

San Francisco Estuary Institute Regional Watershed Program

Concentrations and Loads of Mercury, PCBs, and OC Pesticides Associated with Suspended Sediments in the Lower Guadalupe River, San Jose, California

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SFEI Contribution 86
October 2004

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EXECUTIVE SUMMARY

Mercury, polychlorinated biphenyls (PCBs), and organochlorine (OC) pesticides 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 Bay is listed as impaired for mercury and PCBs (high priority), and OC pesticides (lower priority). Mercury, PCBs, and OC pesticides 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. 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. The Guadalupe River watershed is one of the larger local basins, is a known source of mercury loads associated with historic mining, and is likely source of trace organic contaminants loads associated with legacy urban and agricultural applications. This study assesses the influence of water and sediment runoff processes on concentrations and loads of mercury, PCBs, and OC pesticides in the Guadalupe River during water year 2003.

Rainfall in San Jose during the study year was 15.02 inches or approximately 100% of the 30-year normal (1971-2000). Runoff during the WY 2003 study year was ~61 Mm³ (68 cfs) or ~111% 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 ~79% 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. These data along with turbidity were used by the USGS to estimate SSC data at 15-minute intervals. Estimated SSC ranged from 5-1,180 mg/L and had a flow-weighted mean concentration (FWMC) of 209 mg/L. During the period November 1st to May 31st a total of 10,787 t of suspended sediment was transported past the study location 68% of which was transported in response to the series of floods that occurred during December.

During water year 2003, 26 water samples were collected during stormflow peaks were analyzed for total mercury, other total trace elements (silver, arsenic, cadmium, chromium, copper, nickel, lead, zinc), and organic carbon. Concentrations of total mercury varied from 0.2-18.7 µg/L with a flow-weighted average of 3.9 µg/L. 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 other trace elements correlated with discharge and other 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 perhaps with the exceptions of chromium and nickel which showed weak correlations with mercury when the data were stratified between rising and falling stages of floods. The observations are consistent with

the knowledge that during large floods mercury is mainly sourced from creeks and reservoirs adjacent to or within the New Almaden Mining District. Rainfall intensity in the historic Mining District appeared to greatly influence the concentrations of mercury at the sampling location. When rainfall exceeded certain thresholds, we suggest that new mercury derived from the mining areas was supplied to the stream network and transported downstream resulting in concentrations in excess of 1 µg/L on the falling stages of the storm hydrographs. During lower rainfall intensity storms and on rising stages, no new mercury entered the stream network from the mining areas and mercury concentrations of <1 µg/L were observed in response to mercury loads derived from urban areas or resuspended from within channels. Daily mercury loads varied from 0.0044–20 kg (~ 4,600x). During the study, 116 ± 32 kg of total mercury was transported into lower South San Francisco Bay. Climate during the study year was approximately average, suggesting the load estimate might approximate long-term average. However, there is evidence of occasional massive inputs of contaminated mining debris probably in response to wetter conditions than experienced during our present study. It is presently unknown what influence very dry and wet years will have on the estimation of long-term average loads. These questions are the primary focus of subsequent years of study.

Twenty-two samples were collected from Guadalupe River during storm events and analyzed for PCBs and OC pesticides. Total 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. Unlike mercury, trace organic contaminant concentrations were positively correlated to suspended-sediment concentrations (SSC; $r^2 = 0.51$ to 0.72). The positive correlations observed in Guadalupe River indicate that these compounds originate from diffusely distributed contaminated watershed soil sources, stream sediment deposits, and locally resuspended stream sediment. However, the relative abundance of individual PCB congeners and DDT compounds in Guadalupe River samples varied with discharge and were suggestive of slightly varying sources contributing to contaminant transport under different flow regimes. Patterns indicated that low flow conditions were influenced more by resuspended sediment, whereas high flows transported relatively unweathered material from sources outside of the immediate stream environment. Furthermore, unique contaminant patterns at the onset of storm events suggest first flush effects in this watershed. Daily contaminant loads varied from 0.45 to 240 g t-PCBs, 0.46 to 200 g t-DDT, 0.26 to 174 g t-Chlordanes, and 0.033 to 16.4 g dieldrin. Loading estimates for the period October 2002 to May 2003 were 1.2 ± 0.21 kg t-PCBs, 1.1 ± 0.27 kg t-DDT, 0.79 ± 0.13 kg t-chlordane, and 0.082 ± 0.017 kg dieldrin. Compared to estimates of contaminant loading from the large tributaries entering the Bay from the Central Valley of California, Guadalupe River loading was less by factors of 3.5 to 50; however, it is suggested that a combined loading from the local urbanized tributaries (6,550 km²) would contribute similar magnitudes of PCBs, DDT, and chlordane loads to runoff from the Central Valley (154,000 km²). The magnitude of these loading estimates will likely contribute to delayed recovery of Bay contamination by PCBs, DDT, and chlordane.

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SECTION ONE

INTRODUCTION

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. Approaches to-date have 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 ignore accepted hydrological principles such as seasonal antecedent moisture conditions and runoff, the influence of slope, soil 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. The ability to quantify potential benefits that can result from management actions in the watershed, wetlands, and Bay is also limited. It is hypothesized that present regional 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 five 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 processing in the Bay (such as described by the PCB single box mass balance model (Davis, 2002). The project will 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 al. 2000) in order to accept or reject its use as a tool for estimating loads for management purposes. The last two of these secondary aims will be handled during SPLWG meetings rather than during formal written reports.

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 County Park. RMP sampling over the past decade has shown high concentrations of Hg and PCBs on the estuary margin near the Guadalupe River mouth (e.g. RMP, 2003). Studies on bed sediment contaminant concentration have found that some urban drainage channels 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

OVERVIEW

The methods section of this report is provided to give the reader a general overview of the watershed, the sampling location, the study components and teams, and the field methods. Most specific field methods for the trace organics component of the study and the mercury component of the study are given in the individual report sections.

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 Alamos 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 500 km² (~190 mi²). 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 (these statistics are exclusive of the Sacramento and San Joaquin watersheds that drain greater California). There are five main tributaries in the Guadalupe watershed: Los Gatos Creek, Ross Creek, Guadalupe Creek, Alamos Creek, and Canas Creek. The subwatersheds of Los Gatos Creek, Ross Creek, Guadalupe Creek, and Alamos 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 Loma Prieta (elevation 1,155 m [3,790 ft]).

Sampling during the study was carried out approximately 100 m (300 ft) upstream from where US Highway 101 passes over the Guadalupe River (Figure 2-1b). The bridge at this site connects the main San Jose International Airport grounds to a rental car service center. This site makes use of the recently established USGS stream gauge, Guadalupe River above Highway 101 at San Jose (11169025) (Area = 414 km² or 160 mi²) that replaces the former USGS stream gauge, Guadalupe River at San Jose (11169000) (Area = 378 km² or 146 mi²). Sampling was carried out from this bridge during flood flow and under the bridge during wading stages (Figure 2-2a, b). The reach has been straightened and widened and the cross-section has been modified to a trapezoid to improve flood-discharge transmission. The upper banks 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, and an in-channel floodplain that marks the height of the bankfull discharge (approximately 1.5 year return interval flood) (Figure 2-3). The bed at the sampling location consists of poorly sorted gravels, sands and silts with a median grainsize (D₅₀) of 2-3 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.

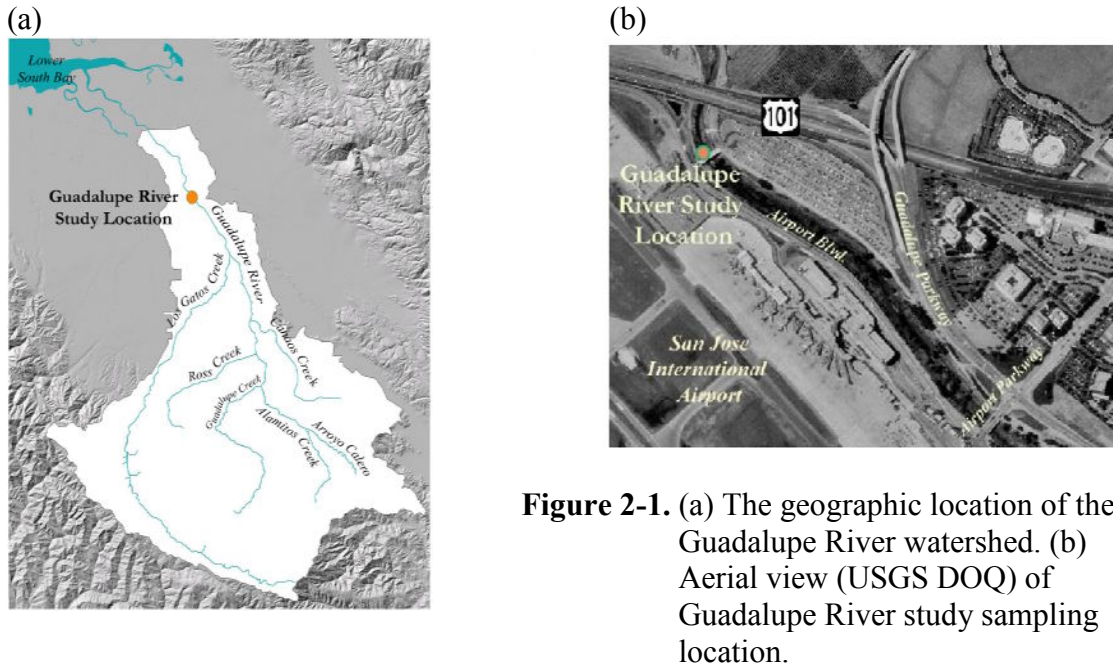


Figure 2-1. (a) The geographic location of the Guadalupe River watershed. (b) Aerial view (USGS DOQ) of Guadalupe River study sampling location.



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.

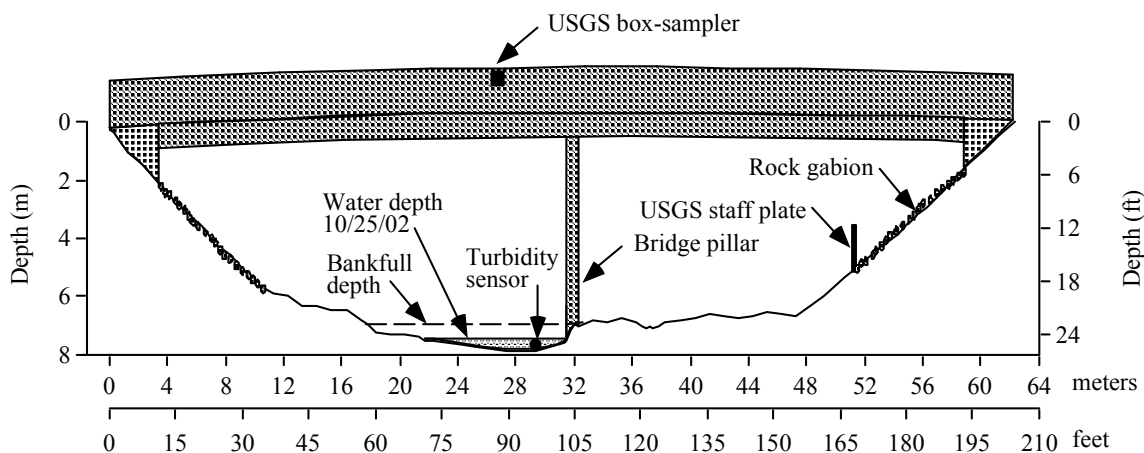


Figure 2-3. Surveyed scale cross-section ($v/h = 2$) of the sampling location indicating the main channel features on October 25, 2002.

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 mercury and other trace elements.

Each component was headed up 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 contaminants 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.

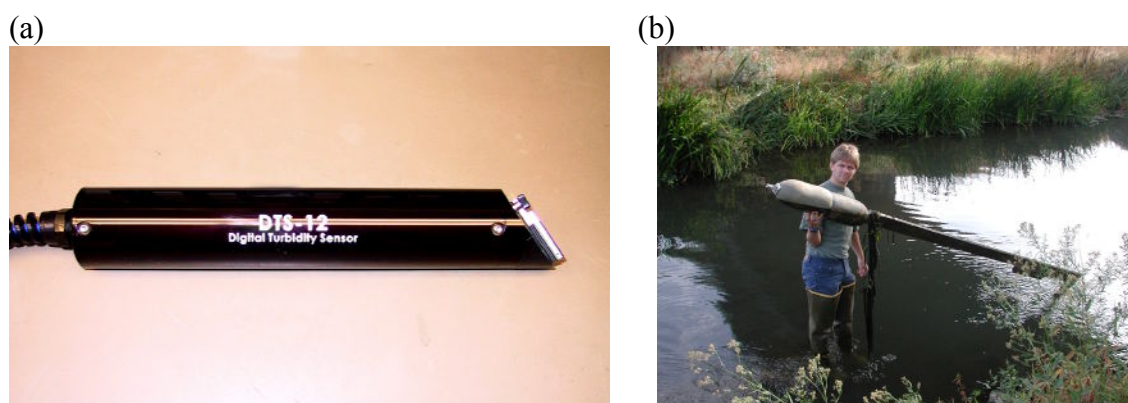


Figure 2-4. The DTS-12 turbidity sensor. a) The DTS-12 Turbidity Sensor. Note the wiper on the right side of the instrument. b) Photo of the installed sensor and bed-mounted boom at the Guadalupe River sampling location.

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-reel 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.

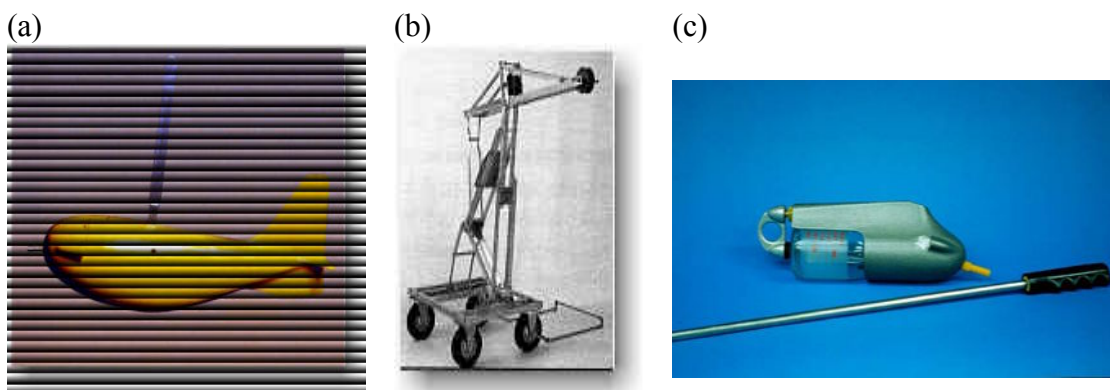


Figure 2-5. The suspended sediment samplers employed by the USGS at the Guadalupe River sampling location. (a) US D-74 depth-integrating sampler, (b) USGS Type A Crane with Type A Four-Wheel Truck and (c) US DH-48 hand-held depth-integrating sampler.

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 other trace elements 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-element 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 element clean polyethylene gloves, did not touch anything with her/his hands except the inner Ziploc™ bag and trace element 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 other trace elements). After operations needing “clean hands” were completed, the trace element 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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SECTION THREE

HYDROLOGICAL PROCESSES

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 gauge 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 2002 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 gauge (11169000) located at St John Street in the City of San Jose (Area = 378 km² or 146 mi²). The average annual runoff for the period WY 1930 - 2003 was 41 Mm³ (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 Mm³ (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 Mm³ (3.21-282 cfs) and averaged ~55 Mm³ (61.8 cfs [daily average]). Runoff during the WY 2003 study year was approximately ~61 Mm³ (68 cfs) or about 111% of the 1971-2000 normal.

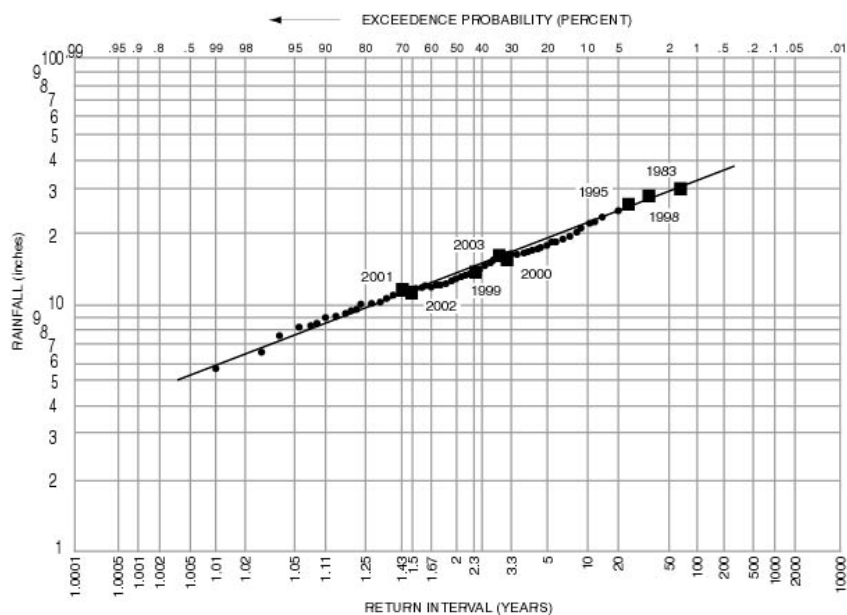


Figure 3-1. Return interval of annual rainfall based on data for the period 1931-2003 (Data downloaded from the Western Region Climate Center web site, WRCC, 2003).

