

# **MEASUREMENT OF SEDIMENT AND CONTAMINANT LOADS FROM THE GUADALUPE RIVER WATERSHED**

## **SAMPLING AND ANALYSIS PLAN**

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## BACKGROUND

### Project objective

The main objective of this project is to improve our knowledge on the magnitude of contaminant loads entering the Bay from local tributaries and in doing so improve our understanding of contaminant process in the Bay (such as described by the PCB single box mass balance model (Davis, 2002). Thereby, this project is designed to assist in the development of TMDLs and the management of the Bay. The project also has a number of secondary objectives. 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.

### Timeline

This Sampling and Analysis Plan (SAP) constitutes the written deliverable of Project Implementation (Table 1). Other activities have included a) the development and negotiation of the required sub-contracts, b) site reconnaissance, c) confirmation of equipment costs, d) budget reevaluation e) equipment purchase, f) turbidity probe installation and testing, and g) web programming to make the turbidity data available real time.

Each year the project continues (2002, 2003, 2004, and 2005) sampling will occur in the winter months each time the watershed sustains storm rainfall that causes flow to increase beyond 200 cubic feet per second (cfs) and an increase in turbidity indicating sediment and contaminant transport (see sections below for definitions and rationale). Each spring, samples will be analyzed in the laboratory and following delivery of results back to San Francisco Estuary Institute (SFEI), the main effort in analysis and reporting will be carried out and completed by late summer.

**Table 1.** Generalized timeline for the Project.

	2002-2003				2003-2004				2004-2005				2005-2006			
	F	W	S	S	F	W	S	S	F	W	S	S	F	W	S	S
Project implementation	■															
Sampling		■				■				■				■		
Laboratory analysis																
Funding request			■	■			■	■			■	■				
Reporting				■			■					■				■

## **Oversight**

Project oversight will consist of members of the CEP technical committee, consulting groups, universities, and members of the Sources Pathways and Loadings Workgroup (SPLWG) of the Regional Monitoring Program for Trace Substances (RMP). The oversight group, their main roles and their affiliations are listed (Table 2). Oversight will occur through four main mechanisms: 1. Monthly CEP technical meetings, 2. Quarterly SPLWG meetings, 3. Mercury and PCB TMDL workgroup meetings, and 4. Solicitations of external peer-review.

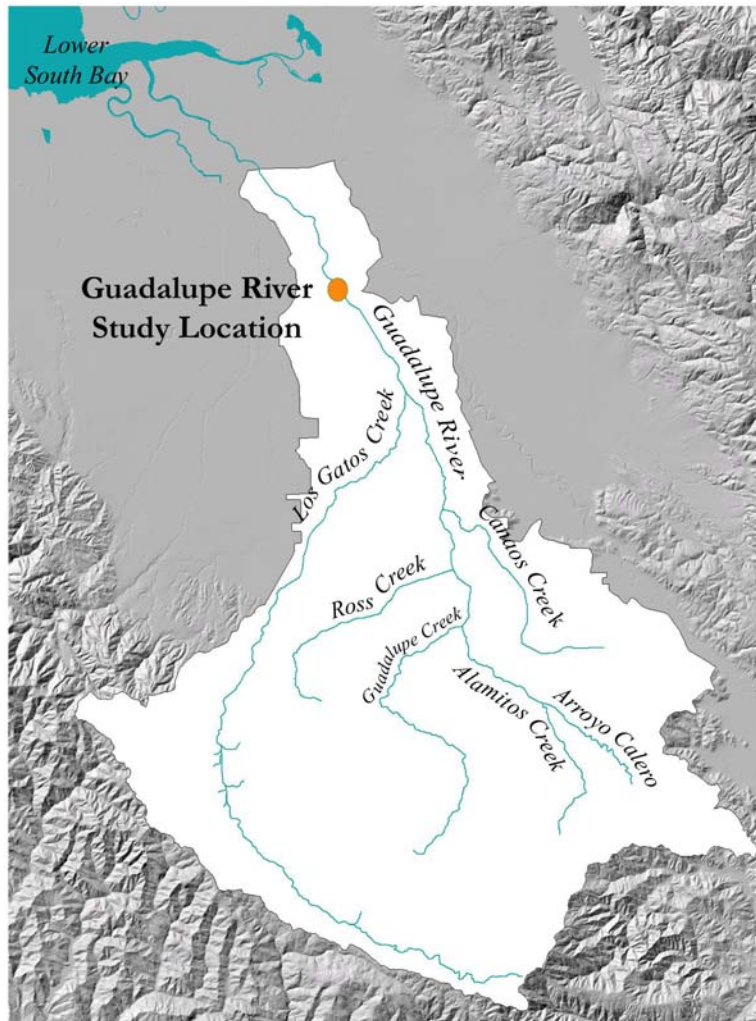
**Table 2.** Oversight group members. Note, where a person has several roles they have been listed more than once.

<b>Name and affiliation</b>	<b>Name and affiliation</b>
<b>CEP technical committee</b>	<b>RMP SPLWG</b>
David Tucker, CSJ, BACWA (Chair)	Tom Mumley, SF RWQCB
Arlene Feng, AC, BASMAA	Khalil Abu-Saba, AMS, CEP
Geoff Brosseau, BASMAA	Andy Gunther, AMS, CEP
Andy Gunther, CEP Program Coordinator	Jim Kuwabara, USGS
Khalil Abu-Saba, AMS	Trish Mulvey CSB, SFEI Board
Fred Hetzel, SF RWQCB	Tom Hall, EOA
Karen Taberski, SF RWQCB	Terry Cooke, URS
Jon Konnan, EOA, SCVURPPP	Russ Flegal, UC Santa Cruz
Chris Sommers, EOA	Jim McGrath, Port of Oakland
Jay Davis, SFEI	Dave Tucker, City of San Jose
	Jim Scanlin, Alameda County
<b>Mercury TMDL Workgroup</b>	Geoff Brosseau, BASMAA
Richard Looker, SF RWQCB	Joseph Domagalski, USGS
Dave Drury, BASMAA	Mike Nolan, USGS
Bill Elgas, BACWA	Fred Hetzel SFBRWQCB
Khalil Abu-Saba, AMS, CEP	Don Yee, SFEI
Carrie Austin, SF RWQCB	Jay Davis SFEI
<b>PCBs TMDL Workgroup</b>	<b>External Peer-review</b>
Fred Hetzel, SF RWQCB	Mike Stenstrom, UCLA
Jon Konnan, BASMAA	
Dan Watson, BACWA	
Andy Jan, Port of Oakland	
Jay Davis, SFEI	

## **Location**

### **Geographic location**

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 1). The Guadalupe River watershed is one of 13 drainages that constitute the basin and the second largest in terms of area. The Guadalupe River watershed is bounded on the west by the San Tomas Creek watershed, on the east by the Coyote Creek watershed and to the south by coastal watersheds.

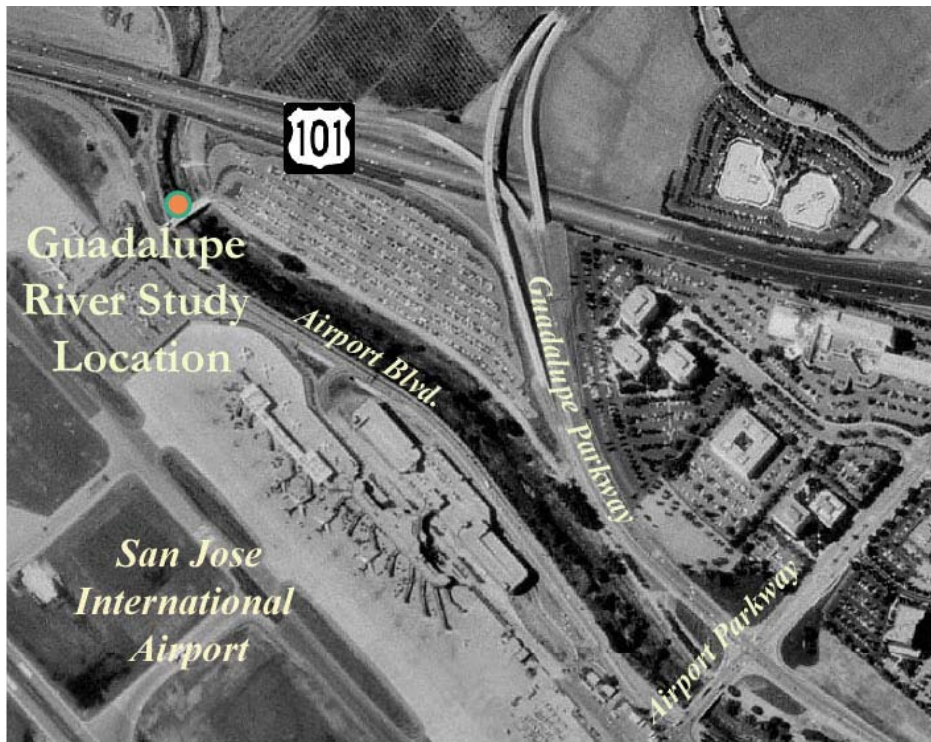


**Figure 1.** The geographic location of the Guadalupe River watershed.

## Sampling location

The Guadalupe River study sampling site is located approximately 0.06 km (0.036 miles) upstream from where US Highway 101 passes over the Guadalupe River (Figure 2). This location is on the northeast side of San Jose International Airport on a bridge that connects the main airport grounds to a rental car service center.

