall of >0.1 mm). Fifty percent of the rainfall fell in just 8 days or 3% of the time (Figure 3-4). Ninety percent of the rainfall occurred in just 30 days or 11% of the time. In terms of runoff, about 50% and 90% of the runoff occurred in just 12 and 120 days respectively (4.5% and 44% of the time) (Figure 3-4).

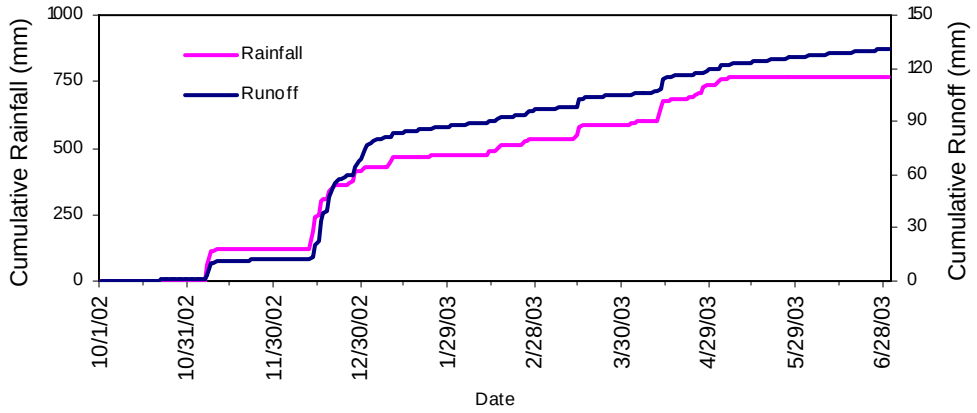

Figure 3-3. Accumulative rainfall and runoff curves for Guadalupe River watershed during WY 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) and a lower watershed location (San Jose). Rainfall data supplied by Santa Clara Valley Water District. Runoff data are provisional supplied by the USGS.

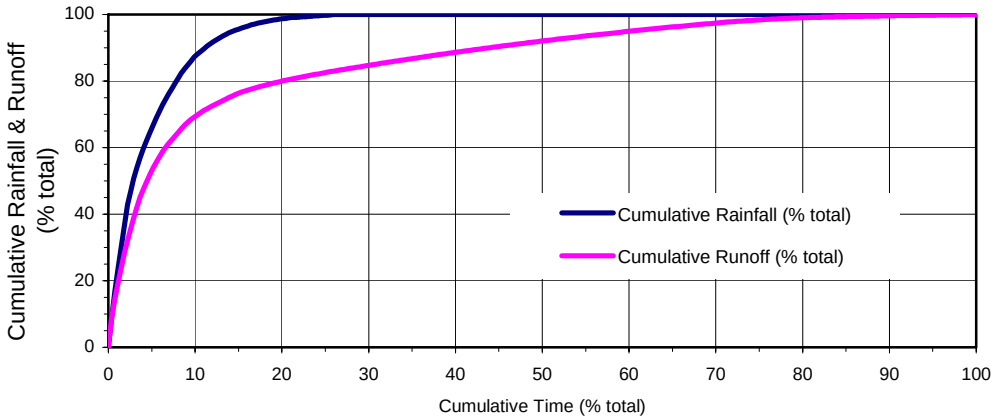

Figure 3-4. Accumulative rainfall and runoff as a percentage of total rainfall and runoff compared to cumulative percentage of time over the period November 1st 2002-June 30th 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) and a lower watershed location (San Jose). Rainfall data supplied by Santa Clara Valley Water District. Runoff data are provisional supplied by the USGS.

INSTANTANEOUS FLOOD PEAK RUNOFF

The USGS has been measuring flood peaks at the Guadalupe River at San Jose stream gage (11169000) since WY 1931. The largest flood recorded since 1931 occurred on March 10th 1995 with a peak of 17.4 feet and an instantaneous discharge of 11,000 cfs. The 7th largest peak occurred on February 3rd 1998 with a peak of 12.6 feet and an

instantaneous discharge of 7,510 cfs. The largest flood during WY 2003 occurred at 9:00 am on December 16th 2002 with a peak of 10.4 feet and an instantaneous discharge of 6,160 cfs. This flood peak followed a smaller peak that occurred on December 14th. The cumulative rainfall from December 13th-16th was in excess of 292 mm (11.5 inches) in the upper watershed or about 25% of the CY 2003 total and 66 mm (2.6 inches) in the City of San Jose or about 17.5% of the CY 2003 total. This flood peak is estimated to have had a return interval of ~5 years (Figure 3-5).

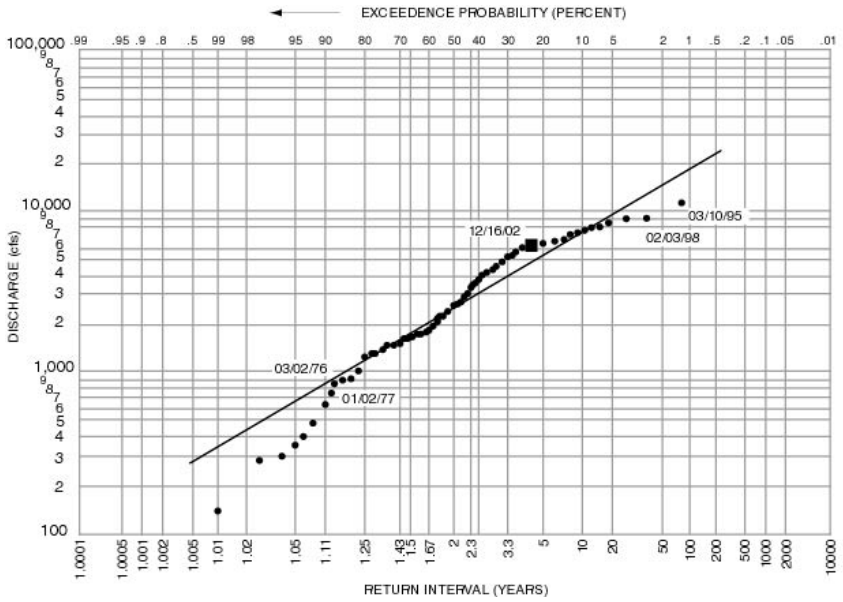

Figure 3-5. Return frequency floods in the Guadalupe River based on the annual series (11169000 data provided by the USGS).

FLOOD PEAKS AND OPERATION OF RESERVOIRS DURING WATER YEAR 2003

Both flood discharge and base flow are influenced by the operation of reservoirs in the Guadalupe River watershed by the Santa Clara Valley Water District. During the study period, there was a series of control releases from Calero, Almaden and Guadalupe reservoirs (Figure 3-6). It is known that sediments both in these reservoirs and in the downstream river channels have concentrations of mercury greater than the natural background (TetraTech, 2003). It seems likely that some of the mercury signal in the lower watershed could be traced back to reservoir management. At no time during the study did the reservoirs spill uncontrollably. A series of floods occurred during the study year (Table 3-2). As the season progressed, various controlled releases where implemented, the most notable from the standpoint of mercury being from the Almaden reservoir beginning 12/17 at 16:45 and from Guadalupe reservoir beginning 12/29 at midday (Table 3-2).

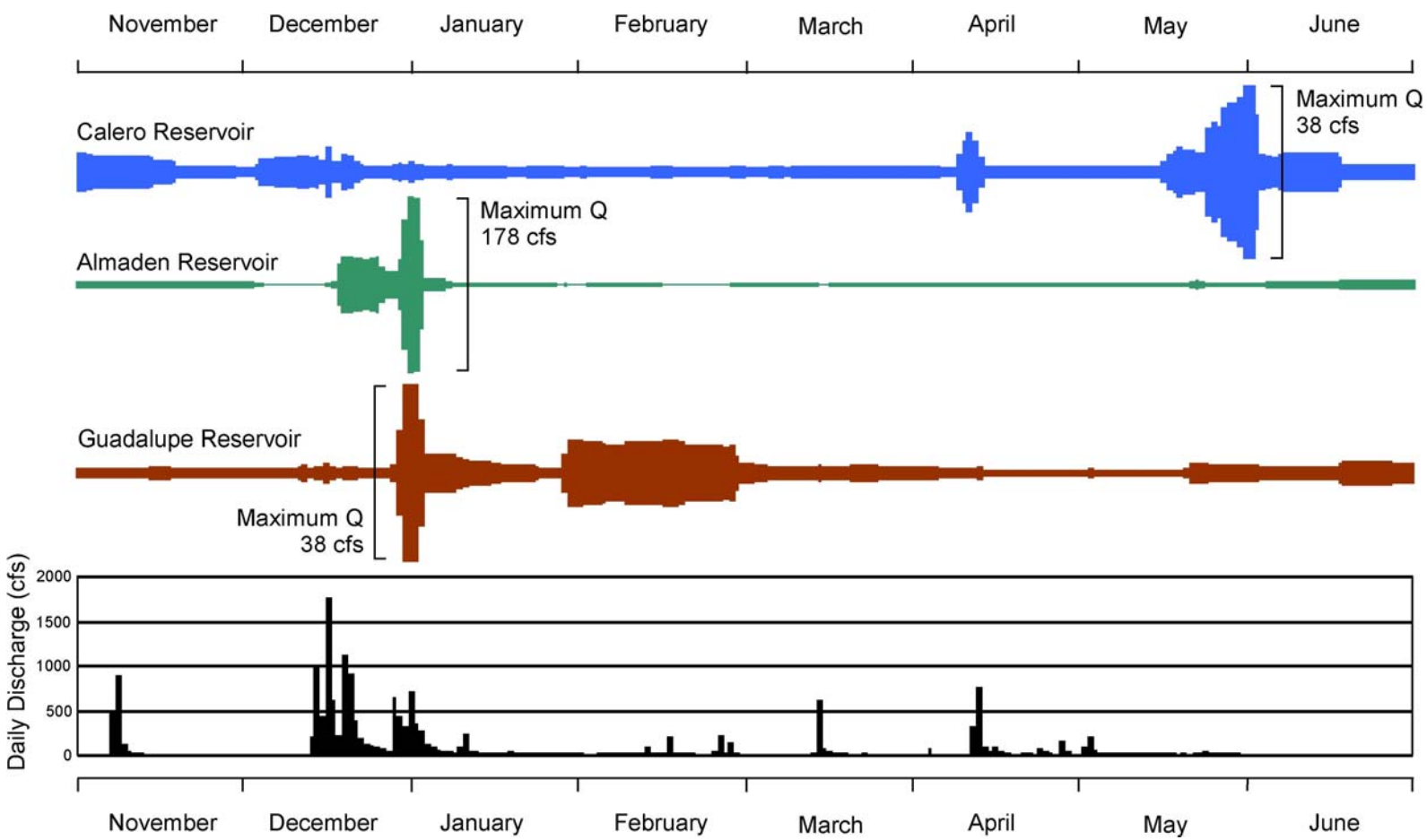

Figure 3-6. Schematic figure illustrating the operation of reservoirs during the study period. The height of each reservoir pulse relative to time was developed by scaling the daily discharge below the reservoir to the maximum daily discharge that occurred during the study period.

Table 3-2. Storms and reservoir operations during WY 2003. Instantaneous discharge data provided by Santa Clara Valley Water District.

			Reservoir discharge		
Event	**Start**	**End**	**Calero (Minimum = 2 cfs)**	**Almaden (Minimum = 1 cfs)**	**Guadalupe (Minimum = 2 cfs)**
Storm 1	Nov. 7 @ 0130	Nov. 9 @ 0700	7 cfs		
Storm 2	Dec. 13 @ 1430	Dec. 14 @ 0500	7 cfs		
Storm 3	Dec. 14 @ 1500	Dec. 15 @ 0700	Peak = 13 cfs @ 17:00		
Storm 4	Dec. 16 @ 0200	Dec. 17 @ 0500	Peak = 31 cfs @ 05:45		
Storm 5	Dec. 19 @ 1200	Dec. 20 @ 0400	Peak =20 cfs @ 16:30	A controlled release of 24 cfs began 12/17 @ 16:45. This was increased to 55 cfs 12/18 @ 10:00 and sustained at 55-60 cfs until 12/26 @ 8:15 with the exception of a short peak of 86 cfs on 12/18 @ 15:30. After 12/26 the discharge was dropped back to 27 cfs.	
Storm 6	Dec. 28 @ 1400	Dec. 29 @ 0400		Discharge maintained at 27-29 cfs	
Storm 7	Dec. 31 @ 0200	Dec. 31 @ 1900		On 12/29 @ 13:45 discharge was increased to 85 cfs. At midday on 12/30, discharge was ramped up as was maintained at 171-184 cfs until 01/02/03 @ 11:00 when it was ramped back down to 13 cfs where it was maintained until 01/07/03 when it was again ramped down to 5 cfs.	On 12/29 @ midday discharge was ramped up and maintained at 37 cfs until 01/02/03 @ 11:45 when it was ramped back down to 8 cfs.
Storm 8	Mar. 14 @ 1900	Mar. 15 @ 1300			Discharge was maintained at 8 cfs from 01/02/03 @ midday to 01/09 when it was ramped down to 6 cfs. Then gradually discharge was ramped down through the rest of January: 01/14 5 cfs; 01/16 4 cfs; 01/23 2 cfs. On 01/28 @ 10:45 discharge was ramped up to 14 cfs and maintained at 12 –14 cfs until 02/28 @ 10:30 when it was ramped back down to 4 cfs.
Storm 9	Apr. 12 @ 1300	Apr. 13 @ 1400	On 04/09/, discharge was ramped up from 2 cfs to 10 cfs, then at 15:45 up to 13 cfs. On 4/11 @ 3:00 discharge was ramped up to 18 cfs where it was maintained until 04/12 @9:15 when is was progressively ramped back down to 10 cfs over a period of 4 hours. On 04/13 @ 9:30 the discharge was ramped down from 10 – 3 cfs over a period of 6 hours.		

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SECTION FOUR

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SUSPENDED SEDIMENT PROCESSES IN GUADALUPE RIVER, WY 2003

690 **Rand Eads, Lawrence Freeman, and Lester McKee**

INTRODUCTION

There is a strong relationship between sediment loads and the transfer of PCBs, OC pesticides and mercury into the Bay (Davis et al., 1999; McKee et al., 2003). There is a strong relationship between suspended sediment and turbidity and therefore a turbidity probe and data logger can be used to estimate time continuous estimates of suspended sediment concentration and loads in situations where suspended sediment grainsize is reasonably constant (e.g. Walling et al., 1997; Eads and Lewis 2001). In this section, the results of the continuous turbidity measurement and water sampling for suspended sediment concentration during WY 2003 will be presented.

PREVIOUS DATA

Suspended sediment has been measured by the U.S. Geological Survey in 26 locations in small tributaries around the Bay Area (McKee et al., 2003). Periods of record range from a few days to more than 15 years. Peak concentrations can be remarkably high at some locations during storm events; six locations recorded in excess of 10,000 mg l^{-1} and a further six locations recorded between 5,000 and 9,999 mg l^{-1}. Only 18 out the 26 locations had at least one full wet season of record. Flow-weighted mean concentrations at many locations were in excess of 1000 mg l^{-1} perhaps indicative of both a tectonically active erosive terrain coupled with a storm dominated rainfall regime and an anthropogenically modified landscape. The USGS made measurements on the Guadalupe River at San Jose (11169000) from February 1957 and May 1962. The discharge during this covered the full range of response and included floods that ranged from 1 year return to the second largest flood in the gage record (4/2/58 peak = 9,150 cfs). Concentrations measured during the period WY 1957 – 1962 ranged from 3-5,970 mg l^{-1} had a flow-weighted mean concentration of 1,319 mg/L.

Sediment loads have been calculated at locations around the Bay where sufficient data exist (McKee et al., 2003). Sediment export in Bay Area tributaries was found to range from 27-1639 t $km^{-2}yr^{-1}$. Using the SIMPLE model, Davis et al. (2000) estimated a sediment load for Guadalupe of 6,200 metric tonnes. An annual average load of 91,044 metric tonnes (702 t $km^{-2}yr^{-1}$) was estimated for the Guadalupe River watershed by the U.S. Army Corps of Engineers (USACE, 2001). Using a flow-weighted mean concentration generated with the historic collected by the USGS between 1957-1962 data and combining this with the mean annual runoff of 55 Mm^3 an historic annual average load is estimated at 72,563 t (560 t $km^{-2}yr^{-1}$).

STUDY PERIOD (WY 2003)

Continuous Turbidity and Suspended Sediment Concentration

Turbidity was measured every 15 minutes during the period November 1st 2002-May 31st 2003 (7 months or 23,327 data points). Turbidity ranged from 3 – 819 NTU and varied during the study period mainly in response to discharge (Figure 4-1). The USGS collected 238 water samples and analyzed these for suspended sediment concentration (SSC). Measured SSC ranged from 5-1,012 mg L^{-1} and as expected, formed a relationship with discharge exhibiting a high degree of scatter (Figure 4-2). A relationship was developed between turbidity and SSC using a loess (Cleveland, 1979) fit (Figure 4-3). A

model was generated that excluded several outliers and used to estimate time continuous suspended sediment concentration (Figure 4-4). This illuminated the detail and complexity of the relationship between discharge and suspended sediment concentration during each flood (Figure 4-5). Hysteresis is the term used to describe differing concentration of the rising and falling stages of a hydrograph for a given magnitude of discharge. During the study there was flood-specific hysteresis. Some floods exhibited clockwise hysteresis (the peak SSC occurred before the peak discharge) and other floods exhibited anticlockwise hysteresis (the peak SSC occurred after the peak discharge). An understanding of this kind of detail allowed for very accurate determination of suspended sediment loads.

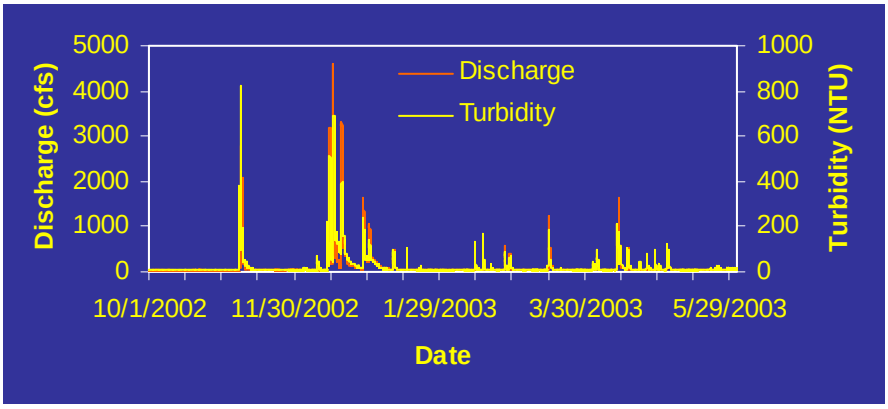

Figure 4-1. The variation of turbidity and discharge during the study period.

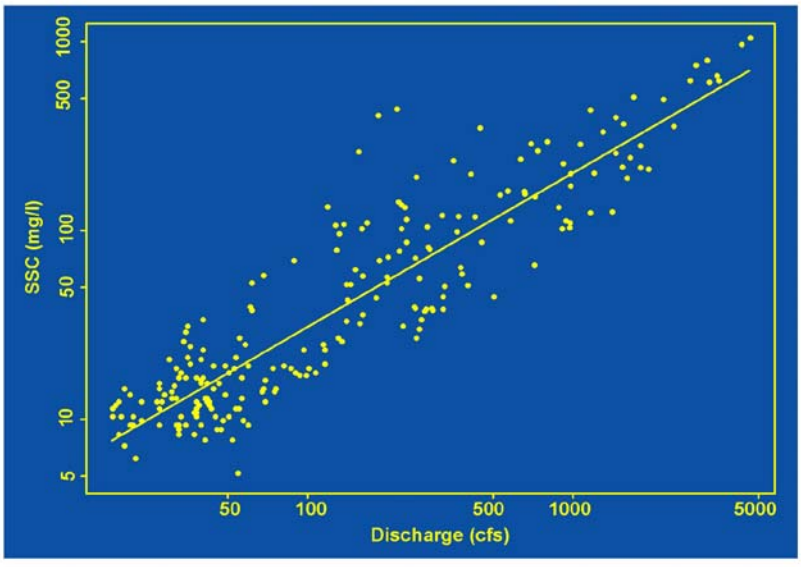

Figure 4-2. Measured suspended sediment concentration as a function of discharge.

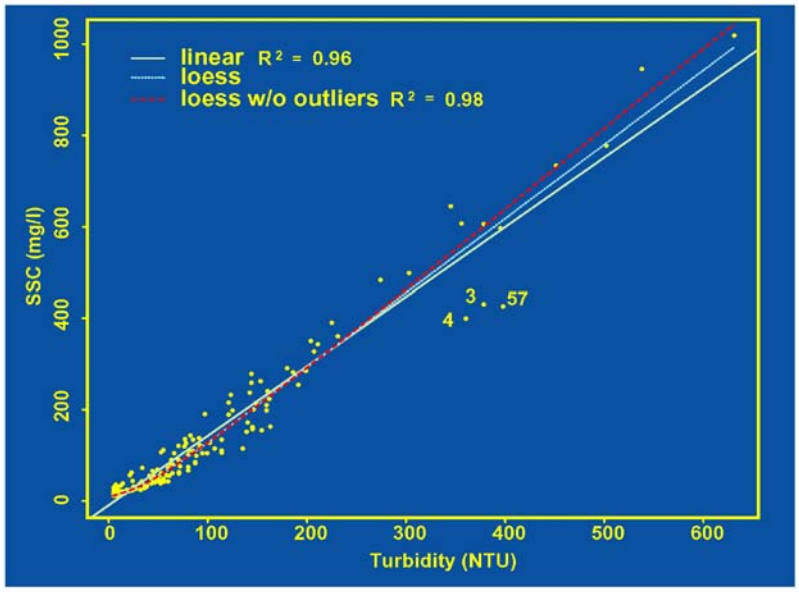

Figure 4-3. Guadalupe WY 2003 Turbidity-SSC model.