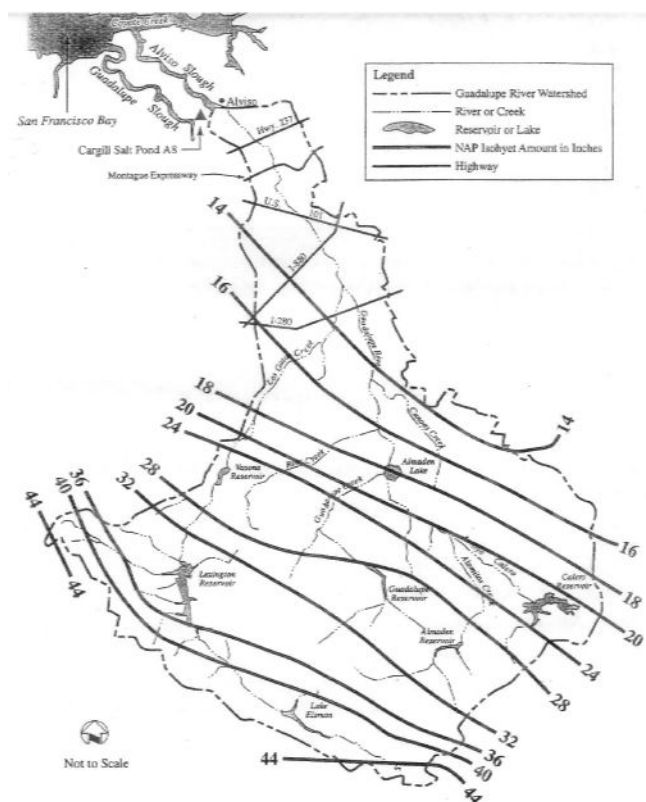


Figure 3-2. Variation of annual average rainfall across the Guadalupe River Watershed (Source: USACE, 2001).

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 79% 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*	1.45	5.39	22.80	5.49	3.87	4.03	6.51	3.48	2.29	1.89	1.79	1.81	60.80
%Annual	2.4	8.9	37.5	9.0	6.4	6.6	10.7	5.7	3.8	3.1	2.9	3.0	100

* Data from new station (11169025). Station 11169000 discontinued after April 2003.

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 relatively short periods of time (hours to a day) with rather longer periods in between (many days to weeks) (Figure 3-3). During the period November 1st 2002 to 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).

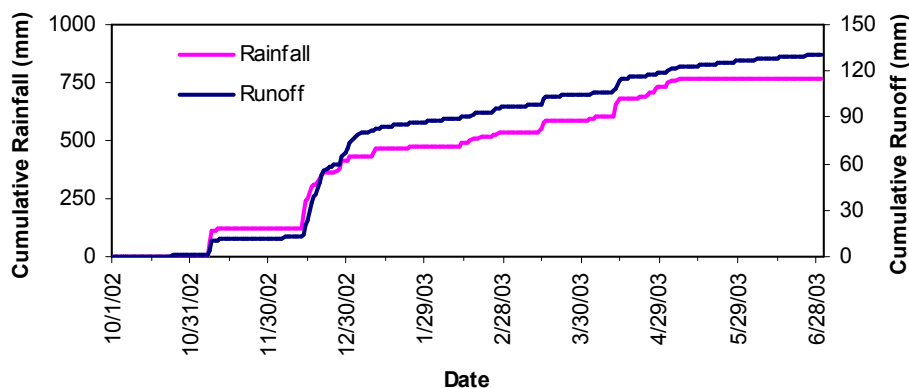


Figure 3-3. Accumulative rainfall and runoff curves for Guadalupe River watershed during WY 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) and a lower watershed location (San Jose). Rainfall data supplied by Santa Clara Valley Water District. Runoff data are supplied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

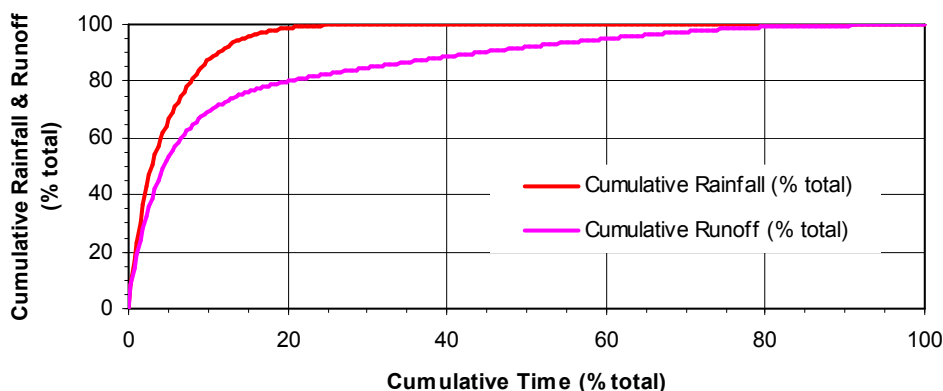


Figure 3-4. Accumulative rainfall and runoff as a percentage of total rainfall and runoff compared to cumulative percentage of time over the period November 1st 2002-June 30th 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) and a lower watershed location (San Jose). 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 gauge (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).

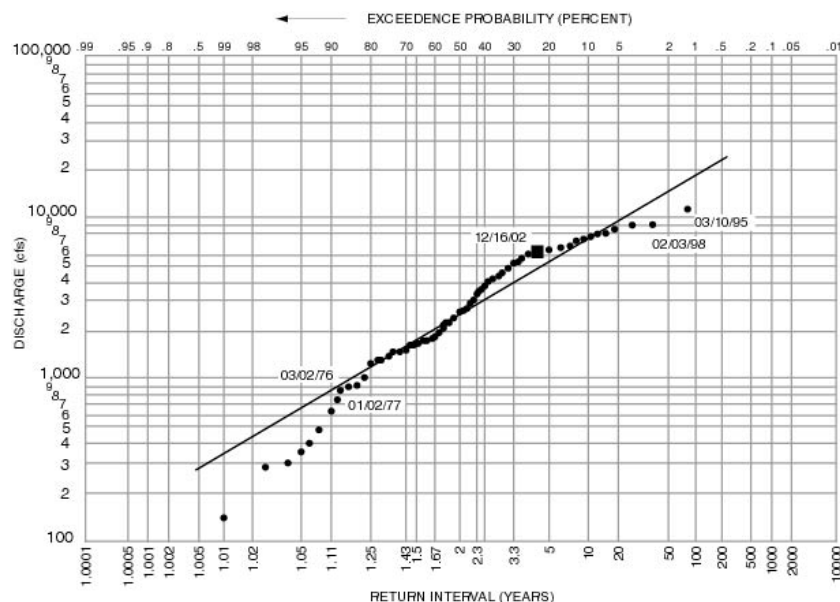


Figure 3-5. Return frequency floods in the Guadalupe River based on the annual series (11169000 data provided by the USGS).

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SECTION FOUR

SUSPENDED SEDIMENT PROCESSES

Rand Eads, Lawrence Freeman, and Lester McKee

INTRODUCTION

There is likely a strong relationship between suspended sediment loads and the transport of PCBs, OC pesticides and mercury into the Bay (Davis et al., 1999; McKee et al., 2003). Water discharge and concentrations of sediments and contaminants vary greatly during storms at time intervals of minutes to hours (McKee et al., 2003). Suspended sediments are relatively cheap to measure at these intervals whereas it is cost prohibitive to sample contaminants during storms at an adequate level to understand transport process. Turbidity is measured in water using optical backscatter and a sensor usually mounted at 90 degrees to the incident light beam. Most turbidity probes are limited to measurement in the range of 0-2000 NTU, but for many applications this range is sufficient to access a river during all climatic conditions. The relationship between turbidity and suspended sediment is confounded by factors such as % organic carbon, floc size and particle density, grain size, and color (Madej et. al., 2002; Pavelich, 2002; Ganju et al., 2003). However, providing these factors either do not vary greatly during floods or vary consistently, a turbidity probe and data logger can be used to estimate time continuous estimates of suspended sediment concentration and loads (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 are 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 show in excess of 10,000 mg/L and a further six locations show between 5,000 and 9,999 mg/L. 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 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 to May 1962. The discharge during this period covered the nearly the full range of river discharge variability and included floods that ranged from 1 year return to the second largest flood in the gauge record (4/2/58 peak = 9,150 cfs). Concentrations measured during the period WY 1957 to 1962 ranged from 3-5,970 mg/L and 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⁻²yr⁻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⁻²yr⁻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 Mm³ an historic annual average load is estimated at 72,563 t (560 t km⁻²yr⁻¹).

STUDY PERIOD (WY 2003)

Continuous Turbidity and Suspended Sediment Concentration

Turbidity was measured at the USGS Hwy 101 gauge on Guadalupe River (11169025) (Area = 414 km² or 160 mi²) 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 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 calibration equation 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 response of suspended sediment concentration to discharge 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.

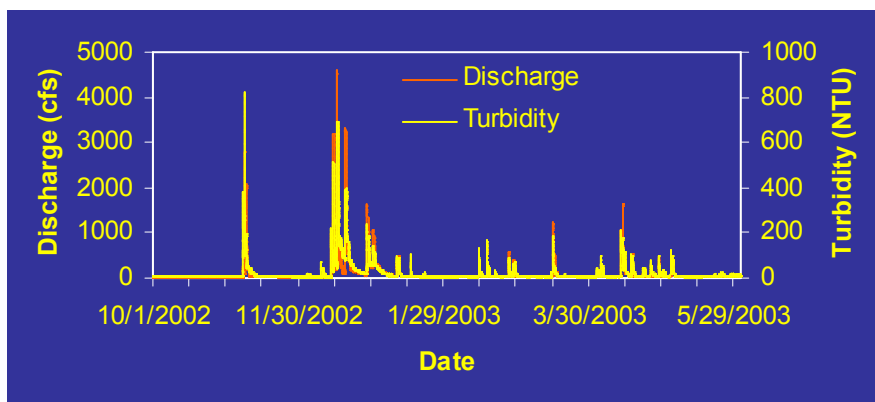


Figure 4-1. The variation of turbidity and discharge during the study period.

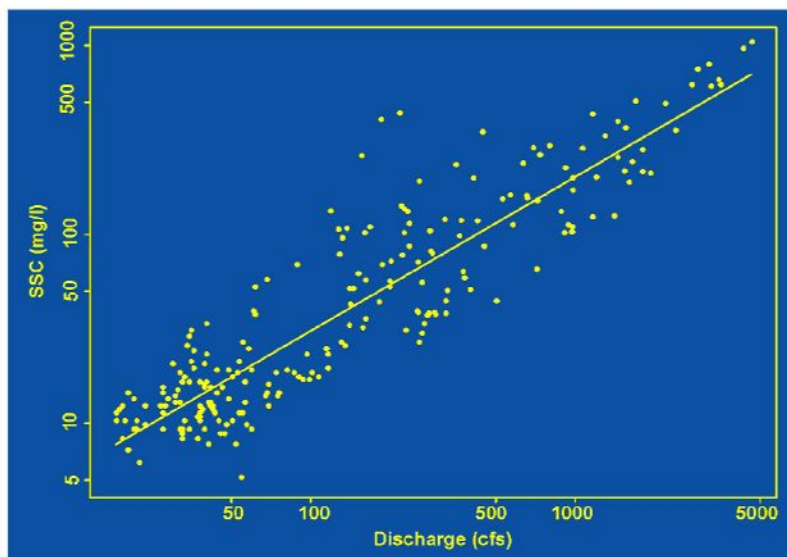


Figure 4-2. Measured suspended sediment concentration as a function of discharge.

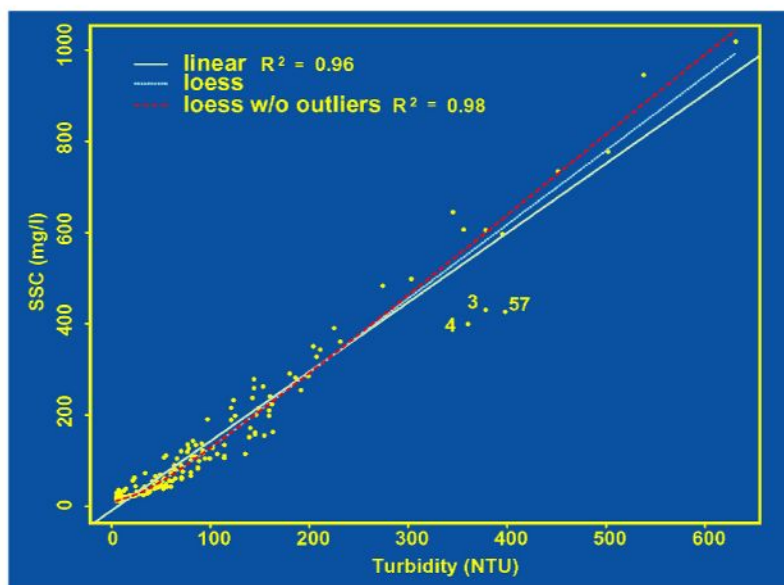


Figure 4-3. Guadalupe WY 2003 Turbidity-SSC calibration.

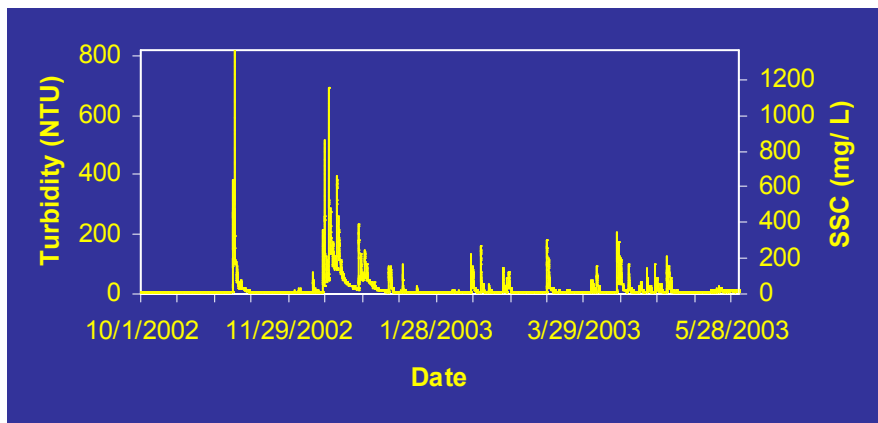


Figure 4-4. Time continuous suspended sediment concentration for the study period generated using the loess (Cleveland, 1979) calibration equation.