*Driving directions:* From the northeast entrance of the airport on Airport Parkway, turn right onto Airport Blvd. Follow Airport Blvd. approximately 1 km (0.6 mi) to the sampling location at the bridge that connects the main airport grounds to a rental car service center. From the southwest entrance of the airport on Coleman Ave, turn onto Airport Blvd. Follow Airport Blvd. past Airport Parkway approximately 1 km (0.6 mi) to the sampling location at the bridge that connects the main airport grounds to a rental car service center.



**Figure 2.** Aerial view (USGS DOQ) of Guadalupe River study sampling location.

## **Watershed characteristics**

### **Physiology**

Guadalupe Creek flows from its headwaters in the eastern Santa Cruz Mountains to its confluence with Alamitos Creek at Coleman Road in the city of San Jose where it becomes Guadalupe River and continues its journey through the city, past the San Jose International Airport and beyond Highway 101. The influence from the ocean tides begins between the Montague Expressway and Highway 237 before the River ultimately discharges to the South Bay via Alviso Slough. The Guadalupe River watershed encompasses approximately 556 km<sup>2</sup> (200 mi<sup>2</sup>). The watershed is the 4<sup>th</sup> largest in the Bay Area by area and the 5<sup>th</sup> largest in terms of annual discharge volume to the Bay. There are five main tributaries in the Guadalupe watershed: Los Gatos Creek, Ross Creek, Guadalupe Creek, Alamitos Creek, and Canaos Creek. The subwatersheds of Los Gatos Creek, Ross Creek, Guadalupe Creek, Alamitos Creek gather runoff from the Santa Cruz Mountains, notable high points being Mt. Thayer (elevation 1,063 m [3,486 ft]) and Mt. Umunum (elevation 1,062 m [3,483 ft]), and the summit of Loma Prieta (elevation 1,155 m [3,790 ft]).

### **Climate and hydrology**

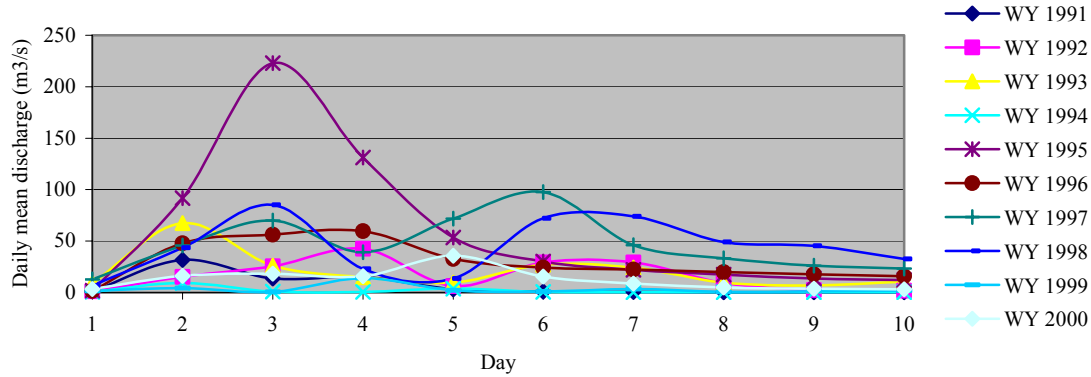
The residents of the Guadalupe River water enjoy a mild climate similar to other locations in the Bay Area that have only limited influence from maritime fogs. Average monthly temperatures have reached a maximum of 27.8 °C (82.1 °F) in San Jose in July and a minimum of 14.4 °C (57.9 °F) in January. Rainfall in the Guadalupe River watershed is predominantly maritime, with regional-scale weather systems moving on shore in response to the position of the Pacific high-pressure zone and westerly winds that bring moist air from the Pacific Ocean. Rainfall measurements began in San Jose in 1898 making that location one of the longest running records in the Bay Area. Annual rainfall in San Jose averages 368 mm (14.5 inches) with the maximum annual rainfall at 200% of the average and the minimum at 40% of the average. Locations in the highest extremities of the watershed can receive in excess of 1,500 mm (60 inches) annually. In addition to annual and spatial rainfall variability, the watershed undergoes periods of drought, the most recent of which occurred from 1987-92 (six years of below average rainfall) and “deluge”, most recently 1993-2000 (eight wetter than average years with only one intervening dry year). Rainfall follows a seasonal pattern with a pronounced wet season that generally begins in November and can last through to May. During this period an average of 89% of the annual rainfall occurs. The wettest month on average is January with an average rainfall of 78 mm or 21% of the annual. On average, rain occurs on 58 days at a depth of  $\geq 0.254$  mm (0.01 in), on 33 days at a depth  $\geq 0.254$  mm (0.1 in), on 9 days at a depth  $\geq 12.7$  mm (0.5 in) and on only 2 days annually at a depth of  $\geq 25.4$  mm (1 in).



Runoff in the Guadalupe River watershed exhibits similar patterns to rainfall; high interannual variability (C.V. = 117), successive years of low or high runoff, and a highly seasonal runoff pattern. To a small extent, the runoff pattern is dampened by the operation of storage reservoirs in the upper parts of tributary creeks. There are five major reservoirs in the watershed with a total storage capacity of 44 Mm<sup>3</sup> (35,778 acre-feet) or about 100% mean annual runoff (MAR). The reservoirs occur on Los Gatos Creek (Lexington Reservoir, and Vasona Reservoir), Guadalupe Creek (Guadalupe Reservoir), Alamitos Creek (Almaden Reservoir), and Calero Creek (Calero Reservoir). The reservoirs were built for water supply but they also provide some flood mitigation.

Gauging on the Guadalupe River at San Jose began in 1930. Since that time annual discharge has varied from 1 mm of runoff (0.422 Mm<sup>3</sup>) to 638 mm of runoff (241 Mm<sup>3</sup>) or about 600 times. The driest year on record occurred in water year (WY) 1933 and the wettest year was WY 1983. MAR is 110 mm (42 Mm<sup>3</sup> or 34,050 acre-feet). Daily discharge varies from zero to 223 m<sup>3</sup>s<sup>-1</sup> (7,870 cfs). The largest in the past decade occurred in 1995 (Figure 3). In fact the 1995 flood is the largest on record with a peak gauge height of 17.4 feet (5.3 m), 11,000 cfs (311 m<sup>3</sup>s<sup>-1</sup>) and a mean daily discharge of 7,870 cfs (223 m<sup>3</sup>s<sup>-1</sup>). During the past decade, the Guadalupe River has averaged seven floods per year with an average daily discharge in excess of 200 cfs (5.7 m<sup>3</sup>s<sup>-1</sup>). On average, five of these were single peak events and two were events with three to five peaks less than seven days apart. These floods are caused by intense rainfall in the watershed over the preceding days (Table 3). Depending on the rainfall in the season-to-date and the rainfall intensity during a particular storm event, a rainfall of only 1.3 inches in a 24 to 48-hour period can cause a small flood to route through the watershed. Rainfall and stream flow information is collected by the Santa Clara Valley Water District as part of their water management and flood alert system and is readily available on the internet <http://alert.valleywater.org/>.

These observations have important implications for flood sampling for suspended sediment and trace contaminants. Sampling teams will need to be responsive to weather forecasts and be willing to remobilize for subsequent peaks that commonly occur less than 7-10 days apart especially later in the wet season. On average, there is a 17% chance that the first flood will occur in September or October, a 45% chance of the first flood being before November 30<sup>th</sup> and a 76% change that the flood season will begin prior to New Year.



**Figure 3.** Daily discharge on Guadalupe River at San Jose (USGS 11169000) during the largest flood of the year for each water year during the past decade.