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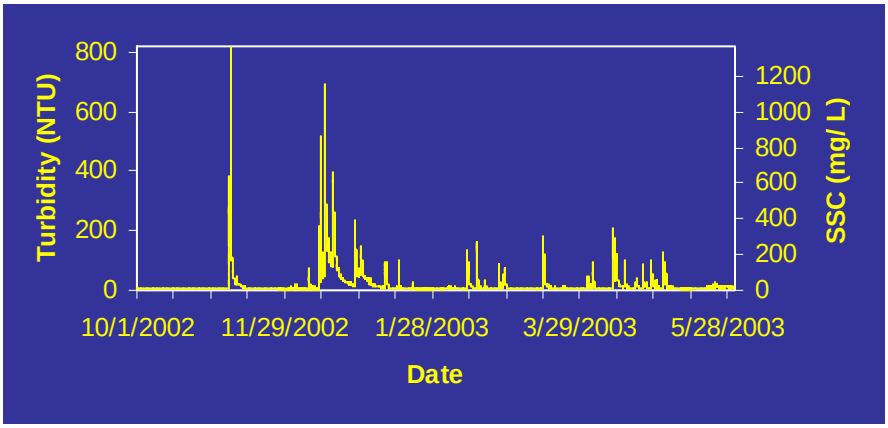
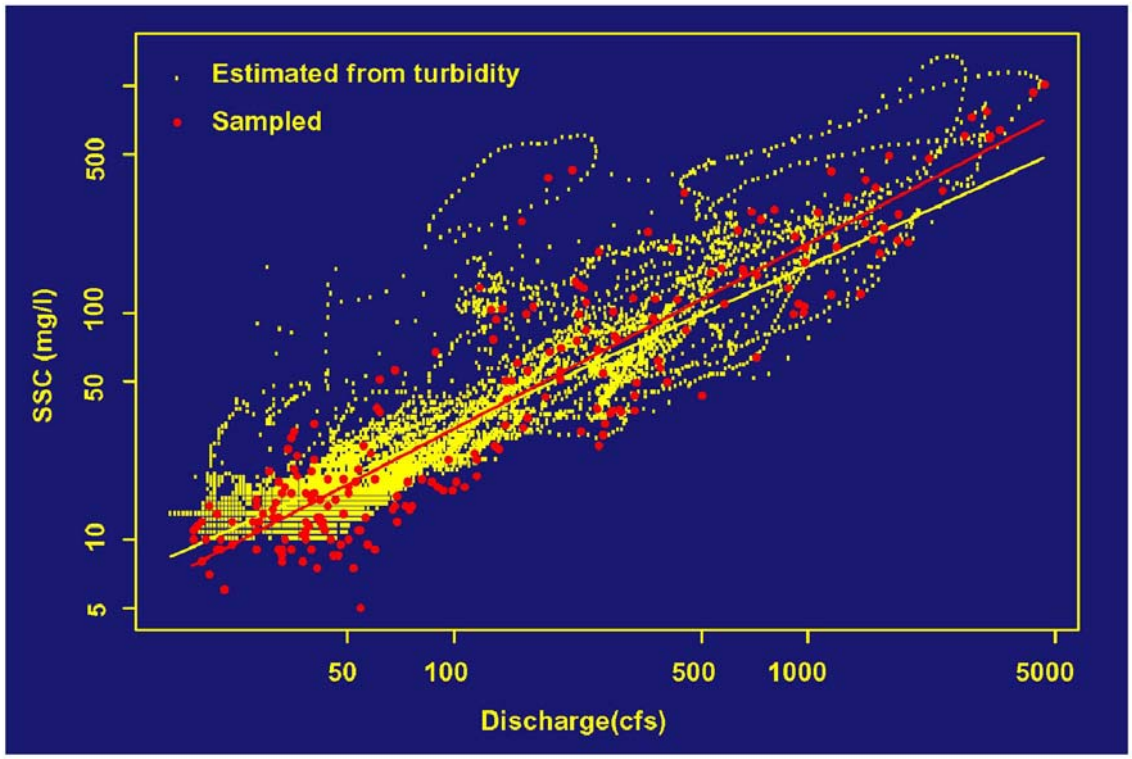


760 **Figure 4-4.** Time continuous suspended sediment concentration for the study period generated using the loess model.



765 **Figure 4-5.** A demonstration of the improved detail generated through the use of continuous turbidity measurement to model suspended sediment concentration. Note the hysteresis loops that are evident in the modeled data that are not evident in the measure data.

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Suspended Sediment Grainsize

During WY 2003 four water samples were analyzed by the USGS for the grainsize of suspended sediment (Table 4-1). During the discharge conditions when particle size was measured, the majority (>90%) of suspended sediment particles were
775 <0.62 mm in diameter. With the exception of an outlier, grainsize appears to increase with increasing discharge, a result consistent with an increase bed stress and turbulence during increased flow. Sediment particle size has a bearing on the relationship between suspended sediment concentration and turbidity. More suspended sediment samples need to be analyzed for particle size distribution to determine what the effect on the
780 concentration vs turbidity relationship is when particle size changes.

Suspended Sediment Loads

USGS water and sediment discharge data for Guadalupe River above highway 101 at San Jose (11169025) are preliminary and subject to change. The data are typically
785 published by the beginning of April following the end of the water year. Suspended sediment concentrations estimated using the loess model ranged from 10-1,366 mg/L and had a flow-weighted mean concentration of 193 mg/L. Suspended sediment loads were

computed by combining 15-minute USGS discharge values (11169025) with the estimated 15-minute suspended sediment concentrations generated by the loess regression turbidity model. The 15-minute load estimates thus calculated was summed for time scales ranging from individual storm events to the seven month total. During the period October 1st to May 31st a total of 10,328 t of suspended sediment was transported past the study location. Sediment load reached a maximum of 493 t hr^{-1} for the hour ending 10 am on December 16th 2002. During that hour, 4.8% of the total load measured was transported through the cross-section at the sampling location. A maximum daily sediment load of 2,823 t (27% of the total) also occurred on December 16th. Fifty percent of the suspended sediment was transported in just 3 days or 1.2% of the time. Ninety percent of the suspended sediment load occurred in just 14 days or 5.8% of the time (Figure 4-6). A total of 7,027 t or 68% of the total annual load was transported in response to the series of floods that occurred during December (Table 4-2). These results are characteristic of climatically variable Bay Area rivers and creeks (e.g. McKee et al., 2003).

Table 4-1. Grainsize of particles in suspension during WY 2003.

Date	Time	Instantaneous discharge (cfs)	SSC (mg/L)	Suspended sediment sieve diameter percent (<.062 mm)	Suspended sediment, sieve diameter percent (<.125 mm)	Suspended sediment, sieve diameter percent (<.25 mm)	Suspended sediment, sieve diameter percent (<.5 mm)	Suspended sediment, sieve diameter percent (<1 mm)
11/7/2002	**10:40**	197	406	98	99	100	--	--
11/8/2002	**13:20**	1830	289	90	96	99	99	100
11/13/2002	**10:35**	28	14	91	--	--	--	--
12/15/2002	**12:00**	252	70	96	--	--	--	--

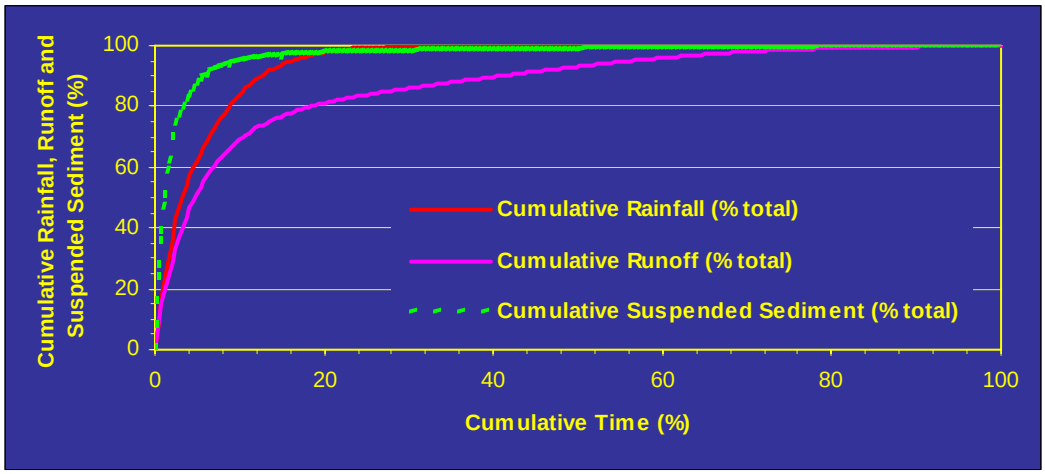

Figure 4-6. Cumulative rainfall, runoff and suspended sediment as a percentage of total rainfall, runoff, and suspended sediment compared to cumulative percentage of time over the period November 1st 2002 – May 31st 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) and a lower watershed location (San Jose). Rainfall data supplied by Santa Clara Valley Water District. Runoff data are provisional supplied by the USGS.

Table 4-2. Suspended sediment loads (metric tonnes) for the study period.

Date	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Total
Load (t)	19	2,085	7,027	165	184	268	486	93	10,328
% Total	0.2	20.2	68.0	1.6	1.8	2.6	4.7	0.9	100.0

Comparisons to Previous Estimates

In terms of annual discharge, WY 2003 was about average (see hydrology section). The measured sediment load for WY 2003 was about 11% of the load estimated by the Army Corps (USACE, 2001) and about 1.7x that estimated by the SIMPLE model (Davis et al., 2000). The likely underestimate by the SIMPLE model has already been discussed (McKee et al., 2003) and the over estimate by the Army Corps probably occurred because they used a regional data set to make an estimate rather then watershed specific data. Most interesting however, is the comparison of concentration data collected by the USGS between 1957-1962 (Figure 4-7). The flow-weighted mean concentration for WY 2003 was 193 mg/L or about 15% of the flow-weighted mean for the 1957-1962 period. During the late 50s and early 60s, the Guadalupe River watershed was undergoing rapid urban development. This might have caused larger supplies of sediment to the river channel that have since waned. In addition, there might have been some middle and lower watershed channel adjustment (bed incision and or bank erosion) following the completion of the reservoirs during the 1950s. Either of these hypotheses seem plausible but would require further study to support or reject.

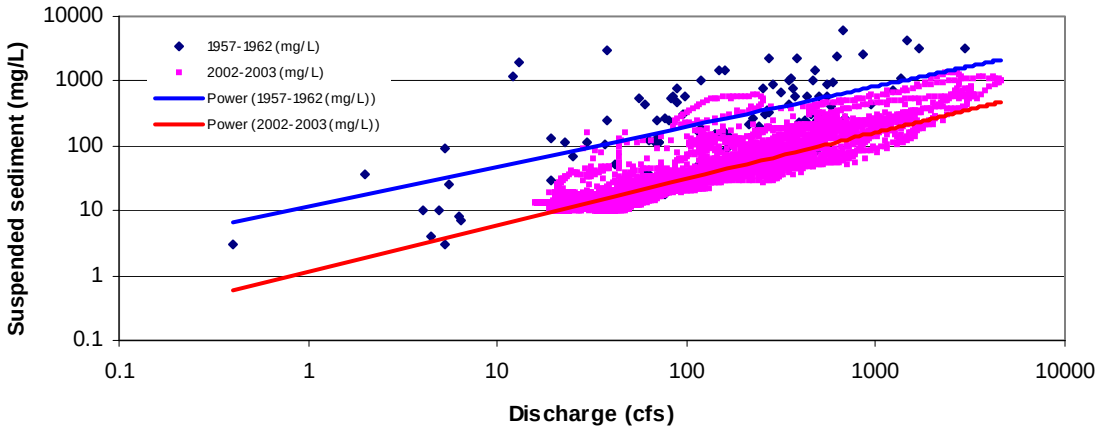

Figure 4-7. Comparison of WY 2003 data with a historical data set collected by the USGS between 1957-1962.

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SECTION FIVE

PCB AND OC PESTICIDE PROCESSES IN GUADALUPE RIVER, WY 2003

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Jon Leatherbarrow and Lester McKee

ABSTRACT

Polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides are organic chemicals of current environmental concern in San Francisco Bay due to their lengthy persistence in the environment and their potentially adverse effects on wildlife and human health. Although these chemicals have been restricted or banned for decades, their concentrations are high enough in Bay sport fish to contribute to the issuance of an interim consumption advisory for fish caught in the Bay. Consistent with this advisory, the Bay is listed as impaired by the State of California in compliance with the Clean Water Act for PCBs (high priority) and OC pesticides (lower priority). This study assesses storm events and the influence of sediment and water runoff processes on concentrations and transport of PCBs and OC pesticides in the Guadalupe River, one of the larger local basins, and a likely source of ongoing loads of trace organic contaminants.

In 22 samples collected during varying stages of storm events, t-PCB concentrations ranged from 3.4 to 90 ng L^{-1} with a flow-weighted mean concentration of 54 ng L^{-1}. In all samples, PCB congener distributions were indicative of predominant contributions of Aroclor 1254 and 1260 with hexa-, hepta-, and octa-chlorobiphenyls comprising approximately 50 to 75% of t-PCB concentrations. Total DDT concentrations ranged from 1.7 to 71 ng L^{-1} with a flow-weighted mean concentration of 48 ng L^{-1}. Total chlordane concentrations ranged from 1.6 to 64 ng L^{-1} with a flow-weighted mean concentration of 40 ng L^{-1}. Dieldrin concentrations ranged from 0.3 to 6.0 ng L^{-1} with a flow-weighted mean concentration of 3.7 ng L^{-1}. All measured contaminants were positively correlated to instantaneous discharge (r^2 = 0.61 to 0.80) and suspended sediment concentration (r^2 = 0.51 to 0.72) with maximum concentrations occurring on December 16th when discharge exceeded 4,000 cfs and suspended sediment concentration exceeded 800 mg L^{-1}. The positive correlations observed in Guadalupe River indicate that contaminant residues transported to the bottom of the watershed are homogeneous relative to suspended sediment and likely originate from diffuse storage of contaminated watershed soils and/or upstream sediment deposits.

The relative abundance of individual PCB congeners and DDT compounds in Guadalupe River samples varied with discharge and were suggestive of different sources contributing to contaminant transport to the bottom of the watershed. As discharge increased, sources of Aroclor 1254 increased in importance while contributions from sources of Aroclor 1260 decreased. Of the individual DDT compounds, DDD (o,p' + p.p'-DDD) was the most predominant compound at low discharge, but decreased in importance at high flows. In contrast, contributions of DDT (o,p'- + p,p'-DDT) increased with discharge suggesting that relatively unweatherd material was being transported from terrestrial sources in the watershed. A first flush effect was evident and indicated by unique contaminant patterns in the early storms of the season.

Using the continuous record of turbidity and regression models between suspended sediment, turbidity, and contaminant concentrations, monthly loads were estimated. Load estimates for the period October 2002 – May 2003 were 1.1± 0.3 kg t-PCBs, 0.91 ± 0.26 kg t-DDT, 0.69 ± 0.12 kg t-chlordane, and 0.075 ± 0.017 kg dieldrin. Due to most of the storm activity occurring in December, most of the sediment (68%) and contaminant load (54-65%) occurred during that month. Compared to estimates of contaminant load from the large tributaries entering the Bay from the Central Valley of California, Guadalupe River load was less by factors of 3.5 to 50; however, it is reasonable to assume that combined load from the local tributaries would contribute similar magnitudes of PCBs, DDT, and chlordanes. The magnitude of these load estimates will likely contribute to delayed recovery of Bay contamination by PCBs, DDT, and chlordane.

INTRODUCTION

Polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides are organic chemicals of current environmental concern in San Francisco Bay due to their lengthy persistence in the environment and their potentially adverse effects on wildlife and human health. The OC pesticides of specific concern for regulation and management in the Bay are DDT (including the o,p'- and p,p'-isomers of DDT, DDE, and DDD), chlordane (including alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide), and dieldrin. PCBs and OC pesticides are sparingly soluble in water and tend to partition into particulate material in soil and sediment and lipid tissue in biota. These properties allow PCBs and OC pesticides to persist in soils, sediments, and biota for time periods of decades or longer (Spencer et al. 1996, Leatherbarrow et al. 2002, Gunther et al. 1999, Davis et al. 2002).

Concerns over the persistence of PCBs and OC pesticides in the Bay and their tendency to biomagnify in the food web have spurred the allocation of considerable resources and effort to monitor these chlorinated hydrocarbons in the Bay over the last few decades. Although these chemicals have been restricted or banned for decades, their concentrations were high enough in Bay sport fish caught in 1994 to contribute to the issuance of an interim consumption advisory for sport fish caught in the Bay (OEHHA, 1994). This health advisory remains in place and has led to the listing of all segments of San Francisco Bay on the Clean Water Act Section 303(d) list as impaired by these contaminants. Since the initial listing in 1998, PCBs have been a high priority concern for the Bay and are currently subject to development of a Total Maximum Daily Load (TMDL) management plan. At the time of the most recent revision to the 303(d) list in 2002, OC pesticides were listed as low priority and were not currently scheduled for TMDL development (SWRCB, 2003).

PCBs were commercially produced in the United States from 1929 to 1979 and were primarily used in industrial applications as insulating fluids in transformers, capacitors, and electromagnets and were also used for other minor purposes: heat exchanger fluids, chemical stabilizers, plasticizers, adhesives, insulating materials, flame-retardents, lubricants, and other products (Wong et al. 2000, Walker et al. 1999). Beginning in the 1940's, OC pesticides were used as insecticides for agricultural purposes and in urban areas for pest control and mosquito abatement (Mischke et al. 1985), as well as for various other industries, such as forestry and transportation (Nowell et al. 1999). PCBs and OC pesticides were used throughout Bay Area watersheds resulting in their widespread distribution in the drainage basins and channels of local tributaries of the Bay (Law and Goerlitz, 1974). The widespread use of these chemicals in Bay Area watersheds eventually contributed to the large reservoir of chlorinated hydrocarbons in the Bay sediment pool and ongoing persistent sources within the watersheds.

Although the large sediment pool in the Bay is expected to be the main driving force influencing water quality and food web contaminant dynamics for persistent organic chemicals (Davis 2003, Gobas and Wilcockson, 2002), existing storage in local watersheds and continuing inputs from these sources warrant investigation into their

impact on overall impairment of the Bay. In 2000-2001, the Bay Area stormwater agencies conducted a synoptic sediment survey of PCBs and OC pesticides (and other contaminants) in storm drains and local tributaries and determined that areas of high contamination still exist in urban areas of local watersheds (KLI 2002, Salop et al. 2002). Results from a previous study in the tidal reach of the Guadalupe River determined that watershed sources most likely contributed to continued inputs of these contaminants to the Bay (Leatherbarrow et al. 2002). In the context of an environmental fate model for PCBs in the Bay, external PCB load on the order of 10 kg yr^{-1} was estimated to be a sufficient amount to significantly delay declining concentrations in Bay sediment and biota (Davis 2003). These findings highlighted the need to understand how continued contaminant load from local tributaries contribute to further contamination of Bay sediment and biota in context of other important pathways of contamination (e.g. inputs from the Central Valley) and the long term recovery of the Bay.

The Guadalupe River drains a heavily urbanized mixed land-use watershed and enters Lower South San Francisco Bay near San Jose, California. This watershed is the 5^{th} largest of the small tributaries that enter the Bay from the urbanized greater San Francisco Bay Area. It represents an ideal watershed to study the influence of sediment and hydrological processes on transport of PCBs and OC pesticides and has the potential to improve our understanding of likely processes in other watershed where sampling has not occurred. Furthermore, this is the first study to use low-level detection techniques sufficient for consistent quantification of these trace organic contaminants in the water column of a San Francisco Bay tributary. Results from this study will provide information that will further assist in refining mass budget models of persistent organic contaminants and the future development of TMDLs in the Bay.

METHODS

Study Site

The study site was located in a downstream reach of the Guadalupe River at a USGS gaging station just upstream from Highway 101 in San Jose, California. The Guadalupe River drains a 556 km^2 basin adjacent to Lower South San Francisco Bay that is approximately 46% urbanized, of which 65% of the urban area is residential, 10% is commercial, and 11% is light or heavy industrial (SCBWMI, 2000). Remaining land uses in the watershed consist primarily of forest (35%), rangeland (15%) and agriculture (~3%) (SCBWMI 2000).

Sample and Data Collection

Twenty-two grab samples were collected from the Guadalupe River for analysis of PCBs and OC pesticides (Table 5-1). Individual PCB congeners were measured to derive total PCB (t-PCB) concentrations in water samples. Total DDT (t-DDT) concentrations accounted for concentrations of o,p' and p,p'-isomers of DDD, DDE, and DDT. Total chlordane (t-chlordane) concentrations were comprised of alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide. Dieldrin was also measured as part of this study.

Table 5-1. Chlorinated hydrocarbons 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	

Grab samples were also collected for analysis of selected water quality parameters: suspended sediment concentrations (SSC_{GRAB}), particulate organic carbon (POC), and dissolved organic carbon (DOC). Turbidity data were collected on 15-minute intervals from November 1st, 2002 to May 31st, 2003 by Redwood Sciences Laboratories following methods described in Section Two of this report. Suspended sediment and grain size were measured by USGS following methods also described in Section Two.