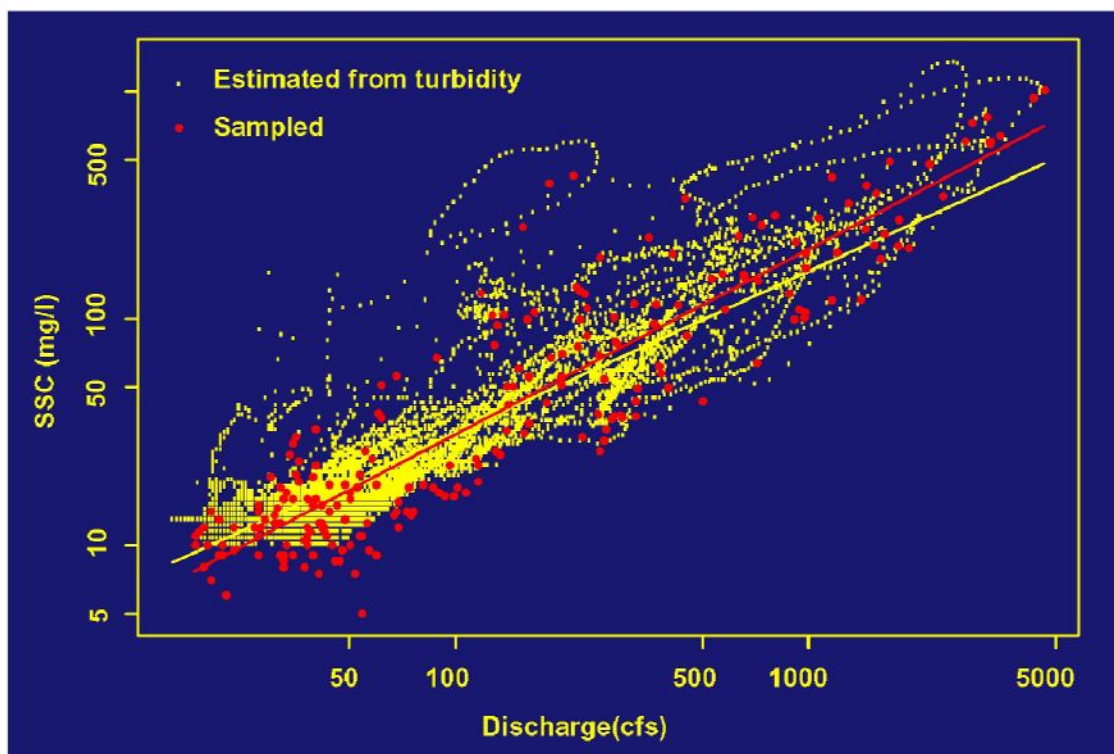


Figure 4-5. A demonstration of the improved detail generated through the use of continuous turbidity measurement to estimate suspended sediment concentration. Note the hysteresis loops that are evident in the estimated data that are not evident in the measured USGS data.

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 <0.062 mm in diameter (silt and clay particles). 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 concentration vs turbidity relationship is when particle size changes.

Suspended Sediment Loads

Daily and monthly WY 2003 suspended sediment data were published by the USGS in May 2004 (Smithson et al., 2004). The water and suspended sediment data at 15-minute time intervals that were used to develop the published daily, monthly and annual summaries are available upon request. Instantaneous suspended sediment concentrations ranged from 5-1,180 mg/L and had a flow-weighted mean concentration of 209 mg/L. Suspended sediment loads were computed at 15-minute intervals and summed for time scales ranging from individual storm events to the seven month total. During the period November 1st to May 31st a total of 10,787 t of suspended sediment was transported past the study location. Sediment load reached a maximum of 619 t hr⁻¹ for the hour ending 9:30 am on December 16th 2002. During that hour, 5.7% of the total load measured during the study was transported through the cross-section at the sampling location. A maximum daily sediment load of 3,275 t (30% 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 (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 (<0.062 mm)	Suspended sediment, sieve diameter percent (<0.125 mm)	Suspended sediment, sieve diameter percent (<0.25 mm)	Suspended sediment, sieve diameter percent (<0.5 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	--	--	--	--

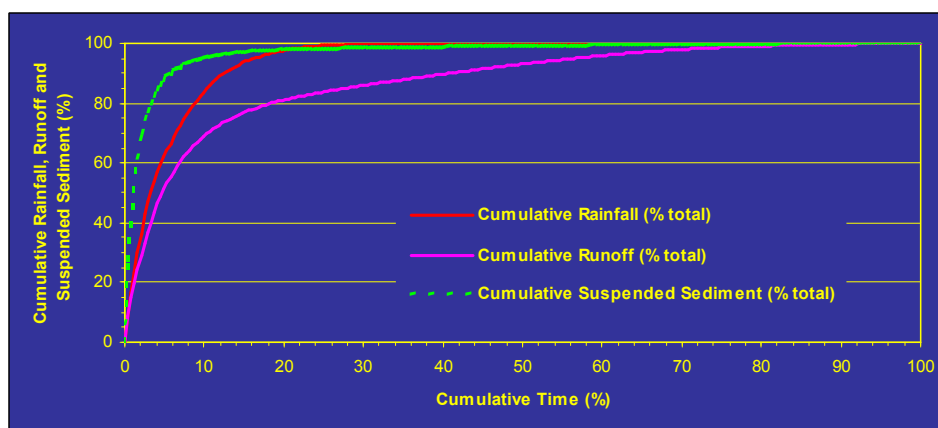


Figure 4-6. Cumulative rainfall, runoff and suspended sediment as a percentage of total rainfall, runoff, and suspended sediment compared to cumulative percentage of time over the period November 1st 2002 to May 31st 2003. Rainfall is the cumulative average of an upper watershed location (Loma Prieta) 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	Nov	Dec	Jan	Feb	Mar	Apr	May	Total
Load (t)	1708.9	7661.2	149.2	192.8	245.4	610.0	219.5	10,787
% Total	15.8	71.0	1.4	1.8	2.3	5.7	2.0	100

Comparisons to Previous Estimates

In terms of annual discharge, WY 2003 was about 111% average (see hydrology section). The measured sediment load for WY 2003 was about 12% 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 than 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 209 mg/L or about 16% 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 Lexington Reservoir during the early 1950s. Both of these hypotheses seem plausible but would require geomorphic study on the history and timing of historic channel cross-section and / or long profile changes to support or reject.

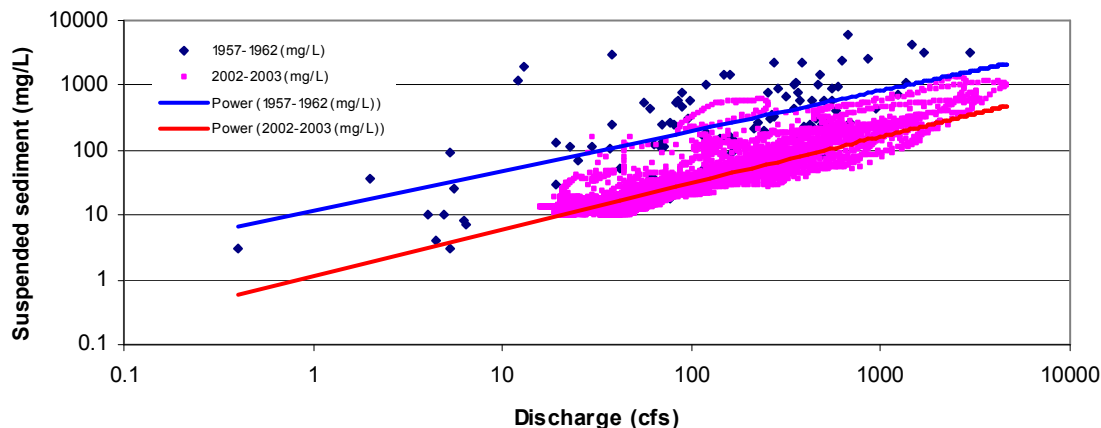


Figure 4-7. Comparison of WY 2003 data with a historical data set collected by the USGS between 1957-1962.

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SECTION FIVE

MERCURY TRANSPORT PROCESSES

Lester McKee and Jon Leatherbarrow

ABSTRACT

San Francisco Bay is listed as impaired for mercury by the State of California and 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; recommendations are more stringent for pregnant woman and children. 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 important for developing load allocation strategies and resolving mercury impairment.

During water year 2003, 26 water samples were collected during stormflow peaks on Guadalupe River at the USGS discharge gauge (11169025) near San Jose International Airport. These samples were analyzed for total mercury, other total trace elements (silver, arsenic, cadmium, chromium, copper, nickel, lead, zinc), and organic carbon. In addition, 238 water samples were gathered for analysis of suspended sediment concentrations and 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 from 0.2–18.7 µg/L with a flow-weighted average of 3.9 µg/L. 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. There were weak correlations between mercury, chromium, and nickel when the data were segregated for rising and falling stage but these were not significant perhaps due to a limited number of data points. In contrast, concentrations of suspended sediment, particulate organic carbon, and other trace elements correlated with discharge and other 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 perhaps with the exceptions of chromium and nickel. The observations are consistent with the knowledge that mercury is mainly sourced from creeks and reservoirs adjacent to or within the New Almaden Mining District. Rainfall intensity in the historic Mining District appeared to greatly influence the concentrations of mercury at the sampling location. When rainfall exceeded certain thresholds, we suggest that new mercury derived from the mining areas was supplied to the stream network and transported downstream resulting in concentrations in excess of 1 µg/L on the falling stages of the storm hydrographs. During lower rainfall intensity storms and on rising stages, no new mercury entered the stream network from the mining areas and mercury concentrations of <1 µg/L were observed in response to mercury loads derived from urban areas or resuspended from within channels.

Short-term relationships between suspended sediment and total mercury, rainfall distributions and intensities, and knowledge of mercury source areas within the watershed were used to estimate loads. Hourly loads of total mercury varied from 0.0002–5.3 kg and daily loads varied from 0.0044–20 kg (~ 4,600x). During the study, 116 ± 32 kg of total mercury was transported into lower South San Francisco Bay. This estimate of total mercury load is ~4x greater than previously reported in studies on the Guadalupe River that did not capture such large floods occurring after intense rainfall. Climate during the study year was approximately average, suggesting the load estimate might approximate long-term average. However, there is evidence of occasional massive inputs of contaminated mining debris probably in response to wetter conditions than experienced during our present study. It is presently unknown what influence very dry and wet years will have on the estimation of long-term average loads. These questions are the primary focus of subsequent years of study.

INTRODUCTION

Mercury is a potent neuro-toxicant 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). Sediment associated mercury is the phase that typically regulates mass transport (loading) to aquatic systems. Once this particulate phase mercury repartitions and transforms into dissolved biologically reactive phases, mercury may bio-accumulate in the tissues of aquatic organisms over their lifespan and bio-magnify up through the food web to fish, birds, aquatic mammals and humans (Davis et al. 2003). Although there is not a direct correlation between total mercury loading to a system and methyl-mercury (the most toxic form of mercury), systems that have high mercury loadings usually have methyl-mercury related water quality problems. The regulatory mechanism immediately available is to assign waste load allocations based on the relative magnitude of each total mercury source to the system.

Continuous monitoring over the past decade by the 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 also poses a significant human health risk (OEHHA, 1997, 1999; Davis et al., 2002). The State of California has listed all segments of San Francisco Bay as water bodies impaired by mercury, and the California Office of Environmental Health Hazard Assessment has issued a health advisory to people who consume fish caught from the Bay (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 waste load allocations (Johnson and Looker, 2003).

Mercury in San Francisco Bay enters via two main external pathways: the Sacramento River and the Guadalupe River (Johnson and Looker, 2003). Beginning in the 1840's, 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. The Sacramento River and Guadalupe River watersheds were contaminated during this long history of mercury and gold mining (Alpers and Hunerlach, 2000). 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. Several recent studies made estimates of mercury loads in the lower Guadalupe River (Leatherbarrow et al., 2002; Thomas et al., 2002), but these studies did not investigate mercury concentration during large flood events when most of the mercury is likely to be transported (McKee et al., 2003). Thus, the processes of mercury transport and the magnitude of mercury loads entering the Bay from the historic New Almaden Mining District in Guadalupe River watershed remains a large uncertainty in the mercury budget of the Bay, yet is of paramount importance for developing load allocations strategies (Johnson and Looker, 2003). This study assists local environmental management efforts by addressing these vital data gaps and makes important contributions to the science of fluvial mercury transport process.

METHODS

Sampling

Between November 11th 2002 and May 29th 2003, water samples were gathered during six storms at the USGS discharge gauge site, Guadalupe River at Highway 101 (11169025) (Figure 5-1). The area upstream from this gauging point is 414 km². The USDA Redwood Sciences Laboratory and USGS collaborated to estimate 15-minute suspended sediment concentration from November 1st 2002-May 31st 2003. This was achieved by the combination of a DTS 12 turbidity probe equipped with a wiper and the USGS standard method for seasonal daily loads (Edwards and Glysson, 1999). In excess of 23,000 turbidity data points and 238 discrete suspended sediment concentrations data points were generated. Daily summaries of the sediment and water discharge data were published by the USGS (Smithson et al., 2004) and 15-minute data are available from USGS upon request.

A total of 26 water samples for mercury and other trace element analysis were collected using clean-hands protocols (e.g. Bloom, 1995; Hurley et al., 1995; Colman and Breault, 2000). 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.

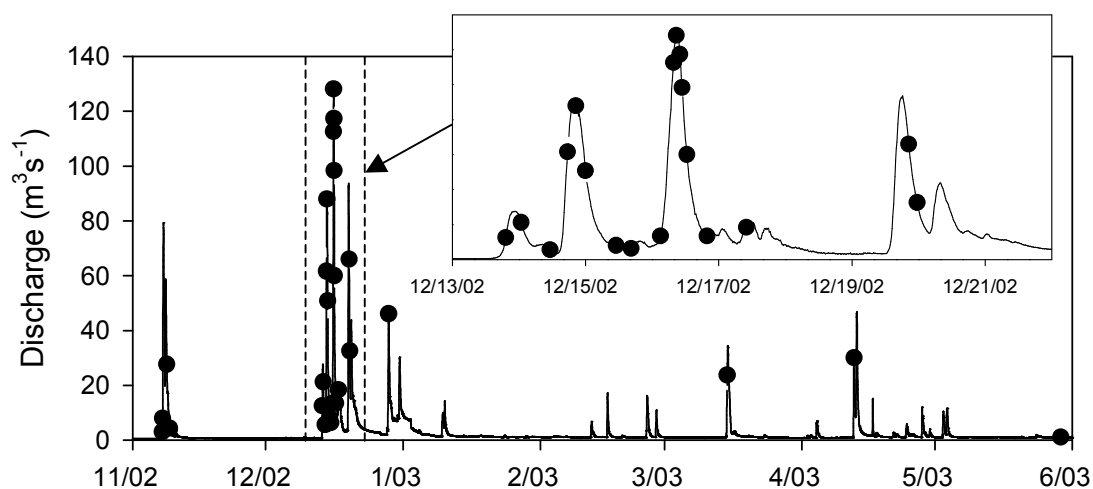


Figure 5-1. Water sampling for total mercury and other total trace elements concentrations relative to discharge during the study period.

Laboratory Analysis Methods

The 26 water samples were analyzed for total mercury (Hg), other total trace elements (silver, arsenic, cadmium, chromium, copper, nickel, lead, zinc), suspended sediment concentration (SSC), dissolved organic carbon (DOC), and particulate organic carbon (POC). Analysis of other trace elements was included in this study to help understand the geochemical differences between runoff derived from the lower versus the upper watershed. SSC, DOC and POC were measured because of their likely association with mercury and their use for improving loads estimation.

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 other trace element analysis were acidified to a final concentration of 1% v/v nitric acid (HNO₃), and SSC, DOC and POC water samples were refrigerated at 4°C in the dark until analysis. Mercury samples were analyzed with cold vapor atomic fluorescence following U.S. EPA method 1631e (USEPA, 2002). Other trace element samples were analyzed using ICP-MS following U.S. EPA method 1638 (USEPA, 1996). SSC was measured gravimetrically following the methods of (Guy, 1969). DOC and POC were analyzed by catalytic combustion using U.S. EPA method 415.1 (USEPA, 1983).

Quality Assurance

The mercury and other trace element 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 analytical duplicates divided by the average of the duplicates was within the target range of ±25% without exception (Table 5-1). A single field replicate yielded a RPD of 7.6% for mercury and 0.4-6.8% for other trace elements. 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 5-1). The quality assurance samples included one method blank for each analytical batch of other trace elements and three method blanks for each batch of mercury analyses. Other 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 5-1). 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 5-1. Quality control parameters of mercury and other 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

Concentrations of total mercury varied over two orders of magnitude (105x) from 0.2-18.7 µg/L with a flow-weighted average of 3.9 µg/L (Table 5-2). Concentrations of other trace elements showed less variability. Maximum total mercury concentrations did not coincide in a predictable way to peaks in discharge (Figure 5-2). 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 as high as December 19th even though both discharge and SSC were greater. Concentrations of the other trace elements more closely followed discharge and SSC. However, silver, arsenic, cadmium, copper, and zinc appear to have 2-4 data points that fall above the general trend in the data (Figure 5-3). A Spearman Rank correlation analysis was performed using the whole data set to determine the relative significance of correlations between parameters (Table 5-3). Mercury did not correlate with any other parameter measured during this study. However, there were weak correlations between mercury and both chromium and nickel when the data were segregated for rising and falling stage but these were not significant perhaps due to a limited number of data points. In contrast, there were significant correlations between all other trace elements and between instantaneous discharge, SSC and all other trace elements. Organic carbon does not appear to strongly influence the transport of mercury and other trace elements, with the exception of copper, during flood stage in the lower Guadalupe River.

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 funding have constrained sampling intervals to either routine or periodic sampling, with minimal reference to discharge (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

Table 5-2. Concentrations measured during discrete sampling in the Guadalupe River from November 2002-May 2003.

Date	Time	Discharge (m ³ /s)	SSC (mg/L)	DOC (mg/L)	POC (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)
11/7/2002	16:30	2.4	43	ND	ND	0.2	0.03	4.2	0.7	9	43	27	19	191
11/7/2002	18:00	5.8	219	ND	ND	0.5	ND	ND	ND	ND	ND	ND	ND	ND
11/8/2002	17:00	20.3	101	ND	ND	0.4	ND	ND	ND	ND	ND	ND	ND	ND
11/9/2002	7:30	3.3	54	ND	ND	4.7	ND	ND	ND	ND	ND	ND	ND	ND
12/13/2002	19:18	9.2	342	8.9	<DL	0.3	0.10	2.9	0.6	23	40	41	31	152
12/14/2002	0:46	15.5	107	6.1	0.5	0.3	<DL	1.8	0.1	9	14	19	8	50
12/14/2002	11:15	4.2	27	5.4	0.5	0.4	0.03	1.7	0.1	4	8	7	3	24
12/14/2002	17:30	56.4	477	4.5	0.3	0.7	0.16	2.4	0.6	28	41	52	44	193
12/14/2002	20:30	110.9	577	3.9	0.8	0.6	0.13	2.6	0.7	57	46	113	47	188
12/15/2002	0:00	60.5	359	4.6	0.3	0.6	<DL	1.9	0.2	30	19	64	16	77
12/15/2002	11:00	7.9	77	5.1	0.3	0.5	<DL	1.7	0.1	14	8	31	3	21
12/15/2002	16:30	6.1	39	5.5	<DL	0.5	0.03	1.7	0.1	8	8	15	3	22
12/16/2002	3:00	13.9	58	4.6	<DL	0.2	<DL	1.5	0.1	6	8	13	5	33
12/16/2002	7:45	145.8	831	4.0	0.7	1.3	0.12	2.1	0.6	63	45	109	46	171
12/16/2002	8:45	168.1	1,016	4.4	0.7	2.1	0.13	2.7	0.7	71	52	149	52	188
12/16/2002	10:00	152.5	1,072	5.2	0.6	2.1	0.13	2.5	0.6	73	46	151	41	152
12/16/2002	10:45	125.5	1,041	5.7	0.9	3.4	0.10	2.2	0.5	98	50	189	38	148
12/16/2002	12:30	72.7	749	6.3	0.4	3.2	0.08	1.8	0.3	86	34	169	24	100
12/16/2002	19:45	14.0	318	7.3	0.5	4.7	0.11	1.7	0.1	34	15	71	9	40
12/17/2002	10:00	19.7	154	5.5	<DL	6.7	0.05	1.4	0.1	21	14	36	9	53
12/19/2002	20:30	80.8	540	4.0	2.7	18.7	<DL	2.4	0.3	7	19	24	18	59
12/19/2002	23:30	37.0	444	5.3	2.3	5.3	0.05	1.8	0.2	49	20	92	13	60
12/28/2002	18:25	54.4	335	2.2	1.4	15.1	0.11	1.7	0.4	38	26	65	25	116
3/15/2003	3:45	26.1	213	6.1	4.3	6.8	0.06	1.7	0.3	22	27	40	20	117
4/12/2003	18:30	33.9	243	ND	ND	5.8	0.27	1.8	0.3	23	24	42	23	105
5/29/2003	10:15	1.1	56	1.8	0.7	5.2	<DL	1.5	0.1	2	6	4	2	9
	Number	26	26	21	17	26	17	23	23	23	23	23	23	23
	Minimum	1.1	27	1.8	0.3	0.2	0.03	1.4	0.1	2	6	4	2	9
	Maximum	168.1	1,072	8.9	4.3	18.7	0.27	4.2	0.7	98	52	189	52	193
	Max/Min	151	40	5	14	105	9	3	13	46	9	51	34	21
	Mean	48.0	365	5.1	1.1	3.5	0.10	2.1	0.3	34	27	66	22	99
	FWMC	-	691	4.7	1.0	3.9	0.12	2.2	0.5	56	38	110	35	137

FWMC = Flow-weighted mean concentration.

<DL = Less than detection limit.

ND = No data.

concentrations found in 34 watersheds around the world were collated (Figure 5-4). The interpretation of Figure 5-4 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 greater 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

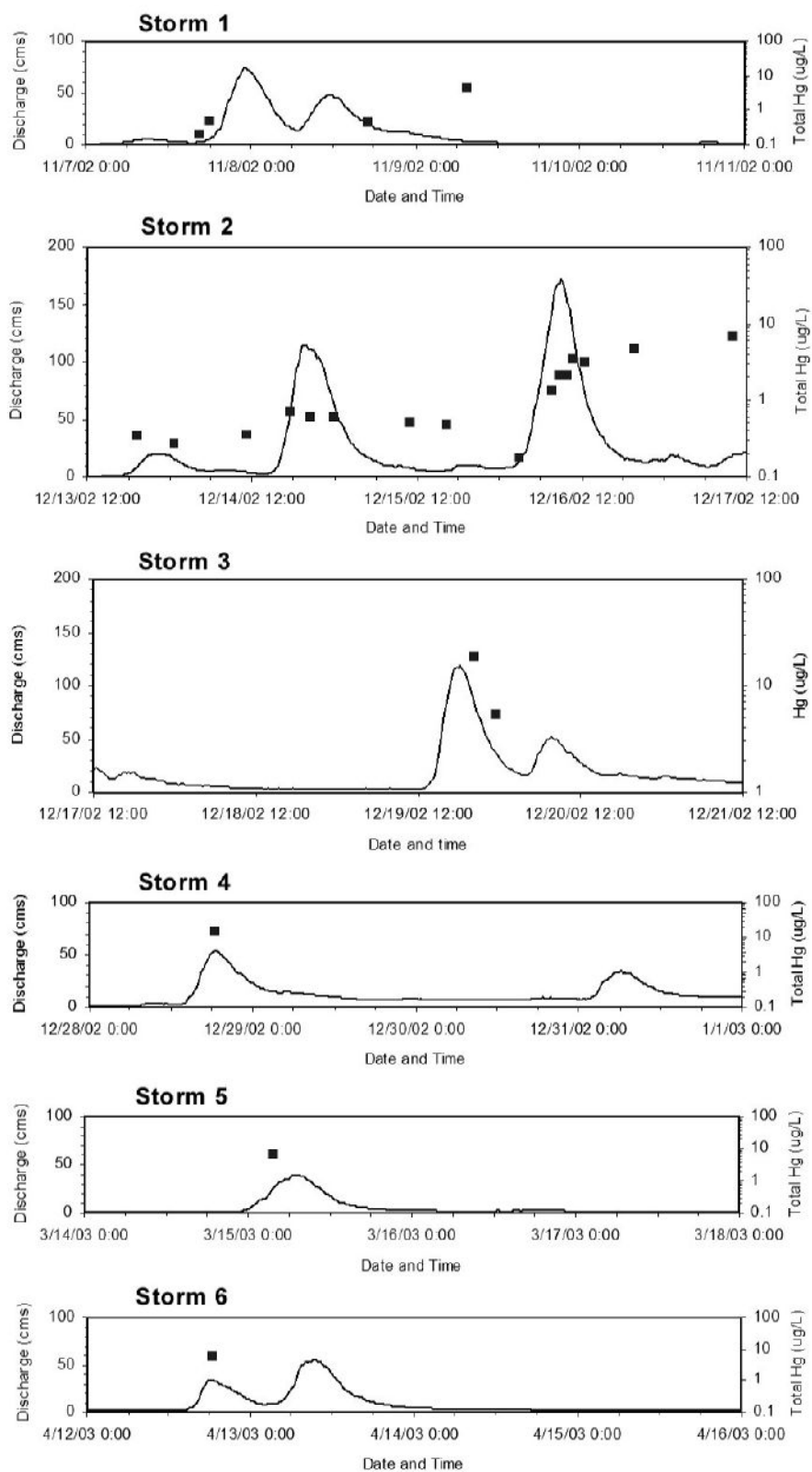


Figure 5-2. Concentrations of total mercury during storms on the Guadalupe River. Note: cms = cubic meters per second (m^3/s).

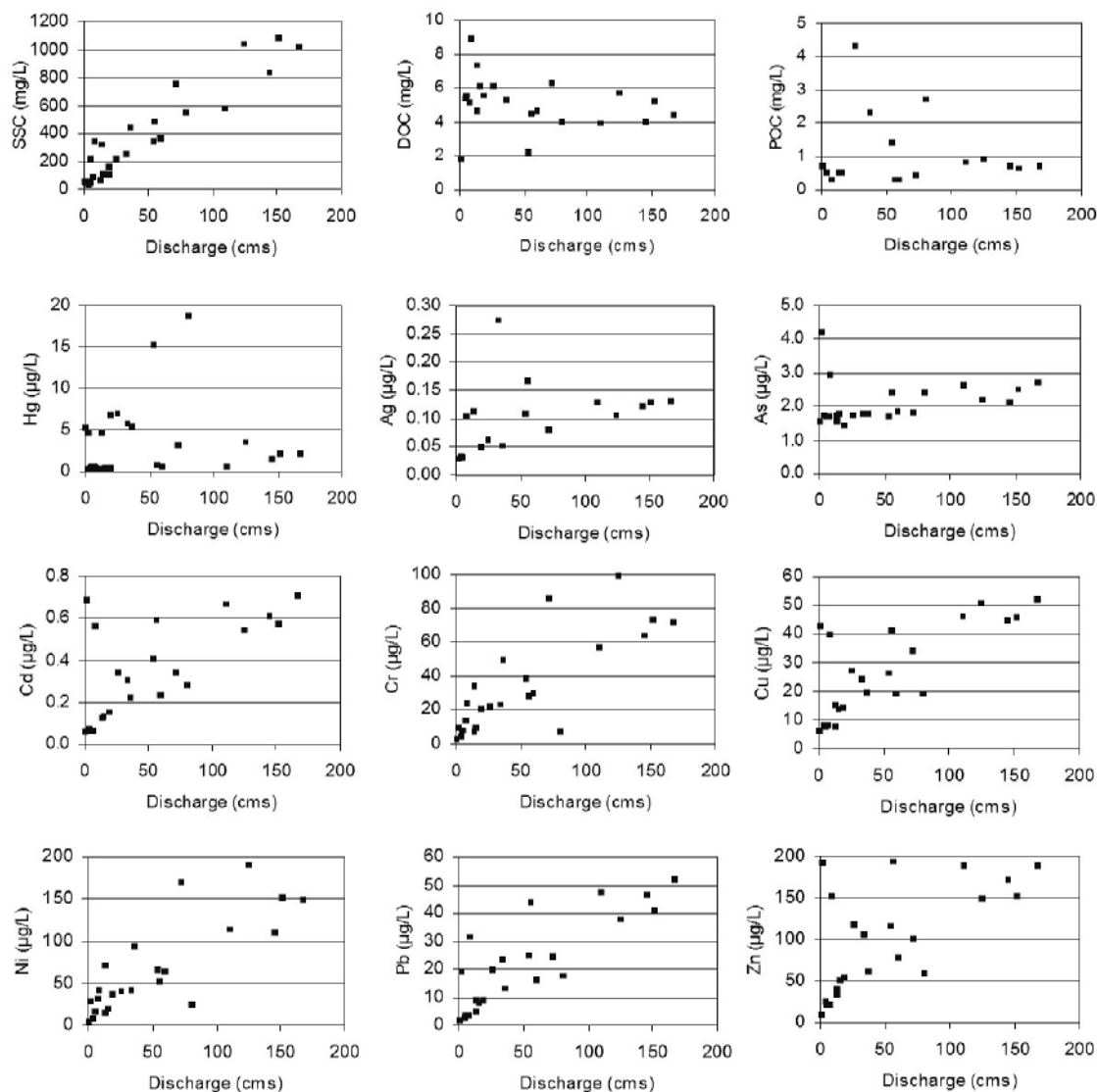


Figure 5-3. Concentrations of suspended sediment, organic carbon, mercury, and other trace elements as a function of discharge.

Table 5-3. Spearman correlation matrix comparing trace element concentrations and instantaneous discharge (Inst. Q), suspended sediment concentrations (SSC), dissolved organic carbon (DOC), and particulate organic carbon (POC).

	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 ***	-----

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

between 30-90 ng/L. Concentrations in excess of 100 ng/L are typically only found in watersheds where there are specific 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 mercury release events (e.g. Gambonini tailings dam failure) (>100,000 ng/L) (Whyte and Kirchner, 2000).

The Guadalupe River exhibits total mercury concentrations of a magnitude consistent with other watersheds around the world that are contaminated with mercury-laden mining debris (Figure 5-4) (e.g. Gray et al., 2000; Carroll et al., 2000; Ganguli et al., 2000; Blum et al., 2001). 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 outlined above, concentrations in the Guadalupe River of <100 ng/L might have

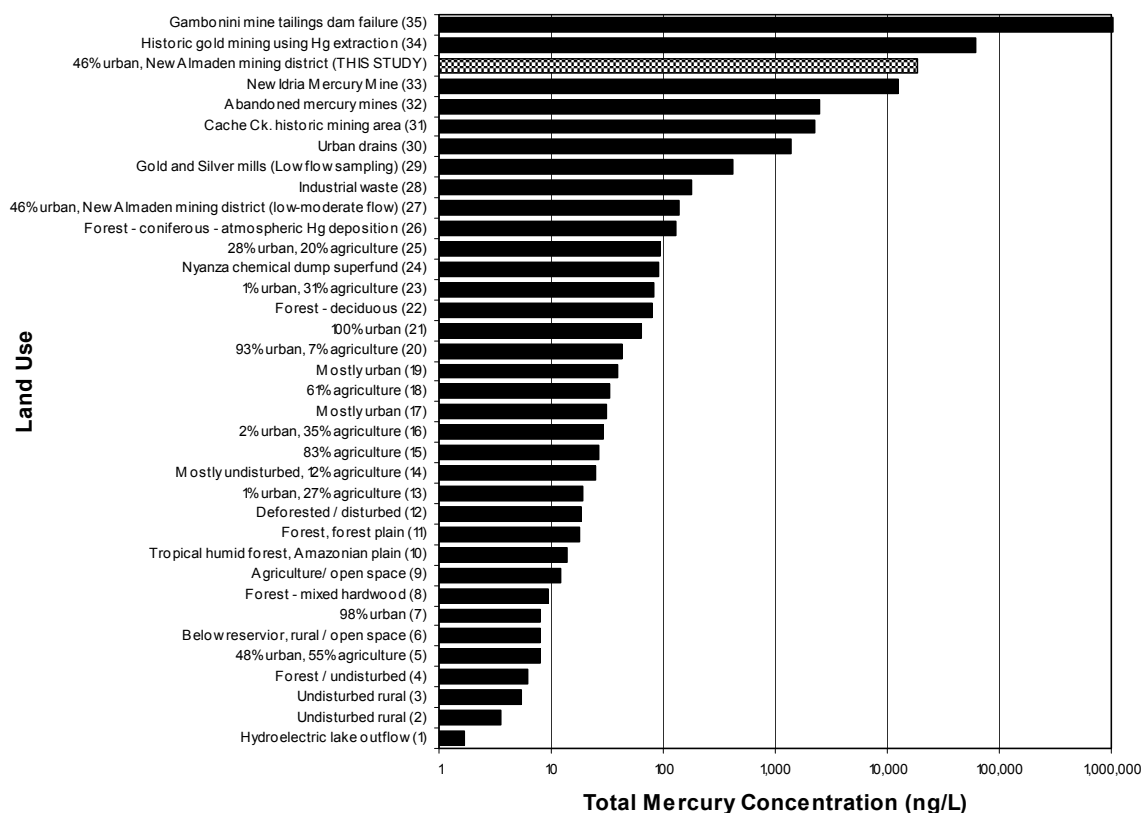


Figure 5-4. Maximum total mercury concentrations reported in the literature for a range of land use and land management conditions. 1. La Grande Hydroelectric Lake outflow, Quebec, Canada (Schetagne et al., 2000); 2. Sudbury R., site B2, Massachusetts (Waldron et al., 2000); 3. Sudbury R., site B1, Massachusetts (Waldron et al., 2000); 4. Serra do Navio experimental site, NE Amazon, Brazil (Fostier et al., 2000); 5. Milwaukee R. at Easterbrook, Wisconsin (Hurley et al., 1995); 6. Sacramento R., below Keswick Dam, California (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. Lehstehach 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).

been predicted. This seems to hold true for the Los Gatos sub-watershed, the largest tributary of the Guadalupe River, 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 historic New Almaden Mining District, the largest mercury mining operation in North America between 1845-1975 (Rytuba and Enderlin, 1999). Although mines comprise <1% of the land use within the watershed area, runoff from historic mining areas and mercury stored behind reservoirs and in stream bed and banks deposits provide an ongoing source of mercury for transport during floods.