**Table 3.** A comparison of rainfall and runoff during the largest flood of each water year over the past decade.

Water Year	Date	Instantaneous Peak (cfs)	Daily Average (cfs)	Peak Gauge Height (ft)	9am Rainfall at Mt Umunhum		
					Preceding 24 hours (in)	Preceding 48 hours (in)	Season to Date (in)
1991	3/24/1991	3,330	1,120	6.5	1.6	1.6	27.9
1992	2/12/1992	4,640	1,500	8.3	2.7	5.4	23.7
1993	1/13/1993	4,920	2,380	8.7	5.4	5.5	33.6
1994	12/11/1993	1,510	330	4.1	1.0	1.3	10.6
1995	3/10/1995	11,000	7,870	17.4	6.4	10.4	61.2
1996	2/20/1996	4,720	1,990	8.4	3.5	7.4	41.6
1997	1/26/1997	5,470	3,450	9.4	2.6	5.4	61.1
1998	2/3/1998	7,510	3,010	12.6	4.6	6.7	44.7
1999	11/30/1998	1,300	492	4.0	2.5	2.7	8.9
2000	2/11/2000	3,340	570	6.5	1.3	2.6	34.1

**Geology and soils**

The Guadalupe River watershed is comprised predominately of flood basin Holocene deposits in the lower watershed, and alluvial fan Holocene and Pleistocene

deposits in the upper watershed. The watershed lies on a series of faults with northwesterly trends: San Jose, Palo Alto, Stanford/Cascade, Monte Vista, and San Andreas. Bedrock that underlies the Guadalupe River watershed northeast of the San Andreas Fault is a composite of the Franciscan Complex, the Coast Range ophiolite, and parts of the Great Valley Sequence. Mineralized mercury is widespread throughout the New Almaden region, which is associated with siliceous and calcareous deposits from hydrothermal alteration of serpentinite. Other metals that are widely distributed in the watershed include magnesium, iron, nickel, and chromium, which are typically found at high concentrations in serpentinitized ultramafic rocks.

### **Watershed and stream geomorphology and habitat**

Based on a public access level reconnaissance (McKee and Leatherbarrow, October 2002), sediment supply to the channels appears to be sourced from urban runoff, bed and bank erosion and agricultural erosion. Very little fresh or even recently active hillslope colluvial processes were observed in the areas visited (excluding Los Gatos Creek watershed) indicating that sediment supply to the streams is confined more to localized failures rather than from the diffuse landscape. There were a number of ranches running cattle and/ or horses observed where over grazing, yard areas or laneways had exposed soils. New developments on hillsides where new roads have been cut also showed evidence of erosion in isolated instances. There were also a number of tree crop areas managed for zero vegetation cover. Areas either managed or accidentally left with exposed soils in rural areas of the watershed will play a role in the overall sediment budget for the watershed.

Riparian areas on the valley floor support native arroyo willow, Fremont cottonwood, box elder, western sycamore, red willow, and sandbar willow (SCBWMI, 2000). Species of oak around upper watershed riparian and hillslope areas and the native meadow grasses and flowers have been the pride of the watershed throughout the mission and mining eras. A steelhead run still exists in the mainstem of the Guadalupe River and lower Los Gatos Creek. Work is presently underway to enhance the habitat by removal of barriers and installation of fish ladders (SCBWMI, 2000). Presently, out of a total survey length of 81 miles of creek lines within the Guadalupe, 21% are concrete or rock-lined culverted, 38% have been straightened, rerouted, or contained by levees, and 40% remain in an “unmodified” state.

### **Land use and population**

The Santa Clara Valley was almost exclusively used for agriculture before the World War II era. As the electronics industry began to develop in the 1960's, the valley experienced large and rapid-paced population growth and subsequent urban development. Current land uses in the Guadalupe River watershed are comprised of a mix of agricultural and rangeland activities in the upper watershed and high-density urban land use in the lower watershed (Table 4). Urban development in the lower watershed has

dramatically increased impervious surface cover, which typically hastens the transport of sediment and associated contaminants via urban runoff in response to storm events.

Between 1940 and 2000, population in Santa Clara County has increased from approximately 175,000 to 1.68 million people (800%) (MTC and ABAG, 2002). As of 2000, approximately 53% of the people in Santa Clara County lived in the City of San Jose, much of which lies within the Guadalupe River watershed. Estimates of projected population in Santa Clara County for the year suggest that population will increase by approximately 480,000 more people or 130% between 2000 and 2025 (SCDF, 2001).

**Table 4.** Land use in the Guadalupe River watershed based on 1995 statistics (SCBWMI, 2000).

Land use	Area		Land use	Area	
	(acres)	(%)		(acres)	(%)
Residential	32230	30.7	Agriculture	3120	3.0
Commercial	4888	4.7	Forest	37810	36.0
Public/ Quasi-public	2777	2.6	Rangeland	16859	16.1
Industry - Heavy	1556	1.5	Urban Recreation	2500	2.4
Industry - Light	996	0.9	Vacant/ Undeveloped	1145	1.1
Transportation and utilities	1027	1.0		61434	58.5
Mines and Quarries	28	0.0			
	43502	41.5			

### Known contaminant sources

Historic agricultural and mercury mining activities and more recent urban development and population growth in the Guadalupe River watershed have resulted in widespread distribution of contaminant sources in the watershed that are associated with various land uses. The inoperative mining district of New Almaden (currently within the Alameda Quicksilver County Park), which at one time was the largest supplier of mercury in North America, is responsible for historic deposits of mercury that continue to flow to the Bay via a drainage network (Abu-Saba and Tang, 2000). Urban conveyance systems also continue to transport PCBs and OC pesticides (DDT, chlordane, and dieldrin) through the Guadalupe River watershed (KLI, 2002; Leatherbarrow et al., 2002). The Silicon Valley Toxics Coalition (SVTC) currently displays maps that identify locations of known point sources of contamination throughout the Santa Clara Valley on their website (SVTC, 2002).

### **Channel modifications (past and ongoing)**

Interpretation of study results may require evaluation of bed and bank disturbance associated with channel modifications that might impact water column concentrations of trace contaminants and suspended sediments at the study location. The Guadalupe River has been subject to morphological modifications since 1866, when a canal was dug to relieve flooding from a then rapidly expanding orchard agriculture (SCBWMI, 2000). In the 1960s, Canoas and Ross Creeks were realigned. In 1975, about 3,000 feet of the Guadalupe River channel was widened and moved eastward and the original channel was filled to make way for the Almaden Expressway. In the late 1970s, Alamos Creek was widened and levees were built from Bertram Bridge downstream to its confluence with Guadalupe Creek, a distance of approximately 6 miles. Recently, the U.S. Army Corps of Engineers has begun a series of three flood control projects along the length of Guadalupe River from Alviso Slough to just upstream of Almaden Lake on Guadalupe Creek. Estimated construction time lines are August 2002 to December 2004 for the Lower Guadalupe River Project, May 2002 to November 2004 for the Guadalupe River Park and Flood Protection Project, and June 2003 to March 2010 for the Upper Guadalupe River Project. Project partners include the Santa Clara Valley Water District, the City of San Jose, and the San Jose Redevelopment Agency. The objectives of the projects are to provide flood protection, protect fish and migratory bird habitat, and provide recreational and open space benefits. Other ongoing or proposed projects in the watershed include; the Los Capitancillos Freshwater Wetlands Project proposed to create wetland habitat next to Guadalupe Creek near the Los Capitancillos Percolation Ponds and compensate for sediment removal from the creek, the Guadalupe Creek Project which will provide a flood protection berm to protect the Los Capitancillos Project, and an ongoing bank stabilization project on Canoas Creek. Several federal and state funded transportation projects are also in various stages of development in the Guadalupe River watershed (MTC, 2002).

### **Watershed character downstream of the sampling location**

The area downstream of the sampling location (and hence that will not be measured) is characterized mainly by industrial and commercial land use with small areas of residential and open space. This area is flood-prone and mostly less than 20 feet above sea level. During large floods it may be difficult to accurately define where in fact the watershed boundary lies. At low flow however, the area is about 10 square miles or less than 1% of the total watershed area.

### **Previous and ongoing investigations of PCBs, OC pesticides and Hg**

Several studies have investigated the distribution and extent of contamination in the Guadalupe River. These previous results will provide context for analysis of data generated in this study. From 1996 to 2001, the RMP conducted seasonal sampling of water and sediment in the tidal reach of the Guadalupe River (Alviso Slough) to

determine that wet-season concentrations of PCBs, OC pesticides and mercury were relatively high in surface water entering the Bay (Leatherbarrow et al., 2002). In an ongoing effort to assist TMDL development that began in 2000, the Santa Clara Valley Urban Runoff Pollution Prevention Program has been monitoring sediment in urban conveyance systems and creeks for PCBs and mercury (KLI, 2002). Both contaminants have been measured at high concentrations in urban/industrial sites within the watershed. A mercury TMDL for the Guadalupe River is currently being developed under the guidance of the Santa Clara Basin Watershed Management Initiative with collaboration from the Santa Clara Valley Water District, Tetra Tech, Inc. and EOA, Inc. A final TMDL report is due by June 2003.