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 chromotagraphy/ 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 $^{13}C_{12}$-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 E1and 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 autosampler, and an Alpha data system running Micromass software. A DB-5 (60 m, 0.25 mm i.d., 0.1 μm 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 water quality parameters in grab samples are discussed in detail in Section Six.

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, $^{13}C_{12}$-labeled surrogate recoveries, and duplicate field samples. Concentrations in samples with $^{13}C_{12}$-labeled surrogate recoveries outside of method specifications (25-150%) were estimated and qualified (q). Attempts to bring recoveries within the normal range by additional clean-up procedures and reanalysis were not possible for some samples due to complete consumption of the low sample volumes collected in the study. These data have greater uncertainty; however, sample concentrations reported with surrogate recoveries were not rejected because concentrations fell within the range of reported concentrations. Concentrations not measured above limits of quantification were assumed to be zero for calculation of t-PCBs, t-DDT, and t-chlordane.

RESULTS

Hydrology

As a result of the Mediterranean-type climate of the Bay Area, greater than 95% of the rainfall in the Guadalupe River watershed during climatic year (CY) 2003 – July 1st to June 30th - fell between November and April. Approximately 50% of the rainfall occurred in eight days or 3% of the time and 90% of the rainfall occurred over 30 days or 11% of the time in the study period (see Section Three). Consequently, approximately 85% of discharge at the study site in water year (WY) 2003 – October 1st to September 30th – occurred during these months. Approximately 50% and 90% of the annual runoff occurred in 12 and 120 days, respectively. During WY 2003, a maximum peak discharge of 6,160 cfs occurred at 9:00 am on December 16th, 2002 (Figure 5-1). Mean annual flow was 59 cfs or 97% of normal flow measured upstream at USGS gaging station 11169000 from 1971 to 2000. Samples were collected during storm events at different points along the hydrograph.

Continuous Turbidity and Suspended Sediment Concentrations (SSC)

Turbidity ranged from 3 nephelometric turbidity units (NTU) in base flow conditions to an annual peak of 819 NTU that occurred during the first seasonal flood event on November 7th, 2002 when discharge was approximately 2,600 cfs. This peak in turbidity was evidence of a first flush of sediment during the first storm of the season. USGS also measured suspended sediment concentrations (SSC_{USGS}) that ranged from 5 to 1,012 mg L^{-1} in 238 water samples. As described in Section Four of this report, a

relationship was developed to correlate turbidity and SSC_{USGS} using a loess fit after removing three outliers ($r^2 = 0.98$, $p < 0.0001$; see Section Four). This model was used to estimate time continuous concentrations of suspended sediment (SSC_{EST}) for WY 2003. The linear relationship between turbidity and SSC_{USGS} yielded a peak estimated SSC_{EST} concentration of 1,370 mg/L. Turbidity exceeded 400 NTU (or 640 mg L^{-1} SSC_{EST}) during three storm events on November 7th, December 14th, and December 16th, 2002.

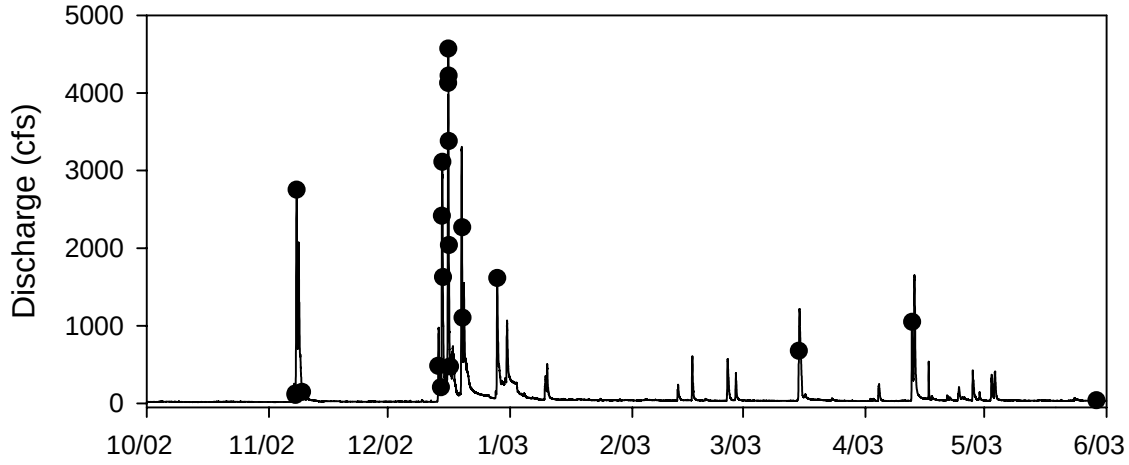

Figure 5-1. Sampling events at Guadalupe River, WY 2003. Sampling events are depicted as black circles on the hydrograph and turbidigraph.

Polychlorinated Biphenyls (PCBs)

Total PCB concentrations ranged from 3.4 to 90 ng L^{-1} and exhibited a flow-weighted mean concentration (FWMC) of 54 ng L^{-1} (Table 5-2). Only four measurements were below detection: three measurements of PCB 008 and one measurement of PCB 183/185. Relative percent differences (RPDs) of PCB congeners measured in the field duplicate sample ranged from 0.5 to 33% (Table 5-3). The RPD of t-PCBs was approximately 8.1%. Total PCB concentrations were positively correlated to instantaneous discharge ($r^2 = 0.61$, $p < 0.0001$) and SSC_{EST} ($r^2 = 0.51$, $p = 0.0002$; Figure 5-2). Concentrations spanned over an order of magnitude between base flow conditions and storm flow with the maximum t-PCB concentration being measured on December 16th, 2002 when discharge exceeded 4,000 cfs and SSC_{EST} exceeded 800 mg L^{-1}. In all samples, hexa-, hepta-, and octa-chlorobiphenyls comprised approximately 50 to 75% of t-PCB concentrations. Concentrations of all individual PCB congeners are listed in Appendix Table A.

Organochlorine Pesticides

Total DDT concentrations ranged from 1.7 to 71 ng L^{-1} and exhibited a FWMC of 48 ng L^{-1} (Table 5-2). Total DDT concentrations were comprised primarily of p,p'-DDE (25 to 50%), p,p'-DDD (11-40%), and p,p'-DDT (11-36%). Total chlordane concentrations ranged from 1.6 to 64 ng L^{-1} and exhibited a FWMC of 40 ng L^{-1}. Abundant chlordane components were alpha-chlordane (26-34%), gamma-chlordane (25-31%), and trans-nonachlor (23-32%). Dieldrin concentrations ranged from 0.3 to 6.0 ng L^{-1} and exhibited a FWMC of 3.7 ng L^{-1}. Of all pesticides measured, only one concentration of heptachlor was below detection. RPDs of individual DDT compounds ranged from 3% for p,p'-DDE to 29% for p,p'-DDT with an overall RPD of 4% for t-DDT. RPDs of chlordane compounds ranged from 0.6% for alpha-chlordane to 56% with an overall RPD of 0.3% for t-chlordane (Table 5-3). The RPD for dieldrin was 6%. As with PCBs, concentrations of measured OC pesticides increased with increasing flow (r^2 = 0.66 to 0.80, $p < 0.0001$) and sediment discharge (r^2 = 0.64 to 0.72, $p < 0.0001$; Figure 5-2). Maximum concentrations of t-DDT, t-chlordane, and dieldrin were measured on December 16th concomitant with maximum instantaneous discharge (4,500 cfs) and SSC_{EST} (1,000 mg/L) observed during sampling. Concentrations of all individual pesticides are listed in Appendix Table B.

Water Quality

Concentrations of discretely measured SSC_{GRAB}, POC, and DOC are presented in Table 5-2. SSC_{GRAB} concentrations ranged from 16.8 to 1,150 mg L^{-1}. POC ranged from 0.3 to 0.9 mg L^{-1}. DOC ranged from 3.9 to 8.9 mg L^{-1}. Of all water quality parameters, only one measured POC concentration was below the method detection limit (0.1 mg L^{-1}). DOC and POC were not significantly linearly correlated to any of the organic contaminants measured in this study ($p > 0.05$).

Table 5-2. Summary of hydrology, water quality, and chlorinated hydrocarbon concentrations in Guadalupe River water samples, WY 2003. Method detection limits (MDLs) represent the maximum MDL reported for all samples. The t-PCB MDL was based on the maximum MDL reported for individual PCB congeners. DDD, DDE, and DDT are the sum of o,p' and p,p'-isomers of each compound. q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries.

Date	Time	Discharge cfs	SSC mg/L	DOC mg/L	POC mg/L	t-PCBs ng/L	t-DDT ng/L	DDD ng/L	DDE ng/L	DDT ng/L	t-CHL ng/L	ACHL ng/L	GCHL ng/L	TNON ng/L	DIEL ng/L
Maximum MDLs[#]				0.1	0.1	0.01*		0.1	0.05	0.2		0.2	0.2	0.25	0.05
11/7/2002	16:45	104	237	.	.	19	42	11	17	13	12	3.5	3.6	3.3	1.1
11/7/2002	17:05	127	242	.	.	17	31	9	14	8.0	11	3.0	3.3	3.0	1.0
11/7/2002	23:40	2,753	928	.	.	54	59	16	31	12	53	14	15	17	3.1
11/9/2002	7:46	146	50	.	.	7.7	5.7	3.0	1.8	0.9	3.7	1.2	1.0	0.9	0.64
12/13/2002	19:29	484	315	8.9	ND	65	33	16	13	4.6	26	7.0	8.0	7.6	2.4
12/14/2002	11:00	206	29	5.4	0.5	4.1	3.3	1.0	1.4	0.9	3.4	1.0	0.9	0.9	0.74
12/14/2002	17:55	2,417	577	4.5	0.3	62	48	12	19	17	50	13	15	15	4.7
12/14/2002	20:24	3,112	641	3.9	0.8	38	34	6.7	14	14	37	10	10	12	3.5
12/15/2002	0:16	1,627	360	4.6	0.3	13	16	3.3	7.2	5.8	13	3.7	3.5	4.2	1.6
12/16/2002	7:55	4,128	845	4.0	0.7	90	55	11	21	23	56	15	15	18	5.8
12/16/2002	8:45	4,525	1024	4.4	0.7	Q 85	71	17	28	26	64	19	19	18	6.0
12/16/2002	9:55	4,223	1130	5.2	0.6	57	52	11	21	19	41	12	11	12	4.2
12/16/2002	10:45	3,473	1148	5.7	0.9	54	Q 50	q 9.0	22	q 19	37	11	10	10	3.2
12/16/2002	12:31	2,039	933	6.3	0.4	Q 37	Q 40	q 7.5	q 16	q 16	Q 26	7.7	7.0	q 7.3	2.7
12/16/2002	19:55	477	427	7.3	0.5	19	15	2.3	7.7	5.1	9.7	2.7	2.4	2.7	1.4
12/19/2002	20:30	2,333	578	.	.	Q 31	Q 30	q 5.6	q 12	q 12	Q 24	q 7.0	q 6.5	q 6.6	2.8
12/19/2002	23:30	1,151	487	.	.	14	Q 18	q 3.2	q 8.2	q 6.4	Q 12	3.6	3.1	q 3.2	2.0
12/28/2002	18:24	1,616	352	.	.	69	Q 36	9.4	14	q 13	Q 35	10	10	q 9.2	3.4
3/15/2003	3:06	676	195	.	.	27	15	5.0	6.4	4.0	15	4.5	4.7	4.0	1.5
4/12/2003	18:40	1,048	220	.	.	15	17	4.0	7.1	5.7	22	6.3	6.4	q 6.1	1.9
5/29/2003	10:33	40	16.8	.	.	3.7	Q 1.7	q 0.97	q 0.44	q 0.30	1.6	0.52	0.46	0.37	0.31
5/29/2003	10:33	40	16.8	.	.	3.4	1.8	0.92	0.46	q 0.40	1.6	0.52	0.43	0.36	0.33

Table 5-3. Quality assurance and control summary. DF = detection frequency (%) of analytes in field samples. RPD = relative percent difference of concentrations measured in field duplicate. Accuracy is the range of matrix spike recoveries in three QA samples.

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Parameter	Blank Conc. (pg/L)	MDL Range	DF	RPD	Accuracy (%)
o,p'-DDD	ND	5.4 - 67	100	10	100 - 140
o,p'-DDE	ND	5 - 36	100	24	72.2 - 89.2
o,p'-DDT	ND	7.9 - 105	100	19	94.2 - 112
p,p'-DDD	ND	7.9 - 83	100	4	111 - 135
p,p'-DDE	ND	8.4 - 49	100	3	92 - 116
p,p'-DDT	ND	11 - 182	100	29	93.5 - 114
alpha-Chlordane	ND	7.8 - 164	100	1	95 - 121
gamma-Chlordane	ND	6.8 - 145	100	6	93.1 - 108
cis-Nonachlor	ND	21 - 350	100	8	93.1 - 118
trans-Nonachlor	ND	8.9 - 237	100	2	96.3 - 112
Heptachlor	ND	5 - 31	95	NA	94.8 - 116
Heptachlor Epoxide	ND - 2.41	2.6 - 14	100	2	90.7 - 109
Oxychlordane	ND	11 - 79	100	56	94.1 - 107
Dieldrin	5.04 - 8	4.9 - 31	100	6	90.3 - 119
PCB 001					97.2 - 121
PCB 003					104 - 112
PCB 004					101 - 127
PCB 008	ND - 17.1	0.31 - 21	86	ND	
PCB 015					90.8 - 112
PCB 018/30	1.58 - 9.26	0.16 - 8	100	4	
PCB 019					104 - 111
PCB 028/20	2.36 - 14	0.24 - 4	100	6	
PCB 031	2.11 - 12.2	0.24 - 5	100	6	
PCB 033/21	1.53 - 7.34	0.24 - 5	100	13	
PCB 044/47/65	2.64 - 7.29	0.02 - 8	100	8	
PCB 049/69	1.16 - 3.02	0.02 - 7	100	7	
PCB 052	1.81 - 7.34	0.02 - 8	100	8	
PCB 056	ND - 1.89	0.61 - 6	100	13	
PCB 060	ND - 1.13	0.61 - 6	100	33	
PCB 066	ND - 3.34	0.58 - 5	100	8	
PCB 070/74/61/76	2.15 - 8.22	0.58 - 5	100	2	
PCB 087/97/86/108/119/125	1.59 - 1.59	0.19 - 6	100	14	
PCB 095/93/98/100/102	1.7 - 6.83	0.21 - 6	100	5	
PCB 099/83	1.11 - 5.11	0.22 - 7	100	4	
PCB 101/90/113	1.68 - 7.04	0.19 - 6	100	13	
PCB 105	0.63 - 2.74	0.52 - 10	100	10	102 - 115
PCB 110/115	1.34 - 8.06	0.16 - 5	100	17	
PCB 114					87.4 - 111
PCB 118	1.19 - 6.46	0.45 - 10	100	7	94.1 - 118
PCB 128/166	0.4 - 0.894	0.43 - 9	100	8	
PCB 132	ND - 1.81	0.56 - 12	100	1	
PCB 138/129/160/163	3.01 - 5.98	0.41 - 9	100	5	
PCB 141	ND - 1.34	0.5 - 11	100	1	
PCB 149/147	2.68 - 2.96	0.51 - 11	100	1	
PCB 151/135/154	1.46 - 1.47	0.01 - 4	100	1	
PCB 153/168	1.5 - 4.79	0.39 - 8	100	8	
PCB 156/157	0.493 - 0.522	0.46 - 9	100	23	86.3 - 110
PCB 158	ND - 0.715	0.34 - 7	100	2	
PCB 167					90.6 - 110
PCB 170	ND - 2.04	0.01 - 5	100	15	
PCB 174	ND - 2.95	0.01 - 4	100	24	
PCB 177	ND - 1.74	0.01 - 5	100	20	
PCB 180/193	1.6 - 6.37	0.01 - 4	100	17	
PCB 183/185	0.983 - 2.13	0.01 - 4	95	24	
PCB 187	ND - 3.93	0.01 - 4	100	25	
PCB 189					90.2 - 118
PCB 194	ND - 0.625	0.19 - 7	100	19	
PCB 195	ND - 0.446	0.2 - 8	100	28	
PCB 201	ND - 0.265	0.01 - 4	100	1	
PCB 203	ND - 0.652	0.01 - 5	100	31	
PCB 205					96.1 - 111
PCB 206					93.1 - 110

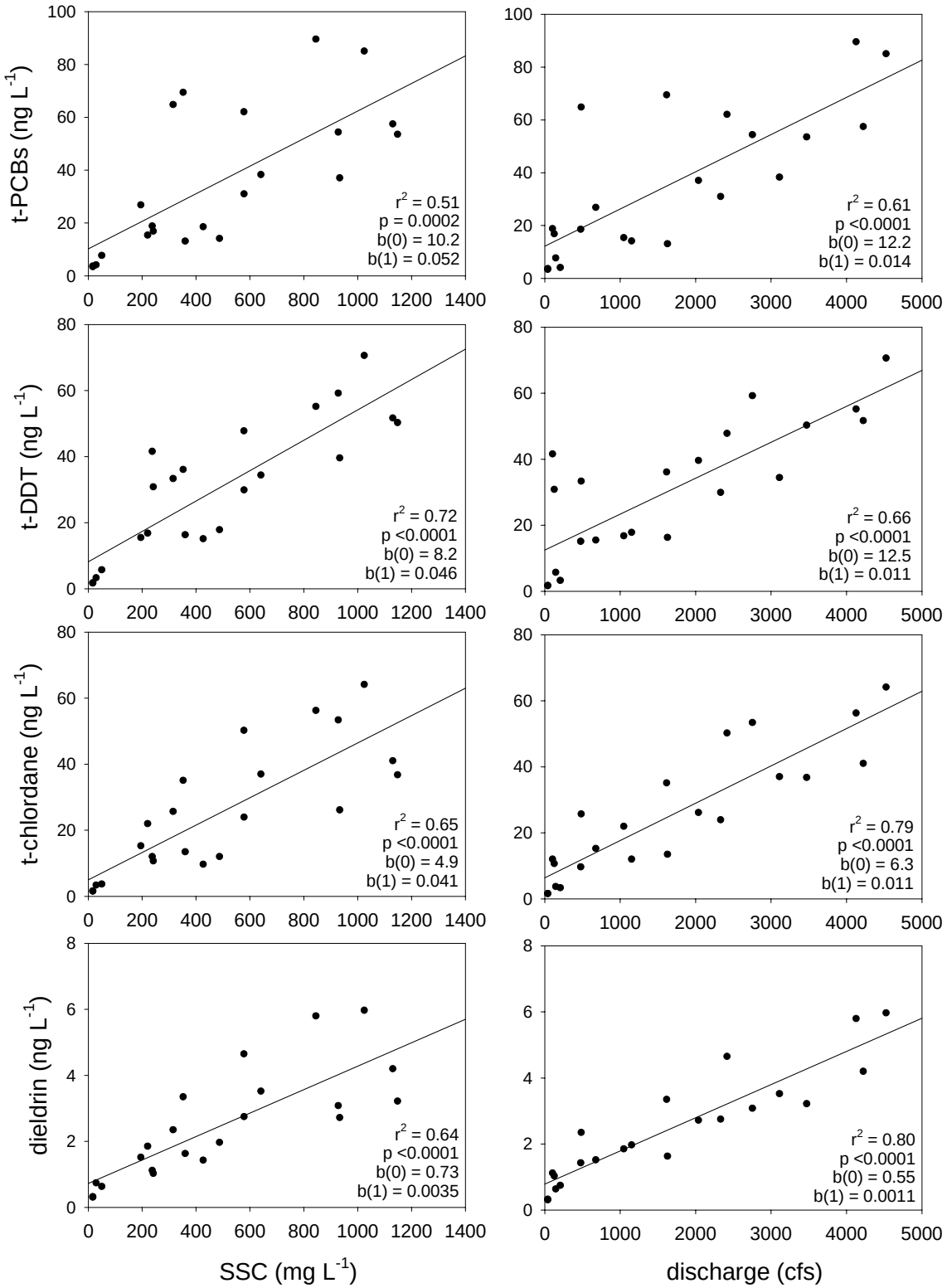


Figure 5-2. Linear regressions of chlorinated hydrocarbon concentrations versus discharge and SSC.

DISCUSSION

Chlorinated Hydrocarbons in Watersheds

Concentrations of PCBs and OC pesticides measured in this study reflected contaminant signals consistent with past usage and current storage of these contaminants in the tributary and its watershed. The primary use of PCBs for industrial and other urban purposes, as well as the application of chlordane as a termiticide in urban areas, has resulted in greater concentrations and loads of these contaminants in urban areas of watersheds compared to nonurban areas (Rostad et al. 1999, Wong et al. 2000, Foster et al. 2000, Pereira et al. 1996). DDT and dieldrin were insecticides used primarily for agriculture, but also for mosquito abatement and termite control in urban areas; therefore, residues of these chemicals have been found in high concentrations in both urban and agricultural areas of watersheds and stream channels (KLI 2002, Salop et al. 2002, Wong et al. 2000, Gilliom and Clifton 1990, Kratzer 1999, Pereira et al. 1996). The Guadalupe River watershed is heavily urbanized, especially in the lower watershed where water is not regulated by dam and reservoir operations. Furthermore, before significant population growth occurred in the post-World War II era, large portions of the watershed were used for agriculture (SCBWMI 2000). Accordingly, findings in this study were consistent with previous studies that established a linkage between past uses of PCBs and OC pesticides with areas of contemporary contamination in watersheds and tributaries (e.g., Wong et al. 2000).