Total Mercury Variation Over the Sampling Period

During the wet season of WY 2003, concentrations of total mercury did not vary consistently in relation to discharge, suspended sediment, organic carbon, or other trace element concentrations when all the data were analyzed together (Figure 5-3; Table 5-3). These results contrast with previous studies on other watersheds that have demonstrated relationships between suspended sediment and mercury concentrations (e.g. Balogh et al., 1997; Whyte and Kirchner, 2000; Domagalski, 2001; Lawson and Mason, 2001) and relationships between organic carbon and mercury (e.g. Hurley et al., 1995; Allen and Heyes, 1998; Scherbatskoy et al., 1998; Schwesig and Matzner, 2001). 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 gauge (about 3 km 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 $\mu\text{g/L}$, and between 92-98% of the mercury was transported in particulate forms (Thomas et al., 2002). There were weak correlations observed between mercury and both chromium and nickel when the data were segregated between rising and falling stages of the hydrographs but these were not significant due probably due to limited number of data. Chromium and nickel are often found in mercury mining areas of silica-carbonate type in association with mercury (Bailey and Everhart, 1964; Rytuba, 2000). In general, our observations on the Guadalupe River are consistent with and reflect the heterogeneous nature (in space and time) of mercury release from mining sources and transport in the watershed during large floods.

Careful stratification of the data showed several shorter time periods when mercury and suspended sediment did co-vary. For example, during the period from the start of the study through to December 16th 2002 at 10 am, a separate linear relationship was observed on both the rising and falling stages of individual flood peaks. We propose that this observation results from a difference in the origin of water. During the rising stage, most of the water emanates from the middle and lower urbanized areas of the watershed where incident rainfall is lower but impervious surfaces and efficient drainage transports urban sources of mercury quickly to the sampling location (Figure 5-5(a)). During the falling stages, water from the upper watershed arrives at the sampling location carrying with it greater concentrations of mercury derived from resuspension and / or bed and bank erosion in contaminated tributary areas (Figure 5-5(a)), a hypothesis consistent with proposals by previous authors (Thomas et al., 2002; Tetra Tech 2003). After December 16th 2002 at 10:00 am, the character of the mercury-suspended sediment relationship changed; increasing in a non-linear fashion during the falling stages of the

December 16th flood peak (Figure 5-5(b)). This observation suggests that the mercury source-transport character in contaminated areas changed relative to the sources of water and sediment from other lesser contaminated areas (Figure 5-5(b)). Some additional sources of mercury were activated and began to provide an increased quantity of mercury to the stream network. In addition, there were a number of outliers that could not be explained using simple regression relationships (Figure 5-5(a, b)). In order to determine the causes of these observations, the operation of contaminated reservoirs and variation in runoff associated with storm rainfall intensity in the New Almaden Mining District were investigated to determine the overall character of mercury concentrations during the entire wet season and develop a defensible conceptual model of sources, pathways and loadings of mercury in the Guadalupe River watershed that would hold true with water years of varying annual discharge.

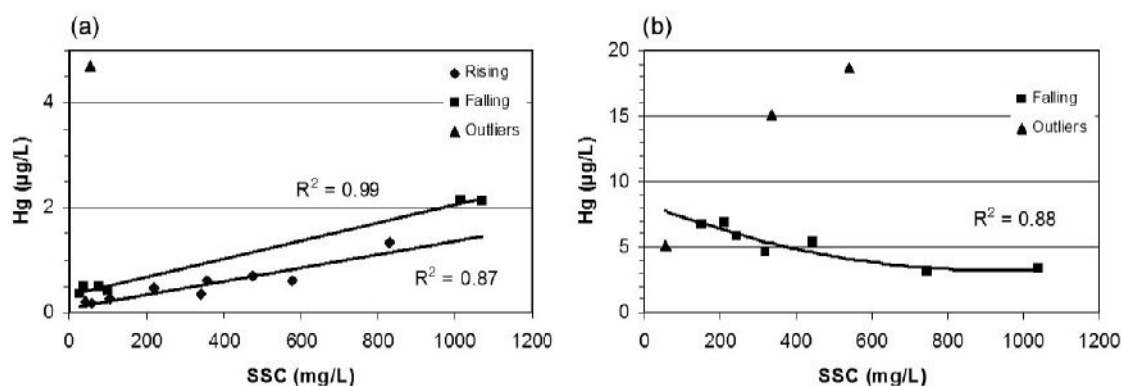


Figure 5-5. Relationships between mercury and suspended sediment for several short periods during water year 2003. (a) Start of the study (11/7/2002) to 12/16/2002 10:00 am. (b) 12/16/2002 10:00 am to the end of study (05/29/2003).

Mercury Source Heterogeneity in the Guadalupe River Watershed

There are five main subwatersheds and four main reservoirs in the Guadalupe River watershed. A number of previous studies have described mercury concentrations in reservoir water and sediments and in stream 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 5-6). 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. 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 large variation of mercury concentrations around the watershed explains the lack of a consistent relationship between mercury and any other parameter collected during this study. Water flowing from each of the subwatershed areas has different geochemical characteristics. The timing and total contribution of each source area differs

depending on the spatial distribution of rainfall and antecedent soil moisture conditions for each flood event.

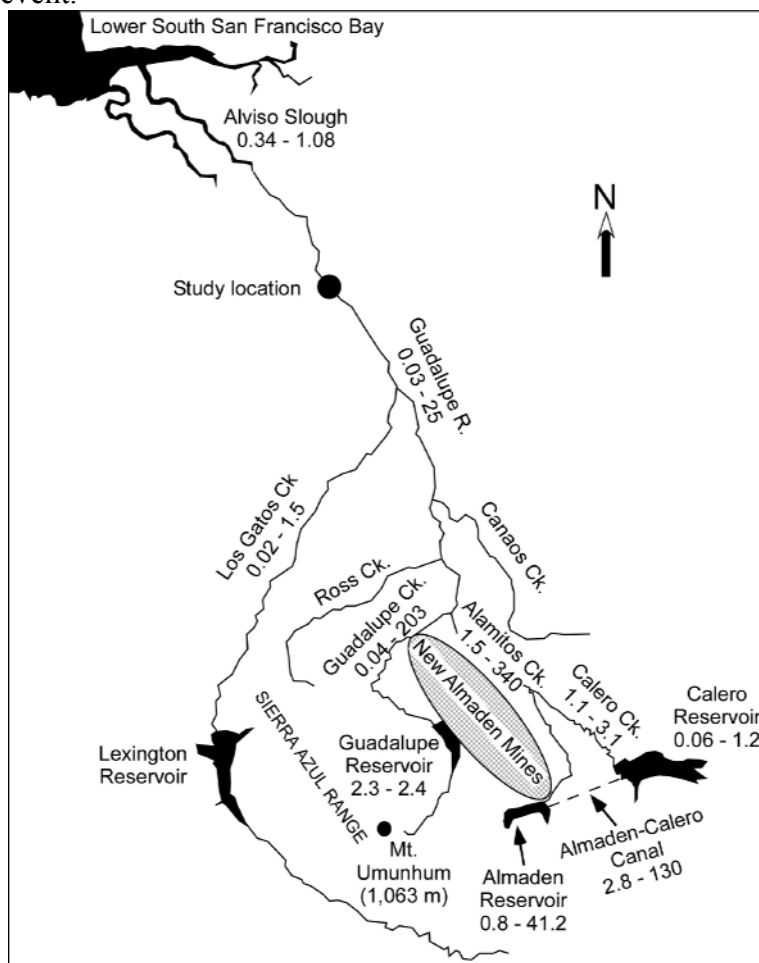


Figure 5-6. Total mercury concentration ($\mu\text{g/g}$) in creek and reservoir sediments of the Guadalupe River watershed (Leatherbarrow et al., 2002; Thomas et al., 2002; Tetra Tech 2003).

Reservoir Hydrology and Mercury Concentrations

Release water from the three reservoirs (Calero, Almaden, and Guadalupe) that receive runoff from the New Almaden Mining District and that are most contaminated might exert some influence on mercury concentrations in the lower watershed. The Calero and Almaden Reservoirs are located in the Alamos Creek subwatershed, whereas, the Guadalupe Reservoir is located in the Guadalupe Creek subwatershed. Previous water column sampling during summer months suggests typical water column concentrations of between 0.005-0.020 $\mu\text{g/L}$ in the Almaden and Guadalupe Reservoirs and 0.001-0.004 $\mu\text{g/L}$ in the Calero Reservoir (Tetra Tech 2003). Tetra Tech (2004) measured concentrations in the out flow waters of the Almaden Reservoir in April 2004 of 0.037 and 0.050 $\mu\text{g/L}$. Summer and winter concentrations are 5 orders of magnitude

less than maximum concentrations found in the lower watershed during the present study and indicate that reservoir discharge, no matter how large, could not be the direct cause of the high concentrations observed in the lower Guadalupe River.

It is perhaps possible that reservoir releases may cause scour of contaminated sediment downstream of the reservoirs. The District increased release from Guadalupe Reservoir to Guadalupe Creek on December 13th from $\sim 0.1 \text{ m}^3/\text{s}$ to $\sim 0.2 \text{ m}^3/\text{s}$. Discharge at this level was maintained until December 20th when it was reduced back to $< 0.1 \text{ m}^3/\text{s}$. It was increased to $1.1 \text{ m}^3/\text{s}$ on December 30th when reservoir storage was over flood control rule curve. On December 19th, release from Almaden Reservoir to Alamitos Creek was increased from $< 0.1 \text{ m}^3/\text{s}$ to $\sim 0.7 \text{ m}^3/\text{s}$. It was maintained at the discharge until December 27th when it was increased to $\sim 1.6 \text{ m}^3/\text{s}$. On December 30th it was increased again to $\sim 2.0 \text{ m}^3/\text{s}$. Releases of this magnitude are much less than the discharges recorded at the gauging stations on these creeks downstream (Guadalupe Creek December 16th-31st: $0.3\text{-}5.3 \text{ m}^3/\text{s}$; Alamitos Creek December 18th-31st: $1.2\text{-}5.0 \text{ m}^3/\text{s}$). These observations suggest that any scouring associated with reservoir release is insignificant compared to scouring associated with runoff directly associated with storm rainfall. Reservoir management does not appear to play a dominant role in the cause of mercury concentrations observed in the Guadalupe River at our sampling location in the lower watershed during this study.

Rainfall Intensity and Mercury Concentrations

Conceptually, new mercury-laden sediment supply to the stream network of the Guadalupe River watershed may be derived by at least four mechanisms: landslides and debris flows directly entering the stream network, bank failures and slumps, bed erosion and resuspension, and overland flow that carries contaminated sediment particles. Overland flow occurs when rainfall intensity exceeds soil infiltration rate and positive pore pressures within shallow soil horizons force some rainwater back to the surface after initial infiltration (called "through-flow"). Most typically this condition is attained at the watershed scale either when rainfall for the season-to-date exceeds some watershed specific threshold amount (a function of soil properties and climatically influenced geomorphic evolution) or when rainfall is sustained over a long period, for example 24-hours, during which soil drainage on slopes is exceeded by sustained moderate rainfall intensity.

In addition to watershed scale surface runoff, these soil conditions can also lead to significant landslide and debris flow activity (Wilson and Jayko, 1997 and references therein). Wilson and Jayko (1997) developed a model to predict significant debris flow activity in the Bay Area based upon rainy day normal (RDN) (the mean annual precipitation (mm) divided by mean annual number of rain days). Once soil moisture deficits are alleviated by early winter rains, they found that significant levels of landslide activity occur when 6-hour rainfall exceed 8.5 RDN or when 24-hour rainfall exceed 14.2 RDN. In the historic mercury mining areas of the Guadalupe River watershed, their model predicts significant landslide activity when rainfall intensity exceeds 50-75 mm in 6 hours or when rainfall intensity exceeds 85-130 mm in 24 hours. We contest that the antecedent rainfall requirement for mercury release should be similar or lesser to that

needed for debris-flow activity. The storm intensity-duration thresholds for mercury release might be lesser than those needed for significant debris-flow activity because of the lesser positive pore pressures required for shallow through-flow and mobilization of mercury contaminated surface soil particles and mining debris as opposed to mechanical slope failure. Never the less, the work of Wilson and Jayko (1997) provides a suitable model as a starting for predicting mercury transport in New Almaden Mining District. We note that the concepts of Wilson and Jayko (1997) were refined further (Wilson, 2000, 2001) however, the regional map provided by Wilson and Jayko (1997) remains the best resource for our current work.

In order to test the influence of rainfall intensity on mercury source-transport in the Guadalupe River, rainfall intensity data were retrieved from the network of rainfall alert gauges operated by the Santa Clara Valley Water District. The data can be obtained at intervals ranging upward from 1 minute. For the purposes of this study, hourly data were retrieved from two rain gauges in the vicinity of the New Almaden Mining District; New Almaden (2080 Almaden RF4) and Guadalupe Creek (1526 Guad WS RF123). The rainfall gauge at New Almaden (2080 Almaden RF4) appeared to be a good indicator of the occurrence and intensity of rainfall in the Mining District but the rain gauge on Guadalupe Creek could also have been utilized. The temporal distribution of rainfall data at New Almaden were compared with the timing of major flood peaks and mercury concentrations observed at the sampling location (Table 5-4).

During the first flush in November, concentrations remained relatively low and correlated with SSC over the rise and fall of the first two peaks. Total mercury in the water column during this period was probably sourced from urban areas and resuspension and erosion of channel sources. The third peak of the first flush event occurred less than 24 hours later. It is hypothesized that the 6-hour intensity during this rainstorm was sufficient to saturate soils in the historic New Almaden Mining District to the point where new mercury load from contaminated soils and mine wastes was able to enter either Alamitos and / or Guadalupe Creek. On the falling stage of the third hydrographic peak, some of this new mercury load passed the sampling location and was sampled at 7:30 am on November 9th (4.7 µg/L total mercury). During the dry period that followed concentrations probably gradually decreased as suspended sediment concentration and load decreased. The second flood series of the season began on December 13th 2002. Again, concentrations of total mercury remained relatively low and correlated with suspended sediment concentrations during the first two hydrographic peaks. Mercury was probably sourced from urban areas and resuspension and erosion of bed and bank sources in Guadalupe River and the contaminated tributaries upstream. During the third peak, we suggest that rainfall intensity was again sufficient to saturate source areas in the historic mining areas and release new mercury to the creeks. Again, on the falling stages of the hydrograph, mercury concentrations increased. This increase was caused by a gradual reduction in dilution from relatively low Hg concentration urban runoff and non-contaminated tributaries. New mercury sourced from mining areas was sampled as it passed the Hwy 101 sampling location. After this event, all subsequent rain events sampled, regardless of intensity, showed concentrations >6µg/L. In addition, the stable flow sample taken on May 29th, approximately 6 weeks after the April flood event, also

showed a concentration (5.2 µg/L) elevated well above those expected from channel resuspension or urban runoff (<1.5 µg/L). We hypothesize that the May sample was dominated by dissolved mercury but have no laboratory analysis to prove this. It appears that once soils in the historic mining areas were saturated, they continued to release mercury load for transport in Guadalupe River well after a storm event. The period of release probably increased as rainfall for the season-to-date increased. An alternate hypothesis for the cause for the observed high mercury concentration on May 29th is a release of mercury due to a disturbance of a unknown mercury source anywhere upstream of the sampling location, but it is impossible to determine at this time. Future sampling efforts might provide evidence to support these hypotheses.

Table 5-4. Rainfall intensities and mercury concentrations during major floods at the Guadalupe River sampling location during WY 2003.

Storm	Peak	Rainfall (mm)				Associated maximum measured Hg (µg/L)
		6-hour	24-hour	Season-to-date	Time of maximum 6-hour intensity	
1	1	15	17	17	11/7/2002 5:00	-
	2	48	81	83	11/7/2002 22:00	0.5
	3	45	130	155	11/8/2002 10:00	4.7
2	1	27	67	226	12/13/2002 19:00	0.4
	2	47	72	283	12/14/2002 18:00	0.7
	3	63	81	373	12/16/2002 6:00	6.7
3	1	44	45	442	12/19/2002 16:00	18.7
4	1	40	55	546	12/28/2002 17:00	15.1
5	1	33	55	721	3/15/2003 5:00	6.8
6	1	25	85	846	4/13/2003 6:00	5.8

Total Mercury Loads

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 1-94 µg/g. This variation is much larger than reported by Thomas et al. (2002) and negates the use of a simple annualized sediment model for calculating mercury loads in the Guadalupe.