## DATA QUALITY OBJECTIVES

### **Data uses**

Section 303(d) of the Clean Water Act requires that impaired water bodies be identified. Impaired water bodies are those where water quality standards are not expected to be met after implementation of best available technological controls, with respect to permitted wastewater. Water quality standards include: (1) designated uses (such as fish and wildlife habitat and recreational use); (2) any narrative or numeric water quality objectives; and (3) anti-degradation or maintenance of ambient water quality.

San Francisco Bay is listed as impaired by the State (Clean Water Act 303(d)) for PCBs, OC pesticides (DDT, chlordane, and dieldrin), and mercury. Once a water body is listed under Section 303(d), the State is required to determine the amount that the contaminants of concern must be reduced to meet the applicable water quality standard and eliminate beneficial use impairment. This allocation of allowable contaminant discharge from various sources is called a Total Maximum Daily Load, or TMDL.

As part of TMDL implementation, the San Francisco Regional Water Quality Control Board (SF RWQCB) and its environmental management partners has specifically requested better estimates of loads of TMDL listed substances from local urbanized small tributaries to inform strategies for water quality attainment. For example, the PCB one-box model for the Bay (Davis, 2002) currently suggests that external annual loads of just 10 kg of PCBs would prevent the total PCB mass in the Bay from ever dropping below one-tenth of the present mass, thus maintaining concentrations in some sport fish that may continue to pose human health concerns. An estimate of loads for PCBs from one of the major urban drainages of the Bay Area will allow environmental managers to focus management on specific sources and pools. In the case of mercury, assessment of concentrations and loads in the Guadalupe River will provide valuable baseline data to quantify ongoing impacts to the Bay in the context of legacy loads and to assess concentration and load trends in a watershed that is itself listed as impaired for mercury. At present there are no estimates of current inputs of OC pesticides. This study will

provide a valuable data set to begin the process of determining current loads of persistent organochlorine contaminants to the Bay.

Therefore in the context of these outlined management needs, the data collected during this study will be used to characterize water, suspended sediment, and trace contaminant transport processes at a downstream cross-section on the Guadalupe River channel. The interest is mainly in the accurate characterization of changes in concentrations of each contaminant during the passing of a storm hydrograph and between storm hydrographs. However, there will also be some effort expended to quantify concentration variations of suspended sediment and trace contaminants at various points in the X-section during selected storm events. After QA/QC Once trace contaminants and suspended sediment concentrations will be combined with estimates of discharge provided by the USGS to estimate loads of contaminants and sediments entering the tidal sloughs and South San Francisco Bay.

### **Expected measurements**

Measurements made during this study will include concentrations determined through laboratory analyses of appropriately sampled and preserved stream water, optical backscatterance measured using a turbidity probe, and ancillary data measured using various calibrated field and laboratory instruments. All expected measurements are listed in the following tables (Table 5). To aid in the interpretation of the expected measurements made in this study, additional hydrological data including precipitation and stream flow will be requested from the Santa Clara Valley Water District. Additional ancillary data may include qualitative visual observations in the watershed after flood events to better understand subwatershed erosion and point source activation processes and their influences on sediment and contaminant supply and transmission to the watershed outlet (sampling location). There is also the possibility of collecting or collating satellite or aerial images of the receiving waters (the South Bay) to obtain a qualitative view of contaminant fate. However it should be emphasized that the processes of source activation and fate are outside the current scope of the project.

### **Expected quality**

Data quality refers to the level of uncertainty associated with a particular data point. All the elements of the sampling event, from the sampling design through the laboratory analysis and reporting, affect the quality of the data. The management questions this project aims to assist in answering help determine what level of uncertainty is acceptable or appropriate. The following decisions on acceptable detection limits, accuracy and precision (Table 6) were derived from existing knowledge of expected concentrations in the immediate receiving water body (Alviso Slough), concentrations of each contaminant known to be toxic or detrimental to beneficial uses, and the cost associated with laboratory processing at higher detection limits.

**Table 5.** Parameters to be analyzed for or measured in the laboratory or field in Guadalupe River water over the 4-year study program. Units are concentrations (mass per unit volume) unless otherwise stated.

PCB Congeners	Organochlorine Pesticides	<sup>1</sup> PAHs	Trace Metals	Ancillary Measurements
8, 18, 28, 31, 33, 44, 49, 52, 56,	<sup>4</sup> Cyclopentadienes	1-Methylnaphthalene	Total Mercury	Optical back scatter (NTU)
60, 66, 70, 74, 87, 95, 97, 99,	Dieldrin	2,3,5-Trimethylnaphthalene	Dissolved Mercury	<sup>3</sup> Suspended sediment
101, 105, 110, 118, 128, 132,		2,6-Dimethylnaphthalene	Methyl Mercury	Particulate Organic Carbon
138, 141, 149, 151, 153, 156,	<b>Chlordanes</b>	2-Methylnaphthalene		Dissolved Organic Carbon
158, 170, 174, 177, 180, 183,	alpha-Chlordane	Biphenyl	<sup>2</sup> Silver	Nutrients
187, 194, 195, 201, 203	cis-Nonachlor	Naphthalene	<sup>2</sup> Copper	pH
	gamma-Chlordane	1-Methylphenanthrene	<sup>2</sup> Lead	Conductivity (ms cm <sup>-1</sup> )
	Heptachlor	Acenaphthene	<sup>2</sup> Nickel	Temperature (°C)
	Heptachlor Epoxide	Acenaphthylene	<sup>2</sup> Cadmium	
	Oxychlordane	Anthracene		
	trans-Nonachlor	Fluorene		
		Phenanthrene		
	<b>DDTs</b>	Benzo(a)anthracene	<b>Notes</b> 1. PAHs will not be analyzed for in the first year of the study (Water Year 2003) unless the CEP approves an increase in the budget. 2. Silver, Copper, Lead, Nickel, and Cadmium will be analyzed for as budget allows. 3. Water samples for analysis of suspended sediment concentration will be collected by the contaminant sampling team (UCSC and SFEI) as well as the sediment loads sampling team (USGS). 4. If budget allows.	
	o,p'-DDD	Chrysene		
	o,p'-DDE	Fluoranthene		
	o,p'-DDT	Pyrene		
	p,p'-DDD	Benzo(a)pyrene		
	p,p'-DDE	Benzo(b)fluoranthene		
	p,p'-DDT	Benzo(e)pyrene		
		Benzo(k)fluoranthene		
		Dibenz(a,h)anthracene		
		Perylene		
		Benzo(ghi)perylene		
		Indeno(1,2,3-cd)pyrene		
		Dibenzothiophene		

**Table 6.** Anticipated data quality of primary data.

	Number of Samples	Precision	Accuracy	Detection Limit (DL)	Field Blank
PCBs	<30	± 25%	Within 10% of reference	1-5 pg l <sup>-1</sup>	Within 10% of DL
OC pesticides	<30	± 25%	Within 10% of reference	1-5 pg l <sup>-1</sup>	Within 10% of DL
PAHs	<30	± 25%	Within 10% of reference	200-500 pg l <sup>-1</sup>	Within 10% of DL
Mercury	30	± 25%	Within 10% of reference	0.1 ng l <sup>-1</sup>	Within 10% of DL
Trace metals	30	± 25%	Within 10% of reference	<0.1 µg l <sup>-1</sup>	Within 10% of DL
Suspended sediments	<150	± 5%	Within 10% of reference	0.1 mg l <sup>-1</sup>	Within 10% of DL
Turbidity	Every 15 minutes	± 2%	Within 10% of reference	0.0 NTU	Within 10% of DL



## **Data quality indicators**

The data quality indicators, precision, accuracy, completeness, detection limits, representativeness and comparability, relate to various aspects of the data gathering, or sampling and analysis. Quality assurance and quality control procedures for laboratory analyses are conducted in accordance with the Quality Assurance Project Plan for the RMP (Yee et al., 2001). Quality control criteria for analyses of trace elements, trace organics, and ancillary water quality parameters are listed in the Appendix. Brief summaries of each indicator are provided in the following paragraphs:

**Accuracy** is the degree of agreement of a measurement with a known or true value. To determine accuracy, a laboratory or field calibration value is compared to the known or true concentration. Accuracy is usually assessed through the use of spiked samples (e.g., matrix spikes or surrogate spikes) or the analysis of a sample of known concentration (e.g., a performance evaluation sample or laboratory control sample [LCS].) In the field, calibration with prepared standards provides information about the accuracy, or bias, of a field instrument. If the data provided from the laboratory does not meet the required accuracy listed in Table 6, the data will be tagged with a qualifier.