In this study, concentrations of t-PCBs (3.4-90 ng L^{-1}), t-chlordane (1.6-64 ng L^{-1}), and dieldrin (0.3-6.0 ng L^{-1}) were likely indicative of urban influences on downstream water quality. Concentrations were of similar magnitude to concentrations of t-PCBs (2.0-29 ng L^{-1}), t-chlordanes (1.0-49 ng L^{-1}) and dieldrin (<0.05-4.8 ng L^{-1}) measured in the Anacostia River, which drains a small (440 km^2), highly urbanized (60%) watershed to Chesapeake Bay (Foster et al. 2000). PCB concentrations in both studies were consistent with concentrations measured in other urbanized river systems: <5.0-33 ng L^{-1} in the Detroit River (Froese et al. 1997), 10-46 ng L^{-1} in the Saginaw River (Verbrugge et al. 1995), 0.13-170 ng L^{-1} in the Milwaukee River (Steuer et al. 1999). In contrast, DDT concentrations in Guadalupe River (1.7-71 ng L^{-1}), were almost an order of magnitude greater than concentrations measured in the Anacostia River, where maximum concentrations of p,p'-DDE, p,p'-DDD, and p,p'-DDT were 1.5 ng L^{-1}, 2.1 ng L^{-1}, and 4.1 ng L^{-1}, respectively. Peak usage of DDT and other organochlorine pesticides preceded the reporting of pesticide use statistics in California; however, relatively high DDT concentrations at the bottom of the Guadalupe watershed are assumed to be a result from contaminated soils and sediments that are mobilized from areas where past urban and agricultural applications occured.

Concentrations in Relation to Storm Events

PCBs and OC pesticide concentrations were highly dependent on stream discharge and suspended sediment as described by the linear relationships between contaminants and explanatory variables (Figure 5-2). Concentrations of all measured contaminants were over an order of magnitude greater in storm flow than in base flow. Positive correlations between organic contaminants and discharge and/or SSC have been attributed to erosional processes of relatively diffuse non-point watershed sources and

resuspension of upstream channel sediments (Foster et al. 2000; Froese et al. 1997). These findings were in contrast to studies that found inverse correlations in areas where downstream contaminant sources were diluted by increased stream discharge, transport of less-contaminated suspended sediment from upstream, or dominance of atmospheric contributions to measured concentrations (Meharg et al. 2003, Verbrugge et al. 1995, Bremle and Larsson 1997). Thus, the patterns observed in Guadalupe River indicate that contaminant residues transported to the bottom of the watershed are homogeneous relative to suspended sediment and likely originate from diffuse storage in contaminated watershed soils and/or upstream sediment deposits.

Potential Sources of Chlorinated Hydrocarbons

Previous studies of organic contaminants in water bodies have inferred potential contaminant sources and relative degrees of contaminant degradation or dissipation by evaluating the relative abundance of PCB congeners (Meharg et al. 2003, Rostad 1997, Johnson et al. 2000) and DDT compounds (Nowell et al. 1999, Pereira et al. 1996, Bergamaschi et al. 2001, Kratzer 1999). Similar rationale was used in this study to develop hypotheses about the source of sediment and associated contaminants transported to the downstream reaches of the Guadalupe River watershed.

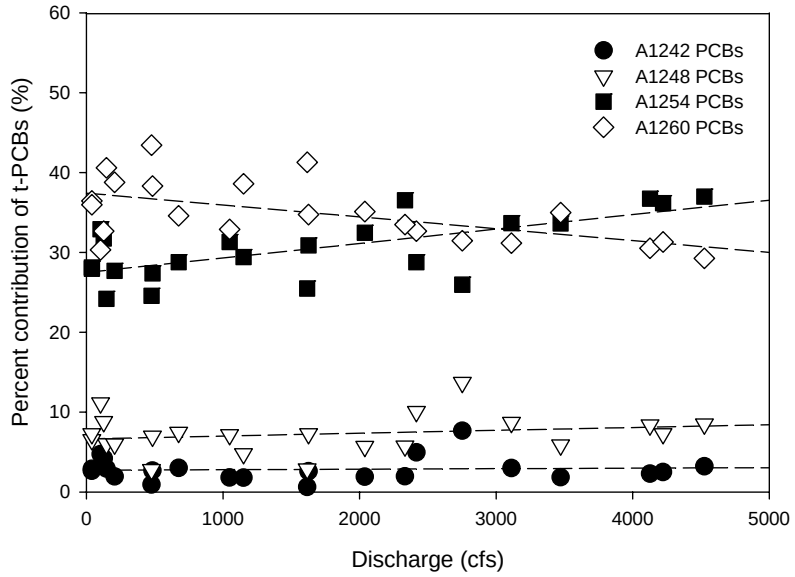
The relative abundance of individual PCB congeners, or fingerprints, in Guadalupe River samples resembled distributions in original technical mixtures of Aroclors 1260, 1254, and 1248. The fingerprints varied over time and were suggestive of different sources contributing to the t-PCB signal at the bottom of the watershed during and between floods (Jay Davis, SFEI, personal communication). Interpretations generated using fingerprints were further supported by observations of patterns of congeners grouped by the number of chlorine atoms in the molecule, or homologs. A high abundance of PCB mass (50 to 75%) composed of six (hexa-) or more chlorine atoms reflects dominant contributions of PCBs from sources of Aroclors 1254 and 1260. Predominance of high-molecular weight PCBs is indicative of erosion from watershed sources or resuspension of channel sediment rather than from atmospherically derived PCBs (Foster et al. 2000), which are typically enriched in tetra-chlorobiphenyls (Tsai et al. 2002, Poster and Baker 1994).

Proportions of PCB congeners were evaluated with respect to instantaneous discharge to assess the hydrological influence on PCB source activation and transport to the bottom of the watershed (Figure 5-3). PCB congeners were selected and summed to represent contributions of Aroclors 1242, 1248, 1254, and 1260 based on their relative abundance listed in Frame et al. (1996). For example, contributions of Aroclor 1260 were represented by the summed relative abundance of the five most predominant congeners: PCBs 138, 149, 153, 180, and 187. Selected congeners comprised approximately 35-50% of individual Aroclors (Frame et al. 1996). Although the PCB congener sums do not comprise exact total concentrations of individual Aroclors, they provide a strong indication of which Aroclor is contributing most to t-PCBs in the Guadalupe River at the sampling location.

As discharge increased, proportions of Aroclor 1260-related PCBs steadily decreased ($r^2 = 0.33$, $p = 0.0052$), while Aroclor 1254-related PCBs increased ($r^2 = 0.46$, $p = 0.0005$) (Figure 5-3). This variation in proportions is suggestive of variation in sources of PCBs transported to the study location. Foster et al. (2003) found similar patterns in two tributaries of Chesapeake Bay. They attributed higher molecular-weight PCBs on suspended particles collected in base flow to resuspended sediment from the channel. During low-flow conditions in the Guadalupe River, sources of Aroclor 1260 contribute the greatest proportions of measured t-PCBs and most likely originate from in-stream sediment via a similar process to that previously described by Foster et al (2003). During storm flows, sources of Aroclor 1254 were increasingly important to t-PCB transport in the Guadalupe River. It is proposed that these exist further upstream in channel sediment or in terrestrial soils located further from the main drainage lines of the watershed that are only mobilized during larger or more intense rain storms.

Results also suggest that sources of Aroclors 1242 and 1248 supply smaller amounts of PCB residues in a relatively consistent manner over the range of observed discharge, except for a few apparently anomalous concentrations at low flow and around 3,000 cfs. The anomalous concentrations can be explained by viewing congener distributions in chronological order of samples collected (Figure 5-4). Greater proportions of lower-molecular weight Aroclors appear to be a result of a unique source of PCBs being activated during the beginning stages of storm events. This first flush effect occurs when rainfall causes scavenging of particles from the atmosphere (Offenberg and Baker 2002, van Ry et al. 2002) and produces surface runoff that entrains readily erodable material that deposited on watershed surfaces (Chevreuil and Granier 1991).

Higher proportions of less chlorinated PCBs in river samples collected early in runoff events have been attributed to inputs from direct or indirect (i.e. runoff) deposition from the atmosphere (Ferreira et al. 2003). In urban air, concentrations of PCBs in particulate, gaseous, and dissolved (rain) fractions are typically dominated by lower-molecular weight PCB congeners (Tsai et al. 2002, Poster and Baker 1994, Park et al. 2001). Furthermore, Tsai et al. (2002) estimated that dry deposition of PCBs in the Bay Area occurs in the range of 0.39 – 2.1 ng m^2 d^{-1}, which causes dry-season accumulation of PCBs on watershed surfaces that potentially add to PCB load when washed into the river system during storm events. Therefore, while the largest proportions of t-PCBs originate from resuspended channel sediment and terrestrial soils, first flush effects likely contributed to the observed pulses of Aroclors 1242 and 1248 particularly in the first storm of the season on November 7th, 2002 (samples 1-3 in Figure 5-4), as well as in the beginning stages of later storms on December 14th, 2002 (sample 7 in Figure 5-4), and December 19th, 2002 (sample 16 in Figure 5-4).



A1242 PCBs = ΣPCB 8, 18, 31, 28, 33
A1248 PCBs = ΣPCB 28, 31, 52, 66, 70
A1254 PCBs = ΣPCB 95, 101, 110, 118, 138
A1260 PCBs = ΣPCB 138, 149, 153, 180, 187

Figure 5-3. Influence of stream discharge on relative abundances of predominant Aroclor-related PCB congeners in Guadalupe River water samples. Five congeners were selected to represent contributions from each Aroclor based on their order of decreasing abundance listed in Frame et al. 1996.

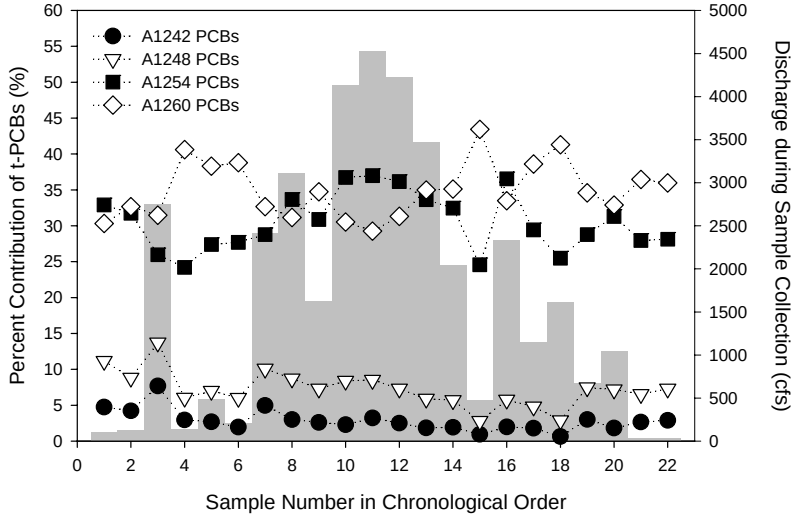


Figure 5-4. Proportions of Aroclor-related PCB congeners in chronological order of samples collected. Arorclor-related PCB congeners were summed as in Figure 5-3. Shaded bars depict instantaneous discharge during sampling.

The relative abundance of DDE, DDD, and DDT compounds (o,p' + p,p' isomers) in Guadalupe River provided further evidence of varying sources contributing to contaminant loads at the bottom of the watershed. Technical DDT was originally prepared in proportions of approximately 80% p,p'-DDT and 20% o,p'-DDT (WHO 1989); however, DDT readily degrades aerobically to DDE and anaerobically to DDD (Corona-Cruz et al. 1999). Thus, degraded or weathered DDT residues in aerated soils tend to be enriched with DDE, while anaerobic or flooded soils and sediments tend to have higher proportions of DDD (Castro and Yoshida 1971, Strömpl and Thiele 1997).

As with PCBs, the relative contributions of DDE, DDD, and DDT were largely dependent on the flow regime of the river (Figure 5-5). Proportions of DDT in water increased with increasing discharge until reaching relatively constant levels of 34 to 42% of t-DDT in samples collected in flows above 1,000 cfs. DDT proportions greater than approximately 10% of t-DDT are thought to be indicative of recent inputs of DDT residues from watershed soils into the aquatic system since DDT degrades more quickly to DDE and DDD in water (Nowell et al. 1999, Agee et al. 1986, Castro and Yoshida 1971). In contrast, DDD proportions were highest (> 50%) during low discharge and then decreased to approximately 18 to 27% of t-DDT when discharge exceeded 1,000 cfs. DDE proportions remained consistently high (38-52%) over the range of discharge except in three samples collected during low-flow conditions (26-32%). High proportions of DDD and low proportions of DDT during low flow conditions were indicative of t-DDT residues transported from sources of anaerobic or flooded sediments, which likely originated from within the channel of the main stem of the river or adjoining tributaries. In stream flows greater than 1,000 cfs, DDE and DDT consistently comprised greater percentages of t-DDT than DDD suggesting that relatively unweathered t-DDT residues were transported from aerated watershed soils as opposed to resuspended sediments from within the channel.

Another similarity between the relative distribution of PCB congeners and DDT compounds was evident in the unique signal from the first major storm event of the season. All high-flow samples were characterized by high proportions of DDE and DDT with the exception of the sample collected on November 7th at 11:40 pm (sample 3 – Figure 5-6). This first flush sample lacked an equally high proportion of DDT, which further implies that a unique contaminant source contributed to load in the lower Guadalupe River during the early stages of the wet season. The sample also had the highest concentration of p,p'-DDE measured in the study. P,p'-DDE has been shown to have greater volatility from soils (Spencer et al. 1996) and has been found in greater abundance in air compared to other DDT compounds (Spencer et al. 1996, McConnell et al. 1998). Thus, washout of particles in air, combined with runoff of atmospherically-deposited particles in the watershed may have contributed to the unique DDT proportions measured during the first storm of the season.

In summary, variation in relative abundances of PCB congeners and DDT compounds with respect to discharge led to proposed hypotheses concerning the influence of hydrologic processes on mobilization and transport of chlorinated hydrocarbon residues from various sources within the watershed. First, a first flush

phenomenon transported material from a unique source during the first storms of the season – possibly of atmospheric origin. Second, base flow conditions transported material that originated from within the stream channel, while higher flows were dominated by less weathered particulate material that originated from terrestrial watershed sources stored further from the stream channel. Although sampling at a single location near the bottom of the watershed precludes confirming sources of upstream contaminants, the data provide further understanding of contaminant transport mechanisms occurring over time scales of storm events and seasons.

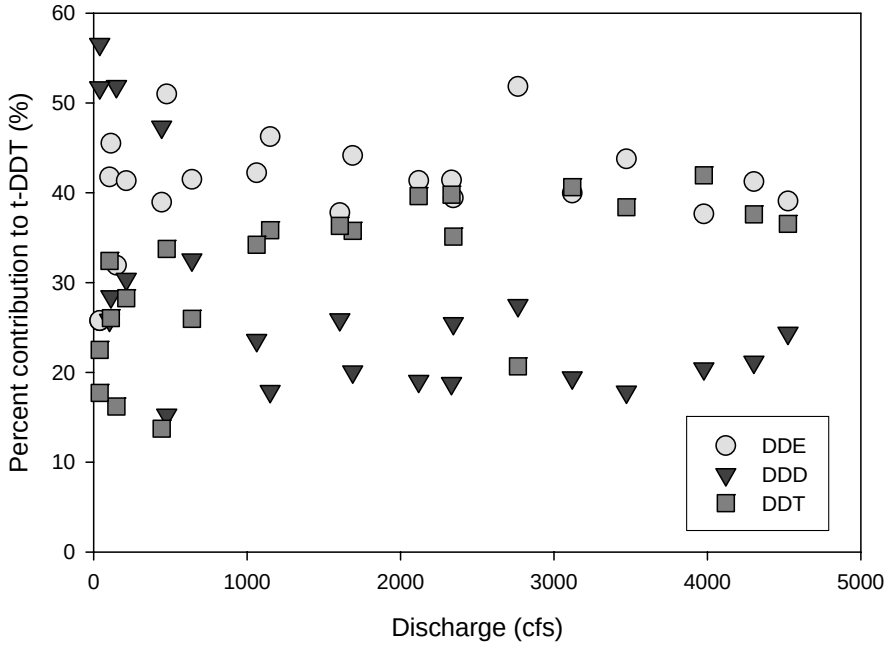


Figure 5-5. Percent contribution to t-DDT from DDE, DDD, and DDT. DDE, DDD, and DDT are the sum of o,p'- and p,p'-isomers for each compound.

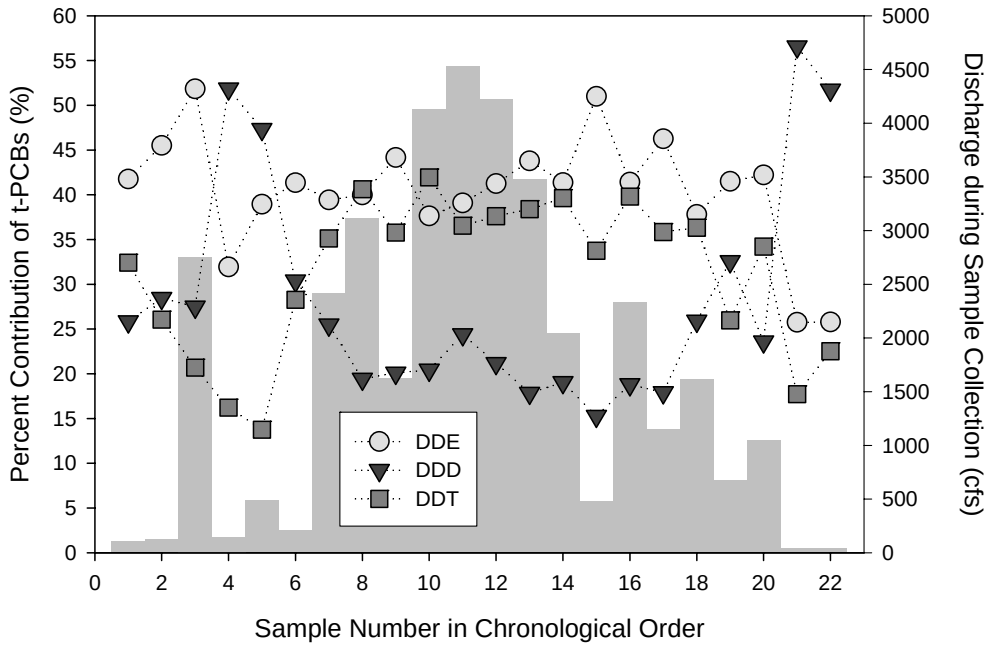


Figure 5-6. Proportions of DDT compounds in chronological order of samples collected. The shaded area depicts instantaneous discharge during sampling.

Load estimates

Continuous data collected for discharge and turbidity facilitated estimation of suspended sediment loads as described in Section Four. Using linear relationships between estimated SSC_{EST} and chlorinated hydrocarbons, the continuous SSC_{EST} record was used to estimate a continuous time series of PCB and OC pesticide concentrations at 15-minute intervals. The estimated continuous time series of chlorinated hydrocarbons were used to estimate loads on a monthly time scale from October 2002 to May 2003.

Load estimates were subject to potential errors from several factors: direct measurement of parameters associated with hydrology, water quality indices and contaminants; cross-sectional variability in SSC in the water column; and regression-based estimates of continuous SSC_{EST} and contaminant concentrations. Estimates of overall error in load (δLOAD/LOAD) were calculated using quadratic sums of fractional uncertainties in the following equations:

$$\frac{\delta LOAD}{LOAD} = \sqrt{\left(\frac{\delta Q}{Q}\right)^2 + \left(\frac{\delta C}{C}\right)^2}$$ = error in overall contaminant load

where:

$$\frac{\delta Q}{Q} = \pm 5\% \text{ = error in stream discharge}$$

$$\frac{\delta C}{C} = \sqrt{\left(\frac{\delta SSC_{EST}}{SSC_{EST}}\right)^2 + \left(\frac{\delta C_{LAB}}{C_{LAB}}\right)^2 + \left(\frac{\delta C_{REG}}{C_{REG}}\right)^2} \text{ = error in contaminant concentrations}$$

$$\frac{\delta SSC_{EST}}{SSC_{EST}} = \sqrt{\left(\frac{\delta SSC_{LAB}}{SSC_{LAB}}\right)^2 + \left(\frac{\delta SSC_{XSEC}}{SSC_{XSEC}}\right)^2 + \left(\frac{\delta SSC_{REG}}{SSC_{REG}}\right)^2} \text{ = error in SSC concentrations}$$

The error associated with stream discharge (δQ/Q) was estimated to be ± 5%. Error associated with SSC ($\delta SSC_{EST}/SSC_{EST}$) was approximately ± 7% based on estimated errors associated with laboratory measurement ($\delta SSC_{LAB}/SSC_{LAB}$; ± 5%), cross-sectional variability ($\delta SSC_{XSEC}/SSC_{XSEC}$; ± 5%), and regression of SSC_{USGS} with turbidity ($\delta SSC_{REG}/SSC_{REG}$; ± 2%) (see Section Four).

Descriptions of terms and approximate errors associated with contaminant concentrations are presented in Table 5-4. The error associated with time continuous contaminant measurements (δC/C) is assumed to be the upper limit of uncertainty since it is probable that the regression term in the equation ($\delta C_{REG}/C_{REG}$) encompasses some error associated with laboratory analysis of contaminants ($\delta C_{LAB}/C_{LAB}$) and overall error associated with suspended sediment concentrations ($\delta SSC_{EST}/SSC_{EST}$), both of which are treated as distinct terms in the equation. Estimates of load error were ± 30% for t-PCBs, ± 29% for t-DDT, ± 17% for t-chlordane, and ± 22% for dieldrin.

Table 5-4. Estimates of error associated with estimating sediment and contaminant load from Guadalupe River.