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 rainfall and hydrology, rainfall intensity in the mining area, 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) and beyond will further refine the understanding of mercury transport processes under differing hydrological and climatic events.

Hourly loads of total mercury varied from 0.0002-5.3 kg reaching a maximum at 8:00 pm on December 19th 2002. Daily loads varied from 0.0044-20 kg or about 4,600x 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 17% of the wet season load for WY 2003. The maximum daily load of total mercury occurred during the second largest peak (119 m³/s) on December 19th rather than the largest flood peak (172 m³/s) on December 16th as a result of greater concentrations of mercury derived from new mercury release in mining areas. In response to the series of floods that occurred in December, 37.5% of the annual discharge (October 1st 2002 to September 30th 2003), 71% of the measured suspended sediment load (November 1st 2002 to May 31st 2003), and 66% of the total mercury load (November 1st 2002 to May 31st 2003) were transported past the sampling location during just one month (Table 5-5). Errors accounted for during loads estimation were discharge ($\pm 10\%$), suspended sediment ($\pm 2\%$), variation of Hg in the cross section ($\pm 10\%$), extrapolation/SSC-mercury regressions ($\pm 10\%$) and laboratory analysis ($\pm 21.5\%$). The total error was estimated to be $\pm 28\%$. For the study period, 116 ± 32 kg of mercury was transported into lower South San Francisco Bay.

Table 5-5. Monthly discharge (million meters cubed), sediment loads (metric tonnes), and mercury loads (kilograms) during the study period.

	2002			2003									Annual
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	
Discharge (Mm ³)	1.45	5.39	22.80	5.49	3.87	4.03	6.51	3.48	2.29	1.89	1.79	1.81	60.80
Percentage annual (%)	2.4	8.9	37.5	9.0	6.4	6.6	10.7	5.7	3.8	3.1	2.9	3.0	100
Suspended sediment (t)	----	1,709	7,661	149	193	245	610	219	----	----	----	----	10,787
Percentage annual (%)	----	15.8	71.0	1.4	1.8	2.3	5.7	2.0	----	----	----	----	100
Total mercury (kg)	----	6.1	77	4.0	5.6	8.5	11	3.4	----	----	----	----	116 \pm 32
Percentage annual (%)	----	5.3	66.3	3.5	4.8	7.3	9.9	2.9	----	----	----	----	100

---- No data gathered.

Taking into account error estimates, total mercury load in the Guadalupe River measured during this study is 4x 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 (100% and 111% 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% Mean Annual Runoff {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 rainfall intensity might influence annual loads.

SUMMARY AND CONCEPTUAL MODEL

The toxicity and persistence of mercury in San Francisco Bay are issues of critical concern to environmental managers, scientists and the public at-large. This study adds a further contribution to the already large body of accumulated knowledge on mercury in and around the Bay and the general processes of mercury release and transport in watershed environments. 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 been mined historically) are the largest components of the mercury budget of San Francisco Bay and the components where the magnitude of loads have the greatest uncertainties yet great influence on planning and management. This study has shown that the Guadalupe River exhibits total mercury concentrations of a magnitude consistent with other watersheds around the world that are contaminated with mercury-laden mining debris. Unlike the findings of many other studies, total mercury concentrations did not relate in a predictable way to discharge and did not significantly correlate over the study period with any other parameter measured. This lack of correlation likely resulted from source heterogeneity for suspended sediments, mercury, other trace elements and organic carbon associated with the range of flow regimes sampled in this study. Water release from contaminated reservoirs did not strongly influence mercury concentrations and transport in the lower watershed. Instead, the release of mercury from contaminated areas varies in response to the distribution of rainfall across sub-watersheds and rainfall intensity in historic mining areas. The following conceptual model for mercury release from source areas in the Mining District is suggested based on rainfall intensities, accumulative rainfall, and mercury concentrations observed during WY 2003.

During the first storms of the year, new mercury release from source areas is not initiated until rainfall in a 6-hour period exceeds 60 mm and/or rainfall in a 24-hour period exceeds 100 mm. If these conditions occur, concentrations in excess of 1.5 µg/L total mercury will be observed on the falling stages of the hydrograph. Otherwise, the majority of mercury transported to the lower Guadalupe River will be sourced from urban runoff during the rising stages of the hydrograph and in-channel resuspension, and or bed or bank erosion from the upper watershed during falling stages. Later in the season once soils become saturated (approximately 350 mm of accumulated rainfall), mercury release is achieved when 6-hour rainfall exceeds 60 mm and 24-hour rainfall exceeds 80 mm. As

the climatic season progresses and soil moisture deficit is reduced, storms of lesser rainfall intensity release mercury. If storms occur in quick succession like those of December soil moisture deficits are also alleviated and 6-hour rainfalls of approximately 40 mm appear to cause mercury release. Beyond about 700 mm of accumulated rainfall as little as 25-30 mm of rainfall in a 6-hour period can cause further mercury release.

Mercury release in response to intensity, duration and accumulated seasonal rainfall appears to occur under slightly more moderate conditions than proposed for significant debris flow activity by Wilson and Jayko (1997). This may have been caused by our choice in rain gauge (2080 Almaden RF4) that may under-predict rainfall across the Mining District. In addition, the rainfall thresholds developed by Wilson and Jayko were based on the level of debris flow activity that occurred during the severe storm of January 1982 when mapped debris flow events in the Bay Area reached a maximum of 25 per km². It seems likely that a lower level of debris flow, in addition to contaminated sediment carried by overland flow, may be responsible for causing the observed mercury concentrations in the lower watershed during our study. In addition, artificially steepened slopes, road cuts, embankments, mine debris piles and tailing dams found in the historic Mining District probably fail under more moderate or at least variable rainfall conditions not described adequately by the regional scale analysis completed by Wilson and Jayko.

Rainfall during WY 2003 was about normal. Maximum annual rainfall in the Guadalupe River watershed during the wettest year on record was about 200% of normal. Under rainfall conditions more severe than WY 2003, our conceptual model forces us to predict much greater loads of new mercury will enter the stream network and cause greater concentrations and loads downstream. There are massive mercury-laden cemented bar and terrace deposits in Alamitos creek and several other tributary creeks adjacent to the historic Mining District. These provide evidence that in the past under extreme rainfall and runoff conditions, massive failures of mining debris have occurred similar to that described by Whyte and Kirchner (2000) for the Gambonini mine located approximately 50 km north of San Francisco. Conversely, our model suggests that during more moderate rainfall years, when rainfall does not exceed the intensity thresholds, only in-channel sources (bed and bank erosion and resuspension) and urban runoff will provide mercury for transport. During such moderate rainfall years, the loads of mercury will be much less. At this time, long-term average loads and annual variability is difficult to predict because runoff and sediment loading alone do not describe the entire process of mercury loading. Furthering knowledge of watershed mercury source-transport processes and refining the conceptual models and hypotheses presented here will be the subjects of ongoing study in the Guadalupe River watershed.

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SECTION SIX

**PCB AND OC PESTICIDE
TRANSPORT PROCESSES**

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 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 warrant the issuance of an interim consumption advisory for fish caught in the Bay. Consistent with this advisory, all segments of the Bay are listed on the Clean Water Act 303(d) list of water bodies impaired by PCBs and OC pesticides. This study assesses 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 to the Bay.

Twenty-two samples were collected from Guadalupe River during varying stages of storm events in water year (WY) 2003 for analysis of PCBs and OC pesticides. Total 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. Contaminant concentrations were positively correlated to suspended-sediment concentrations (SSC; $r^2 = 0.51$ to 0.72). Maximum concentrations were measured in samples collected on December 16th when discharge exceeded 150 m³ s⁻¹ and SSC exceeded 900 mg L⁻¹. The positive correlations observed in Guadalupe River indicate that suspended sediments transported to the bottom of the watershed are relatively homogeneous with respect to concentrations of PCBs and OC pesticides. These compounds originate from diffusely distributed contaminated watershed soil sources, stream sediment deposits, and locally resuspended stream sediment. However, the relative abundance of individual PCB congeners and DDT compounds in Guadalupe River samples varied with discharge and were suggestive of slightly varying sources contributing to contaminant transport under different flow regimes. Patterns indicated that low flow conditions were influenced more by resuspended sediment, whereas high flows transported relatively unweathered material from sources outside of the immediate stream environment. Furthermore, unique contaminant patterns at the onset of storm events suggest first flush effects in this watershed.

Daily, monthly, and seasonal loads were estimated using a continuous record of turbidity, regression models between suspended sediment, turbidity, and contaminant concentrations. Daily contaminant loads varied from 0.45 to 240 g t-PCBs, 0.46 to 200 g t-DDT, 0.26 to 174 g t-Chlordanes, and 0.033 to 16.4 g dieldrin. Maximum daily loads of all contaminants were measured on December 16th, which constituted approximately 19 to 22% of total loads estimated over the eight-month period from November 2002 to May 2003. Loading estimates for the period November 2002 to May 2003 were 1.2 ± 0.21 kg t-PCBs, 1.1 ± 0.27 kg t-DDT, 0.79 ± 0.13 kg t-chlordane, and 0.082 ± 0.017 kg dieldrin. Compared to estimates of contaminant loading from the large tributaries entering the Bay from the Central Valley of California, Guadalupe River loading was less by factors of 3.5 to 50; however, it is suggested that a combined loading from the local urbanized tributaries (6,550 km²) would contribute similar magnitudes of PCBs, DDT, and chlordane loads to runoff from the Central Valley (154,000 km²). The magnitude of these loading estimates will likely contribute to delayed recovery of Bay contamination by PCBs, DDT, and chlordane.

INTRODUCTION

Concerns over the persistence of polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides in San Francisco Bay and their tendency to biomagnify in the food web have spurred the allocation of considerable resources and effort to monitor chlorinated hydrocarbons over the past few decades. 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. Although these chemicals have been restricted or banned for decades, their concentrations were high enough in Bay sport fish caught prior to 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 (SWRCB, 2003). 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 (SFBRWQCB, 2004).

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-retardants, lubricants, and other products (ATSDR, 2000). Beginning in the 1940s, 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 use of these chemicals in Bay Area watersheds contributed to ongoing persistent sources of chlorinated hydrocarbons in eroding soils and sediments of watersheds and tributaries and the current reservoir of contaminated sediment within San Francisco Bay (Phillips and Spies, 1988; Flegal *et al.*, 1994; Venkatesan *et al.*, 1999).

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), sources in local watersheds and continuing release from these sources and transport via hydrological pathways warrant investigation. In 2000-2001, the Bay Area stormwater management agencies conducted a synoptic survey of PCBs and OC pesticides (and other contaminants) in bed sediments of 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). These findings highlighted the need to understand how continued contaminant loading from local tributaries contribute to further contamination of Bay sediment and biota in context of other important

transport pathways of contamination (e.g. inputs from the Central Valley) and the long-term recovery of water quality in the Bay.

This study was implemented in water year (WY) 2003 to improve our knowledge of the magnitude of contaminant loads entering the Bay from local tributaries and improve our understanding of contaminant transport in relation to hydrologic and geomorphic processes. A study location was selected in a lower reach of Guadalupe River, which drains a heavily urbanized mixed land-use watershed and enters Lower South San Francisco Bay near San Jose, California. The Guadalupe River watershed is the fifth largest of the small tributaries that enter the Bay from the urbanized greater San Francisco Bay Area. It represents an ideal watershed for studying the influence of sediment and hydrological processes on transport of PCBs and OC pesticides to the Bay. 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 have important implications in developing and refining mass budget models of persistent organic contaminants and TMDL management strategies in the Bay.

METHODS

Sample and Data Collection

Twenty-two grab samples were collected from the Guadalupe River during varying stages of storm events for analysis of PCBs and OC pesticides (Figure 6-1, Table 6-1). 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. Individual grab samples were also collected for analysis of selected water quality parameters: suspended sediment concentration (SSC), suspended sediment grainsize, 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.

Sample Preparation and Analysis

Trace organic contaminants were analyzed by AXYS Analytical Services Limited, Sidney, British Columbia, Canada. PCBs were analyzed using high-resolution gas chromatography/ high-resolution mass spectrometry (HRGC/ HRMS) following EPA method 1668 revision A (USEPA, 1999). Pesticides were analyzed using isotope dilution HRGC/ HRMS. Prior to analysis, two liters were sub-sampled from four-liter sample bottles, spiked with ¹³C₁₂-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

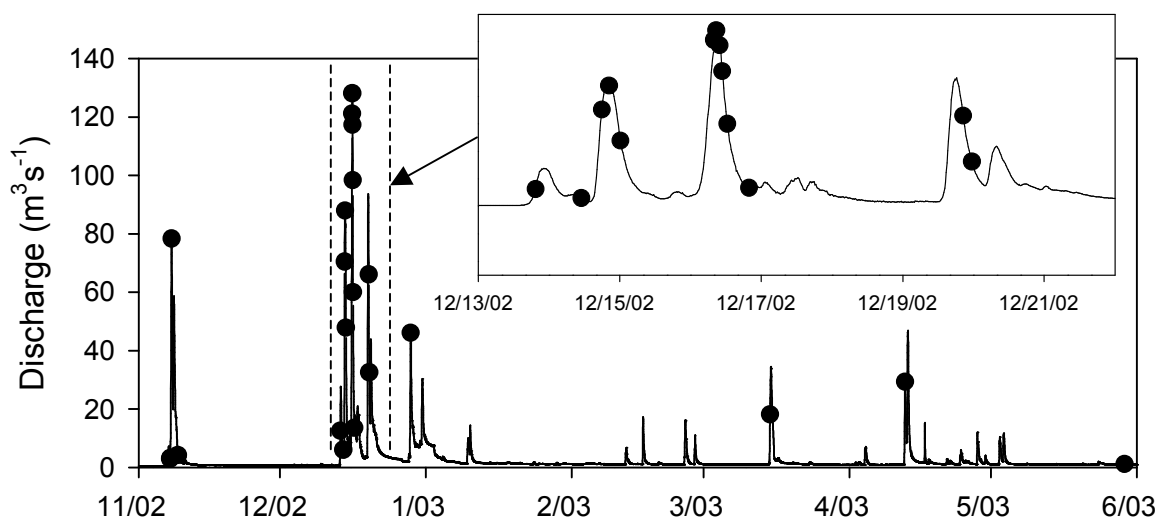


Figure 6-1. Sampling events at Guadalupe River, WY 2003. Sampling events are depicted as black circles on the hydrograph.

Table 6-1. 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	

less polar pesticides, and fraction E2, containing the more polar pesticides) using a Florisil chromatographic column. The E1 and E2 fractions were separately spiked with labeled recovery (internal) standards prior to instrumental analysis. Samples were analyzed using HRGC/HRMS with a VG 70 VSE HRMS equipped with an HP 5890 gas chromatograph, a CTC autosampler, and an Alpha data system running Micromass software. A DB-5 (60 m, 0.25 mm i.d., 0.1 μ m film thickness) chromatography column was coupled directly to the MS source. The MS was operated at 8000 (static) mass resolution in the electron impact mode using multiple ion detection, acquiring at least two ions for each target and surrogate compound. SSC was measured gravimetrically following the methods of (Guy, 1969). DOC and POC were analyzed by catalytic combustion using U.S. EPA method 415.1 (USEPA, 1983).

Quality Assurance and Control

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

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 6-2). Only four measurements were below detection. Relative percent differences (RPDs) of PCB congeners measured in the field duplicate sample ranged from 0.5 to 33% (Table 6-3). The RPD of t-PCBs was 8.1%. Total PCB concentrations were positively correlated to SSC ($r^2 = 0.51$, $p = 0.0002$; Figure 6-2) and instantaneous discharge ($r^2 = 0.61$, $p < 0.0001$). Concentrations spanned an order of magnitude variation between base flow conditions and storm flow. The maximum t-PCB concentration was measured on December 16th, 2002 at 7:55 AM when discharge was 158 m^3s^{-1} and SSC was 900 mg L^{-1} . In all samples, hexa-, hepta-, and octa-chlorobiphenyls comprised 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 6-2). 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

Table 6-2. 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	Q m ³ s ⁻¹	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	2.3	43	ND	ND	19	42	11	17	13	12	3.5	3.6	3.3	1.1
11/7/2002	17:05	2.5	43	.	.	17	31	9	14	8.0	11	3.0	3.3	3.0	1.0
11/7/2002	23:40	72	760	.	.	54	59	16	31	12	53	14	15	17	3.1
11/9/2002	7:46	3.2	53	.	.	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	11	361	8.9	ND	65	33	16	13	4.6	26	7.0	8.0	7.6	2.4
12/14/2002	11:00	4.5	27	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	73	626	4.5	0.3	62	48	12	19	17	50	13	15	15	4.7
12/14/2002	20:24	111	577	3.9	0.8	38	34	6.7	14	14	37	10	10	12	3.5
12/15/2002	0:16	57	69	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	158	901	4.0	0.7	90	55	11	21	23	56	15	15	18	5.8
12/16/2002	8:45	168	1016	4.4	0.7	Q 85	71	17	28	26	64	19	19	18	6.0
12/16/2002	9:55	152	1072	5.2	0.6	57	52	11	21	19	41	12	11	12	4.2
12/16/2002	10:45	125	1041	5.7	0.9	54	Q 50	q 9.0	22	q 19	37	11	10	10	3.2
12/16/2002	12:31	73	749	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	14	317	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	81	540	4.0	2.7	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	37	444	5.3	2.3	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	54	335	2.2	1.4	69	Q 36	9.4	14	q 13	Q 35	10	10	q 9.2	3.4
3/15/2003	3:06	19	188	6.1	4.3	27	15	5.0	6.4	4.0	15	4.5	4.7	4.0	1.5
4/12/2003	18:40	33	228	ND	ND	15	17	4.0	7.1	5.7	22	6.3	6.4	q 6.1	1.9
5/29/2003	10:33	1.1	56	1.8	0.7	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	1.1	56	1.8	0.7	3.4	1.8	0.92	0.46	q 0.40	1.6	0.52	0.43	0.36	0.33

Table 6-3. Quality assurance and control summary. DF = detection frequency (%) of analytes in field samples. MDL = method detection limit. NA = not available. ND = not detected. RPD = relative percent difference of concentrations measured in field duplicate. Accuracy is the range of matrix spike recoveries in three QA samples.

Parameter	Blank Conc.	Field Sample	MDL Range	DF	RPD	Accuracy
	pg/L	pg/L	pg/L	%	%	%
o,p'-DDD	ND	189 - 4470	5.4 - 67	100	10	100 - 140
o,p'-DDE	ND	11.6 - 897	5 - 36	100	24	72.2 - 89.2
o,p'-DDT	ND	59.3 - 3050	7.9 - 105	100	19	94.2 - 112
p,p'-DDD	ND	729 - 13700	7.9 - 83	100	4	111 - 135
p,p'-DDE	ND	429 - 29800	8.4 - 49	100	3	92 - 116
p,p'-DDT	ND	244 - 22800	11 - 182	100	29	93.5 - 114
alpha-Chlordane	ND	516 - 18600	7.8 - 164	100	1	95 - 121
gamma-Chlordane	ND	428 - 18800	6.8 - 145	100	6	93.1 - 108
cis-Nonachlor	ND	135 - 6250	21 - 350	100	8	93.1 - 118
trans-Nonachlor	ND	361 - 18400	8.9 - 237	100	2	96.3 - 112
Heptachlor	ND	0 - 603	5 - 31	95	NA	94.8 - 116
Heptachlor Epoxide	ND - 2.41	73.6 - 1510	2.6 - 14	100	2	90.7 - 109
Oxychlordane	ND	30 - 1050	11 - 79	100	56	94.1 - 107
Dieldrin	5.04 - 8	307 - 5970	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	ND - 197	0.31 - 21	86	ND	
PCB 015						90.8 - 112
PCB 018/30	1.58 - 9.26	17.3 - 535	0.16 - 8	100	4	
PCB 019						104 - 111
PCB 028/20	2.36 - 14	33.9 - 2190	0.24 - 4	100	6	
PCB 031	2.11 - 12.2	16 - 1130	0.24 - 5	100	6	
PCB 033/21	1.53 - 7.34	6.53 - 258	0.24 - 5	100	13	
PCB 044/47/65	2.64 - 7.29	56 - 1850	0.02 - 8	100	8	
PCB 049/69	1.16 - 3.02	34.9 - 1150	0.02 - 7	100	7	
PCB 052	1.81 - 7.34	89.4 - 2910	0.02 - 8	100	8	
PCB 056	ND - 1.89	12.4 - 335	0.61 - 6	100	13	
PCB 060	ND - 1.13	6.38 - 129	0.61 - 6	100	33	
PCB 066	ND - 3.34	29.3 - 998	0.58 - 5	100	8	
PCB 070/74/61/76	2.15 - 8.22	58.3 - 2060	0.58 - 5	100	2	
PCB 087/97/86/108/119/125	1.59 - 1.59	92.7 - 3830	0.19 - 6	100	14	
PCB 095/93/98/100/102	1.7 - 6.83	178 - 4870	0.21 - 6	100	5	
PCB 099/83	1.11 - 5.11	87.8 - 3890	0.22 - 7	100	4	
PCB 101/90/113	1.68 - 7.04	164 - 6560	0.19 - 6	100	13	
PCB 105	0.63 - 2.74	43.5 - 1900	0.52 - 10	100	10	102 - 115

Table 6-3 (continued). Quality assurance and control summary. DF = detection frequency (%) of analytes in field samples. MDL = method detection limit. ND = not detected. RPD = relative percent difference of concentrations measured in field duplicate. Accuracy is the range of matrix spike recoveries in three QA samples.

Parameter	Blank Conc.	Field Sample	MDL Range	DF	RPD	Accuracy
	pg/L	pg/L	pg/L	%	%	%
PCB 110/115	1.34 - 8.06	200 - 8310	0.16 - 5	100	17	
PCB 114						87.4 - 111
PCB 118	1.19 - 6.46	104 - 5010	0.45 - 10	100	7	94.1 - 118
PCB 128/166	0.4 - 0.894	40 - 1400	0.43 - 9	100	8	
PCB 132	ND - 1.81	106 - 2790	0.56 - 12	100	1	
PCB 138/129/160/163	3.01 - 5.98	309 - 8450	0.41 - 9	100	5	
PCB 141	ND - 1.34	56.6 - 1480	0.5 - 11	100	1	
PCB 149/147	2.68 - 2.96	302 - 8030	0.51 - 11	100	1	
PCB 151/135/154	1.46 - 1.47	163 - 6020	0.01 - 4	100	1	
PCB 153/168	1.5 - 4.79	262 - 6820	0.39 - 8	100	8	
PCB 156/157	0.493 - 0.522	22.6 - 957	0.46 - 9	100	23	86.3 - 110
PCB 158	ND - 0.715	29.4 - 897	0.34 - 7	100	2	
PCB 167						90.6 - 110
PCB 170	ND - 2.04	90.6 - 1900	0.01 - 5	100	15	
PCB 174	ND - 2.95	104 - 2630	0.01 - 4	100	24	
PCB 177	ND - 1.74	74.8 - 2050	0.01 - 5	100	20	
PCB 180/193	1.6 - 6.37	216 - 4890	0.01 - 4	100	17	
PCB 183/185	0.983 - 2.13	69.6 - 1580	0.01 - 4	95	24	
PCB 187	ND - 3.93	143 - 4530	0.01 - 4	100	25	
PCB 189						90.2 - 118
PCB 194	ND - 0.625	57 - 1040	0.19 - 7	100	19	
PCB 195	ND - 0.446	22.6 - 387	0.2 - 8	100	28	
PCB 201	ND - 0.265	9.07 - 234	0.01 - 4	100	1	
PCB 203	ND - 0.652	41.9 - 940	0.01 - 5	100	31	
PCB 205						96.1 - 111
PCB 206						93.1 - 110

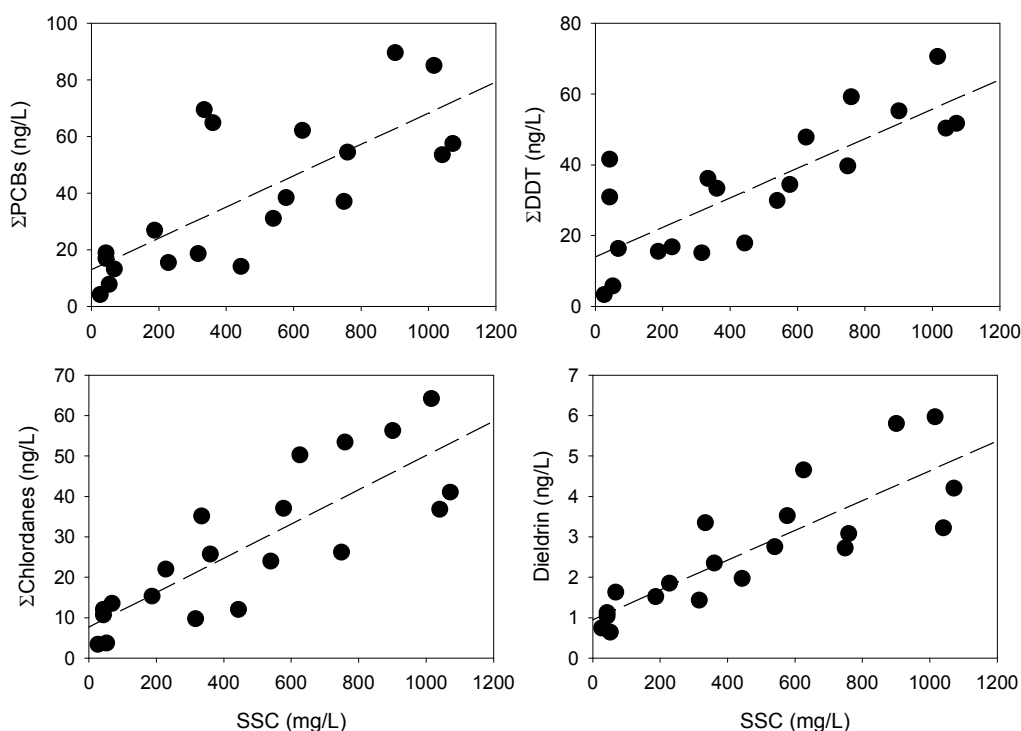


Figure 6-2. Linear regressions of chlorinated hydrocarbon concentrations and SSC.

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 6-3). The RPD for dieldrin was 6%. As with PCBs, concentrations of measured OC pesticides increased with SSC ($r^2 = 0.64$ to 0.72 , $p < 0.0001$; Figure 6-2) and flow ($r^2 = 0.66$ to 0.80 , $p < 0.0001$). Maximum concentrations of t-DDT, t-chlordane, and dieldrin were measured on December 16th at 8:45 AM when discharge was 168 m³s⁻¹ and SSC was approximately 1,020 mg L⁻¹. Concentrations of all individual pesticides are listed in Appendix Table B.

DISCUSSION

Chlorinated Hydrocarbons in Watersheds

Concentrations of PCBs and OC pesticides measured in this study reflect contaminant signals consistent with past usage and diffuse sources of these contaminants in urbanized watersheds. The primary use of PCBs for industrial and other urban

purposes, as well as the application of chlordane as an insecticide in urban areas, has resulted in greater concentrations and loadings of these contaminants in urban areas of watersheds compared to non-urban 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 pest control in urban areas. 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. Runoff from urbanized portions of the watershed 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 (SCBWM 2000). Findings in this study appear to support previous studies that established a linkage between past uses of PCBs and OC pesticides and areas of contamination in watersheds and tributaries (e.g., Wong *et al.* 2000).

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) measured in this study were of similar magnitude to concentrations measured in other urban systems. For example, Foster *et al.* (2000) measured 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) in the Anacostia River, which drains a small (440 km²), 60% urbanized watershed tributary to Chesapeake Bay. PCB concentrations were also consistent with concentrations measured in the Detroit River (<5.0-33 ng L⁻¹; Froese *et al.* 1997), Saginaw River (10-46 ng L⁻¹; Verbrugge *et al.* 1995), and Milwaukee River (0.13-170 ng L⁻¹; 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 (Foster *et al.* 2000). Peak usage of DDT and other organochlorine pesticides preceded the reporting of pesticide use statistics in California; however we suggest that the relatively high DDT concentrations in the Guadalupe River are a result from contaminated soils and sediments that are mobilized from areas where past urban and agricultural applications occurred.

Study results indicate that Guadalupe River runoff may continue to negatively impact downstream water quality in the Bay. From 1997 to 2001, the RMP measured organic contaminant concentrations in seasonal water samples in a tidal reach of Guadalupe River and in Lower South San Francisco Bay (Leatherbarrow *et al.* 2002, SFEI 2003, SFEI 2004). Concentrations in this study were greater than tidal reach water concentrations of t-PCBs (3.6-6.1 ng L⁻¹), t-DDT (2.4-3.6 ng L⁻¹), t-chlordane (1.0-3.1 ng L⁻¹), and dieldrin (0.0027-0.27 ng L⁻¹). Both locations had greater concentrations than Lower South Bay water samples. This gradient of decreasing contaminant concentrations downstream from river to Bay has also been observed in the Chesapeake Bay by Ko and Baker (2004), who attributed the downstream trend to either rapid settling of particles or dilution by other sources once freshwater reaches the tidally influenced reaches of the tributary and Bay. We propose that similar processes are occurring in the Lower South Bay tributaries. If these transitional zones on the Bay margin might be important areas of

biological assimilation decisions on how to manage contaminants in the Bay might benefit from a greater understanding of the fate of contaminants and sediment upon entering tidally influenced waters.

Concentrations in Relation to Storm Events

PCBs and OC pesticide concentrations were over an order of magnitude greater in storm flow than in base flow and were highly dependent on discharge and SSC. 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 stream sediment (Foster *et al.* 2000, Froese *et al.* 1997, Ko and Baker 2004). 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). Observations in the Guadalupe River appear to be consistent with Foster *et al.* (2000), Froese *et al.* (1997), and Ko and Baker (2004). The contaminant concentrations increased with increasing discharge during all floods and likely originate from diffuse storage of contaminated watershed soils, upstream sediment deposits, and locally resuspended stream sediment.

Hydrologic characteristics (the source of water) during individual storm events, however, do influence the gradient of the least squares regression relationships found between contaminant concentrations and SSC. Contaminant particle concentrations during rising stages of flood peaks were greater than particle-based concentrations measured on falling stages (Figure 6-3). Differences in particle-based concentrations might be attributed to differences in suspended sediment character (e.g., grain size or organic carbon concentration) and/or varying sources of sediment sampled at the study location. These patterns help develop a working hypothesis that rising stage samples collected before the flood peak represent greater contributions of runoff originating from the lower watershed as opposed to runoff from the upper watershed. In turn, greater concentrations of contaminants measured during the rising stages of storm events likely reflect an urban runoff signal from the predominantly urbanized lower watershed. The variation between rising and falling stages was greatest for PCBs relative to the OC pesticides, an observation consistent with our understanding of sources in the watershed. A second year of monitoring in WY 2004 will provide a greater number of samples to test hypotheses and understand any influence of suspended sediment character on trace organic concentrations in water from different origins in the watershed.

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.

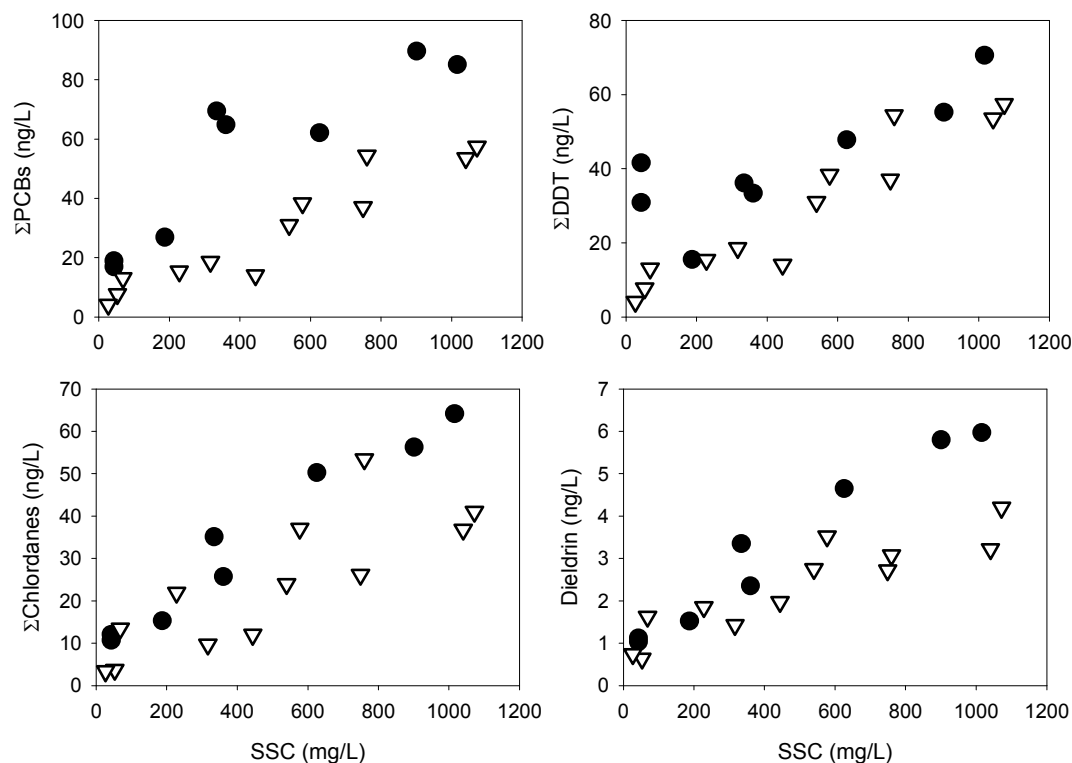


Figure 6-3. Linear regressions of chlorinated hydrocarbon concentrations and SSC in samples collected during rising and falling stages of storm events. Rising stage samples appear as black circles. Falling stage samples appear as open triangles.

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. 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 (Figure 6-4). A high abundance of PCB mass (50 to 75%) composed of six (hexa-) or more chlorine atoms reflects predominant contributions of PCBs from sources of Aroclors 1254 and 1260 (Frame *et al.* 1996). Predominance of high-molecular weight PCBs has been shown to be 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 lower-molecular weight PCBs (Tsai *et al.* 2002, Poster and Baker 1994).

The distribution of mass among individual PCB congeners were evaluated with respect to instantaneous discharge to assess the potential influence of hydrology and sediment transport on PCB source activation and transport. During low-flow conditions in the Guadalupe River, hexa- and hepta-CB congeners (e.g., PCB 180) contributed the

greatest proportions of measured t-PCBs. As storm flow increased, the contribution of these congeners decreased, whereas the contribution of penta-CB congeners (e.g., PCB 118) increased (Figure 6-5). This variation in PCB distribution between low and high flow conditions has been observed in previous studies (Foster *et al.* 2003, Rostad 1997). The patterns have been attributed to varying sources of sediment originating from resuspended finer grain material at low flow and erosion of watershed soils and sediment at high flow (Foster *et al.* 2003). Furthermore, the large proportions of high-molecular weight PCB congeners observed in low flow may be a result of greater degradation of low-molecular weight PCB congeners (Rostad 1997). We propose that similar processes are taking place in Guadalupe River, and, thus, PCB congener patterns distinguish between variable sources of resuspended river sediment at low flow and eroded material carried by overland flow at high flow.

Tri- and tetra-CB congeners contribute smaller amounts of t-PCB residues in a relatively consistent manner over the range of observed discharge, except for samples collected in the early stages of storm events. At the onset of storms, greater proportions of low-molecular weight PCBs appear to be a result of the activation or release of a unique source of PCBs. This pattern may indicate a first flush effect that occurs when rainfall scavenges particles from the atmosphere (Offenberg and Baker 2002, van Ry *et al.* 2002) and produces surface runoff that entrains readily erodible material that deposited on watershed surfaces (Chevreuil and Granier 1991). Greater proportions of less chlorinated PCBs in river samples collected early in runoff events have been attributed to inputs from direct deposition or indirect deposition (via runoff) 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). Therefore, although the largest proportions of t-PCBs originate from resuspended channel sediment and terrestrial soils, first flush effects likely contributed to observed pulses of low-molecular weight PCBs during the beginning stages of storm events.

The relative abundance of DDE, DDD, and DDT compounds (o,p' and 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, whereas anaerobic or flooded soils and sediments tend to have greater proportions of DDD (Castro and Yoshida 1971, Strömpl and Thiele 1997).

The relative contributions of DDE, DDD, and DDT compounds (o,p' + p,p' isomers) to t-DDT were largely dependent on the flow regime of the river (Figure 6-6). 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 30 m³s⁻¹. 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,

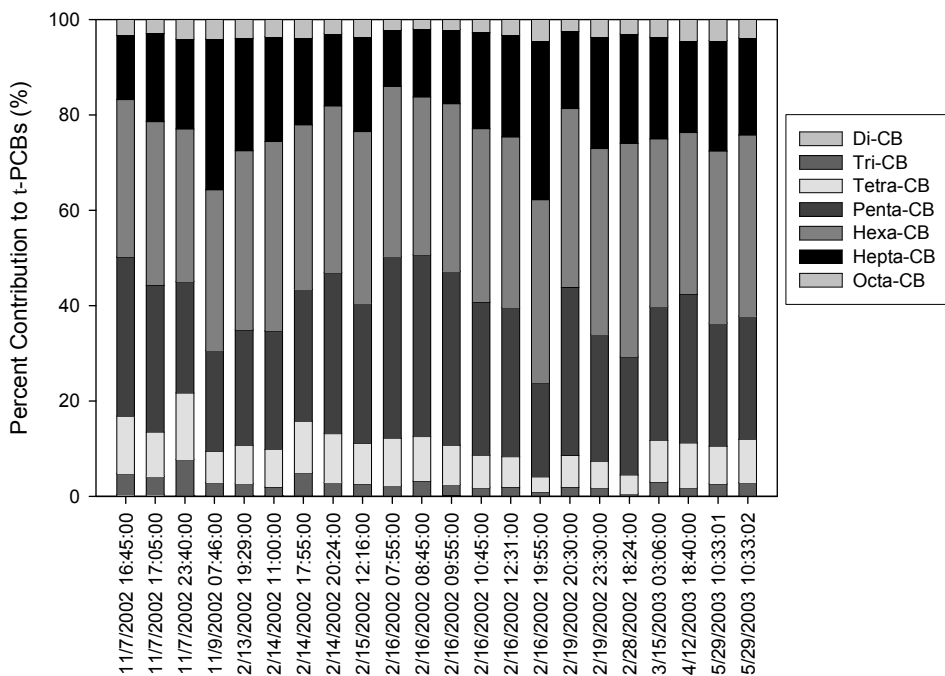


Figure 6-4. Relative abundance of PCB homologs in Guadalupe River water samples.

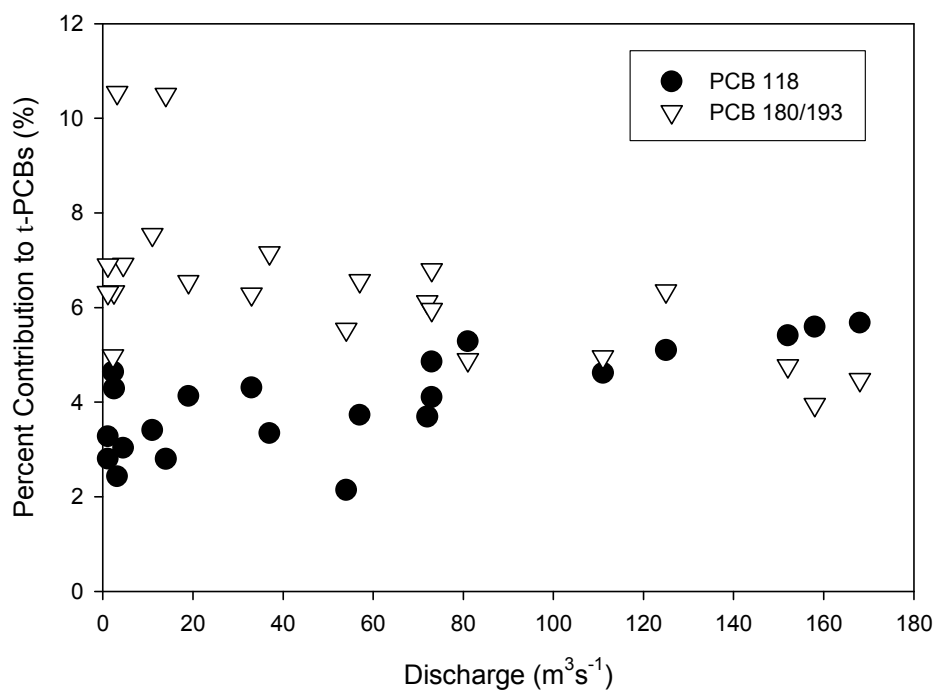


Figure 6-5. Percent contribution to t-PCBs from PCB 118 and PCB 180.

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 $30 \text{ m}^3 \text{ s}^{-1}$. 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 $30 \text{ m}^3 \text{ s}^{-1}$, 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. This first flush sample lacked an equally high proportion of DDT, which further implies that a unique contaminant source contributed to loading 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. The p,p' isomer of 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.

Hypotheses and Conceptual Model

Variation in relative abundances of PCB congeners and DDT compounds with respect to discharge led us to hypotheses concerning the influence of hydrologic processes on mobilization and transport of chlorinated hydrocarbon residues from various sources within the watershed and the following conceptual model of transport processes for the Guadalupe River watershed. First, greater concentrations on the rising stages of floods relative to falling stages suggest that runoff from urban areas is more contaminated than runoff from the non-urban upper watershed. Second, a first flush phenomenon transported material from a unique source during the first storms of the season – possibly of atmospheric origin. Third, base flow conditions transported material that originated from within the stream channel, whereas 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.

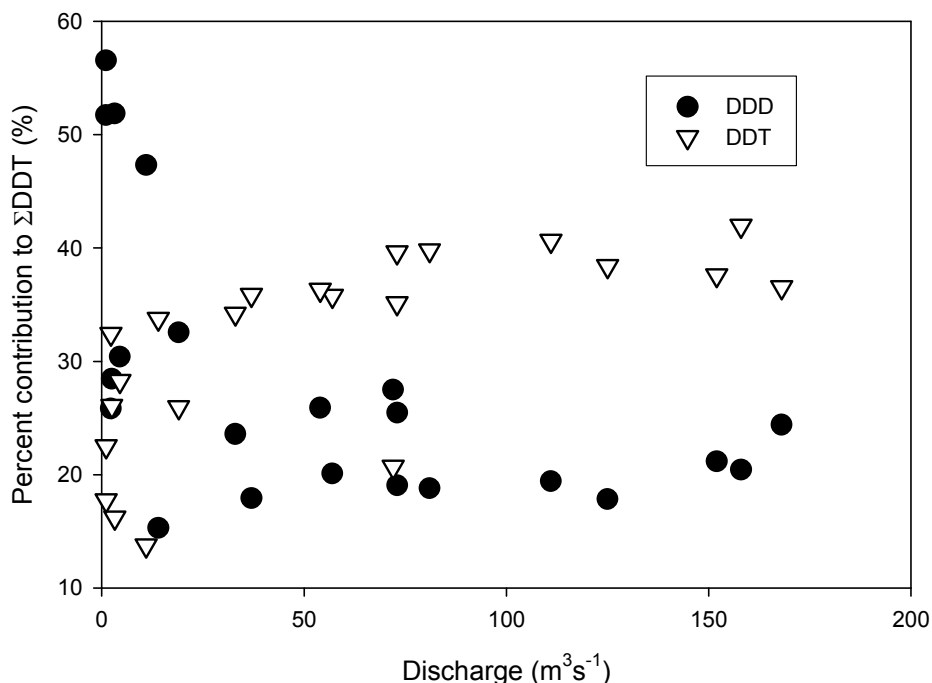


Figure 6-6. Percent contribution to t-DDT from DDD and DDT compounds. DDD and DDT are the sum of o,p'- and p,p'-isomers for each compound.

Load estimates

Continuous data collected for discharge and turbidity facilitated the estimation of loads of organic contaminants related to suspended sediment in Guadalupe River for our study period (WY 2003). Using linear relationships between estimated SSC and contaminants, the continuous SSC 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 daily and monthly time scale from November 2002 to May 2003.

Loading estimates were subject to potential errors. Sources of error associated with measurement or estimation of physical factors included measurement of stream flow ($\pm 5\%$), laboratory measurement of SSC ($\pm 5\%$), cross-sectional variability in SSC ($\pm 5\%$), and regression of SSC with turbidity ($\pm 2\%$). Additional errors were associated with regressions between SSC and organic contaminants, as well as errors associated with laboratory analyses of contaminants. Regression errors for contaminants were approximately $\pm 19\%$ for t-PCBs, $\pm 16\%$ for t-DDT, $\pm 14\%$ for t-Chlordanes, and $\pm 13\%$ for dieldrin. Based on QA data (Table 6-3), analytical accuracy was estimated to be $\pm 15\%$ for t-PCBs, $\pm 24\%$ for t-DDT, $\pm 13\%$ for t-Chlordanes, and $\pm 19\%$ for dieldrin. Total errors were estimated by the propagation of errors method. Total errors for loads

estimates were $\pm 18\%$ for t-PCBs, $\pm 26\%$ for t-DDT, $\pm 16\%$ for t-chlordane, and $\pm 21\%$ for dieldrin.

Estimates of loads generated on a 15-minute interval were summed for each day and month of study. Daily contaminant loads varied from 0.45 to 240 g t-PCBs, 0.46 to 200 g t-DDT, 0.26 to 174 g t-Chlordanes, and 0.033 to 16.4 g dieldrin. Maximum daily loads of all contaminants were measured on December 16th, which constituted approximately 19 to 22% of total loads estimated over the eight-month period from October 2002 to May 2003 (Table 6-5). In addition, approximately 45 to 50% of total loads occurred over a seven-day period from December 14th to December 20th, 2002. As expected, most of the suspended sediment (71%) and contaminant loading (57-65%) occurred during the month of December when most of the storm activity and 49% of the water discharge occurred. Combined loading in November and December contributed greater than 70% of the total load of sediment and contaminants in the Guadalupe River.

Table 6-5. Monthly loading of sediment and chlorinated hydrocarbons in Guadalupe River, WY 2003.

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Total
Sediment (tonnes)	19	1,709	7,661	149	192	245	610	220	10,805
t-PCBs (grams)	16	176	583	67	51	60	91	41	1,200 \pm 210
t-DDT (grams)	13	149	496	54	41	49	75	33	1,100 \pm 270
t-chlordane (grams)	8	119	396	35	28	34	52	21	790 \pm 130
Dieldrin (grams)	1	12	40	5	4	4	6	3	82 \pm 17

Loading estimates using flow-weighted mean concentrations and the flow (47.8 Mm³) occurring during the study period (October 2002 to June 2003) resulted in loading estimates that were greater by a factor of 2 to 3: 2,600 \pm 800 g t-PCBs, 2,300 \pm 700 kg t-DDT, 1,900 \pm 300 kg t-chlordane, and 180 \pm 40 kg dieldrin. The difference between SSC-based loading 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 loading. In this case, the use of a flow-weighted mean concentration and total discharge generated positively biased loading 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 6-5.

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 loading 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 loading from Bay Area watersheds. The Guadalupe River watershed encompasses approximately 8% of the non-tidal watershed area directly adjacent to the Bay (6,650 km²) – excluding the Central Valley (McKee *et al.* 2003). If all Bay Area watersheds contributed to contaminant loading equally based on watershed area, combined loading 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, loading 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 loading 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 km² in the Central Valley of California. As expected, Guadalupe River loads were lower than estimates of loading from the Central Valley in WY 2003: 23 kg PCBs, 9.7 kg t-DDT, 1.5 kg t-chlordane, and 3.0 kg dieldrin (Leatherbarrow *et al.* 2004). In consideration of total contaminant loads from the combined Bay watersheds, our present hypothesis is that allochthonous loadings 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 urbanized tributaries to San Francisco Bay within the nine counties directly adjacent to the Bay.

CONCLUSIONS AND IMPLICATIONS

This study assessed the influence of storm events on runoff processes, suspended sediment transport, 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. During low flows, contaminants appeared to be associated primarily with resuspended sediment, whereas 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 concentrations and loads. Most of the loading of PCBs and OC pesticides was associated with the large storm events that occurred in November and mainly December. Although estimates of contaminant loading from Guadalupe River were less than estimated loads from the Central Valley, we suggest that, if measured, the combined loading from the local tributaries would contribute a similar magnitude of

PCBs, DDT, and chlordanes to loads emanating from the Central Valley watersheds via the Sacramento / San Joaquin River Delta.

Recent mass budget modeling of organic contaminants in San Francisco Bay indicates that continued PCB and OC pesticide loading of these magnitudes are likely to delay the recovery of water quality in the Bay (Davis 2004, Leatherbarrow *et al.* 2004). Model results also suggest that the Bay is very responsive to relatively small reductions in loading 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 of contaminant processes in the Bay have illustrated the importance of deriving realistic estimates of contaminant loading from local tributaries and the large rivers of the Central Valley. This would best be achieved through a combined effort of further empirical data collection especially during years with above-average discharge and suspended sediment loads and extrapolation of existing data using rainfall-runoff process based models. Accurate loading estimates in the context of refined mass budget models will help prioritization of management actions aimed at reducing contaminant inputs from various pathways and evaluating the effectiveness of those actions.

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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

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

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, other 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