**Precision** is the degree of mutual agreement between or among independent measurements of a similar property (standard deviation [SD] or relative percent difference [RPD]). This indicator relates to the analysis of duplicate laboratory or field samples. If the precision of the data does not meet the criteria laid out in Table 6, the data will be tagged with a qualifier.

**Completeness** is expressed as the amount of usable data obtained compared to the amount that was expected to have been obtained. Due to a variety of circumstances, sometimes not all samples collected can be analyzed. The percent completeness required will depend on data use and decisions to be made based on those data. Expectation of completeness will be higher the fewer the number of samples taken per event.

**Representativeness** is the expression of the degree to which data accurately and precisely represent a characteristic of an environmental condition or a population. It relates both to the sampling area and to the sampling procedures. The sampling methodology was designed to assess representativeness via two main mechanisms. 1. We will collect both point data and depth/ X-sectionally integrated samples (DCS). The DCS samples will be used to test the degree to which the point sampling explains both the temporal and spatial variation of concentration in the water column. The issue of representativeness will be incorporated into interpretation and discussion of the results in the *Final Report*.

**Comparability** expresses the confidence with which one data set can be compared to another. The use of standard, published methods allows the data to be compared to data from other projects; using the same methods throughout allows for

comparison of data within a project. Expressing data using consistent units also addresses comparability. The project aim to collect data using standard published methods and briefly outlined in this *Sampling and Analysis Plan*. The aim is to ensure that the data collected is specifically comparable with other mercury and PCB data collected in the Bay, and Guadalupe River during the development and implementation of TMDLs.

## **Data Management**

Both the UCSC and AXYS analytical labs provide data to SFEI in both written and electronic form. Electronic data files are provided in Excel spreadsheet format. Once the data is checked for quality control, SFEI will upload the data into an Access Data Base and then into Oracle Data Base. It can then be extracted at will and on request via appropriate staff at SFEI or via the web ([www.sfei.org](http://www.sfei.org)). The data will also be formatted and provided in raw tables within the final report. The following check list provides a brief overview of data management procedures.

1. Data Manager: Receipt of data – conduct an inventory to check that all types of data have been provided
2. QA Officer: Carryout QA/QC procedure
3. Data Manager: Format the data ready for archiving
4. Data Manager: Archive data in Access Data Base and Oracle
5. Lead Scientist: Carry out interpretation and prepare draft report
6. Lead Scientist: Submit draft report for management and external peer-review
7. Lead Scientist: Address reviewers comments and prepare final report
8. Lead Scientist: Submit final report and a reply to the reviewers
9. Lead Scientist: Give oral presentation to Science Oversight Group
10. Lead Scientist: Prepare report as a peer-reviewed Journal article

## **Final report outline**

The final 1<sup>st</sup> year report will be completed in late Fall, 2003. It is anticipated that it will be approximately 30 pages in length with additional appendices as necessary containing raw data. It is anticipated that the report will contain the following sections:

Cover (with site photograph)

Abstract

Acknowledgements

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Introduction

Methods

    Turbidity

    Suspended sediments

    Trace metals

- Trace organics
- Results
  - Turbidity
  - Suspended sediments
  - Trace metals
  - Trace organics
- Discussion
- Recommendations
- References
- Appendices

## SAMPLING DESIGN

### Bridge description

All sampling during high flow will occur off the “Rental Car Return Bridge” located on the property of the San Jose International Airport. The bridge was built and is maintained by the airport authority. The bridge is a two lane bi-directional all-concrete steel reinforced structure with a slight arch and a single center pillar support in the middle of the river channel (Figure 4A. and 4B.). Traffic speed on the bridge is subdued by a traffic light on the western end of the bridge. There is a raised footpath with a width of 1.5 m (4.8 ft) on each side of the carriageway. The footpath on the downstream side of the bridge will be used for operating the field equipment and collecting samples. The bridge rail measures 9.0 m (29.4 ft) above the current thalweg. The rail has a height of 1.1 m (3.7 ft) above the footpath.

A.



B.



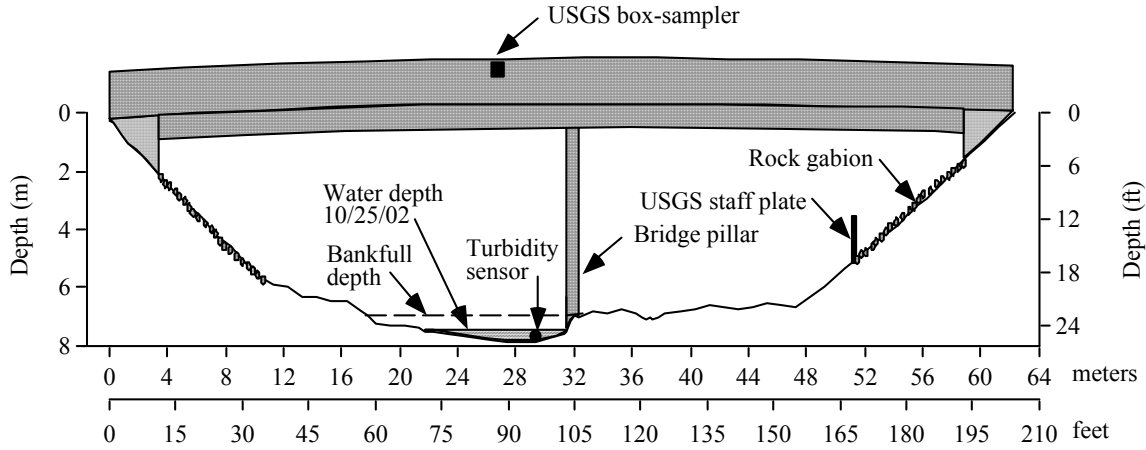
**Figure 4.** A view of the “Rental Car Return Bridge” (the study sampling location) looking from (A) the bottom of left bank, and (B) the top of the left bank of the Guadalupe River.

## **Reach character**

The reach has been straightened and widened and the X-section geometry has been modified to a trapezoid to improve the transmission of flood discharge. The upper banks in the vicinity of the bridge have been secured from erosion by wire covered rock gabion. Presently the low-flow channel meanders left to right as it passes downstream (Figure 5A and 5B). The main features of the channel at the sampling location include the low-flow channel, a low-flow channel partially submerged bar, a low-flow channel left bank, an in-channel floodplain that marks the height of the bankfull discharge (approximately 1.5 year return interval flood), and the upper (high flow) trapezoidal banks (Figure 6). The bed at the sampling location consists of poorly sorted gravels, sands and silts with a median grainsize ( $D_{50}$ ) of 10 mm (visual estimate). The in-channel floodplain is vegetated with grasses, reeds and other soft-stemmed riparian plants. There are a number of larger trees both upstream and downstream that were perhaps part of the original riparian vegetation before the channel was modified. The turbidity sensor and USGS box sampler (suspended sediment point samples) are presently positioned to sample the thalweg of the current low-flow channel (Figure 6). Under moderate or high flood conditions it is likely that the thalweg may move laterally. This may necessitate the repositioning of the point sampling locations for turbidity and suspended sediments. Although the sampling location is relatively free of trash and other urban debris, during a reconnaissance upstream (October 2000), there were a number of reaches that were littered with trash such as bottles, cans, and various types of plastic and metal objects, such as a shopping trolley. These may pose a problem should they catch on the turbidity sensor housing.



**Figure 5.** The character of the low-flow channel at the sampling location (A) looking upstream and (B) looking downstream with the Highway 101 Bridge near the top of the photo.



**Figure 6.** Scale X-section of the sampling location indicating the main channel features.

**Field health and safety**

The sampling location on Guadalupe River presents a suite of hazards that must be addressed by any field investigator. During the wet season, stream flows will be too high to enter and all sampling will occur from the bridge. If field personnel must enter the channel (in particular during the maintenance of the turbidity probe) there are localized hazards due to steep and potentially unstable banks, unsure footing, perhaps unstable recently deposited large debris, exhaustive work, urban pollution, and crime that might pose problems. To counter these hazards, SFEI has developed a “Safety Sheet” for fieldwork (Table 7). It presents general guidelines for health and safety in the field that will be followed during this Project; however, “common sense”, concentration on the job at hand, and care for others remain the best defense against potential and real field hazards.

**Table 7.** Field health and safety guidelines for the Guadalupe River watershed Study.

<u>General</u>	<u>When using chemicals</u>
1. Always have at least two people in the field at any time.	1. Wear safety glasses and gloves.
2. Always notify Airport Security prior to or upon arrival.	2. Know your equipment/ sampling methods before you begin.
3. Carry a first aid kit.	3. Avoid contact between reagents and shin, eye, nose, and mouth.
4. If possible, carry a cellular phone.	4. Do not eat or drink while monitoring.
5. Be aware of team members with allergies to insects or vegetation.	5. DO NOT pour chemicals or samples containing reagents onto the ground or into the creek.
6. Never drink the stream water.	6. Close all reagent containers after use to avoid accidental spills.
7. Take care on unstable stream banks.	7. Wipe up spill immediately if they occur.
8. DO NOT attempt to wade swift flowing water.	
9. If you are afraid for your safety, stop monitoring.	