Error term	Description of error	Error Estimate (±%)			
		t-PCBs	t-DDT	t-chlordane	Dieldrin
δLOAD/LOAD	overall error in load	30	29	17	22
δC/C	overall error in contaminant concentrations	30	29	16	21
$\delta C_{LAB}/C_{LAB}$	measurement of contaminant concentrations	15	24	13	19
$\delta C_{REG}/C_{REG}$	regression between SSC and contaminants	25	14	7	8

Estimates of loads generated on a 15-minute interval were summed for each month of the study (Table 5-5). As expected, most of the sediment (68%) and contaminant load (54-65%) occurred during the month of December when most of the

storm activity and 49% of the water discharge occurred. Combined load in November and December contributed greater than 70% of the total load of sediment and contaminants in the Guadalupe River.

Load estimates using flow-weighted mean concentrations and the flow (47.8 Mm^3) occurring during the study period (October 2002 – June 2003) resulted in load estimates that were greater by a factor of 2 to 3: 2,600 ± 800 g t-PCBs, 2,300 ± 700 kg t-DDT, 1,900 ± 300 kg t-chlordane, and 180 ± 40 kg dieldrin. The difference between SSC-based load estimates and estimates derived from flow-weighted mean concentrations illustrates the importance of capturing the full range of variability associated with streamflow and suspended sediment transport for accurate estimation of particle-associated contaminant load. In this case, the use of a flow-weighted mean concentration and total discharge generated positively biased load estimates because the sampling scheme was so biased towards high flow. The best estimates at this time are those generated using the regression method of extrapolation and shown in Table 5-5.

Table 5-5. Monthly load of sediment and chlorinated hydrocarbons in Guadalulpe River, WY 2003.

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Total
Sediment (tons)	19	2,085	7,027	165	184	268	486	93	10,330
t-PCBs (grams)	16	176	583	67	51	60	91	41	1,100 ± 300
t-DDT (grams)	13	149	496	54	41	49	75	33	910 ± 260
t-chlordane (grams)	8	119	396	35	28	34	52	21	690 ± 120
Dieldrin (grams)	1	12	40	5	4	4	6	3	75 ± 17

CONCLUSIONS AND IMPLICATIONS

This study assessed the influence of storm events on sediment transport, runoff processes and transport of PCBs and OC pesticides in the Guadalupe River, a highly urbanized, mixed land-use watershed of San Francisco Bay. Study results indicate that diffuse sources of contaminants in stream deposits and terrestrial soils were activated over the entire range of discharge. The relative importance of different contaminant sources varied with stream discharge, except for an observed first flush effect at the beginning of the wet season. During low flows, contaminants appeared to be associated primarily with resuspended sediment, while an increase in discharge increased the importance of terrestrial watershed sources on downstream transport of contaminants. Since samples were only collected near the bottom of the watershed, confirmation of these patterns of source activation would require coordinated source identification efforts or nested sampling approaches in upstream areas of the watershed.

Contaminant loads at the bottom of the watershed were highly dependent on discharge and suspended sediment. Most of the load of PCBs and OC pesticides was associated with the large storm events that occurred in November and December.

Although estimates of contaminant load from Guadalupe River were less than estimated loads from the Central Valley, it is reasonable to assume that combined load from the local tributaries would contribute similar magnitudes of PCBs, DDT, and chlordanes. This is a particularly important concern considering management actions that reduce contaminant inputs to the Bay from external pathways are probably more feasible in the local watersheds.

To highlight the important implications of this study, it is necessary to understand how contaminant load from Guadalupe River reflects potential load from other Bay Area watersheds; compares to other pathways of contaminant inputs to the Bay; contributes to the long-term fate of contaminants in the Bay; and impacts the overall water quality in the Bay.

Given that most Bay Area watersheds have densely urbanized areas, particularly in lowland areas adjacent to the Bay, as well as histories of agricultural use, similar characteristics and watershed processes are likely contributing to PCB and OC pesticide load from local tributaries on a regional scale. The diverse characteristics of individual watersheds preclude an accurate extrapolation of Guadalupe River results to other watersheds within the scope of this study (i.e. without the development of a model) however, a simple area-based calculation allows for a first order approximation of combined load from Bay Area watersheds. The Guadalupe River watershed encompasses approximately 8% of the non-tidal watershed area directly adjacent to the Bay (6,650 km^2) – excluding the Central Valley (McKee et al. 2003). If all Bay Area watersheds contributed to contaminant load equally based on watershed area, combined load in WY 2003 would have been 14 kg PCBs, 11 kg t-DDT, 9 kg t-chlordane, and 0.9 kg dieldrin. Considering that Guadalupe River had average streamflow and rainfall in WY 2003, load of sediment and associated contaminants from local tributaries is expected to be greater in years with above-average rainfall and runoff and lower in drier years.

Although comparisons of Guadalupe River to other pathways of contamination are difficult due to limited data availability, some conclusions can be made about the role of Guadalupe River in overall contaminant load to the Bay. A similar study funded through the RMP is currently being conducted in the Sacramento-San Joaquin River Delta (at Mallard Island), which drains a watershed area of 154,000 km^2 in the Central Valley of California. As expected, Guadalupe River loads were lower than preliminary estimates of load from the Central Valley averaged over an eight-year period from 1995 to 2002: 13 kg PCBs, 17 kg t-DDT, 2.4 kg t-chlordane, and 3.8 kg dieldrin (SFEI, unpublished data); however, the eight-year averages are influenced by several years of well-above average Delta Outflow. Therefore, our present hypothesis is that allocthonous loads of PCBs and organochlorine pesticides derived from watershed runoff are approximately evenly distributed between the large river pathways (Sacramento and San Joaquin Rivers) and stormwater issuing from local small tributaries to San Francisco Bay.

Continued PCB and OC pesticide load of these magnitudes are likely to slow down recovery of improved water quality in the Bay (Davis 2003, Leatherbarrow et al. 2003). In context of the overall impact of continued load to the Bay, mass budget models

of PCBs and OC pesticides in San Francisco Bay have concluded that continued inputs of PCBs and OC pesticides on the order of 10 kg yr^{-1} could significantly prolong recovery times of the Bay with respect to declining concentrations in Bay sediment and biota (Davis 2003, Leatherbarrow et al. 2003). Moreover, the modeling studies also suggested that the Bay is very responsive to relatively small reductions in load from external contaminant pathways. Therefore, remediation of contaminated areas in the watersheds may produce observable improvements in water quality on time scales of years to decades. Modeling efforts have illustrated the importance of deriving realistic estimates of contaminant load from local tributaries and the large rivers of the Central Valley through further empirical data collection or extrapolation of existing data, especially during years with above-average discharge and suspended sediment loads. Thus, accurate load estimates in the context of refined mass budget models will help improve prioritization of management actions aimed at reducing contaminant inputs from various pathways and evaluating the effectiveness of those actions.

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SECTION SIX

MERCURY PROCESSES IN THE GUADALUPE RIVER, WY 2003

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Lester McKee and Jon Leatherbarrow

ABSTRACT

San Francisco Bay is listed as impaired for mercury by the State of California in compliance with Section 303(d) of the Clean Water Act administered by the U.S. Environmental Protection Agency. The California Office of Environmental Health Hazard Assessment has issued a health advisory recommending that adults consume no more than two meals of fish caught from San Francisco Bay per month. Mercury in San Francisco Bay originates from a range of sources and pathways, but the magnitude of mercury loads from historic mining areas in small tributaries surrounding the Bay remains one of the largest uncertainties in the mercury budget. Knowing the magnitude of this pathway is of paramount importance for determining solutions for managing and resolving mercury impairment.

Between November 11th 2002 and May 29th 2003, using clean hands protocols, 26 water samples were taken during nine stormflow peaks at the USGS discharge gage (11169025) near San Jose International Airport. Samples were analyzed for total mercury, other total trace elements (silver, arsenic, cadmium, chromium, copper, nickel, lead, zinc), organic carbon, and suspended sediment concentration. In addition, a real-time turbidity probe provided 15-minute estimates of suspended sediment concentration after calibration using a regression between suspended sediment and turbidity. Concentrations of total mercury varied two orders of magnitude (0.2-18.7 µg/L) with a flow-weighted average of 3.7 µg/L. Maximum total mercury concentrations did not coincide in a predictable way to peaks in discharge. Total mercury correlated for short periods with discharge and suspended sediment, but when all the data were grouped, total mercury was not significantly correlated with any other parameter measured. In contrast, concentrations of suspended sediment, particulate organic carbon, and all other trace elements correlated with discharge and trace elements correlated with each other.

These results suggest that sources of mercury relative to suspended sediment vary from storm to storm and that the dominant sources of other trace elements are separated from the dominant sources of total mercury. These observations are consistent with the knowledge that mercury is mainly sourced from creeks and reservoirs adjacent to the New Almaden Mining District and not ubiquitous across the watershed. On December 16th 2002, a series of reservoir releases began from Calero, Almaden and Guadalupe Reservoirs. These releases had a profound influence on mercury concentration and load at the sampling location, defining two distinct periods (pre- and post-reservoir release). During the pre-reservoir release period, total mercury concentrations ranged from 0.2-4.7 µg/L and had a flow-weighted mean concentration (FWMC) of 0.76 µg/L. During the post-reservoir release period, total mercury concentrations ranged from 1.3-18.7 µg/L and had a FWMC of 5.1 µg/L. The source of mercury is most likely sediments stored in Calero, Alamitos, and Guadalupe Creeks that are mobilized by relatively "clean" water with low suspended sediment concentration that is released from the reservoirs.

Load estimates were generated for the study period. Hourly loads of total mercury varied from 0.2 - 5,240 g and daily loads varied from 0.0046 - 32 kg (~ 7,000x). During the study, 312 ± 82 kg of total mercury was transported into lower South San Francisco Bay. This estimate of total mercury load is ~10x greater than previously reported in studies on the Guadalupe River that did not capture such large floods or the effects of release of water from the Calero, Almaden or Guadalupe Reservoirs. Climate during the study year was approximately average, suggesting the load estimate might approximate long-term average. However, it is presently unknown what influence relatively dry climate during 2001 and 2002 might have had on the magnitude of the loads, and it is presently not clear how inter-annual differences in reservoir operation might influence annual loads. These questions are the primary focus of subsequent years of study.

INTRODUCTION

Mercury is a potent toxin that may contribute to an increase in hatching failures in aquatic bird species and is a developmental neurotoxin that can lead to birth defects, infant mortality, and learning disorders in humans (e.g. Fitzgerald and Clarkson, 1991; Clarkson 1992). Mercury is usually found in the environment bound to sediments and is readily bio-accumulated into the tissues of aquatic organisms over their lifespan and biomagnified up through the food web to fish, birds, aquatic mammals and humans (Davis et al. 2003). The toxicity and persistence of mercury in the aquatic environment are issues of critical concern to environmental managers, scientists and the public at-large.

Continuous monitoring over the past decade by the San Francisco Bay Regional Monitoring Program for Trace Substances (RMP) (Thompson et al., 2000; Hoenicke et al., 2003, SFEI, 2003) and a number of focused studies have determined that mercury in San Francisco Bay may impact birds, including threatened and endangered species (Schwarzbach and Adelsbach, 2003), and poses a significant human health risk (OEHHA, 1997, 1999; Davis et al., 2002). As a result, in compliance with Section 303(d) of the Clean Water Act, the State of California has listed all segments of San Francisco Bay as water bodies impaired by mercury. The California Office of Environmental Health Hazard Assessment has issued a health advisory recommending that adults consume no more than two meals of fish from San Francisco Bay per month. Nursing women, women who may become pregnant, and children less than six years old are advised to consume only one meal per month (OEHHA, 1997, 1999). Regulatory agencies are addressing mercury issues in the Bay through ongoing education programs, the coordination of scientific studies, and planning the implementation of control actions. Recently, the Regional Water Quality Control Board released a report that synthesized current knowledge and uncertainties pertaining to long-term objective to resolve mercury impairment in the Bay (Johnson and Looker, 2003).

Much of the mercury contamination in the Bay is linked to historic mercury and gold mining (e.g., Alpers and Hunerlach, 2000) and probably entered the Bay 50-150 years ago via the Sacramento and San Joaquin Rivers. Today, the Sacramento and Jan Joaquin Rivers are still transporting a considerable load of mercury to the Bay (SFEI, unpublished data) although the magnitude is probably less than it was historically. A mercury load of similar magnitude is probably derived from local small tributaries (the home to >6,000,000 Bay Area residents and the location of a number of discontinued mercury mining operations) (McKee et al., 2003). An understanding of the processes of erosion and resuspension in the Bay (Jaffe et al., 1996, 2001; Foxgrover et al., 2003) combined with a knowledge of bed concentrations generated through the RMP suggests that resuspension of legacy mercury associated with the historic mining era is of a similar magnitude to allochthonous loads from the rivers and local urbanized tributaries (Johnson and Looker, 2003). Studies have shown that atmospheric deposition, non-urban stormwater, and point sources provide relatively small loads of total mercury to the Bay annually (Tsai and Hoenicke, 2001; Steding and Flegal, 2002; Johnson and Looker, 2003). The magnitude of mercury loads from historic mining areas in the small tributaries directly adjoining the Bay remains a very large uncertainty in the mercury budget of the

Bay, yet is of paramount importance for determining solutions for managing and resolving mercury impairment.

Beginning in the 1840s, mercury was mined from the Coast Range of California from 51 major ore deposits (Rytuba and Enderlin, 1999). The extraction of mercury reached a maximum of 79,396 flasks (2,737,066 kg) per year in 1877. In total, the coastal mineral belt produced 2.8 million flasks of mercury most of which was used in the processing of gold and silver in the Sierra Nevada mountains on the eastern side of California. The New Almaden mining district located in the Guadalupe River watershed, South San Francisco Bay, was the largest producer of mercury in North America and provided most of the mercury for use in California. It is known that water and sediments in reservoirs and creeks adjacent to the historic mines exhibit high concentrations of mercury relative to other tributaries in the Guadalupe River watershed (Thomas et al., 2002; also see review: Tetra Tech, 2003). Several recent studies have made estimates of mercury loads in the lower Guadalupe River (Leatherbarrow et al., 2002; Thomas et al., 2002), but these studies did not capture mercury concentration associated with large flood events when most of the mercury is likely to be transported. Presently, the processes of mercury transport from known source areas and magnitude of mercury loads that enter South San Francisco Bay is poorly understood.

This study assists local environmental management efforts by addressing these vital data gaps and makes important contributions to the science of fluvial mercury processes.

METHODS

Sampling

Between November 11th 2002 and May 29th 2003, 26 water samples were taken during nine stormflow peaks at the “rental car return bridge” at San Jose International Airport approximately 100 m upstream from where Hwy 101 crosses the Guadalupe River (Figure 6-1). The DTS 12 turbidity probe equipped with a wiper mounted in the thalweg of the channel provided an estimate every 15 minutes of suspended sediment concentration from November 1st 2002-May 31st 2003. The samples for mercury and trace metal analysis were collected using clean-hands protocols (e.g. Bloom, 1995; Hurley et al., 1995; Colman and Breault, 2000). This involved two persons: one designated “clean hands” wearing a pair of trace metal clean polyethylene gloves directly handling sample bottles and interior bags; the other, designated “dirty hands”, handled exterior bags, coolers, and other uncleaned materials. Double-bagged (Ziploc™) sample bottles were prepared for mercury and trace elements by Moss Landing Marine Laboratory, and 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 aiming for a mid-depth filling of the bottle. More typically, during high flow, a depth of 0.5-1.5 m below water surface was achieved. During wading stage, samples were taken by hand dipping at approximately mid-depth directly under the bridge in the deepest portion of the stream near the turbidity probe.

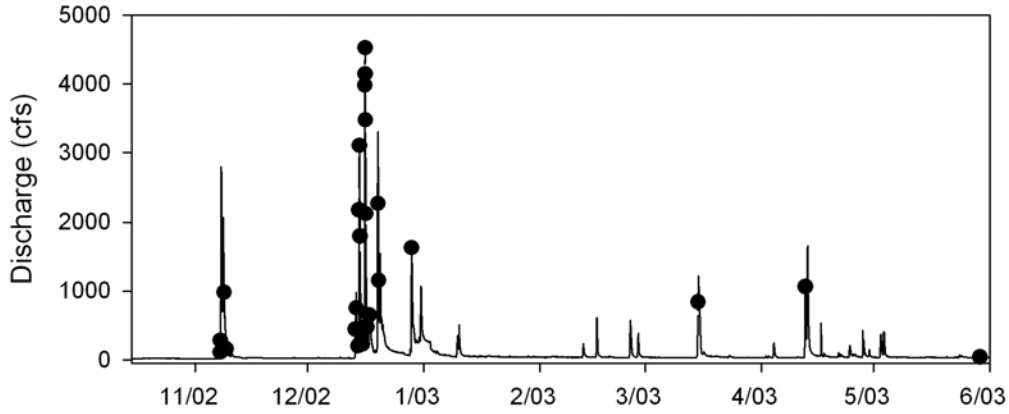

Figure 6-1. Water sampling for mercury and trace elements relative to discharge during the study period.

Laboratory Analysis Methods

Water samples were analyzed for total mercury (Hg), total trace elements (silver, arsenic, cadmium, chromium, copper, nickel, lead, zinc), suspended sediment concentration (SSC), dissolved organic carbon (DOC), and particulate organic carbon (POC). Upon receipt at the lab (commonly within 36 hours), water samples for total mercury analysis were preserved with a final concentration of 0.5% v/v bromine monochloride (BrCl), water samples for trace metal analysis were acidified to a final concentration of 1% v/v nitric acid (HNO_3), and SSC, DOC and POC water samples were refrigerated at 4°C in the dark until analysis. Trace metal samples were analyzed using ICP-MS following U.S. EPA method 1638 (U.S.E.P.A., 1996). Mercury samples were analyzed with cold vapor atomic fluorescence following U.S. EPA method 1631e (U.S.E.P.A., 2002). SSC samples were vacuum filtered onto glass-fiber filter disks. Filters were dried overnight at 104°C, then placed in a vacuum-sealed desiccator until reaching room temperature. Filters were then weighed on an analytical balance with ± 0.0001g precision. DOC and POC were analyzed by catalytic combustion using U.S. EPA method 415.1 (U.S.E.P.A., 1983).

Quality Assurance

The trace metal analysis methods were chosen to ensure the expected concentrations were beyond the detection limits (DL). Silver concentrations were closest to the detection limit with 5% of the data <4x greater than the DL. On the other end of the spectrum, 95% of the Cu, Ni, Pb, Zn, and Hg concentrations were >1,000x DL. Relative percent difference (RPD), calculated as the difference in concentration of a pair of duplicates divided by the average of the duplicates was within the target range of ±25% without exception (Table 6-1). With the exception of one batch of silver analyses, the percent recoveries for standard reference materials were within the target range (75-125%). Silver values in this batch are considered acceptable as the matrix spike and

duplicate recoveries are within ±25%. Also, the percent recovery was 74%, which is barely outside the data quality objective limits. The percent recoveries for matrix spikes were without exception within the target range (75-125%) (Table 6-1). The quality assurance samples included one method blank for each analytical batch of trace elements and three method blanks for each batch of mercury analyses. Trace element concentrations in blank samples were generally not detected, therefore samples were not blank corrected with the exception of copper for one batch (Table 6-1). Field blanks were <DL with the exception of Hg, which on one occasion, had a blank concentration of 0.0065 µg/L. This blank concentration was 27x lower than the minimum concentration found in the field samples and therefore deemed acceptable.

Table 6-1. Quality control parameters of mercury and trace elements analyzed in this study.

Substances Analyzed	Detection Limit (DL) (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 – 21.5	85-110	80-106	<DL	0.0065
Total Silver	0.008	1.5 – 6.4	74-92	86-92	<DL	<DL
Total Arsenic	0.1	0.3 – 9.3	93-94	98-100	<DL	<DL
Total Cadmium	0.002	0.1 – 5.9	98-103	100-117	<DL	<DL
Total Chromium	0.03	0.5 – 1.2	95-100	97-102	<DL	<DL
Total Copper	0.003	0.2 –3.8	99-105	94-99	<DL-0.03	<DL
Total Nickel	0.006	0.4 –9.7	96-98	94-97	<DL	<DL
Total Lead	0.002	0.1 – 0.9	98-102	93-107	<DL	<DL
Total Zinc	0.02	0.1 – 1.1	97-104	97-106	<DL	<DL

RESULTS

Nine storm peaks were sampled to generate an understanding of the variation in total mercury concentration in stormwater both during individual events and between events. Concentrations of total mercury varied over two orders of magnitude (105x) from 0.2-18.7 µg/L with a flow-weighted average of 3.7 µg/L (Table 6-2). Concentrations of other trace elements did not show such great variability. Maximum total mercury concentrations did not coincide in a predictable way to peaks in discharge (Figure 6-2). Although the highest concentration measured appeared to be associated with the flood peak on December 19th 2002, the well-sampled flood peaks that occurred on December 14th, 15th and 16th 2002 did not exhibit peak total mercury concentrations that would be expected from the flood magnitude (Figure 6-2). Concentrations of the other trace elements more closely followed discharge. However, silver, arsenic, cadmium, copper, and zinc appear to have 2-4 data points that fall above the general trend in the data (Figure 6-3). A Spearman Rank correlation analysis was performed using the whole data set to determine the relative significance of correlations between parameters (Table 6-3). Mercury did not correlate with any other parameter measured during this study. In contrast, there were significant correlations between all other trace elements and between instantaneous discharge, SSC and all other trace elements. With the exception of copper, organic carbon does not influence the transport of mercury and other trace elements during flood stage in the lower Guadalupe River.

Table 6-2. Concentrations measured during discrete sampling in the Guadalupe River from November 2002-May 2003. The number in brackets is the calculated flow-weighted mean concentration (FWMC).

Month		SSC (mg/L)	DOC (mg/L)	POC (mg/L)	Hg	Ag	As	Cd	Cr	Cu	Ni	Pb	Zn
					(µg/L)								
Nov	Min	50	-	-	0.2	-	-	-	-	-	-	-	-
	Max	191	-	-	4.7	-	-	-	-	-	-	-	-
	FWMC	95 (n=4)	- -	- -	0.8 (n=4)	0.03 (n=1)	4.2 (n=1)	0.69 (n=1)	9 (n=1)	43 (n=1)	27 (n=1)	19 (n=1)	191 (n=1)
Dec	Min	32	3.9	0.3	0.2	0.03	1.4	0.06	4	8	7	3	21
	Max	967	8.9	0.9	18.7	0.16	2.9	0.70	98	52	189	52	193
	FWMC	660 (n=19)	4.2 (n=16)	0.5 (n=12)	3.8 (n=19)	0.10 (n=14)	2.2 (n=19)	0.48 (n=19)	55 (n=19)	38 (n=19)	109 (n=19)	34 (n=19)	136 (n=19)
Jan	-	-	-	-	-	-	-	-	-	-	-	-	-
Feb	-	-	-	-	-	-	-	-	-	-	-	-	-
Mar	Conc.	282 (n=1)	- -	- -	6.8 (n=1)	0.06 (n=1)	1.7 (n=1)	0.33 (n=1)	22 (n=1)	27 (n=1)	40 (n=1)	20 (n=1)	117 (n=1)
Apr	Conc.	225 (n=1)	- -	- -	5.8 (n=1)	0.27 (n=1)	1.8 (n=1)	0.30 (n=1)	23 (n=1)	24 (n=1)	42 (n=1)	23 (n=1)	105 (n=1)
May	Conc.	18 (n=1)	- -	- -	5.2 (n=1)	- -	1.5 (n=1)	0.05 (n=1)	2 (n=1)	6 (n=1)	4 (n=1)	2 (n=1)	9 (n=1)
Total	Min	18	3.9	0.3	0.2	0.03	1.4	0.05	2	6	4	2	9
	Max	967	8.9	0.9	18.7	0.27	4.2	0.70	98	52	189	52	193
	FWMC	615 (n=26)	3.8 (n=16)	0.5 (n=12)	3.8 (n=26)	0.10 (n=17)	2.1 (n=23)	0.46 (n=23)	51 (n=23)	36 (n=23)	101 (n=23)	32 (n=23)	130 (n=23)
	Max/min	52	2.3	3.0	105	9.3	3.0	13	46	8.6	51	34	21

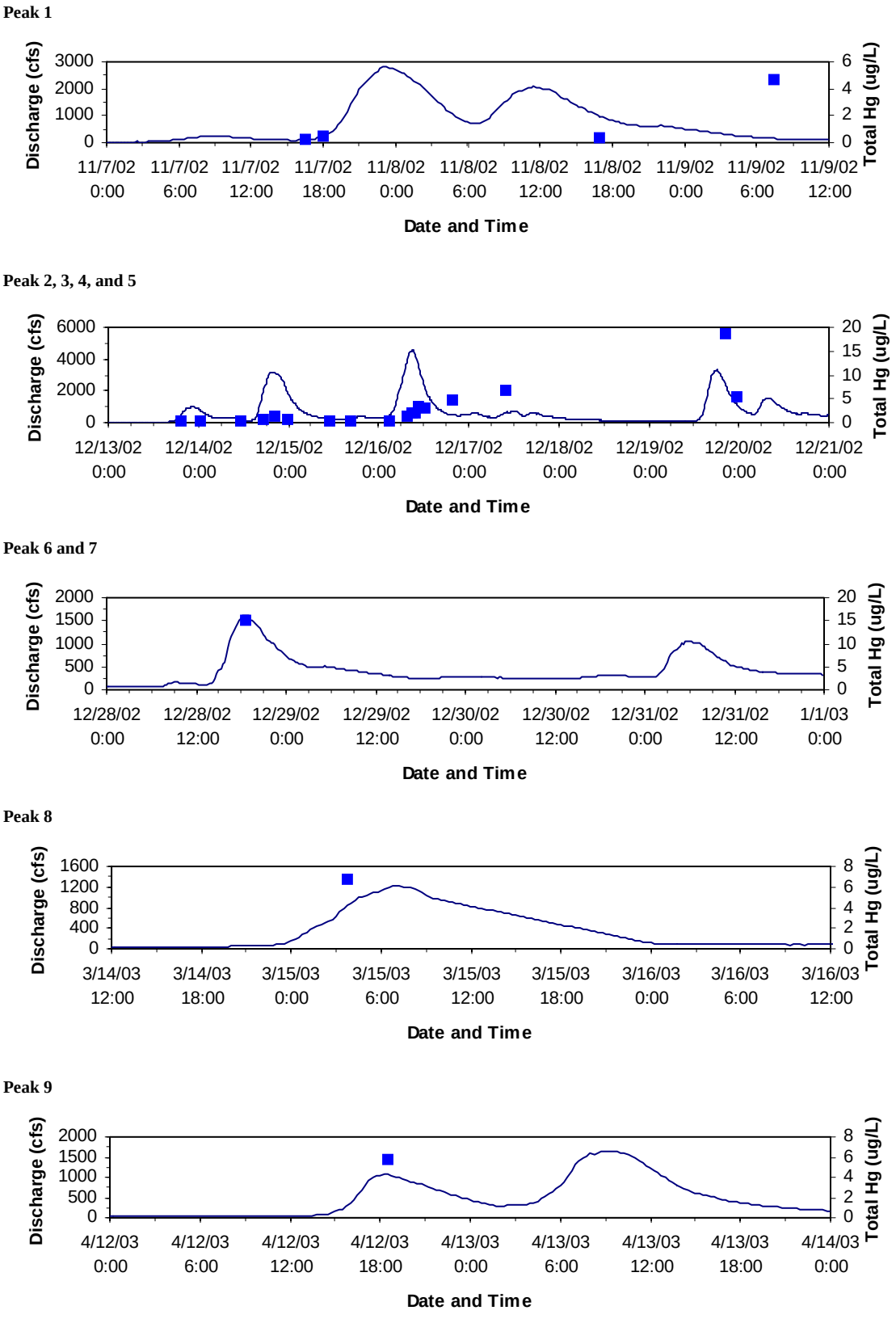

Figure 6-2. Concentrations of total mercury during storms on the Guadalupe River.

1940

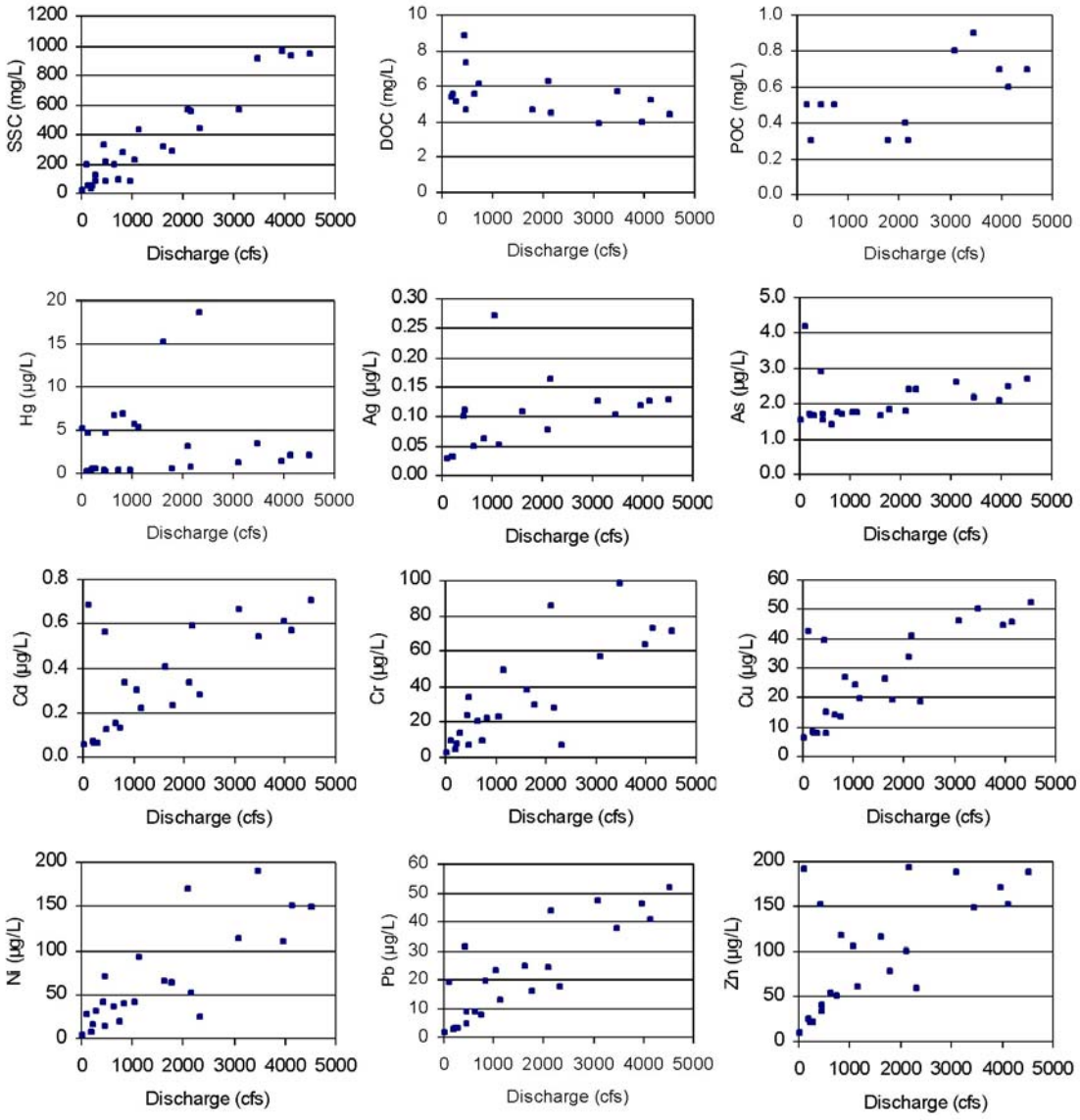

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Figure 6-3. Concentrations of suspended sediment, organic carbon, mercury, and other trace elements as a function of discharge.

Table 6-3. Spearman correlation matrix comparing trace metal concentrations and instantaneous discharge (Inst. Q), suspended sediment concentrations (SSC), dissolved organic carbon (DOC), and particulate organic carbon (POC).

.	Inst. Q	SSC	DOC	POC	Hg	Ag	As	Cd	Cr	Cu	Ni	Pb	Zn
Inst. Q	-----	.	.	.	.	.	.	.	.	.	.	.	.
SSC	0.905 ***	-----	.	.	.	.	.	.	.	.	.	.	.
DOC	.	.	-----	.	.	.	.	.	.	.	.	.	.
POC	0.611 *	0.636 *	.	-----	.	.	.	.	.	.	.	.	.
Hg	.	.	.	.	-----	.	.	.	.	.	.	.	.
Ag	0.701 **	0.627 **	.	.	.	-----	.	.	.	.	.	.	.
As	0.512 *	0.668 ***	.	.	.	.	-----	.	.	.	.	.	.
Cd	0.607 **	0.774 ***	.	.	.	0.487 *	0.858 ***	-----	.	.	.	.	.
Cr	0.786 ***	0.855 ***	.	.	.	0.524 *	0.455 *	0.589 **	-----	.	.	.	.
Cu	0.743 ***	0.879 ***	.	0.695 *	.	0.530 *	0.798 ***	0.935 ***	0.789 ***	-----	.	.	.
Ni	0.798 ***	0.868 ***	.	.	.	0.539 *	0.477 *	0.603 **	0.994 ***	0.798 ***	-----	.	.
Pb	0.811 ***	0.915 ***	.	.	.	0.755 ***	0.733 ***	0.915 ***	0.776 ***	0.953 ***	0.782 ***	-----	.
Zn	0.612 **	0.764 ***	.	.	.	0.518 *	0.799 ***	0.954 ***	0.610 **	0.934 ***	0.616 **	0.922 ***	-----

* $p<0.05$
** $p<0.01$
*** $p<0.001$

DISCUSSION

Concentration Comparisons

Concentrations of total mercury have been measured in a number of watersheds in other parts of the world. In many cases, either study objectives or budgets have constrained sampling intervals to either routine or periodic sampling, with minimal variation in discharge. The pristine nature of some watersheds or known low variability of mercury concentration did not necessitate a focus on particular storm events when mercury transport is likely to reach a maximum (e.g. Bonzongo et al., 1996, Hurley et al., 1995; Fostier et al., 2000; Schetagne et al., 2000). In other cases, the sampling interval has allowed a detailed understanding of concentration variation during floods (e.g. Lawson and Mason, 2001; Schwesig and Matzner, 2001). Without regard to the sampling interval, the maximum concentrations found in 34 watersheds around the world were collated (Figure 6-4). The interpretation of figure 6-4 provides a conceptual model for the magnitude of concentrations that could be expected under a variety of land use and land and water management scenarios. Maximum total mercury concentrations of between 1-18 ng/L are typical of watersheds with pristine “open space” land use and reservoirs with forest or open space catchments (a range slightly higher than suggested by a previous review (Bonzongo et al., 1996). Concentrations ranging from 8-90 ng/L are typical of

mixed land use watersheds comprised of various proportions of urban, agriculture, and open space. When urban area dominates land use within a watershed, concentrations typically range between 30-90 ng/L. Concentrations in excess of 100 ng/L are typically only found in watersheds where there are specific (usually known) mercury sources. These include areas of high atmospheric burden (e.g. areas adjacent to heavy industrial sites) (100-200 ng/L) (e.g. Schwesig and Matzner, 2001), urban storm drains where there is little within-channel/within-pipe mercury retention in sediment deposits (13-1,370 ng/L) (e.g. Soller et al., 2003), historic mercury mining areas or gold mining areas where mercury was used for gold processing (200-60,000) (e.g. Gray et al., 2000; Carroll et al., 2000; Ganguli et al., 2000), and lastly catastrophic events (e.g. Gambonini tailings dam failure) (<1,000,000 ng/L) (Whyte and Kirchner, 2000).

The Guadalupe River watershed is a mixed land use watershed comprised of open space and forestland mostly in the upper watershed (35%), agriculture and rangeland in the middle watershed (18%), and urban areas in the middle and lower watershed (46%) (WMI, 2000). Based on land use statistics and the conceptual model (Figure 6-4) concentrations in the Guadalupe River of <100 ng/L might have been predicted. The Los Gatos sub-watershed, the largest tributary of the Guadalupe River, is a mixed land use watershed comprised of open space, agriculture, residential and rural residential land uses. Total mercury concentrations of 28.5 ng/L have been previously reported for Los Gatos Creek (Thomas et al., 2002). However, the Guadalupe watershed is also home to the New Almaden Mining District, the largest mercury mining operation in North America between 1845-1975 (Rytuba and Enderlin, 1999; Thomas et al., 2002). Although mines comprise <1% of the land use within the watershed area, leachate and runoff from historic mining areas, and mercury stored behind reservoirs and in stream banks and bed deposits provide an ongoing source of mercury for transport during floods. As a result, the Guadalupe River exhibits total mercury concentrations of between 200-18,700 ng/L, a magnitude consistent with other watersheds around the world that are contaminated with mercury laden mining debris (Figure 6-4) (e.g. Gray et al., 2000; Carroll et al., 2000; Ganguli et al., 2000; Blum et al., 2001).

Total Mercury Variation During Floods

The accurate evaluation of mercury loads in a watershed necessitates a detailed understanding of the processes of transport and how mercury concentrations vary during high flow (e.g. Balogh et al., 1997; Balogh et al., 1998; Hurley et al., 1998; Allan and Heyes, 1998; Whyte and Kirchner, 2000). The Guadalupe River has a pronounced wet season. On average, 89% of the annual rainfall occurs in just 58 rain days (rainfall >0.25 mm) and 91% of the annual runoff occurs between November 1st and April 30th. During WY 2003 there were 73 rain days and 94.5% of the WY 2003 rainfall and 85.4% of the WY 2003 runoff occurred during the wet season (November – April). A sampling design that focused on floods was implemented similar to that used in other watersheds with a more pronounced runoff season (e.g. Whyte and Kirchner, 2000).

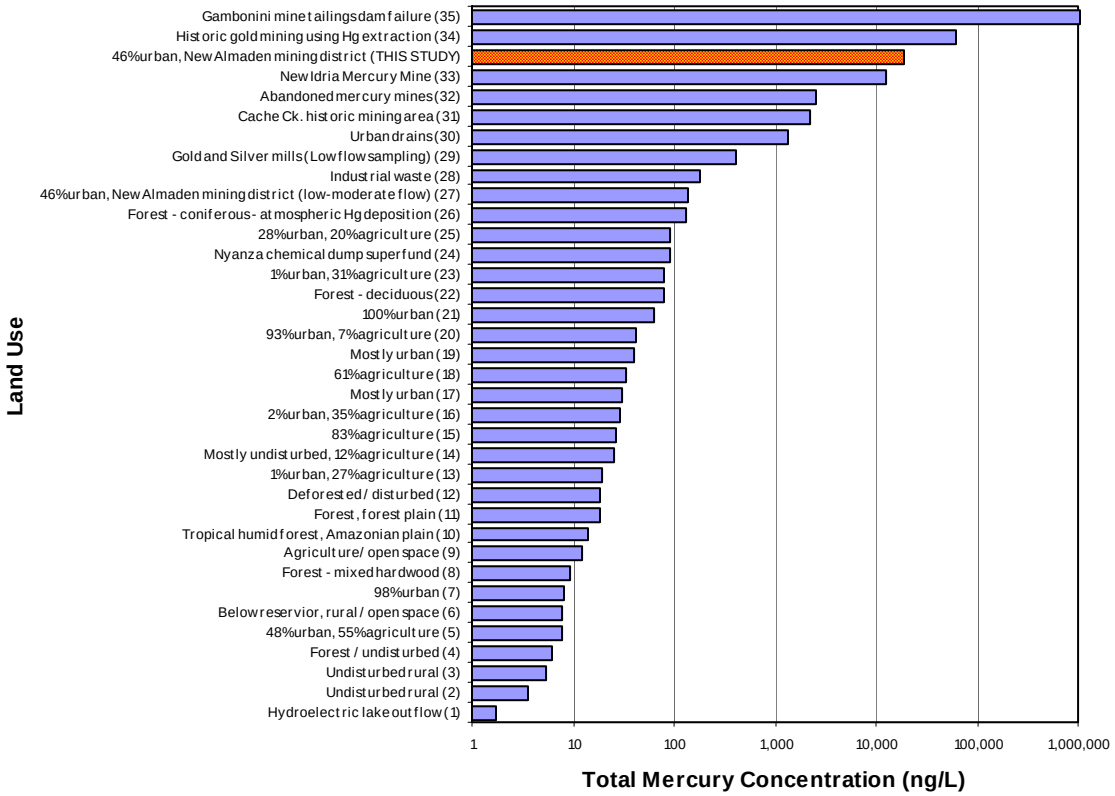

Figure 6-4. Maximum total mercury concentrations reported in the literature for a range of land use and land management conditions. 1. La Grande Hydroelectric Lake outflow, Quebec, Canada (Schetagne et al., 2000); 2. Sudbury R., site B2, Massachusetts (Waldron et al., 2000); 3. Sudbury R., site B1, Massachusetts (Waldron et al., 2000); 4. Serra do Navio experimental site, NE Aamazon, Brazil (Fostier et al., 2000); 5. Milwaukee R. at Easterbrook, Wisconsin (Hurley et al., (1995); 6. Sacramento R., below Keswick Dam, Califonia (Domagalski and Dileanis, 2000; Roth et al., 2001); 7. Lincoln Ck., Wisconsin (Hurley et al., (1995); 8. Coweeta observation watersheds, Northern Carolina (Allen and Heyes, 1998); 9. Lake Naivasha watershed, Kenya (Bon Zango et al., 1996); 10. Rio Negro, Amazon, Brazil (Maurice-Bourgoin et al., 2003); 11. Rio Negro, Amazon, Brazil (Maurice-Bourgoin et al., 2003); 12. Serra do Navio experimental site, NE Amazon, Brazil (Fostier et al., 2000); 13. Sacramento R. above Bend Bridge, California (Domagalski and Dileanis, 2000; Roth et al., 2001); 14. Rappahannock R., Chesapeake (Lawson et al., 2001); 15. Choptank R., Chesapeake (Lawson et al., 2001); 16. Sacramento R. at Freeport, California (Domagalski and Dileanis, 2000; Roth et al., 2001); 17. Anacostia R. NW. Branch (Mason and Sullivan, 1998); 18. Susquehanna R., Chesapeake (Lawson et al., 2001); 19. Anacostia R. NE. Branch (Mason and Sullivan, 1998); 20. Kinnickinnic R., Wisconsin (Hurley et al., (1995); 21. Herring Run R., Chesapeake (Lawson et al., 2001); 22. Nettle Brook, Northern Vermont (Scherbatskoy et al., 1998); 23. Sacramento R. at Colusa, California (Domagalski and Dileanis, 2000; Roth et al., 2001); 24. Sudbury R. site M1, Massachusetts (Waldron et al., 2000); 25. Potomac R., Chesapeake (Lawson et al., 2001); 26. Lehstenhach catchment, NE Bavaria, Germany (Schwesig and Matzner, 2001); 27. Guadalupe R., Bay Area, California (Thomas et al., 2002); 28. Lower Fox R., Wisconsin (Hurley et al., 1998); 29. Steamboat Ck. Nevada (Blum et al., 2001); 30. Santa Clara Valley, Bay Area, California (Soller et al., 2003); 31. Cache Ck., California (Domagalski and Dileanis, 2000); 32. Kuskakwim R. basin, SW Alaska (Gray et al., 2000). ; 33. San Carlos Ck., San Joaquin R. Valley, California (Ganguli et al., 2000); 34. Carson R., Nevada (Carroll et al., 2000); 35. Walker Ck., California (Whyte and Kirchner, 2000).

Many studies have demonstrated a strong relationship between suspended sediment and mercury concentrations (e.g. Balogh et al., 1997; Whyte and Kirchner, 2000; Domagalski, 2001; Lawson and Mason, 2001). For example, Whyte and Kirchner (2000) found a correlation between total mercury and suspended sediment in a mercury mine impacted Tomales Bay watershed (r^2 = 0.98 P=0.0001), which they suggested occurred because mercury and sediment sources upstream remained unchanged throughout monitoring. Typically distribution coefficients (log k_d) for mercury range between 3.7-6.6 for natural fresh waters (Benoit et al., 1998; Mason and Sullivan, 1998; Ganguli et al., 2000; Babiarz et al., 2001; Lawson et al., 2001). A distribution coefficient of 5.5-5.7 was previously calculated for the Guadalupe River at the old USGS gage (about 2 miles upstream from the present sampling location) during a small first-flush flood (Thomas et al., 2002). During that small storm event, concentrations on particles ranged between 0.5-4 μg/L, and between 92-98% of the mercury was transported in particulate forms. These observations supported the use of a sediment model to estimate a mercury load of 4-30 kg per year (Thomas et al. (2002).

In watersheds with agricultural, forest and/or open space land uses, the organic content of suspended particles has been found to strongly influence total mercury concentrations (e.g. Scherbatskoy et al., 1998) and in other cases dissolved organic carbon has played a significant role in transport particularly in (e.g. Hurley et al., 1995; Allen and Heyes, 1998; Schwesig and Matzner, 2001). In a study of Wisconsin rivers of varying land use, Hurley et al. (1995) found a strong relationship between total mercury and dissolved organic carbon during low flow conditions, During high flow conditions, the degradation of this relationship was attributed to particulate matter becoming a more important vector for transport.

The sampling design implemented in the Guadalupe River watershed incorporated the use of a turbidity probe installed in the channel thalweg at the sampling location. The logged data from this instrument provided an estimate of suspended sediment concentration every 15 minutes (once calibrated using a correlation model between turbidity and suspended sediment concentration). During the wet season of 2002/2003, concentrations of total mercury did not vary consistently in relation to either discharge or suspended sediment concentrations (Figure 6-3; Table 6-3). Organic carbon concentrations (DOC or POC) did not vary consistently with total mercury concentrations or suspended sediment concentrations (Table 6-3), suggesting that the sources of sediments, mercury, and organic carbon are highly heterogeneous and vary within the time scales of floods and periods between floods at the Guadalupe River sampling location. If the assumption is made that most of the mercury is bound to particles (the results of Thomas et al. (2002) and Lawson et al. (2001) suggest that when suspended sediment concentrations are >100 mg/L, the particulate fraction dominates total mercury), mercury concentrations on particles in samples collected WY 2003 ranged from approximately 1-280 μg/g. This variation is much larger than reported by Thomas et al. (2002) and tends to negate the use of a simple annualized sediment model for calculating mercury loads in the Guadalupe. Careful stratification of the data showed several short periods when mercury and suspended sediment did co-vary. However, even during these periods, the variation was not linear; instead the concentrations of mercury on sediment

particles were progressively increasing (Figure 6-5a,b). When all the data are considered together and plotted with respect to time, a complex series of mercury hysteresis loops is revealed (hysteresis is the term used to describe differing concentration of the rising and falling stages of a hydrograph for a given magnitude of discharge) (Figure 6-6) that differ greatly from simple regression relationships found in many other watersheds (e.g. Balogh et al., 1997; Whyte and Kirchner, 2000; Domagalski, 2001; Lawson and Mason, 2001). In the Guadalupe River, the hysteresis patterns are caused by large variations in the origin of both sediment and mercury during each sampling event and flood.

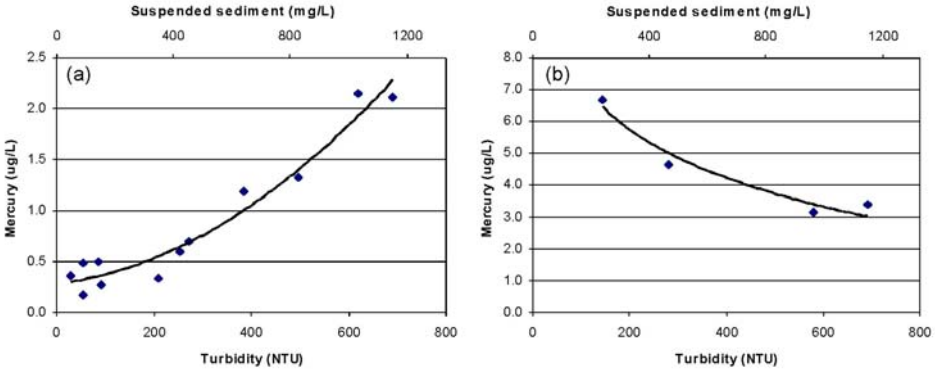

Figure 6-5. Relationships between mercury and suspended sediment for several short periods during water year 2003. (a) December 13th 2002 at 7:15 pm - December 16th at 10:00 am. (b) December 16th at 10:45 am - December 17th at 10:00 am.

Reservoir Hydrology and Mercury Source Heterogeneity

There are five main subwatersheds and four main reservoirs in the Guadalupe River watershed. A number of previous studies have sampled mercury concentrations in reservoir water and sediments and in streams sediment in various tributary channels (see review by Tetra Tech Inc. [Tetra Tech, 2003]). The Almaden Reservoir has the greatest concentrations of mercury in bottom sediment among the reservoirs (Figure 6-7). Alamitos Creek below Almaden Reservoir and Guadalupe Creek below Guadalupe Reservoir appear to have the greatest concentrations of mercury stored in bed and bank sediments (Figure 6-7). Los Gatos Creek has relatively low concentrations of sediment mercury and might be considered characteristic of the natural background found locally (Thomas et al., 2002). The Calero, Almaden and Guadalupe reservoirs were periodically released during the study year. A detailed analysis of the timing of those releases helped to explain the complex total mercury concentration pattern found at the sampling location (Figure 6-6).

During the first flush (November 7th-9th 2002), total mercury concentrations remained low and relatively constant throughout the storm peaks. It is likely that any

mercury signal from contaminated areas was diluted by relatively clean water and sediment from the lower urbanized watershed and Los Gatos Creek and the western tributaries of Guadalupe Creek that flow from Mt Umumhum and other high peaks in the Sierra Azul Range. Releases from Calero (7 cfs), Almaden (2 cfs), and Guadalupe (7 cfs) reservoirs were minimal. Late on the falling stage of the last peak, discharge from Guadalupe Creek became a significant portion of the flow. It is suggested that the high concentration of total mercury found on November 9th was from channel sediments downstream of Guadalupe Reservoir.

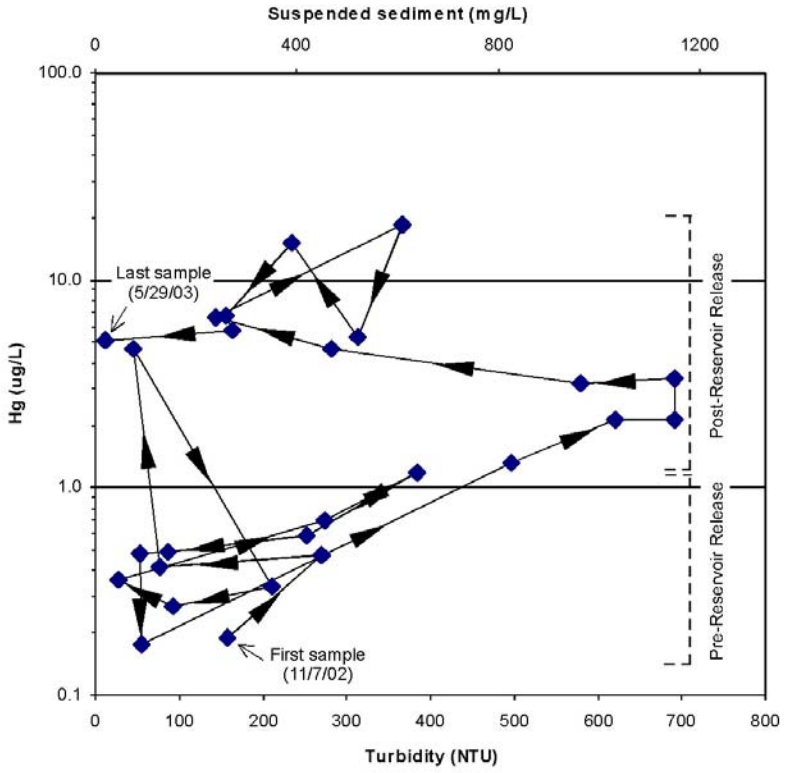

Figure 6-6. Variation of total mercury and instantaneous discharge with respect to time (termed hysteresis). Black arrows indicate time starting at the first sample collected and ending with the last sample collected. During the study there was flood-specific hysteresis. Some floods exhibited clockwise hysteresis (the peak mercury occurred before the peak discharge) and other floods exhibited anti-clockwise hysteresis (the peak mercury occurred after the peak discharge). An understanding of this kind of detail improves the determination of mercury loads.

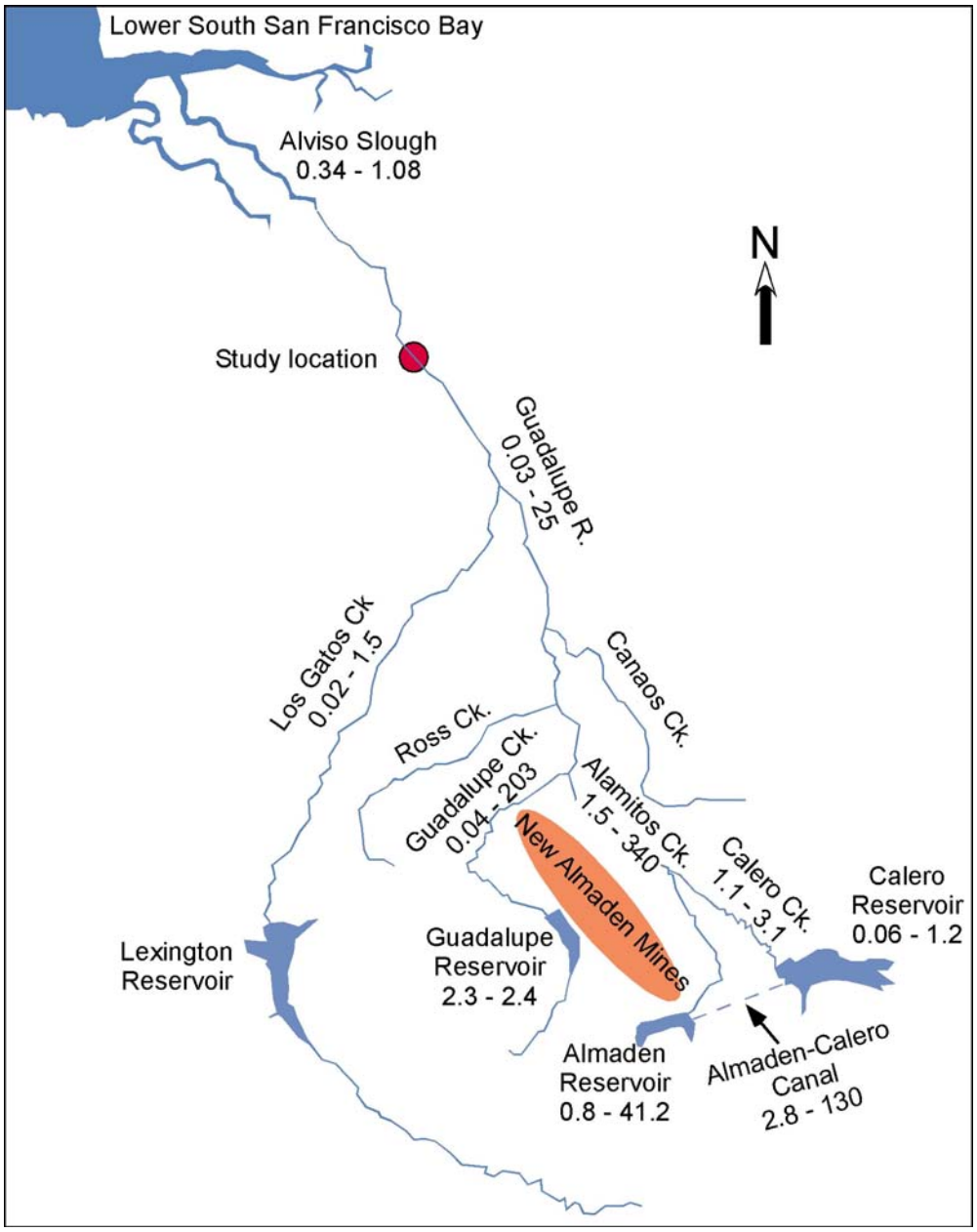

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Figure 6-7. Total mercury concentration (μg/g) in creek and reservoir sediments of the Guadalupe River watershed (Leatherbarrow et al., 2002; Thomas et al., 2002; Tetra Tech 2003).

During the series of storm peaks that occurred from December 14th – 17th 2002, a change occurred in the release of mercury from contaminated source areas. During rising and falling stages of the December 14th and 15th peaks and the rising stage of the December 16th/17th peak (the largest storm peak of the season), total mercury showed a reasonable correlation with suspended sediment (Figure 6-5a). During the falling stage of the 3rd peak, there was a new source of suspended sediment evidenced by sustained suspended sediment concentrations during the falling limb. These sediments were enriched with mercury. On December 16th 2002 Calero Reservoir was released for 12 hours with a peak discharge of 31 cfs between 6:00 and 7:30 am. Discharge from Almaden Reservoir increased to 7.8 cfs and discharge from Guadalupe Reservoir increased to 13 cfs, with both also peaking at 6:00 am. On December 17th at 5 pm, release from Almaden Reservoir was increased to 24 cfs. The release was increased to 55 cfs at 10:00 am on December 18th and maintained at 55-60 cfs until December 26th at 8:00 am with the exception of a short peak of 86 cfs on December 18th at 3:30 pm. The curve in the regression (Figure 6-5a) is likely a result of small releases from Calero, Almaden and Guadalupe Reservoirs flushing mercury-laden sediments from creek beds downstream from these reservoirs. The increase in total mercury concentration on the falling stage of the December 16th/17th peak after 10 am was likely caused by reduced dilution by relatively clean water and sediment from the urban areas as well as from Los Gatos Creek and the western tributaries of Guadalupe Creek. The peak mercury concentrations of 18.7 μg/L on December 19th and 15.1 μg/L were mostly the result of the release of water from the Almaden Reservoir.

Total mercury concentrations remained elevated above 2.1 μg/L from December 16th 2002 at 8:45 am through to the completion of the sampling on May 29th 2003 as a direct result of released water from reservoirs. Thus, the mercury signals at the lower watershed sampling location show two distinct periods (pre- and post-reservoir release). During the pre-reservoir release period, concentrations ranged from 0.2-4.7 μg/L and had a flow-weighted mean concentration of 0.76 μg/L. During the post-reservoir release period, concentrations ranged from 1.3-18.7 μg/L and had a flow-weighted mean concentration of 5.1 μg/L. Given concentrations of mercury in sediments in the Calero, Almaden and Guadalupe Reservoirs are lower than concentrations found in sediments in their respective creeks downstream, the major source of mercury is not thought to be the released water. More likely, the released water is low in suspended sediment concentration and is "hungry" and thus highly effective at scouring loose mercury laden sediments stored in Guadalupe River, Calero Creek, Alamitos Creek, and Guadalupe Creek.

Total Mercury Loads

Mercury load estimates for the Guadalupe River watershed were confounded by the lack of a simple relationship between total mercury and either suspended sediment or discharge. The series of discrete data points gathered were extrapolated in time by combining two methods: (a) short term suspended sediment-mercury relationships, and (b) linear interpolation modified with a knowledge of subwatershed hydrology and subwatershed mercury sources. The loads estimates for WY 2003 are provided with a caveat and expectation that the interpretation of data generated in the second year of

sampling (WY 2004) will further refine the temporal extrapolation method. Hourly loads of total mercury varied from 0.2 - 5,240 grams reaching a maximum at 6:30 pm on December 19th 2002. Daily loads varied from 4.6 g - 32 kg or about 7,000x also reaching a maximum on December 19th. The magnitude of temporal variation found in the Guadalupe River is characteristic of other contaminated systems (Whyte and Kirchner, 2000; Blum et al., 2001; Domagalski et al., 2003). For example daily loads vary in excess of 1000x in Cache Creek, another California Coast Range mining area contaminated with historic mining debris (Domagalski et al., 2003). The load transported on December 19th was 10% of the wet season load for WY 2003. The maximum daily load of total mercury occurred during the second largest peak (3,308 cfs) on December 19th rather than the largest flood peak (4,617 cfs) on December 16th as a result of greater concentrations of mercury derived from reservoir releases. In response to the series of floods that occurred in December, 49% of the discharge, 68% of the sediment load, and 44% of the total mercury load occurred during just one month (Table 6-4). For the study period, 312 ± 82 kg of mercury was transported into lower South San Francisco Bay.

This estimate of total mercury load in the Guadalupe River is ~10x greater than previously reported in studies that did not capture such large floods or the effects of release of water from the Calero, Almaden or Guadalupe Reservoirs (Leatherbarrow et al., 2002; Thomas et al., 2002). Rainfall and discharge for the study year were approximately average (103% and 97% of normal respectively) suggesting that the load estimate might approximate long-term average load. However, it is presently unknown what influence several dry years (water year 2001 [65% MAR] and 2002 [40% MAR]) might have had on the magnitude of the load during the study period. In addition, it is presently not clear how inter-annual differences in reservoir operation might influence annual loads. These questions are the primary focus of subsequent years of study.

Table 6-4. Monthly discharge (million meters cubed), sediment loads (metric tonnes), and mercury loads (kilograms) during the study period.

	2002			2003					
	Oct	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Total**
Discharge (Mm^3)	0.3	4.3	23.4	5	3.4	3.2	5.4	2.8	47.8
Percent transported (%)	0.6	9.0	49.0	10.5	7.1	6.7	11.3	5.9	100
Suspended sediment (t)	19	2,085	7,027	165	184	268	486	93	10,328
Percent transported (%)	0.2	20.2	68.0	1.6	1.8	2.6	4.7	0.9	100
Total mercury load (kg)	0.28	3.7	137	58	27	29	37	19	312±82
Percent transported (%)	0.1	1.2	43.8	18.7	8.8	9.3	11.9	6.2	100

SUMMARY

The toxicity and persistence of mercury in the aquatic environment are issues of critical concern to environmental managers, scientists and the public at-large in the Bay Area. Continuous monitoring over the past decade by the San Francisco Bay Regional Monitoring Program for Trace Substances (RMP) and a number of focused studies have determined that mercury concentrations in San Francisco Bay are of sufficient magnitude to threaten species of birds and mammals and pose a significant human health risk to those who consume fish caught in the Bay. This study adds a further contribution to the already large body of accumulated knowledge on mercury in and around the Bay. The main points are summarized:

- Resuspension of legacy mercury stored in benthic sediments, loads from the large rivers (Sacramento and San Joaquin), and mercury loads from small urbanized tributaries (particularly those where mercury has be mined historically) are the largest components of the mercury budget of the Bay and the components where the magnitude of loads have the greatest uncertainties.
- Concentrations of total mercury in the Guadalupe River from 11/7/03 to 5/29/03 varied by over two orders of magnitude from 0.2-18.7 μg/L with a flow-weighted average of 3.7 μg/L.
- These concentrations are 26x greater than results reported previously for lower Guadalupe River and 655x those previously reported for the relatively pristine Los Gatos sub-watershed.
- The Guadalupe River exhibits total mercury concentrations of between 200-18,700 ng/L, a magnitude consistent with other watersheds around the world that are contaminated with mercury laden mining debris.
- Total mercury concentrations did not relate in a predictable way to discharge and did not correlate over the study period with any other parameter measured.
- Sources of sediments, mercury, and organic carbon are highly heterogeneous and vary within the time scales of floods and between floods at the Guadalupe River sampling location.
- Reservoir releases from Calero, Almaden and Guadalupe Reservoirs had a profound influence of the mercury concentration and load at the sampling location, defining two distinct periods (pre- and post-reservoir release).
- During the pre-reservoir release period, concentrations ranged from 0.2-4.7 μg/L and had a flow-weighted mean concentration of 0.76 μg/L.
- During the post-reservoir release period, concentrations ranged from 1.3-18.7 μg/L and had a flow-weighted mean concentration of 5.1 μg/L.
- The source of mercury is most likely sediments stored in Calero, Alamitos, and Guadalupe Creeks that are mobilized by relatively “clean” water with low suspended sediment concentration that is released from the reservoirs.
- Hourly loads of total mercury varied from 0.2 - 5,240 grams.
- Daily loads varied from 4.6 g - 32 kg or about 7,000x.
- The load transported on December 19th was 10% of the wet season load for WY 2003.

- The maximum daily load of total mercury occurred during the second largest peak (3.308 cfs) on December 19th rather than the largest flood peak (4,617 cfs) on December 16th as a result of greater concentrations of mercury derived from reservoir releases.
- In response to the series of floods that occurred in December, 49% of the discharge, 68% of the sediment load, and 44% of the total mercury load occurred during just one month.
- From October 1st 2002 to May 31st 2003, 312±82 kg of mercury was transported into lower South San Francisco Bay.
- This estimate of total mercury load is ~10x greater than previously reported in studies on the Guadalupe River that did not capture such large floods or the effects of release of water from the Calero, Almaden or Guadalupe Reservoirs.
- Climate during the study year was approximately average, suggesting the load estimate might approximate long-term average. However, it is presently unknown what influence relatively dry climate during 2001 and 2002 might have had on the magnitude of the loads during the study year.
- It is presently not clear how inter-annual differences in reservoir operation might influence annual loads.

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SECTION SEVEN

APPENDICES

Appendix Table A. PCB concentrations in Guadalupe River samples, WY 2003. ND = concentration was below detection limit. b = method blank had a concentration greater than the MDL and 10% of the field sample concentration. e = concentration estimated based on peak that was detected but did not meet quantification criteria. q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries. All units are in pg/L.

Date	Time	t-PCBs	PCB 008	PCB 018/30	PCB 028/20	PCB 031	PCB 033/21	PCB 044/47/65	PCB 049/69	PCB 052	PCB 056	PCB 060	PCB 066	PCB 070/74/61/76
Range of MDLs			0.31 - 21	0.16 - 8	0.24 - 4	0.24 - 5	0.24 - 5	0.02 - 8	0.02 - 7	0.02 - 8	0.61 - 6	0.61 - 6	0.58 - 5	0.58 - 5
11/7/02	16:45	18,853	b 75	132	347	240	102	388	220	653	103	50	250	619
11/7/02	17:05	16,914	b 63.5	110	277	187	76.8	264	157	418	78.6	38.4	171	438
11/7/02	23:40	54,416	80.5	535	2190	1130	258	1850	1150	2180	279	129	645	1360
11/9/02	7:46	7,723	b, q 13.9	b 55.1	b 91	b 53.9	b 12.9	q 90.7	q 62.4	q 166	q 21.6	q 11	q 50.1	q 105
12/13/02	19:29	64,818	94.4	232	685	496	233	869	571	1470	260	121	556	1330
12/14/02	11:00	4,123	b, q 7.01	b 17.3	33.9	b 16	b 6.53	65.6	39.2	108	15.1	6.38	32.3	58.3
12/14/02	17:55	62,091	178	496	1330	837	256	1300	825	1930	318	128	688	1500
12/14/02	20:24	38,331	44.5	128	608	284	82.5	790	451	1340	156	58.9	363	752
12/15/02	0:16	13,113	26.4	37.7	160	85	32.1	207	118	387	58	20.5	111	217
12/16/02	7:55	89,564	84.4	237	1020	547	167	1520	963	2910	335	115	998	2060
12/16/02	8:45	Q 85,054	q 197	406	1200	683	251	q 1310	q 801	q 2610	q 327	q 125	q 852	q 1910
12/16/02	9:55	57,469	108	206	625	355	148	765	474	1550	192	76.1	514	1160
12/16/02	10:45	53,543	q 52.4	117	483	245	89	578	363	1150	165	67.3	422	862
12/16/02	12:31	Q 37,064	q 32.1	q 82.9	q 363	q 175	q 60.4	q 398	q 251	q 805	q 106	q 40.7	q 253	q 522
12/16/02	19:55	18,565	11.5	22.6	71.3	43.8	e 24	94.7	53.8	218	27.7	8.69	63.8	124
12/19/02	20:30	Q 31,033	29.2	q 68.3	q 301	q 159	q 54.6	q 388	q 221	q 772	q 82.8	q 27.3	q 185	q 373
12/19/02	23:30	14,119	14.7	27.3	123	64.6	24.7	146	84.6	279	39.7	14.4	78.2	133
12/28/02	18:24	69,452	21.7	46.4	225	103	34.2	470	394	1050	127	40.9	240	386
3/15/03	3:06	26,879	47.1	132	330	211	92	408	276	653	119	57.9	267	557
4/12/03	18:40	15,418	ND	51.4	140	61.8	26.1	271	162	474	75.9	e 35.8	161	274
5/29/03	10:33	3,710	q ND	e 30.6	34.2	b 25.3	b 8.11	56	34.9	89.4	e 12.4	6.96	e 31.6	62.3
5/29/03	10:33	3,420	ND	29.5	36.3	b, e 23.9	b, e 9.21	60.4	e 37.3	96.6	e 14.1	9.75	e 29.3	63.8

2495 **Appendix Table A (continued). PCB concentrations in Guadalupe River samples, WY 2003.** e = concentration estimated based on peak that was detected but did not meet quantification criteria. q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries. All units are in pg/L.

Date	Time	t-PCBs	PCB 087/97/86/108/119/125	PCB 095/93/98/100/102	PCB 099/83	PCB 101/90/113	PCB 105	PCB 110/115	PCB 118	PCB 128/166	PCB 132	PCB 138/129/160/163	PCB 141	PCB 149/147	PCB 151/135/154
Range of MDLs			0.19 - 6	0.21 - 6	0.22 - 7	0.19 - 6	0.52 - 10	0.16 - 5	0.45 - 10	0.43 - 9	0.56 - 12	0.41 - 9	0.5 - 11	0.51 - 11	0.01 - 4
11/7/02	16:45	18,853	854	965	572	1190	337	1490	875	294	531	1700	298	1150	528
11/7/02	17:05	16,914	703	813	469	951	290	1260	725	231	537	1630	310	1080	493
11/7/02	23:40	54,416	1430	2020	1150	2230	844	3040	2010	744	1500	4900	854	3450	1430
11/9/02	7:46	7,723	q 165	q 281	q 167	q 374	64.4	q 390	188	82	177	638	150	531	276
12/13/02	19:29	64,818	1670	2640	1520	3130	923	3600	2210	752	1830	6200	1220	5260	2530
12/14/02	11:00	4,123	105	186	99.4	212	55.6	241	125	44.8	126	381	81.6	379	200
12/14/02	17:55	62,091	1960	2730	1570	3170	1090	4100	2550	828	1930	5390	1070	4630	2000
12/14/02	20:24	38,331	1500	2090	1200	2430	709	3220	1770	601	1310	3430	638	2920	1170
12/15/02	0:16	13,113	417	659	355	743	206	974	489	180	430	1200	229	1030	444
12/16/02	7:55	89,564	3790	4870	3890	6560	1900	8100	5010	1350	2790	8450	1480	6620	2670
12/16/02	8:45	Q 85,054	q 3830	q 4800	q 3170	q 5780	1730	q 8310	4830	1400	2770	7800	1300	5640	2260
12/16/02	9:55	57,469	2450	3090	2070	3730	1150	5330	3110	944	1940	5580	928	4070	1710
12/16/02	10:45	53,543	1960	2410	1690	3040	1020	4370	2730	894	1750	5510	917	3780	1610
12/16/02	12:31	Q 37,064	q 1210	q 1700	q 1200	q 2050	685	q 2940	1800	q 599	q 1140	q 3580	q 608	q 2610	q 1270
12/16/02	19:55	18,565	356	631	330	723	197	899	520	252	538	1800	402	1500	710
12/19/02	20:30	Q 31,033	q 1170	q 1700	q 1020	q 1950	599	q 2860	1640	q 545	q 1070	q 3220	q 542	q 2350	q 1010
12/19/02	23:30	14,119	377	678	384	713	199	944	472	186	459	1360	256	1220	624
12/28/02	18:24	69,452	1550	3120	2760	4240	625	3390	1490	561	2410	5480	1010	8030	6020
3/15/03	3:06	26,879	819	1230	839	1430	470	1670	1110	353	775	2340	418	2030	1080
4/12/03	18:40	15,418	561	764	468	843	309	1200	664	224	452	1370	233	1060	535
5/29/03	10:33	3,710	107	188	91.4	186	43.5	236	104	40	e 106	325	56.6	305	163
5/29/03	10:33	3,420	92.7	178	87.8	164	e 48.3	200	112	e 43.3	107	309	57.3	302	165

Appendix Table A (continued.). PCB concentrations in Guadalupe River samples, WY 2003. ND = concentration was below detection limit. e = concentration estimated based on peak that was detected but did not meet quantification criteria. q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries. All units are in pg/L.

Date	Time	t-PCBs	PCB 153/168	PCB 156/157	PCB 158	PCB 170	PCB 174	PCB 177	PCB 180/193	PCB 183/185	PCB 187	PCB 194	PCB 195	PCB 201	PCB 203
Range of MDLs			0.39 - 8	0.46 - 9	0.34 - 7	0.01 - 5	0.01 - 4	0.01 - 5	0.01 - 4	0.01 - 4	0.01 - 4	0.19 - 7	0.2 - 8	0.01 - 4	0.01 - 5
11/7/02	16:45	18,853	1360	174	188	370	431	226	938	ND 0	581	243	75.1	47.1	257
11/7/02	17:05	16,914	1240	134	153	392	497	275	1070	369	517	181	59.7	51.7	203
11/7/02	23:40	54,416	3510	518	500	1380	1570	915	3330	1030	2020	889	303	162	900
11/9/02	7:46	7,723	656	40	53.5	331	331	207	814	257	500	124	48.1	22.7	122
12/13/02	19:29	64,818	5420	541	592	1900	2410	1440	4890	1580	3100	1040	387	189	927
12/14/02	11:00	4,123	359	31.6	36.2	105	136	88	285	91.5	199	65.6	22.6	10.8	50.5
12/14/02	17:55	62,091	4420	596	557	1490	1730	974	3700	1170	2230	985	324	171	940
12/14/02	20:24	38,331	2610	376	355	788	888	508	1900	610	1120	483	175	78.1	394
12/15/02	0:16	13,113	979	121	119	342	402	227	861	263	501	206	76.2	33.1	167
12/16/02	7:55	89,564	6740	957	897	1430	1550	887	3540	1110	2070	853	276	133	685
12/16/02	8:45	Q 85,054	5380	752	795	1720	1900	1140	3810	1320	2310	580	240	144	671
12/16/02	9:55	57,469	3950	542	546	1210	1460	868	2740	965	1700	454	157	111	491
12/16/02	10:45	53,543	3980	512	532	1490	1630	1020	3400	1140	2120	543	203	128	570
12/16/02	12:31	Q 37,064	q 2750	345	q 344	1090	1170	771	2520	803	1600	455	168	101	466
12/16/02	19:55	18,565	1630	136	158	862	934	592	1950	634	1200	338	149	64.6	296
12/19/02	20:30	Q 31,033	q 2270	299	q 324	670	789	481	1520	523	1060	312	122	65.8	260
12/19/02	23:30	14,119	1160	112	124	406	515	320	1010	331	716	215	88.9	42.3	178
12/28/02	18:24	69,452	6820	325	436	1430	2630	2050	3850	1460	4530	822	342	234	699
3/15/03	3:06	26,879	1980	225	217	740	873	581	1760	550	1240	393	155	80.6	370
4/12/03	18:40	15,418	1070	141	132	388	438	267	969	297	618	267	119	e 39.3	257
5/29/03	10:33	3,710	285	28.5	e 29.4	105	133	91.5	256	e 88.4	184	69.1	e 30.6	e 9.07	57.1
5/29/03	10:33	3,420	262	e 22.6	29.9	90.6	104	74.8	e 216	69.6	143	57	e 23	e 9.12	e 41.9

Appendix Table B. Pesticide concentrations in Guadalupe River samples, WY 2003. e = concentration estimated based on peak that was detected but did not meet quantification criteria. q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries. All units are in pg/L.

Date	Time	t-DDT	o,p'-DDD	o,p'-DDE	o,p'-DDT	p,p'-DDD	p,p'-DDE	p,p'-DDT
Range of MDLs			5.4 - 67	5 - 36	7.9 - 105	7.9 - 83	8.4 - 49	11 - 182
11/7/2002	4:45:00 PM	41,586	3980	666	1780	6760	16700	11700
11/7/2002	5:05:00 PM	30,862	3440	542	1390	5340	13500	6650
11/7/2002	11:40:00 PM	59,217	4470	897	1750	11800	29800	10500
11/9/2002	7:46:00 AM	5,724	688	58	169	2280	1770	759
12/13/2002	7:29:00 PM	33,346	4280	585	e 761	11500	12400	3820
12/14/2002	11:00:00 AM	3,297	252	43.4	185	750	1320	747
12/14/2002	5:55:00 PM	47,804	3360	644	2190	8810	18200	14600
12/14/2002	8:24:00 PM	34,411	1910	351	1980	4770	13400	12000
12/15/2002	12:16:00 AM	16,310	905	161	944	2370	7040	4890
12/16/2002	7:55:00 AM	55,187	2980	e 567	3050	8290	20200	20100
12/16/2002	8:45:00 AM	70,610	3520	590	3000	13700	27000	22800
12/16/2002	9:55:00 AM	51,679	2400	409	2430	8540	20900	17000
12/16/2002	10:45:00 AM	Q 50,293	q 2030	313	q 2510	q 6940	21700	q 16800
12/16/2002	12:31:00 PM	Q 39,624	q 1740	q 284	q 2100	q 5800	q 16100	q 13600
12/16/2002	7:55:00 PM	15,105	687	141	747	1620	7560	4350
12/19/2002	8:30:00 PM	Q 29,904	q 1290	q 184	q 1600	q 4330	q 12200	q 10300
12/19/2002	11:30:00 PM	Q 17,832	q 853	q 127	q 912	q 2340	q 8120	q 5480
12/28/2002	6:24:00 PM	Q 36,105	1540	345	1810	7810	13300	q 11300
3/15/2003	3:06:00 AM	15,484	1050	145	509	3990	6280	3510
4/12/2003	6:40:00 PM	16,776	856	172	798	3100	6910	q 4940
5/29/2003	10:33:00 AM	Q 1,712	q 208	q 11.6	q 59.3	q 760	429	q 244
5/29/2003	10:33:00 AM	1,775	189	14.7	71.7	729	443	q 328

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Appendix Table B (continued). Pesticide concentrations in Guadalupe River samples, WY 2003. ND=concentration was below detection limit. b=method blank had a concentration greater than the MDL and 10% of the field sample concentration. e=concentration estimated based on peak that was detected but did not meet quantification criteria. q=concentration estimated based on low surrogate recovery. Q= concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries. All units are in pg/L.

Date	Time	t-chlordane	alpha-chlordane	gamma-chlordane	cis-nonachlor	trans-nonachlor	heptachlor	heptachlor epoxide	oxy-chlordane	dieldrin
Range of MDLs			7.8 - 164	6.8 - 145	21 - 350	8.9 - 237	5 - 31	2.6 - 14	11 - 79	4.9 - 31
11/7/2002	4:45:00 PM	12,012	3500	3640	983	3290	55	154	390	1120
11/7/2002	5:05:00 PM	10,665	3040	3250	984	2970	e 35	153	233	1030
11/7/2002	11:40:00 PM	53,415	14000	14800	6250	17200	87.4	562	516	3080
11/9/2002	7:46:00 AM	3,721	1160	999	274	918	q 31	e 250	e 89	636
12/13/2002	7:29:00 PM	25,706	6990	8020	2430	7640	44.8	353	e 228	2350
12/14/2002	11:00:00 AM	3,375	972	857	326	949	e 11.7	188	e 71	742
12/14/2002	5:55:00 PM	50,216	13100	15300	5450	15100	123	718	425	4650
12/14/2002	8:24:00 PM	36,995	9850	10100	4200	11600	151	706	388	3520
12/15/2002	12:16:00 AM	13,471	3710	3500	1430	4150	e 50.3	455	e 176	1630
12/16/2002	7:55:00 AM	56,259	15200	15300	6140	17700	171	1100	e 648	5800
12/16/2002	8:45:00 AM	64,150	18600	18800	5510	18400	280	1510	1050	5970
12/16/2002	9:55:00 AM	41,031	11600	11400	3890	12100	190	1240	611	4200
12/16/2002	10:45:00 AM	36,779	10900	10200	q 3630	10400	e 159	924	566	3220
12/16/2002	12:31:00 PM	Q 26,166	7730	6990	q 2640	q 7300	133	852	521	2720
12/16/2002	7:55:00 PM	9,685	2690	2390	901	2690	44.3	579	391	1430
12/19/2002	8:30:00 PM	Q 23,965	q 7030	q 6460	q 2450	q 6630	121	853	421	2750
12/19/2002	11:30:00 PM	Q 12,006	3570	3110	q 1100	q 3170	106	675	275	1970
12/28/2002	6:24:00 PM	Q 35,110	9970	10300	q 3860	q 9200	603	735	442	3350
3/15/2003	3:06:00 AM	15,281	4490	4720	1560	4040	e 33.5	255	182	1520
4/12/2003	6:40:00 PM	21,963	6290	6380	2440	q 6060	93.7	410	289	1850
5/29/2003	10:33:00 AM	1,582	519	456	b 135	368	ND	73.6	30	307
5/29/2003	10:33:00 AM	1,587	516	428	b 146	361	e 7.31	75	e 53.2	325

Appendix Table C. Mercury, trace element, and organic carbon concentrations in Guadalupe River samples, WY 2003. NS= no water sample taken. ND = concentration was below detection limit.114

. Sample	. Date	. Time	SSC (mg/L)	POC (mg/L)	DOC (mg/L)	Hg (µg/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)
Field Blank	11/8/2002	17:30	NS	NS	NS	0.0065	NS	NS	NS	NS	NS	NS	NS	NS
GR 01	11/7/2002	16:30	190.5	NS	NS	0.19	0.029	4.20	0.685	9.18	42.5	26.6	19.0	191
GR 02	11/7/2002	18:00	126.8	NS	NS	0.47	NS	NS	NS	NS	NS	NS	NS	NS
GR 03A	11/8/2002	17:00	83.3	NS	NS	0.45	NS	NS	NS	NS	NS	NS	NS	NS
GR 03(Duplicate)	11/8/2002	17:00	NS	NS	NS	0.39	NS	NS	NS	NS	NS	NS	NS	NS
GR 04	11/9/2002	7:30	49.6	NS	NS	4.66	NS	NS	NS	NS	NS	NS	NS	NS
GR 10	12/13/2002	19:18	332.8	ND	8.9	0.34	0.101	2.92	0.560	23.4	39.5	40.6	31.4	152
GR 11	12/14/2002	0:46	94.5	0.5	6.1	0.27	ND	1.77	0.131	9.38	13.5	18.9	7.78	49.7
GR 12	12/14/2002	11:15	32.0	0.5	5.4	0.36	0.032	1.70	0.0709	4.00	8.16	7.17	2.76	24.2
GR 13	12/14/2002	17:30	550.9	0.3	4.5	0.70	0.164	2.38	0.591	28.3	41.1	51.8	43.7	193
GR 14	12/14/2002	20:30	567.6	0.8	3.9	1.19	0.126	2.62	0.661	56.5	45.9	113	47.1	188
GR 15	12/15/2002	0:00	287.5	0.3	4.6	0.60	ND	1.85	0.232	29.7	19.2	64.0	16.0	76.9
GR 16	12/15/2002	11:00	80.0	0.3	5.1	0.49	ND	1.65	0.0617	13.8	7.85	30.9	3.17	21.0
GR 17	12/15/2002	16:30	51.3	ND	5.5	0.48	0.031	1.68	0.0611	7.50	7.72	14.9	2.98	21.5
GR 18	12/16/2002	3:00	83.2	ND	4.6	0.18	ND	1.53	0.122	6.44	7.75	13.2	4.75	33.1
GR 19	12/16/2002	7:45	810.0	0.7	4	1.33	0.120	2.08	0.609	63.2	44.6	109	46.4	171
GR 20	12/16/2002	8:45	947.3	0.7	4.4	2.15	0.130	2.69	0.702	71.0	52.2	149	51.8	188
GR 21	12/16/2002	10:00	929.0	0.6	5.2	2.12	0.126	2.46	0.567	73.3	45.6	151	40.5	152
GR 22	12/16/2002	10:45	913.7	0.9	5.7	3.38	0.104	2.17	0.542	98.2	50.3	189	37.5	148
GR 23	12/16/2002	12:30	563.3	0.4	6.3	3.18	0.078	1.81	0.334	85.6	33.8	169	24.1	99.9
GR 24	12/16/2002	19:45	217.5	0.5	7.3	4.65	0.111	1.70	0.123	33.5	14.8	70.9	8.63	40.0
GR 25	12/17/2002	10:00	199.0	ND	5.5	6.70	0.048	1.42	0.149	20.6	14.1	36.3	8.85	52.6
GR 30	12/19/2002	20:30	437.2	NS	NS	18.67	ND	2.40	0.277	6.68	18.8	23.8	17.5	58.5
GR 31	12/19/2002	23:30	433.0	NS	NS	5.29	0.0513	1.76	0.222	49.2	19.6	91.6	12.9	59.7
GR 40	12/28/2002	18:25	315.4	NS	NS	15.11	0.108	1.67	0.401	38.2	26.2	64.6	24.5	116
GR 50	3/15/2003	3:45	282.0	NS	NS	6.81	0.061	1.69	0.332	22.3	27.0	39.7	19.7	117
GR 51	4/12/2003	18:30	225.0	NS	NS	5.77	0.271	1.77	0.304	22.5	24.2	41.8	23.0	105
GR 60A	5/29/2003	10:15	18.1	NS	NS	4.96	ND	1.54	0.0536	2.14	6.18	3.56	1.54	9.40
GR 60(Duplicate)	5/29/2003	10:20	18.8	NS	NS	5.36	ND	1.52	0.0506	2.10	5.93	3.81	1.51	9.36