## **Field equipment (description, calibration and maintenance)**

### **Turbidity**

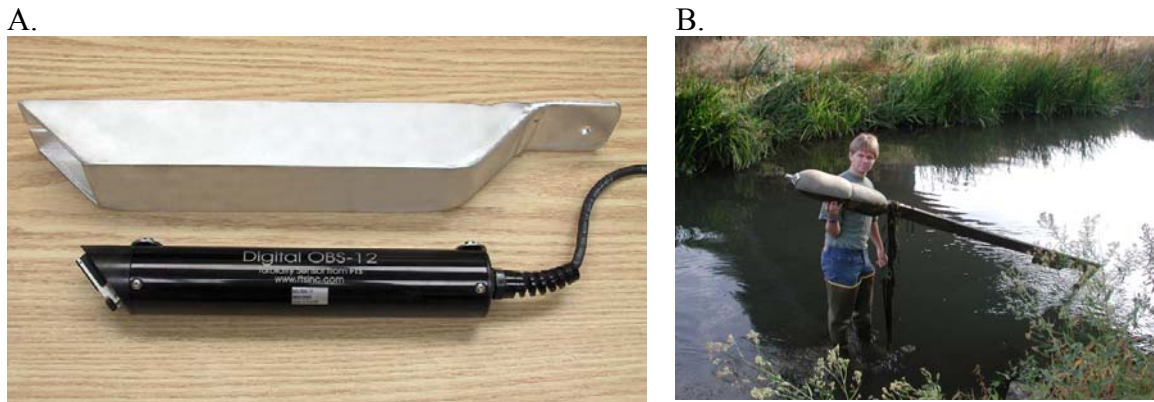
#### *Turbidity Sensor*

This component of the study is being led by Rand Eads of the USDA Forest Service, Redwood Sciences Laboratory. Recent advances in turbidity sensors have reduced biofouling by employing a mechanical wiper that is activated before each turbidity measurement (Eads, 2002). Biofouling by macroinvertebrates and algae occlude the sensor's optical window and can quickly degrade data quality in streams that have warm temperatures and high nutrient loads. We have purchased and installed a DTS-12 turbidity sensor (Figure 7A), manufactured by Forest Technology Systems Limited (FTS), at the Guadalupe site. Digital communication between the sensor and data logger allows for long cable runs (160 feet from the instrument shelter) without signal degradation. We anticipate that the sensor's wiper will successfully remove small contaminants from the optical sensor. Field crews will need to remove larger organic debris if material becomes lodged near the sensor. Field trials, laboratory testing, and statistical analysis at Redwood Sciences Laboratory has led us to conclude that a median turbidity value (from 100 samples in the case of the DTS-12) is more robust in rejecting outliers than the mean or other commonly collected parameters. We will store the median value from each 15-minute wakeup in the USGS Design Analyses data logger (these values, in addition to water stage, will also be available on the USGS web site). The DTS-12 records turbidity in NTUs and is auto-scaling from 0-200 and 0-2000 (the DTS-12 manual is available in electronic form). The DTS-12 will be compared periodically, and only at lower turbidities, to a Hach 2100P portable turbidimeter (widely considered a standard device for field measurements). This will provide assurance that the sensor is operating correctly. The DTS-12 will be returned periodically to the factory for a 6-point calibration in Formazin standards.

#### *Sensor Deployment*

Two methods of deployment for the turbidity sensor were discussed at length with the study team. The original method entailed mounting an articulated sampling boom (plans and photos published on the Redwood Sciences Laboratory web site at: [www.rsl.psw.fs.fed.us/projects/water/tts\\_webpage](http://www.rsl.psw.fs.fed.us/projects/water/tts_webpage)) on the bridge (access to the car rental facilities) and routing the cable to the USGS instrument shelter. A second deployment method was selected that would allow the sensor and boom to be installed in a more timely fashion (the boom and sensor (Figure 7B) were installed and connected to the USGS data logger on 10/9/2002). The deployment that was selected is based on a prior design concept that uses a depth-proportional boom that is anchored to the streambed (Eads and Thomas, 1983). The boom was modified from its original design to incorporate the turbidity sensor. The geology of the basin and the potential effects on bedload transport on the sampling boom were discussed with Tom Lisle, a fluvial geomorphologist with Redwood Sciences Laboratory. The conclusion was that dune, or bed form, migration during storms would not be a likely occurrence and therefore the

predicted height of sensor above the bed is thought to be suitable. An advantage of a bed-mounted boom is that debris is less likely to foul the sensor. A disadvantage is that the bed-mounted boom cannot be accessed during storm flows should the equipment require servicing. Another potential disadvantage is that the bed-mounted boom may only have an effective angle in the water column during high flow of about 30 degrees (when velocity and depth overcome flotation). We expect that the 13 foot-long boom will be fully submerged at storm flows about six feet of stage, and greater, placing the sensor at a maximum distance of about 3 feet above the bed. The boom is anchored to the streambed and protected from impacts by a large block of concrete immediately upstream. In addition to the anchor, a safety stainless steel cable attaches the boom to the concrete block. The boom is constructed of non-rusting aluminum and flotation is provided by two high-density foam floats.

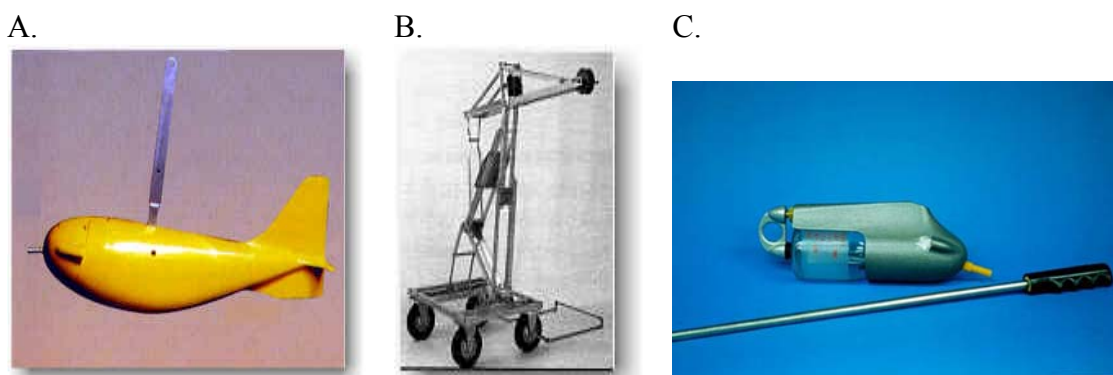


**Figure 7.** The DTS-12 turbidity sensor. A) The DTS-12 Turbidity Sensor and purpose-built housing, and B) Photo of the installed sensor and bed-mounted boom at the Guadalupe River sampling location.

### Suspended sediments

The purpose of sampling the water column for suspended sediment analysis is to determine the instantaneous mean discharge-weighted suspended sediment concentration in the water column. When such concentrations are combined with estimates of discharge, suspended sediment loads are computed. There are a number of sampling devices that have been developed by the Federal Interagency Sedimentation Project (FISP) and its industry partners for sampling wadeable streams (Handheld samplers) and non-wadeable streams (Cable and Real Samplers). For a description of the full range of devices, the reader is referred to Edwards and Glysson (1999). The USGS (Larry Freeman) will lead this part of the Guadalupe River project. They own and maintain two samplers that will be used in this project. During periods of high flow when the

Guadalupe River is not wadeable at the sampling location, a US D-74 depth-integrating sampler (Figure 8A). The D-74 is designed for sampling stream of less than 4.5 m (15 feet) depth. The D-74 weighs 62 pounds and will be deployed from the bridge footpath using a four-wheel boom truck and a cable-and-reel system (Figure 8B). The D-74 has a streamlined cast body that completely encloses a pint bottle. At lower flows when the stream is wadeable, the US DH-48 hand-held depth-integrating sampler will be used (Figure 8C). This sampler is a streamlined aluminum casing about 13 in long that partly encloses the pint sample bottle. Including the sampling container, the whole device weighs 4.5 lbs. During this study we will use a ¼ inch sampling nozzle on both the US D-74 and the US DH-48.



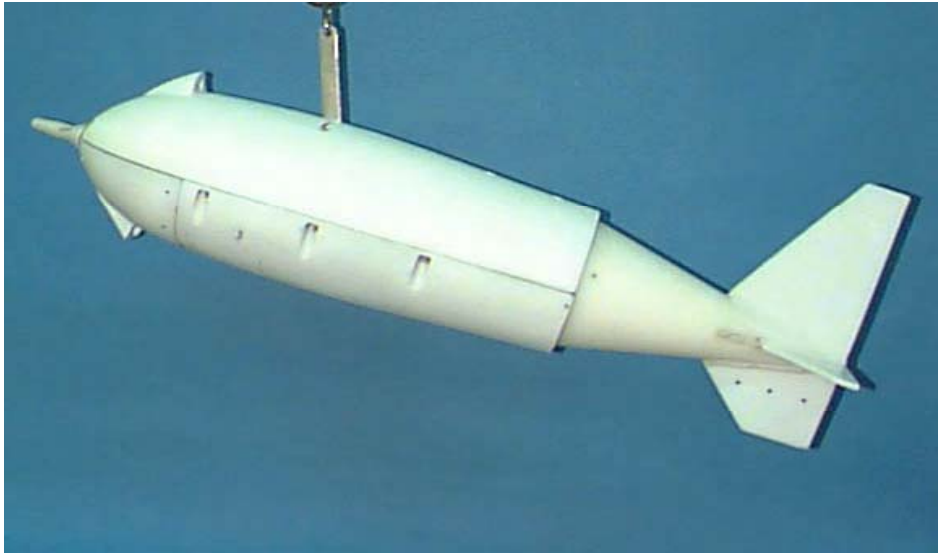
**Figure 8.** The suspended sediment samplers employed by the USGS at the Guadalupe River sampling location. A) US D-74 depth-integrating sampler, B) USGS Type A Crane with Type A Four-Wheel Truck and C) US DH-48 hand-held depth-integrating sampler.

## Trace contaminants

### *Description of Sampling Equipment*

The equipment used for sampling water for analysis of trace contaminants and ancillary water quality parameters is similar to equipment used for RMP Status and Trends Monitoring as outlined in the RMP Field Sampling Manual (David et al., 2001). Field operations procedures and equipment are slightly modified to adapt to logistical factors for conducting stationary sampling from the above-channel bridge location. Major modifications to routine RMP sampling equipment include the addition of a US D-96 depth-integrating collapsible bag suspended-sediment/water quality sampler (Figure 9). An operation manual for the D-96 sampler is accessible via the Internet from the Federal Interagency Sedimentation Project (FISP, 2002). Other primary components of sampling equipment include Teflon™, C-flex™ and polypropylene sample tubing and fittings, trace metals filter (for dissolved trace metals sampling) and assorted sample containers.





**Figure 9.** US D-96 depth-integrating collapsible bag suspended-sediment/water quality sampler

#### *Preparation of Sampling Equipment*

Sampling equipment and containers used for collecting samples for analysis of trace elements and ancillary parameters are prepared by UCSC prior to sampling using trace metal clean techniques described by Flegal et al. (1991) in accordance with the RMP Field Sampling Manual (David et al., 2001).

Samples collected for analysis of PCBs, OC pesticides, and PAHs are collected using the same apparatus used for trace element samples. Sample containers for trace organic samples are prepared by AXYS and shipped to SFEI prior to the date of sample collection. Sample containers are 4-liter amber-colored glass bottles prepared by AXYS prior to sampling by washing and baking or solvent-rinsing using standard laboratory operating procedures. Sample bottles are then shipped to SFEI for sample collection.

### **Sampling procedures**

#### **The sampling team**

##### *Turbidity*

SFEI will collaborate with colleagues at Redwood Sciences Laboratory (RSL) to achieve the goals of this project task. Rand Eads (RSL) has experience in deploying optical probes for continuous suspended sediment monitoring in more than 25 watersheds

on the west coast. SFEI has assisted RSL with the installation of the sensor, logger and other equipment at the USGS gauge. RSL will train SFEI in the protocols for probe maintenance during the first months of probe operation. Henceforth, SFEI will be responsible for probe maintenance include cleaning any accumulated materials from either the sensor or boom housing. Electronic data from the gauging station will periodically be retrieved by USGS and sent to Redwood Sciences Laboratory. RSL will perform data cleanup and quality assurance. RSL will also receive the raw suspended sediment data set from USGS after the USGS has completed quality assurance. A second sediment data set will be collected by UCSC/ SFEI as part of the ancillary data set of the trace contaminants sampling program (see below). RSL will use both of these sediment data sets to compute daily-suspended sediment concentrations and loads. Both finalized turbidity and daily-suspended sediment data sets will then be provided back to SFEI for interpretation and reporting.

#### *Suspended sediments*

The USGS has been collecting data on the discharge of sediment in Bay Area watersheds for the past 40 years and are recognized local experts in the collection and analysis of water discharge and suspended sediment loads in small tributaries of the Bay Area. There are 18 locations in the Bay Area where the USGS has collected at least one full wet season of data and three locations where there is more than 15 years of data. In addition, the same teams that collect sediment data also maintain the discharge gauging in the Bay Area that includes continual reassessment of cross-sectional geometry and rating.

The USGS (Larry Freeman and his team) will be responsible for collection and interpretation of suspended sediment data at the Guadalupe gauge. The USGS has a standard protocol called “seasonal daily suspended sediment loads” that they will initiate to achieve this goal. USGS will seek, train and pay a local “observer” (usually a local landowner, local resident or university student). Once QA/QC is complete, the USGS will provide sediment data to RSL for comparisons to the turbidity method and to SFEI for interpretation and reporting in the context of the contaminant data.

#### *Trace contaminants and ancillary data*

This task will be completed by collaboration with UCSC, led by Dr. Russ Flegal. They have been working with SFEI and other Bay Area groups for more than a decade. UCSC has been primarily responsible for the collection and analysis of trace metals and ancillary data for both the “Status and Trends Program” and the “Special Studies” components of the Regional Monitoring Program for Trace Substances (RMP). They have a set of standard protocols for “Clean” data collection, have years of experience working with the RMP and its partners, and have demonstrated important contributions to improved management of the Bay as well as numerous technical and peer-reviewed publications. The contaminant field team will consist of two team members from UCSC and one team member from SFEI. One person will carry out the “clean hands” field duties, one person will carry out “dirty hands” field duties, and the third person will be responsible for general duties and site logistics. Given the fast response time of the

Guadalupe River, real-time data including rainfall, discharge gauging in the upper watershed and turbidity from this study will be accessed via the Internet for the team members.

## **Sample Collection**

### *Turbidity*

The DTS-12 turbidity sensor has been set to wake up every 15 minutes and send data to the data logger located in the USGS gauge house. The position that the sensor takes the data within the water column is fixed horizontally in the thalweg; however, the vertical position will change depending on the stage height but will remain no greater than about 1 m (3.28 ft) above the bed at maximum stage.

### *Suspended sediments*

The USGS will collect water samples for suspended sediment analysis using two methods. On a routine basis (2-3 times per week) and during floods (up to 2-3 times per day), the “observer” will collect single vertical samples (Edwards and Glysson, 1999). The objective of collecting a single-vertical sample is to obtain a sample that represents the mean discharge-weighted suspended-sediment concentration in the vertical being sampled at the time the sample was collected. Depending on the stage height, the US DH-48 or the US D-74 will be used. The sampling is taken by passing either sampler down and then up through the water column at an even rate so that the sample bottle fills to the base of the neck at the time the device reaches the surface.

In addition to the single vertical samples, the USGS will also collect 10-20 samples using the “Equal-Width-Increment” (EWI) method (Edwards and Glysson, 1999). A cross-sectional suspended-sediment sample obtained by the equal-width-increment (EWI) method requires a sample volume proportional to the amount of flow at each of several equally spaced verticals in the cross section. This equal spacing between the verticals (EWI) across the stream and sampling at an equal transit rate at all verticals yields a gross sample volume proportional to the total stream flow. It is important, obviously, to keep the same size nozzle in the sampler for a given measurement. The Guadalupe River sampling location will be divided into 15-20 verticals. The estimated volume of the composite sample therefore will be about 5-6 pints.

### *Trace contaminants and ancillary water quality parameters*

Collection of water samples for trace contaminant analyses is performed by UCSC staff using trace metal-clean sampling techniques (EPA, 1996) in accordance with the RMP QAPP (Yee et al., 2001). A ‘clean hands/dirty hands’ approach is used when collecting samples in this manner. The ‘dirty hands’ person assists the primary ‘clean hands’ sampler by controlling the flow controller for the peristaltic pump, holding on to or adjusting the sampler components, adjusting the outlet tubing or filter cartridge, and handing sample containers to the ‘clean hands’ person. The ‘dirty hands’ person does not touch the trace-metal clean bottles, but opens the Ziploc™ bags so that the “clean hands”

person may remove them from the bags. The “clean hands” person, wearing at least one pair of polyethylene gloves, does not touch anything with her/his hands except the inner Ziploc™ bag and trace metal clean sampling components. The clean hands/dirty hands system is not critical for the ancillary samples, and these bottles may be rinsed just three times with sample water before collecting the sample.

Unfiltered samples are collected for analysis of SSC, particulate organic carbon, total trace elements (including mercury and methyl mercury) and total PCBs, PAHs, and OC pesticides. Filtered samples are collected for analysis of dissolved trace elements (including mercury and methyl mercury), dissolved nutrients, and dissolved organic carbon (DOC). Collection of filtered samples involves using a 0.45 µm filtration cartridge attached to the sample tubing outlet and secured to sampler components.

## **Sample documentation and shipment**

### **Labeling**

A sample record is maintained for each sampling event. The sample record contains the following information:

1. Site name
2. Collection date
3. Arrival and departure time at each station
4. Station coordinates (latitude and longitude)
5. Water depth at time of sampling
6. A record of every sample bottle filled, with discrete bottle identification code number and quantity of bottles
7. Collecting personnel's names
8. Other remarks (i.e. any conditions that could possibly influence sample analysis or data interpretation, including present and past weather conditions)

The sample collection form, coupled with a chain of custody record and a laboratory analysis record, allows tracing of the complete history of a sample from time of collection to final entry of data to a computer database.

### **Sample storage and shipment to the laboratory**

Water samples collected for analysis of trace metals (including mercury and methyl mercury), nutrients, DOC, POC, and SSC are maintained by UCSC personnel and transported to the UCSC laboratory immediately following the sampling event. Nutrient samples and mercury samples are frozen on dry ice and maintained frozen until they are transferred to laboratory freezers. All other trace metal and related samples are stored in sealed buckets at room temperature during the sampling event and transferred to the laboratory at the conclusion of the event. Sample contamination is avoided by double

bagging the sample containers, handling the containers with clean gloves, and transferring the samples into sealed buckets/coolers immediately after sampling.

Water samples collected for analysis of PCBs, PAHs, and OC pesticides are maintained by SFEI staff during the sampling event and shipped to AXYS within 48 hours of collection. Sample bottles are stored and shipped in coolers using ice packs to maintain a nominal temperature of  $4 \pm 2$  °C (39.2 °F).

## **ANALYTICAL METHODS**

### **Turbidity**

Turbidity will be plotted and checked for outliers. In some cases, outliers can be identified from experience and in other cases a corresponding SSC is required to determine whether a spike is a valid rise in turbidity. Once the physical samples are analyzed in the USGS water lab the SSC data will be forwarded to Redwood Sciences Laboratory. The density and timing of SSC samples will determine both the validity of the turbidity spikes and the goodness of the relationship of SSC and turbidity. A regression of SSC versus turbidity will be done on an annual basis. This relationship will then be used to estimate SSC from the nearly continuous record of turbidity. Once an estimated SSC for each 15-minute record exists the load can be computed from the sum of the product of each SSC and water discharge pair for any desired period. Redwood Sciences Laboratory has developed analysis software for plotting, error correction, and load estimates that operate on a UNIX platform running Splus.

### **Suspended sediments**

There are two categories of laboratory measurement of suspended sediments in water – total suspended solids (TSS) and suspended sediments concentration (SSC). The method of analysis for TSS usually entailed filtration of a sub-sample of water, and then drying and re-weighing the filter and retained sediment to produce a mass per unit volume. The process of sub-sampling either in the field or in the laboratory has been found to cause major analytical bias (Gray et al., 2000). The method that shall be used in the Guadalupe River study is the SSC method and the standard method of the USGS (Guy, 1969) now designated ASTM standard test method D 3977-97 (Gray et al., 2000). This method differs from the TSS method in that it does not allow for sub-sampling either in the field or in the lab. This ensures that all particle sized in the sample are represented in the final determination of concentration. Once suspended sediment concentration is determined the daily loads record will be calculated using the methods outlined in Porterfield (1972). These methods have been adopted by the USGS as the standard methods for computation of the sediment record.

## **Trace contaminants**

### **Mercury and methyl mercury**

Water samples are analyzed for mercury and methyl mercury by UCSC using cold vapor atomic fluorescence spectrometry (CVAFS). Total mercury is measured in accordance with methods outlined in previously published studies (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988; Mason and Fitzgerald, 1990; USEPA, 1999). Methyl mercury is separated from water samples using distillation techniques described in Horvat et al. (1993). The distillate is analyzed for methyl mercury using direct ethylation purge-and-trap techniques (Bloom, 1989).

### **Trace metals**

Water samples are analyzed for trace metals by UCSC using graphite furnace atomic absorption spectroscopy (GFAAS) or inductively coupled plasma-atomic emission spectrometry (ICP/AES). Prior to analysis, samples are prepared with a near-total extraction using an ammonium 1-pyrrolidone dithiocarbonate/ diethylammonium diethyldithiocarbonate (APDC/DDDC) procedure described by Bruland et al. (1985).

### **Trace organics**

Water samples are analyzed for organic contaminants (PCBs, PAHs, and OC pesticides) by AXYS Analytical Services, LTD. PCBs and OC pesticides are measured in accordance with EPA method 1668 revision A (USEPA, 1999) using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). PAHs are measured in accordance with a method comparable to EPA Method 8270 using gas chromatography/mass spectrometry (GC/MS).

### **Ancillary data**

Water samples are analyzed for dissolved nutrients (phosphate, silicate, nitrate, nitrite, and ammonia), dissolved organic carbon (DOC), and suspended sediment concentrations (SSC) by UCSC following methods outlined by Flegal et al. (1991). Conventional water quality parameters (conductivity, salinity, dissolved oxygen, pH, and temperature) are measured onsite by UCSC using a Solomat™ 520C multi-functional chemistry and water quality monitor. This hand-held monitor has several probes, which are submerged approximately 3 feet into the water column to collect readings. The meter is calibrated for conductivity with a KCl standard, dissolved oxygen using a mixture of CoC<sub>12</sub> and NaSO<sub>3</sub> and for pH using buffers of pH 7 and 10.

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## APPENDIX

**Table A.** Quality control criteria for analysis of organic compounds.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Instrument Blank</b>	<b>Cross contamination</b>	NA	Set by laboratory	NA
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	NA	NA	NA
<b>Replicates:</b> (analytical and/or laboratory)  Applies to replicates of field samples, CRMs, matrix spike samples, etc.	<b>Precision</b> Instrument and/or overall reproducibility of a result.	One per batch	RPD or RSD < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, identify and eliminate source of imprecision and reanalyze.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery > 50%	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
<b>Surrogate Spike</b>	<b>% Recovery</b> used to adjust sample results	One per sample	Set by analyzing laboratory (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed
<b>Continuing Calibration Check solutions</b>	<b>Accuracy &amp; Precision</b>	At least every 12 hours	Known values for 90% of analytes shall not deviate more than $\pm 25\%$ for PAHs, and $\pm 20\%$ for PCBs and Pesticides.	Beginning with last sample before failure, recalibrate and reanalyze. Compare RPD and reanalyze.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation (see page24 for equations)

Table B. Quality control criteria for analysis of trace elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	1 per 20 field samples	Within 20–25% of the certified 95% confidence interval	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
<b>Replicates:</b> (analytical and/or laboratory)  Applies to replicates of field samples, CRMs, matrix spike samples, etc.	<b>Precision</b>	One per batch	RPD or RSD < 15%; Hg, As, Se < 25%  RSD of last 7 CRMs < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery > 50%	Check CRM or LCS recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
<b>Laboratory Control Material (LCM; optional)</b>	<b>Accuracy, Laboratory precision</b>	1 per 20 field samples	Within 20–25% of consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table C. Quality control criteria for analysis of cognates.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
<b>Toxicity</b>				
<b>Ammonia, nitrate, nitrite, phosphate, silicate, chlorophyll <i>a</i>, TSS</b>				
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	Once per sample set. NA for chlorophyll <i>a</i> or TSS	NA	NA
<b>Replicates:</b> (analytical and /or laboratory)  Applies to replicates, CRMs, matrix spike samples, etc.	<b>Precision</b>	One per batch. NA for TSS	RPD or RSD < 5%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery > 50%	Review data reports and chromatographs. Check instruments.
<b>DOC (Dissolved Organic Carbon)</b>				
<b>Method Blank</b>	<b>Contamination</b>	One per batch	< MDL or < 10% of lowest sample	Reanalyze samples
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	Once per sample set	RPD < 5%	Recalibrate and reanalyze
<b>Replicates</b>	<b>Precision</b>	One per batch	RPD or RSD < 5%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation