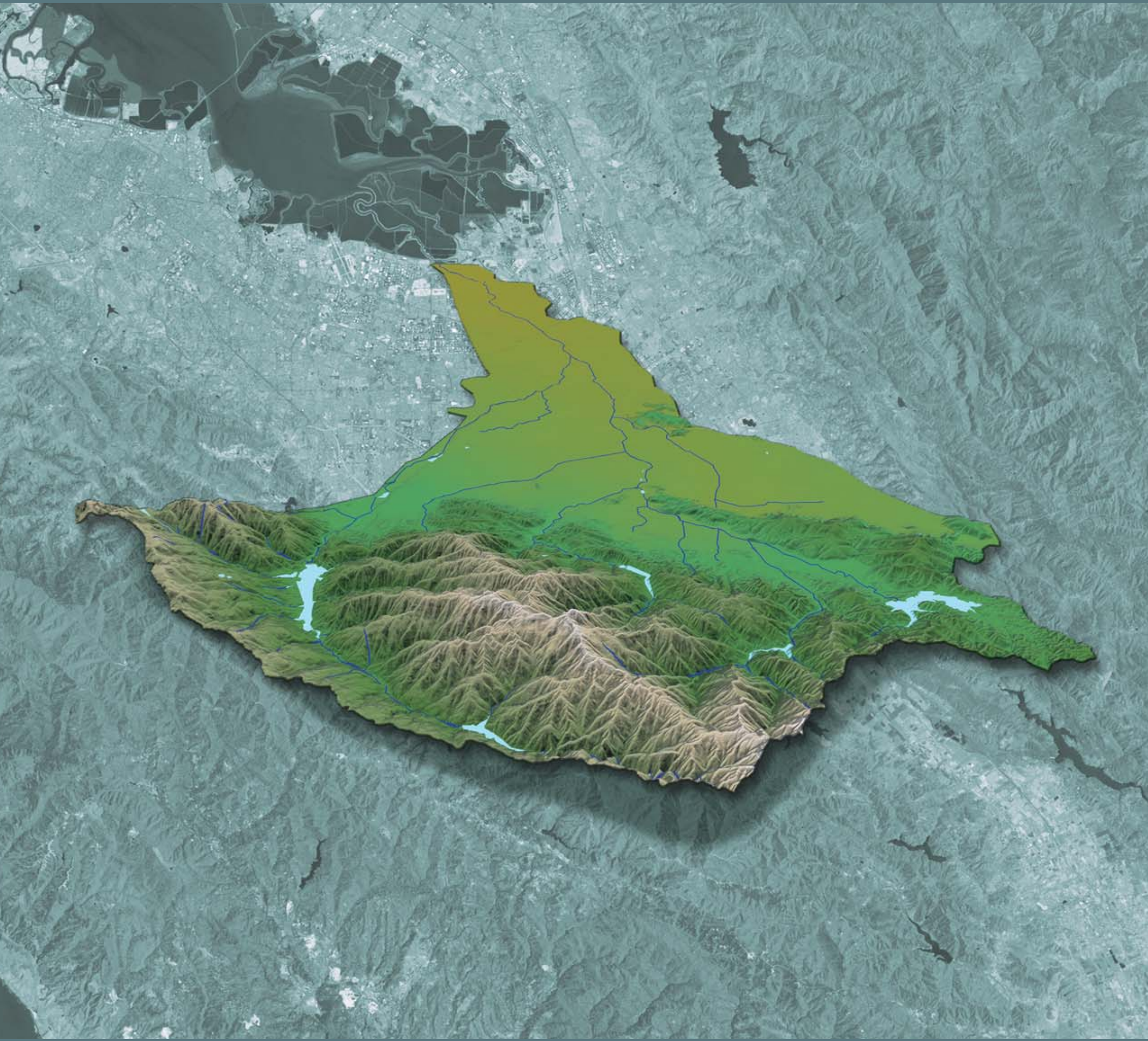
Guadalupe River Watershed Mercury TMDL Project

Final Conceptual Model Report

May 20, 2005



Prepared for:

San Francisco Bay Regional Water Quality Control Board
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ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

The Watershed: The Guadalupe River Watershed is a large (170 sq. mi.) complex hydrologic system, comprised of six major reservoirs and over 80 miles of streams and rivers. The watershed includes dense forests in its headwaters, at elevations greater than 3,000 feet, and in its mid and lower sections large expanses of housing, and extensive commercial development, the latter supporting services, manufacturing, and the Silicon Valley technology enterprise. At sea level, the Guadalupe River discharges into San Francisco Bay (Figure ES-1).

Mercury Concern: The watershed also contains the New Almaden mercury-mining district, the largest mercury producer in North America. From 1846 to 1975 over 84 million pounds of mercury were produced and shipped, mostly to support the California gold rush. Elemental mercury, a liquid metal at room temperature, was used during the extraction of gold from ore. A comparison of mercury data from water and sediment samples from other gold and mercury mines showed that creeks near mercury mines have higher mercury concentrations than gold mines.

Not all of the mercury left the mining district, however. Most of the mercury remaining in the watershed exists as relatively insoluble mercury sulfides in mine wastes that have accumulated in reservoir deposits and sediments, and in stream bottoms, banks and flood plains. Because of the strong association of mercury with solids, the movement of mercury in the watershed is closely tied to the transport of sediments. The high variability of mercury transport is related to the highly variable flow, sediment load, and transported mercury concentrations measured during the wet season.

Total mercury concentrations in the streams that drain the mining areas were up to 6,667 ng/L in the Mine Hill tributary to Jacques Gulch, which enters Almaden Reservoir (SCPD, 2003). The range of total mercury concentrations measured in the outlets of four reservoirs during the dry season of 2003 was 2.7 – 12.8 ng/L and 7.2 to 49.2 ng/L in the dry season of 2004, compared to 1.4 to 20.0 ng/L in 2003 and 3.5 to 42.8 ng/L in 2004. Methylmercury concentrations in the reservoirs within the mining area are exceptionally high. Maximum methylmercury concentrations in the samples

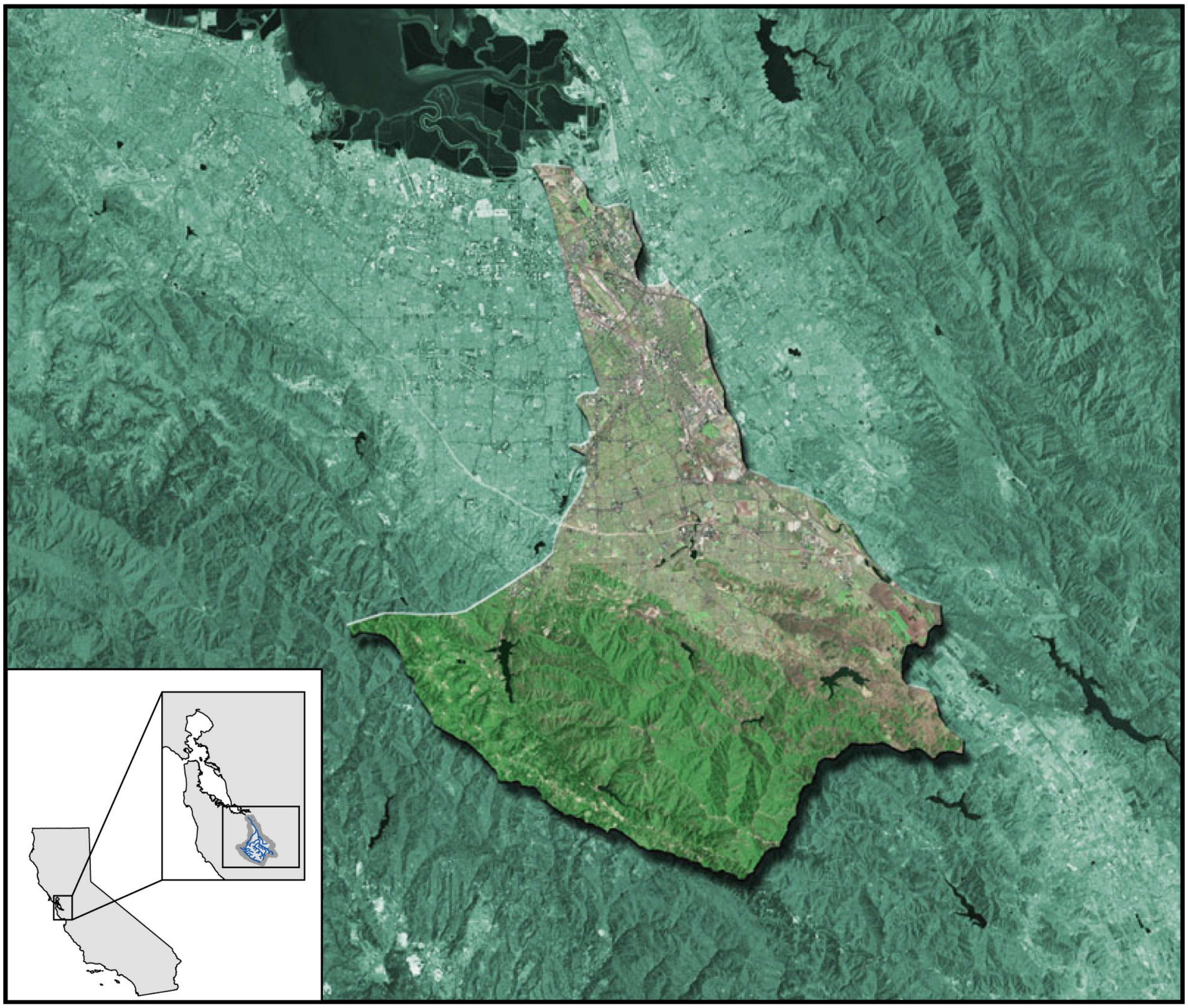


Figure ES-1. Location of Guadalupe River Watershed.

from the reservoir outlets, representing the deeper portion of the hypolimnion, were 7.2 ng/L in Almaden Reservoir and 12.8 ng/L in Guadalupe Reservoir. The problem with mercury, in particular methylmercury, is that it bioconcentrates in the aquatic food chain, producing high mercury concentrations in fish. Fish mercury levels in some of the waterbodies exceed consumption criteria. This has led to fish advisories and postings.

In 1998, in accordance with Section 303 (d) of the Clean Water Act, the California State Water Resources Control Board and the Regional Water Quality Control Board, San Francisco Bay Region listed several waterbodies in the Guadalupe River Watershed as being impaired due to mercury:

- Guadalupe River
- Guadalupe Creek
- Alamitos Creek

- Guadalupe Reservoir
- Calero Reservoir

This impairment listing necessitates the calculation of a Total Maximum Daily Load (TMDL) of mercury for the watershed. The TMDL in essence identifies the maximum amount of mercury that can enter the waterbodies without resulting in the contravention of water quality based standards.

For complex pollutants such as mercury, and in a complex watershed, such as the Guadalupe, the calculation of a TMDL is similarly complex. Formulation of a conceptual model for the system that describes the current understanding of mercury behavior in the watershed can be extremely helpful. In particular the conceptual model describes the processes likely to be controlling mercury transport and fate and identifies additional data needed to address important uncertainties.

The conceptual model is actually a set of statements that describe the current understanding of mercury behavior in the watershed. The uncertainties identified during the conceptual model formulation become the basis for additional field and laboratory investigation. For most other pollutants this is a relatively straightforward process. For mercury, arguably the most complex of all water quality constituents, this requires ongoing efforts of analysis and refinement.

The Conceptual Model: From analyses of the historical data and new results, a conceptual model is emerging for mercury behavior in the Guadalupe River Watershed. The watershed has two distinct hydrologic seasons, a wet winter season and a long dry summer season.

Wet Season: The winter season is punctuated by the advective storms that create large flows in the streams and in the main stem of the Guadalupe River. These large flows are superimposed upon lower flows not that different quantitatively from those of the dry weather season, except that water temperatures are lower. The large storms lead to flows on the main stem that may increase from 10 to over 1000 cubic feet per second (cfs) in less then 24 hours. The high flows recede over 1-2 days. In the upper part of the watershed, the reservoirs typically limit the variability of flow.

The larger rain events, particularly those preceded shortly in time by similar events, create conditions where large quantities of mercury-bearing solids are routed downstream. These solids are believed to originate from hillside drainage, stream sediments, banks, and in some cases flood plains. The larger-sized, mobilized solids in the streams are collected by impoundments created by drop structures and in-stream zones of aggregation. However, during large storms, flows can overtop these drop structures. Above the reservoirs, only suspended sediment is transported downstream, since spilling is extremely rare. Vasona Reservoir, downstream on Los Gatos Creek, spills more often, causing higher suspended solids and mercury to be transported further downstream.

The wet season is largely a season of transport. Methylmercury concentrations are much lower than observed in the outlets of the reservoirs during the warm dry season. But reagents for methylation are being moved into locations where under warmer conditions methylation can occur.

Dry Season: Biogeochemical reactions predominate during the warm dry season. The periodic high flows of winter are past and surface water temperatures increase to values of 65 to 85 ^{o}F. Over the summer, the reservoirs become stratified. Settling of particulate organic matter in summer depletes the lower waters of dissolved oxygen. The reservoirs now are net methlyators of mercury. The methylmercury concentrations in the discharges of Almaden and Guadalupe Reservoirs are high, up to 12.8 ng/l. Methylmercury concentrations in the epilimnetic and upper hypolimnetic waters are less than in the discharge.

Unlike the reservoirs, the creeks in the summer were net demethylators of mercury, with most of the methylmercury in the reservoir releases being lost from the stream water within the first few miles. Although the stream sediment methylmercury concentrations indicate that methylation is occurring at some locations in the creeks, the amount of methylmercury produced is not enough to offset the loss of methylmercury.

Mercury load estimates were made based upon flow and mercury data and modeled flows for selected subwatersheds. Findings from this effort are described below:

1. Most of the total mercury is transported in the wet season, particularly during high flow events.

2. Two major reservoirs, Guadalupe and Calero are sinks for total mercury; they release less total mercury than they receive.

3. Inputs of mercury derived from mine wastes are substantially greater than atmospheric deposition inputs for Guadalupe and Almaden Reservoirs, and for Alamitos and Guadalupe Creeks.

4. The urban creeks contribute less total and methylmercury than the mine-influenced creeks.

5. The total mercury loads from the Guadalupe River have high variability due to varying rainfall from year to year, as seen in the results of a Monte Carlo analysis of loads at the Highway 101 gauging station.

6. While there are multiple uncertainties in the sources of the total and methylmercury load from the Guadalupe River to San Francisco Bay, resuspension of sediments along the main stem of the Guadalupe River and urban storm drains appear to be important contributors.

Mercury Bioaccumulation: The results of the 2004 sampling program established a baseline for fish mercury concentrations in the watershed and have demonstrated the ability to establish a predictive relationship between methylmercury concentrations in water and mercury concentrations in fish tissue. Age-1 largemouth bass (*Micropterus salmoides*) and California roach (*Lavinia symmetricus*) have been shown to be sensitive biosentinels that can be used to monitor recovery in the impoundments and creeks of the watershed. These data from the 2004 sampling program are believed to provide a strong foundation on which to build fish-tissue and aqueous methylmercury numeric targets.

The conceptual model identifies the methylmercury produced in the hypolimnion of impoundments during stratification as an important internal source of methylmercury in the watershed and also a significant entry point of mercury into the food web.

Data Gaps and Uncertainties: The *Final Conceptual Model Report* completes a series of documents developed in Phase 1 of the TMDL for Mercury in the Guadalupe River Watershed. Each document has summarized new information and contributed to the understanding of the biogeochemical processes controlling mercury transport and fate in the watershed. Several data gaps remain and additional data are needed to reduce uncertainties:

- There are large uncertainties in the source of the mercury loads estimated for the Guadalupe River at the Highway 101 gauging station. Additional mercury sampling at high flows of the main tributaries and the main stem of the river are needed to refine the present estimate.

- The predictive relationship between methylmercury concentrations in water and mercury concentrations in fish tissue are based primarily on a single set of samples. The fish data exhibit low variability and are the stronger element of the predictive relationships. An emphasis should be placed on the collection of additional water samples to more fully describe the variability of methylmercury concentrations in the water column.

1.0 INTRODUCTION

The Conceptual Model for Mercury in the Guadalupe River Watershed describes our understanding of the biogeochemical processes controlling mercury transport and fate in the watershed. There are sufficient data available to support a strong scientific basis for this TMDL (Total Maximum Daily Loads) including the magnitude and location of sources, numeric targets, linkage from targets to sources, seasonal variations and critical conditions, and the implementation plan and monitoring plan.

The Final Conceptual Model Report completes a series of documents developed in Phase 1 of the TMDL for Mercury in the Guadalupe River Watershed (Tetra Tech, 2003a). The other documents in this series are:

- **Preliminary Problem Statement**. *Technical Memorandum 1.2 Preliminary Problem Statement* (Tetra Tech, 2003b) provides a preliminary description of the processes or factors that are most relevant to controlling mercury in the watershed. The Problem Statement describes the basis for listings of Guadalupe and Calero Reservoirs, Guadalupe River, and Guadalupe and Alamitos Creeks on the Mercury TMDL List.

- **Synoptic Survey**. *Technical Memorandum 2.1.2 Synoptic Survey Plan* (Tetra Tech, 2003c) and *Technical Memorandum 2.2 Synoptic Survey Report* (Tetra Tech, 2003d) describe the preliminary field sampling effort designed to provide an overview of mercury contamination in the watershed. This survey was conducted in July and August 2003, and the results have been incorporated into the development of the conceptual model.

- **Data Collection Plan.** Based on the draft conceptual model, the data collection plan identifies the minimum additional data needed to develop a defensible TMDL and Implementation Plan. *Technical Memorandum 5.2.3 Data Collection Plan* (Tetra Tech, 2004b) identifies data required to reduce uncertainty associated with key aspects of the TMDL, e.g., 1) the relative importance of individual processes to the transport and fate of mercury in the watershed, 2) estimated magnitudes of mercury loads from different sources, and 3) the effectiveness of alternative control measures.

- **Data Collection Report**. The Data Collection Program was conducted in two parts: Part 1 Wet Season Sampling that was conducted primarily to assess the magnitude of mercury loading to the watershed during the wet season, and Part 2 Dry Season Sampling that was conducted to estimate methylmercury production in reservoirs and to measure bioaccumulation in fish within the watershed. *Technical Memorandum 5.3.2 Data Collection Report* (Tetra Tech, 2005a) presents the results of field and laboratory studies and provides loading estimates based on the most up-to-date information on mercury sources and transport processes in the watershed.

The development of conceptual models was one of the primary recommendations of the National Research Council (NRC) in its assessment of the scientific basis of the TMDL approach to Water Quality Management (NRC, 2001). Conceptual models provide an explicit description of our understanding of the relationships among important environmental variables. The use of conceptual models was recommended to describe the link between environmental stressors (as well as control actions) and environmental responses. The NRC recommendation for building conceptual models was also made with the recognition of the "inevitable limits on our conceptual understanding of these complex natural systems" and with the warning that the science behind water quality management must be utilized with an acknowledgement of uncertainties that exist.

1.1 ROLE OF THE CONCEPTUAL MODEL IN THE DEVELOPMENT OF THE GUADALUPE RIVER WATERSHED MERCURY TMDL

The conceptual model report provides a synthesis of existing information. Mercury sources, loadings, mercury inventories within the system, and tissue levels within biota are summarized. Water quality, physical data, and significant system characteristics are summarized to describe the variables that affect mercury behavior in the watershed. The existing data include historical data that have been collected over the past several decades as well as the results of the Synoptic Survey (Tetra Tech, 2003d) and Data Collection Program (Tetra Tech, 2005a), which provide an up-to-date overview of mercury contamination in the watershed.

The processes affecting mercury behavior in creeks, reservoirs, and river systems in general are identified, and their roles in individual waterbodies within the watershed are described. Emphasis is also placed on the importance of the hydrologic connectivity within the watershed. There are six waterbodies within the watershed that have been affected by past mercury mining (Almaden Reservoir, Calero Reservoir, Guadalupe Reservoir, Alamitos Creek, Guadalupe Creek, and Guadalupe River). It is believed that mercury concerns in these waterbodies can most efficiently be addressed by undertaking a single TMDL project that concurrently considers all mercury sources in the Watershed (RWQCB, 2003a). The Guadalupe River

Watershed Mercury TMDL is also viewed as the primary regulatory vehicle for reducing mercury loads to San Francisco Bay (RWQCB, 2003b).

This report makes extensive use of graphics to communicate the information that has been developed on the extent of mercury in the watershed (sources) and how mercury behaves (i.e., fate, transport, and bioaccumulation). Graphic tools have been prepared for effectively communicating the existing information to a wide audience of interested stakeholders. It is intended that the diagrams presented in this document can be used to facilitate the discussion of important issues and individual elements of the TMDL.

The *Final Conceptual Model Report* builds on a *Draft Conceptual Model Report* (Tetra Tech, 2004a) that summarized the historical data and the results of the Synoptic Survey. A product of the draft report was a series of hypotheses that were used as a guide for the development of the data collection program. With the completion of the Data Collection Program and the evaluation of the results (Tetra Tech, 2005), these hypotheses are revisited. This revision of the conceptual model considers all new data that were collected in the Data Collection Program and evaluates our ability to confirm or refute the original hypotheses. Emphasis is placed on identifying the remaining data gaps, alternative working hypotheses, and the effect of these data gaps on the development of the TMDL. Recommendations are made on how to proceed to reduce the remaining uncertainties.

1.2 Guide to the Conceptual Model – Report Organization

In addition to this introduction, the Conceptual Model Report is organized into six chapters:

2.0 Watershed Characterization and Description of Mercury Sources

Much of the information presented in the Conceptual Model assumes a fundamental understanding of the watershed characteristics (topography, geology, meteorology, and hydrology) and historical mercury mining operations in the watershed. The reader familiar with this information may choose to skip this section. However, this section also provides a comparison of the data from mercury mines in the New Almaden Mining District to other mercury and gold mines in California.

3.0 Data Summary

The most recent mercury measurements in the watershed, including the results of the recently completed Data Collection Program (Tetra Tech, 2005a) are summarized in this section.

4.0 Estimated Mercury Loads

Mercury loads are assessed separately for the wet and dry season based on the knowledge that most mercury transport occurs during the wet season, and most methylmercury production occurs in the warm, dry season. Using historical streamflow data from 1950 to 2001, annual total mercury loads for the Guadalupe River are also estimated.

5.0 Conceptual Model of Mercury Behavior in the Guadalupe River Watershed

The important processes affecting mercury behavior in creeks, reservoirs, and the Guadalupe River are summarized in a series of diagrams. The accompanying descriptions summarize the current understanding of mercury behavior in the watershed. These descriptions are summarized in a series of hypotheses that identify the essential information needed to develop a defensible TMDL and Implementation Plan.

6.0 Summary and Strategy for Developing the Data Collection Plan

The findings of the Conceptual Model Report are summarized, and the use of this information to develop the TMDL is discussed.

7.0 References

The references cited in all chapters of this report are presented at the end of the report in Chapter 7.0.

2.0 WATERSHED CHARACTERIZATION

This section provides a general description of the watershed. The topography, precipitation, hydrology, geology, land uses and mercury sources are described to provide essential background information to those who are not familiar with the watershed.

2.1 WATERSHED DESCRIPTION AND SYSTEM CHARACTERISTICS

2.1.1 TOPOGRAPHY

The Guadalupe River headwaters are in the eastern Santa Cruz Mountains near the summit of Loma Prieta (elevation 3,790 feet). As seen in Figure 2-1, the upper portion of the watershed is mountainous with several ridges extending out into the alluvial valley. The Guadalupe River begins at the confluence of Alamitos and Guadalupe Creeks, below Almaden Lake, and flows 19 miles through heavily urbanized portions of San Jose, ultimately discharging into South San Francisco Bay through Alviso Slough (Figure 2-2). Three urban creeks: (1) Ross, (2) Canoas, and (3) Los Gatos Creeks, join the river as it flows toward San Francisco Bay. Guadalupe River has a total drainage area of approximately 170 square miles south of Highway 237. The river then flows into a 5-mile tidally-influenced reach through Alviso Slough to San Francisco Bay. Prior to 1866, when the south Bay salt ponds began to be developed, the river flowed into Guadalupe Slough.

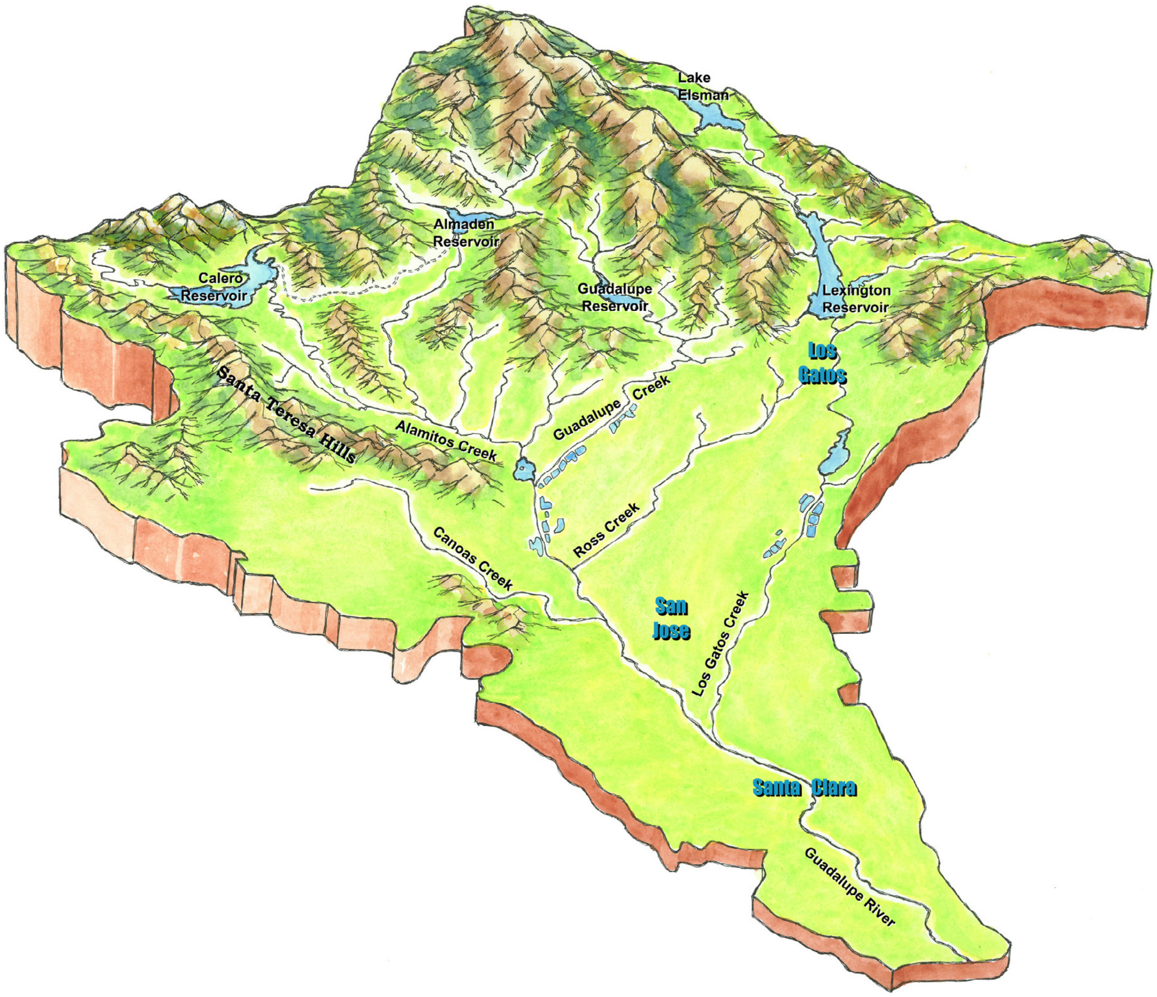


Figure 2-1. General topography of Guadalupe River Watershed.

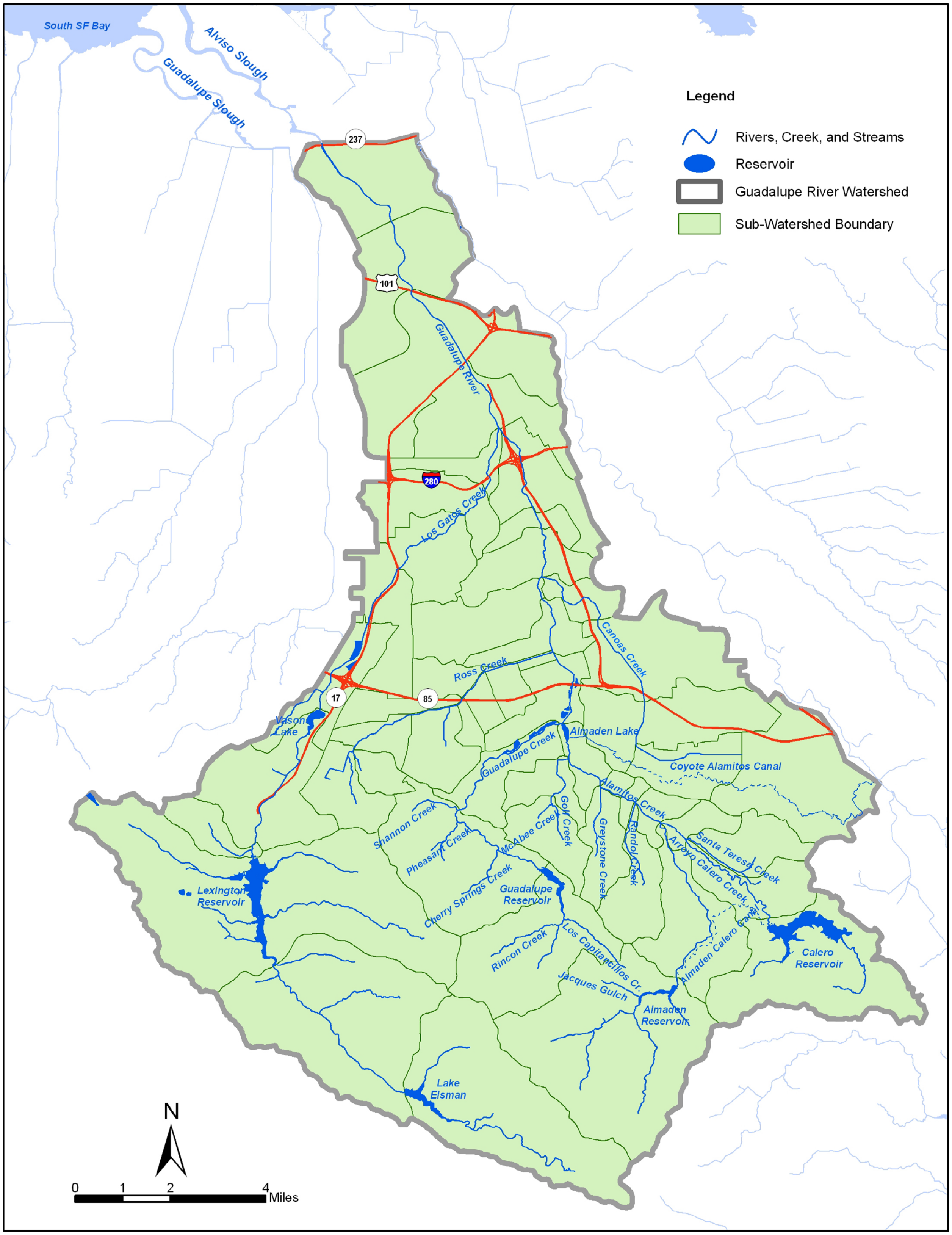


Figure 2-2. Major waterbodies and subwatersheds of Guadalupe River system.

2.1.2 METEOROLOGY

The watershed has a Mediterranean-type climate generally characterized by moist, mild winters and dry summers. The measurable precipitation is in the form of rainfall, 85 percent of which occurs between November and April. Mean annual precipitation ranges from 48 inches in the headwaters above the Guadalupe and Almaden Reservoirs to 14 inches at the Central San Jose rain gauge (station 131). Figure 2-3 shows the variation in rainfall between the upper and lower parts of the watershed. Temperatures range from below freezing in the mountains for a few days in winter to nearly 100 °F in the hottest parts of the valley in the summer.

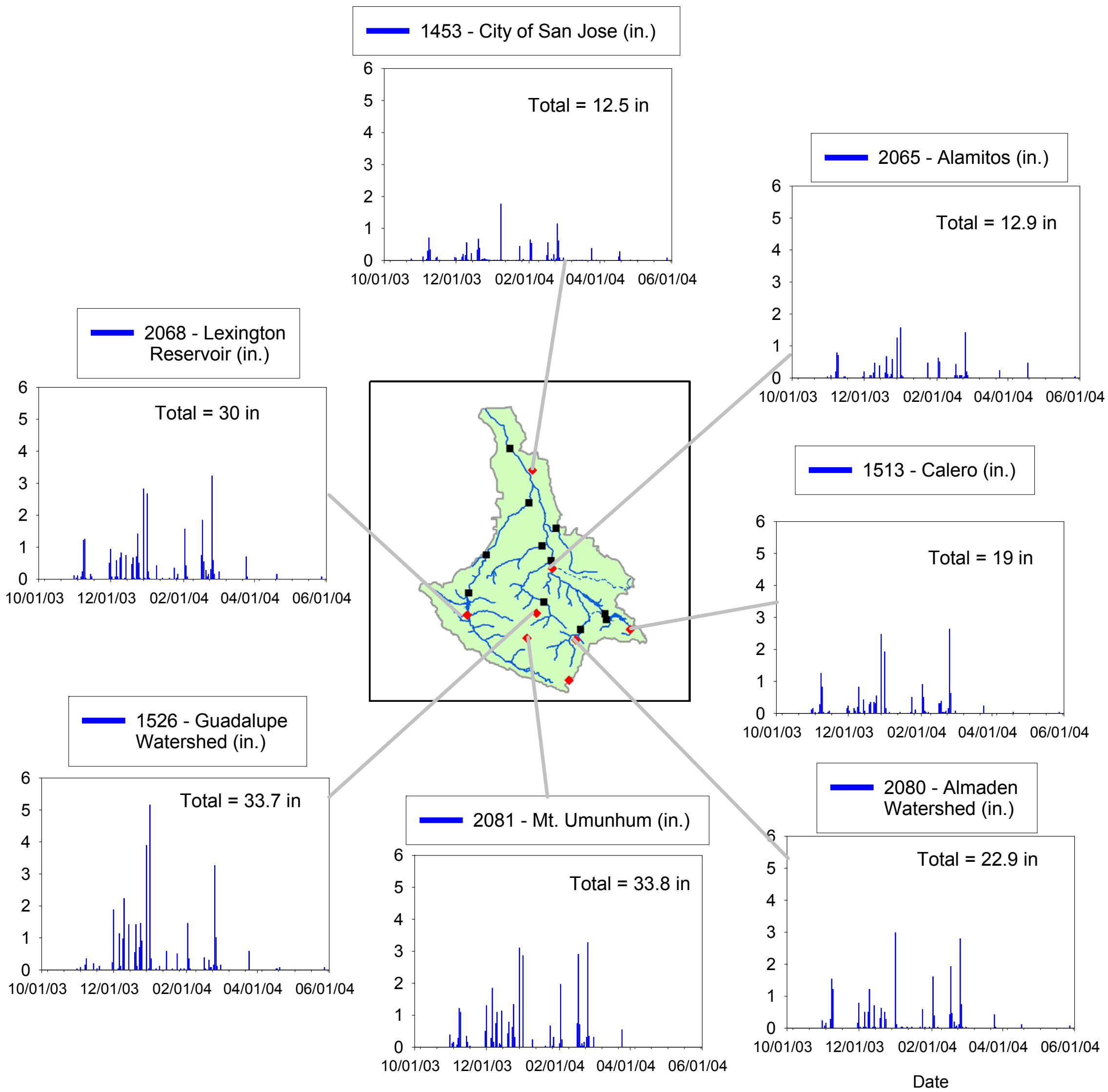


Figure 2-3. Measured rainfall for selected rain gauges in the Guadalupe River Watershed. The numbers at the top of each plot are the identifiers for the individual gauges. Data were obtained from the SCVWD ALERT system (http://alert.valleywater.org/). The y-axis in each plot shows rainfall in inches and the x-axis shows the date between 10/1/2003 and 5/31/2004.

Limited information is available in the San Jose and greater San Francisco Bay Area on wet and dry deposition of mercury. The closest air monitoring station for mercury to the Guadalupe River Watershed is the one at Moffett Field in Sunnyvale. The annual rainfall at this monitoring station during a 1999-2000 pilot study was 14.33 in, and the volume-weighted average total mercury concentration in the rain was 9.7 ng/L (SFEI, 2001). The computed wet deposition flux was 3.5 $\mu g/m^2/yr$ in the South Bay. The total mercury concentration in ambient air at the South Bay station was 2.2 ng/m^3. The total mercury in the air was divided into 95 percent Hg^0, 2 percent RGM (reactive gaseous mercury considered to be Hg^{2+}), and 3 percent particulates based on literature values. An estimate of total deposition flux was made by multiplying the concentration of each species by the appropriate deposition velocity. The total dry deposition flux was estimated to be 19 $\mu g/m^2/yr$. Wet and dry deposition is expected to be higher in the upper parts of the watershed because of the higher rainfall (e.g., up to 48 in/yr) and higher dry deposition due to increased capture in the forested areas. Due to retention of deposition in the watershed, the portion of the total deposition flux that actually reaches surface water is less than the above estimates.

Methylmercury is found at low concentrations in wet deposition (e.g., 0.015-0.35 ng/L) as summarized for samples from the United States and Canada by St. Louis et al., 1995. No local data for methylmercury in rainfall are currently available.

2.1.3 HYDROLOGY

The Guadalupe River has different flow characteristics in the dry and wet seasons. This pattern is also observed in the urban creeks, compared to the less variable outflows from the reservoirs. Figure 2-4 shows the flow gauges used in the loading analysis for this watershed and flow data for each gauge from October 2003 through May 2004. The long-term flow record from 1950 to 2002 comes from the old USGS gauging station at St John's Street, which was removed due to channel modification after May 2002. A new USGS gauging station was set-up downstream near the San Jose Airport by Highway 101. The median flow in the Guadalupe River at the old USGS gauge at St. John's Street was 4.5 cfs between 1960 and 2002 (ALERT, 2003). The maximum daily flow was 7,870 cfs, while the average daily flow was 54.3 cfs over this same period of record. In the wet season, flows increase substantially during storm events. Between 1930 and 1998, peak flows at the old USGS gauge varied from 125 cfs in 1960 to 10,500 cfs on March 10, 1995. The large flows, such as in 1995 and 1998, resulted in flooding of the downtown area of San Jose. There has been an increase in flows from the 1950s and 1960s to the 1990s in the lower part of the river as seen in Figure 2-5, partly as a result of the increased urbanization.

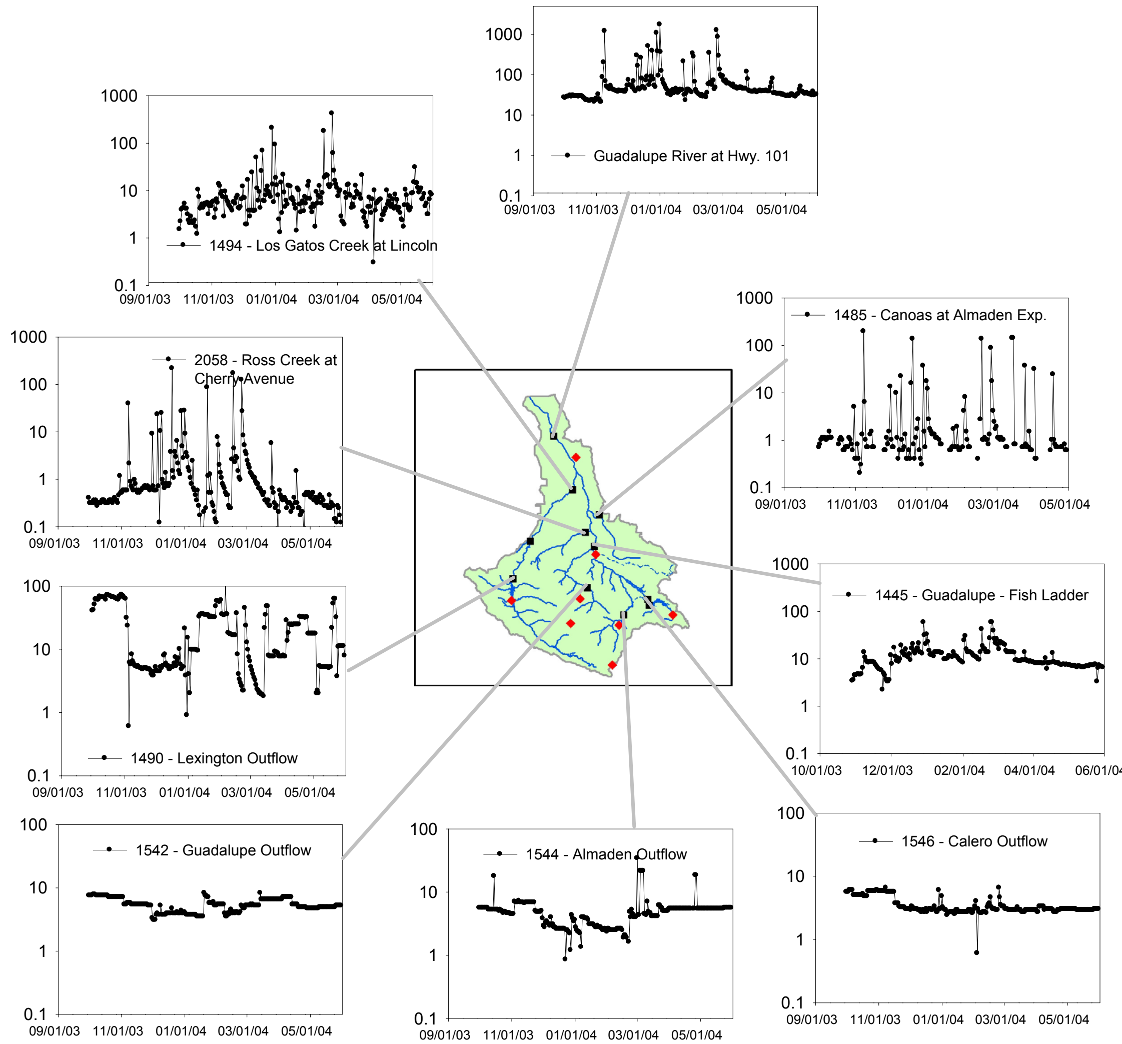


Figure 2-4. Measured flow for selected gauges in the Guadalupe River Watershed. Data were obtained from the SCVWD ALERT system (http://alert.valleywater.org/). The y-axis in each plot shows flows in cfs and the x-axis shows the date between 10/1/2003 and 5/31/2004. The red symbols identify rain gauges and data from them is plotted in Figure 2-3.

The Guadalupe River plays an important role in flood control for the Santa Clara Basin and has been subject to modification since 1866. In 1963, the lower Guadalupe River was channelized including adding new levees along Alviso Slough, out to its confluence with South San Francisco Bay. In the early 1960s, Canoas and Ross Creeks were rerouted to flow into Guadalupe River at different locations, and both lower creek sections were channelized. More recently, the river channel was modified as part of the 1975 Almaden Expressway construction project, where approximately 3,000 feet of channel was widened and moved eastward; the original channel was filled to allow construction of the northbound expressway. In 1999, a fish ladder was added to bypass the Alamitos Drop Structure below Lake Almaden.

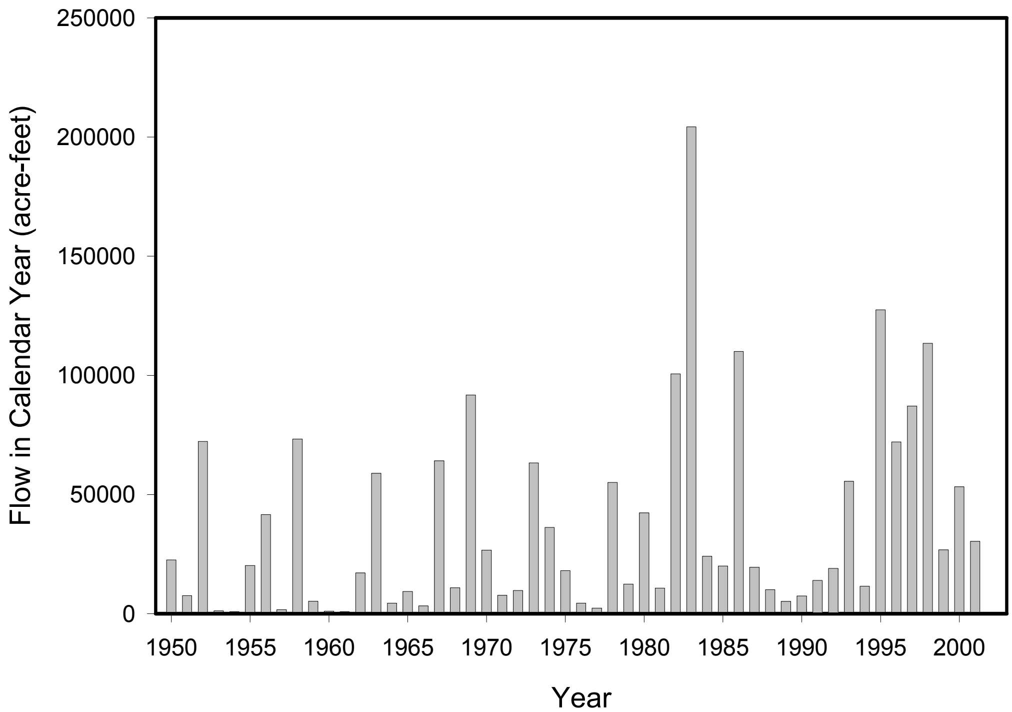


Figure 2-5. Year-to-year variability in total wet weather outflows from the Guadalupe River Watershed, based on the USGS gauge station just below the confluence of Guadalupe River and Los Gatos Creek. Note that there is an increase in total outflows possibly as a result of greater urbanization.

Three flood control projects are underway for the Guadalupe River. The Lower Guadalupe River Project is designed to increase the capacity of the river channel to handle the one-in-a-100-year flood between Highway 101 and the Union Pacific Bridge in Alviso. The Downtown Project is designed to make channel improvements along a 3-mile stretch from Highway I-880 to I-280. The Upper Guadalupe Project extends from I-280 to Blossom Hill Road along the Guadalupe River and from I-880 to Highway 101 along Ross and Canoas Creek. In 2004, the construction of a 3,000 cfs bypass channel to route flood flows underground, instead of in the natural river channel, was completed as part of the Downtown project.

Channel modifications to improve stream habitat were made in 2001 along a portion of Guadalupe Creek above its confluence with Alamitos Creek and below Masson Dam. Sediment was also removed in conjunction with this project and a 1999 project to improve fish passage along Guadalupe Creek where a fish ladder was built to bypass Masson Dam. In the late 1970's, channel modification was done on the lower reaches of Randol, Greystone, and Golf Creeks to provide improved flood protection, and levees were built along Alamitos Creek from the Harry Road bridge to the confluence with Almaden Lake. Flood control projects can also decrease the extent of erosion along stream banks by installing bank protection measures and by changing the energy gradient to reduce high velocity segments.

As part of flood control measures, the SCVWD removes sediment from the various drop structures and flood control structures for routine maintenance as shown for various parts of the Guadalupe River watershed in Table 2-1. The sediment quantities removed by the District provide confirmation of sediment accumulation in the tributaries. Removal of sediment also removes mercury and prevents it from reaching San Francisco Bay. Additional data are needed to quantify sediment transport in the various creeks and to evaluate the reduction in mercury loading due to the District's sediment removal activities. In addition to the removal operations, stream bank protection projects have also been conducted. For example, in the Guadalupe River watershed, about 13,000 linear feet of bank was reworked from 1986 to 1995, and the estimated amount of future bank protection work in this watershed is 12,000 linear feet.

Table 2-1
Past Sediment Removal Operations in Guadalupe River Watershed

Creek	Sediment Removed 1980 - 89 (cu yds)	Sediment Removed 1990 - 98 (cu yds)	Sediment Removal for Next 10 Years (cu yds)
Alamitos Creek	NA	NA	NA
Canoas Creek	38,056	3515	48,000
Guadalupe Creek	330	NA	1,500
Almaden-Calero Canal	NA	NA	NA
Coyote-Alamitos Canal	NA	NA	NA
Greystone Creek	3630	15	5,000
Randol Creek	7,110	NA	3,000
Guadalupe River	12,107	33,062	94,000
Ross Creek	6,720	3,462	8,000
Golf Creek	2090	200	NA
Lone Hill Creek	NA	20	NA
Los Gatos Creek	350	NA	NA

Data are from SCVWD, 2002.
NA = Data not available at time of printing.

There are six water conservation and storage reservoirs in the watershed. These reservoirs are Calero Reservoir on Calero Creek; Guadalupe Reservoir on Guadalupe Creek; Almaden Reservoir on Alamitos Creek; and Vasona Reservoir, Lexington Reservoir, and Lake Elsman on Los Gatos Creek, the latter above Lexington Reservoir. The three reservoirs in or near the former mining area, Almaden, Guadalupe and Calero, were built in the creek canyons. Mine wastes and merury-contaminated sediment are present in the sediments of Almaden and Guadalupe Reservoirs. The storage capacity of the reservoirs is provided in Table 2-2. Water is transferred to Calero Reservoir from Almaden Reservoir via the Almaden-Calero Canal and from the Central Valley Project (CVP). The volume of water retained in the reservoirs changes over the year, depending on the releases to the streams and evaporation. Vasona Reservoir is small, and spills when large storms occur such as for Feb 25-27, 2004. The other reservoirs rarely spill. Hydraulic modeling for Almaden Reservoir using the HEC-5 model estimated that it would spill 6 percent of the time in 100 years (Saah, 1994). The four reservoirs, besides Vasona, may spill in a 1 in a 100 year flood event, but did not spill in 2003 or 2004.

Table 2-2
Reservoir Capacity and Drainage Area of Reservoirs of Guadalupe River System (ALERT, 2003)

Reservoir (Creek)	Drainage Area Above Reservoir (sq miles)	Reservoir Capacity (acre-ft)	Year Built
Almaden (Alamitos)	12	1,586	1935
Guadalupe (Guadalupe)	6	3,228	1935
Calero (Calero)	7	10,050	1935
Lexington (Los Gatos)	37.5	19,834	1952
Vasona (Los Gatos)	44	400	1935
Lake Elsman (Los Gatos)	9.9	6,280	1951

The Guadalupe River system has 15 subwatersheds, as shown in Figure 2-2. Guadalupe Creek and Alamitos Creek subwatersheds, which drain the former mining areas comprise 26,206 acres, representing 24 percent of the entire Guadalupe River watershed (108,911 acres) (see Table 2-3). The area of these watersheds above the reservoirs is 16,000 acres or 14.7 percent of the total watershed. Streamflow decreases in the summer downstream of the reservoirs due to percolation through the stream bottom and diversion to recharge facilities.

Table 2-3
Size of Subwatersheds in Guadalupe River Watershed

Creek	Acres
Alamitos Creek	11,808
Calero Creek	6,762
Santa Teresa Creek	1,285
Randol Creek	1,416
Greystone Creek	1,116
Golf Creek	844
McAbee Creek	1,232
Guadalupe Creek	9,489
Ross Creek	3,197
East Ross Creek	1,311
Short Creek	519
Lone Hill Creek	1,276
Canoas Creek	11,899
Los Gatos Creek	35,261
Guadalupe River	21,496
Total Guadalupe Watershed	**108,911**

2.1.4 LAND USES

The Guadalupe River Watershed is located in the Santa Clara Basin and is largely undeveloped in its upper zone above the reservoirs, with pockets of high-density residential areas. Three-quarters of this area is protected. Virtually all headwaters drain from the protected areas, except for Upper Los Gatos Creek. The lower zone is typical of watersheds in the Santa Clara Basin, with high-density residential use predominating and commercial and public/quasi-public developments being interspersed. The lower zone is atypical of other watersheds in the area due to the continued presence of agriculture (Santa Clara Basin Watershed Management Initiative, 2000) (Table 2-4).

Table 2-4
Acreage of Existing (1995) Land Uses for the Guadalupe River Watershed

Land Use	Acreage
Residential	32,230
Commercial	4,888
Public/Quasi-Public	2,777
Industry-Heavy	3,397
Industry-Light	2,049
Transportation/Communication	1,700
Utilities	15
Landfills	–
Mines, Quarries	28
Agriculture	3,120
Forest	37,810
Rangeland	16,859
Vacant, Undeveloped	1,145
Wetlands	–
Bays, Estuaries	–
Freshwater	399
Total Acres	108,900

Adapted from: Santa Clara Basin Watershed Management Initiative. Table 4-2. (2000).

2.1.5 GEOLOGY

The Guadalupe River watershed can be divided into three regions: 1) an upland region with bedrock outcrops, 2) an alluvial plain, and 3) a baylands region. The upland region is underlain by sedimentary and metamorphic formations, chiefly belonging to the Franciscan Formation. Common sedimentary rock types include sandstone, shale, graywacke, limestone, and conglomerates. Common metamorphic and volcanic rocks include chert, serpentinite, greenstone, basalt, and schist. The alluvial plain overlies a deep structural basin filled with up to 1,500 feet of Plio-Pleistocene and Quaternary unconsolidated alluvial materials. The alluvial deposits consist of well-graded, interbedded fine sands and silts with some gravels. Coarse gravel deposits are present in some reaches of the Guadalupe River where it flows across the ancestral channel, rather than in relocated channels. The portion of the watershed south of Highway 237 is underlain by Bay muds and fine-grained silts and clays.

Mercury mineralization in the South San Francisco Bay Region is chiefly associated with serpentine intrusions into the Franciscan Formation, where the serpentine has been hydrothermally-altered to silica carbonate (Bailey and Everhart, 1964). The naturally occurring mercury is principally in the form of the mineral cinnabar (mercury sulfide) in the silica carbonate. Because the rock types in the Franciscan Formation contain limestone and carbonates, soils derived from these deposits are alkaline, as is the runoff and mine seeps. The alkaline seeps are in contrast to other mining areas with acid-mine drainage where the ore was associated with pyrites and other sulfide minerals, such as the gold mines in the Sierra Nevada (Alpers and Hunerlach, 2000) and the New Idria Mine, where the mercury ore was formed due to hot springs solution deposits (Ganguli et al., 2000).

The Franciscan Formation and its related serpentine beds underlie the New Almaden Mining District of the upper Guadalupe River Watershed (reference Plate 1 from the Bailey and Everhart, 1964 report and the new geologic maps in McLaughlin et al, 2001). Silica carbonate bedrock is found in scattered areas of the New Almaden Mining District, the largest mercury mine in North America. Over 99 percent of the ore was extracted from deep underground shafts and tunnels (Bailey and Everhart, 1964). The mines where silica carbonate outcrops were at the surface include the Mine Hill area with multiple mines and open-cuts on Los Capitancillos Ridge.The Providencia Mine, and the Guadalupe and Senador Mines were located along the extension of Los Capitancillos Ridge. Smaller outcrops were associated with the Enriquita fault zone that cuts across the present location of Guadalupe Reservoir. This zone was exploited by three small mines: San Mateo, San Antonio, and Enriquita. There were other small outcrops along the eastern portion of Los Capitancillos Ridge. A placer deposit in thick gravels was found in the lower portion of Deep Gulch Creek. However, dispersed cinnabar may be present in small silica carbonate outcrops and in the remaining unexplored subsurface veins. Soils overlying the silica carbonate deposits have elevated total mercury. The range of five soil sampling areas within the former mining area had total mercury concentrations ranging from 3.2 to 570 mg/kg; the median total mercury concentrations were 17 to 200 mg/kg (Dames and Moore, 1989). Other rock types that had some cinnabar in a few locations, as noted in the report on the New Almaden Mining District (Bailey and Everhart 1964) include graywacke and shale in the Harry area and altered greenstone or tuff in the nearby upper Cora Blanca and Los Angeles areas of the New Almaden Mining District (all near Mine Hill).

Recently produced geologic maps for the Los Gatos area shows isolated, small silica carbonate deposits in the Limekiln Canyon area of the Lexington watershed (McLaughlin et al, 2001). There were no other mercury deposits identified in the Lexington Reservoir watershed. The Limekiln Canyon did not have elevated total or particulate mercury when sampled in the wet season of 2004. Other silica carbonate deposits outside the New Almaden Mining District include small deposits along the route of the Almaden-Calero Canal near its discharge point to Calero Reservoir and in several places east of the reservoir, and in small areas near Cherry Creek on the west side of the reservoir. The Santa Teresa Hills between Canoas and Calero Creeks also have limited areas with silica carbonate formations; mining operations were limited.

2.1.6 MINING OPERATIONS AND EXISTING CONDITIONS

The mercury deposits were first discovered by Indians and Mexicans prior to 1845. The New Almaden Mining District (a group of seven adjacent mines, most underground, in the upper part of the Guadalupe Creek and Alamitos subwatersheds) operated from 1846 to 1975. Figure 2-6 shows the major mine-related features in the

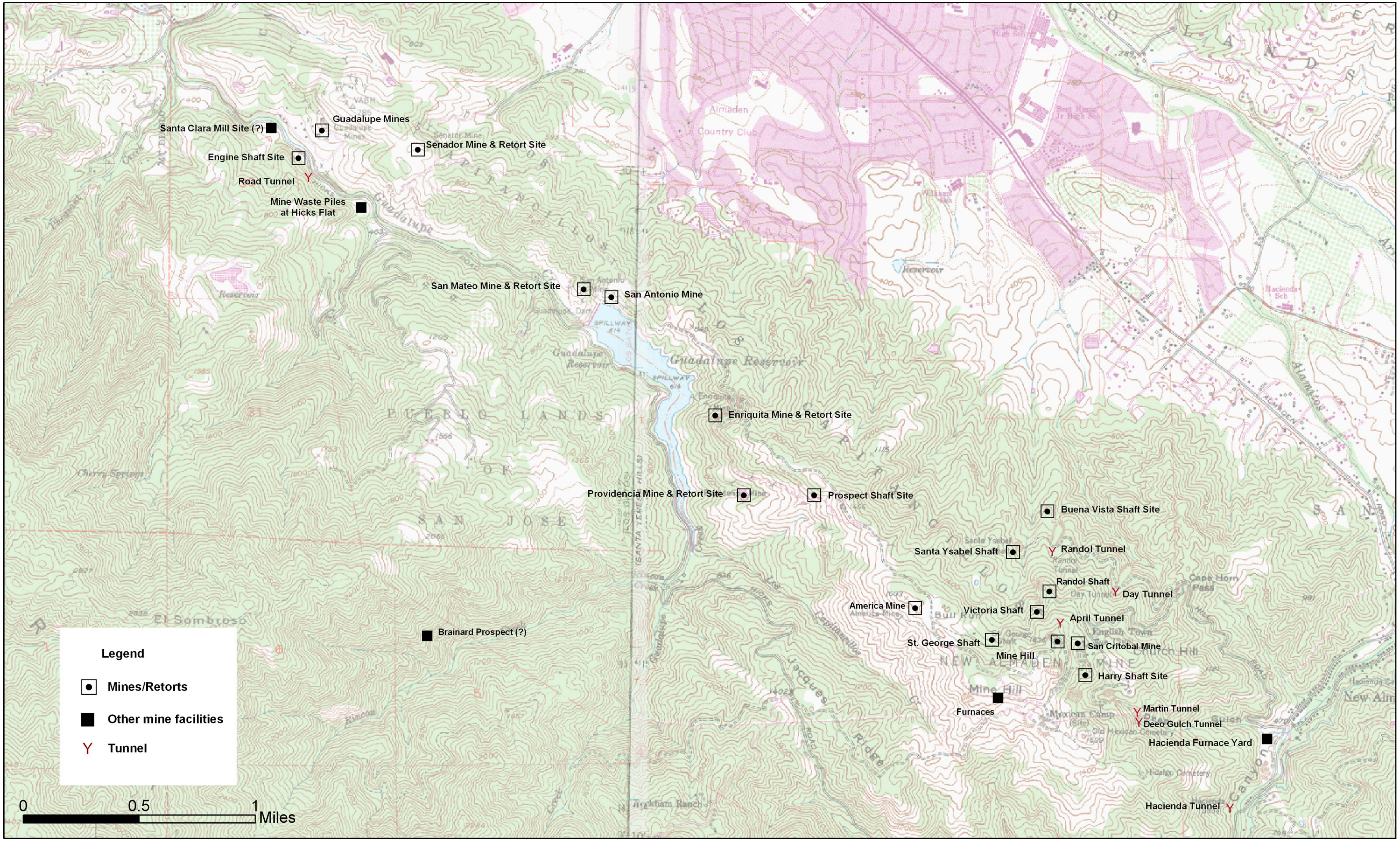


Figure 2-6. Map of major mine-related features (Mine Hill had multiple shafts and open-cut operations, not shown here).

upper Guadalupe River Watershed. Most of the ore was derived from cinnabar in silica carbonate deposits, but there was some native mercury in the underground veins such as in the Harry area near Mine Hill. A placer deposit of cinnabar nuggets in stream gravels was mined from 1945 to 1947 in lower Deep Gulch Creek where it joined Almaden Canyon (Bailey and Everhart, 1964).

A total of about 38.4 million kilograms of mercury was produced; about 70 percent of the production came before 1875, and about 80 percent before 1935. Prior to construction of the Guadalupe and Almaden Reservoirs in 1935, roasted mine wastes, called calcines, and other mine wastes were disposed of in or near the creeks so the materials would be transported downstream by winter flows. Calcines and other mine wastes are still present along the banks of Alamitos Creek on the opposite slope from Hacienda Yard and in some downstream reaches of Alamitos Creek from Bertram Road to Greystone Lane, Deep Gulch, Jacques Gulch, and Guadalupe Creek above Camden Avenue. Because the ore was from silica carbonate deposits, the mine wastes are sometimes found as cemented deposits along the creek banks.

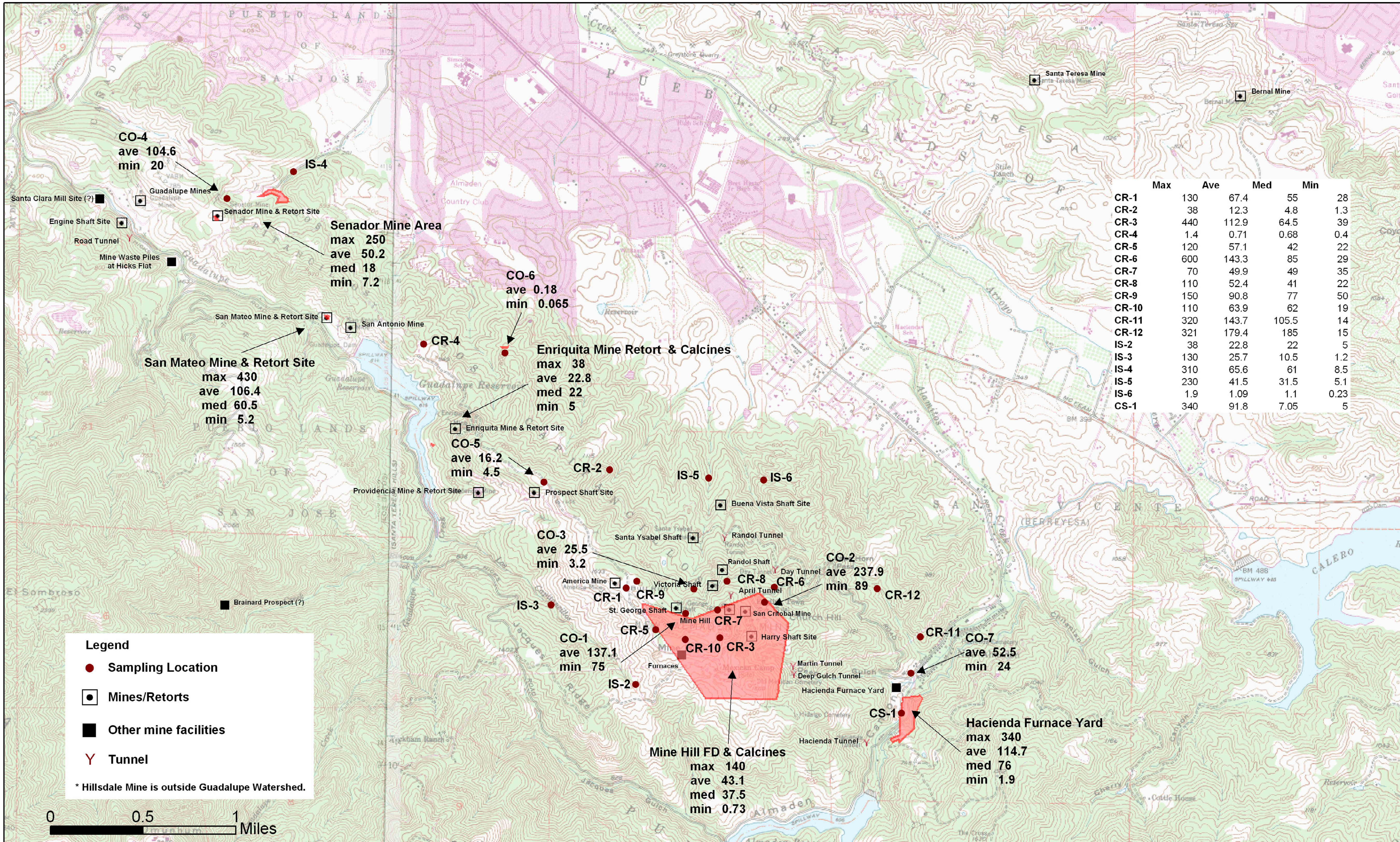
The production activities at the New Almaden Mining District are well characterized, and there is considerable information regarding concentrations of total mercury remaining in the soils. The early veins mined had rich ore of up to 20 percent mercury, which was hand-sorted prior to processing in furnaces and retorts (Bailey and Everhart, 1964). In later years, the percent mercury in the ore declined to 0.5 percent. The average grade of the ore processed over the 100-year life of the mines was nearly 4 percent, about a flask of mercury per ton of rock. As seen in Table 2-5, most of the production came from the mines on Mine Hill within the New Almaden Mining District. The ore was roasted in retorts or furnaces at a temperature of 700 to 1,200 °F; the efficiency of the equipment varied, resulting in varying mercury content in the waste calcines. Large furnaces and retorts were present in Hacienda Yard and on Mine Hill, which generated significant waste deposits. A group of 14 small furnaces were used on the banks opposite the Hacienda Furnace Yard. Mine wastes from these retorts are present on the slopes opposite the Hacienda Furnace Yard above Alamitos Creek. Retorts, used for shorter periods of time, were present at the Guadalupe, Senador, Enriquita, and San Mateo Mines, resulting in smaller waste dumps at these sites. Small retorts, which were sometimes portable units, were used at the Day Tunnel, upper Deep Gulch Creek, and San Cristobal Tunnel. Visible waste dumps were not observed at the latter site (WCC, 1992).

Table 2-5
Production of Mercury from Major Mines in New Almaden Mining District (Bailey and Everhart, 1964 and Cox, 2000)

Mine	Period of Operation	Mercury Produced (Flasks)
New Almaden Mines	1846 to 1975	1,096,411
America Mine	1800s to 1960s	<2,500
Guadalupe Mine	1846, 1920-1930 & 1947-75	112,623
Enriquita	1859-75,1892, 1927-1935	10,571 by 1865, then <100
San Mateo	1860-70s, 1890-1901,1915-1917, 1935-40	At least 1,000
San Antonio	1848, 1915-1917	Small amounts
Providencia	1860-1870,1882, 1909,1942	<2,000
Senador	1860-1900, 1916-1926, 1940s	About 24,500

Prior to remediation, mercury concentrations in the mine wastes within the boundaries of Almaden Quicksilver County Park ranged from 10 to 1,000 mg/kg; the median of 37 sites was 84 ppm (CDM, 1992). Samples of calcines and waste piles around the major mines were collected, along with the unpaved roads, exposed soil overlying silica carbonate and other types of bedrock, streambed sediment, and mine seeps (Dames and Moore, 1989). A summary of the total mercury concentrations in the AQC Park that were not removed or buried is provided in Figure 2-7. Calcines and furnace dust piles around the main retort sites at Hacienda Yard, on top of Mine Hill, and near the Senador, Enriquita, and San Mateo Mines were removed in 1990, covered with soil, re-graded, and re-vegetated. Most of the calcines were placed in the San Francisco Open Cut on Mine Hill, where they were covered with soil, and revegetated. The remaining calcines at the Hacienda Furnace Yard were covered with a 2-foot soil cap (DTSC, 2002). Calcines present on the opposite bank of Alamitos Creek from the Yard were not removed or covered. Calcines at Enriquita and San Mateo were buried near the former retort sites. Overburden piles remain at some of the mines such as near the Providencia and Senador Mines. Erosion control measures were implemented on the steep slopes around the former furnaces and retorts. On the Hacienda Yard next to Alamitos Creek, a concrete cutoff wall and gabion and rock slope protection were installed on the western bank.

Observations from recent site visits to the former mines show that the calcine disposal areas within Almaden Quicksilver County Park are being protected from erosion by the vegetation and runoff control measures implemented. Mine waste piles at former mines; such as near the Senador Mine, have been seeded with grass, but there are places where active erosion is occurring. Runoff from the Senador Mine reaches McAbee Creek, which discharges into Golf Creek, and then into Alamitos Creek. For the boundaries of the subwatersheds within Almaden Quicksilver County Park, see Figure 2-10, which is included in Section 2.1.7 as part of the discussion on the runoff data from the streams in the AQC Park. Calcines and other mine wastes are present in Jacques Gulch, which discharges into Almaden Reservoir, and Deep Gulch, which discharges into Alamitos Creek. The location of known mine seeps and mine wastes are shown in Figure 2-8. Within Almaden Quicksilver County Park, there are former mine roads where isolated mine wastes are evident in the larger cobble and gravel size materials, which are actively eroding. Runoff in some of these areas could reach Jacques Gulch, which discharges into Almaden Reservoir. Other areas would discharge into North Los Capitancillos Creek, which discharges into Guadalupe Reservoir, and directly into this reservoir. Mine seeps are present from former tunnels and adits such as at the Day Tunnel and above Randol Creek, which both ultimately could reach Randol Creek, and then Alamitos Creek, also shown in Figure 2-8.



	Max	Ave	Med	Min
CR-1	130	67.4	55	28
CR-2	38	12.3	4.8	1.3
CR-3	440	112.9	64.5	39
CR-4	1.4	0.71	0.68	0.4
CR-5	120	57.1	42	22
CR-6	600	143.3	85	29
CR-7	70	49.9	49	35
CR-8	110	52.4	41	22
CR-9	150	90.8	77	50
CR-10	110	63.9	62	19
CR-11	320	143.7	105.5	14
CR-12	321	179.4	185	15
IS-2	38	22.8	22	5
IS-3	130	25.7	10.5	1.2
IS-4	310	65.6	61	8.5
IS-5	230	41.5	31.5	5.1
IS-6	1.9	1.09	1.1	0.23
CS-1	340	91.8	7.05	5

Figure 2-7. Map of former mining area with summary of total mercury data following remediation in AQC Park in 1994-1996 (Dames and Moore, 1989 and CDM, 1994) CO = colluvium, CR = road samples, IS = intermittent streambed sediments. CS-1 was collected from Alamitos Creek sediment.

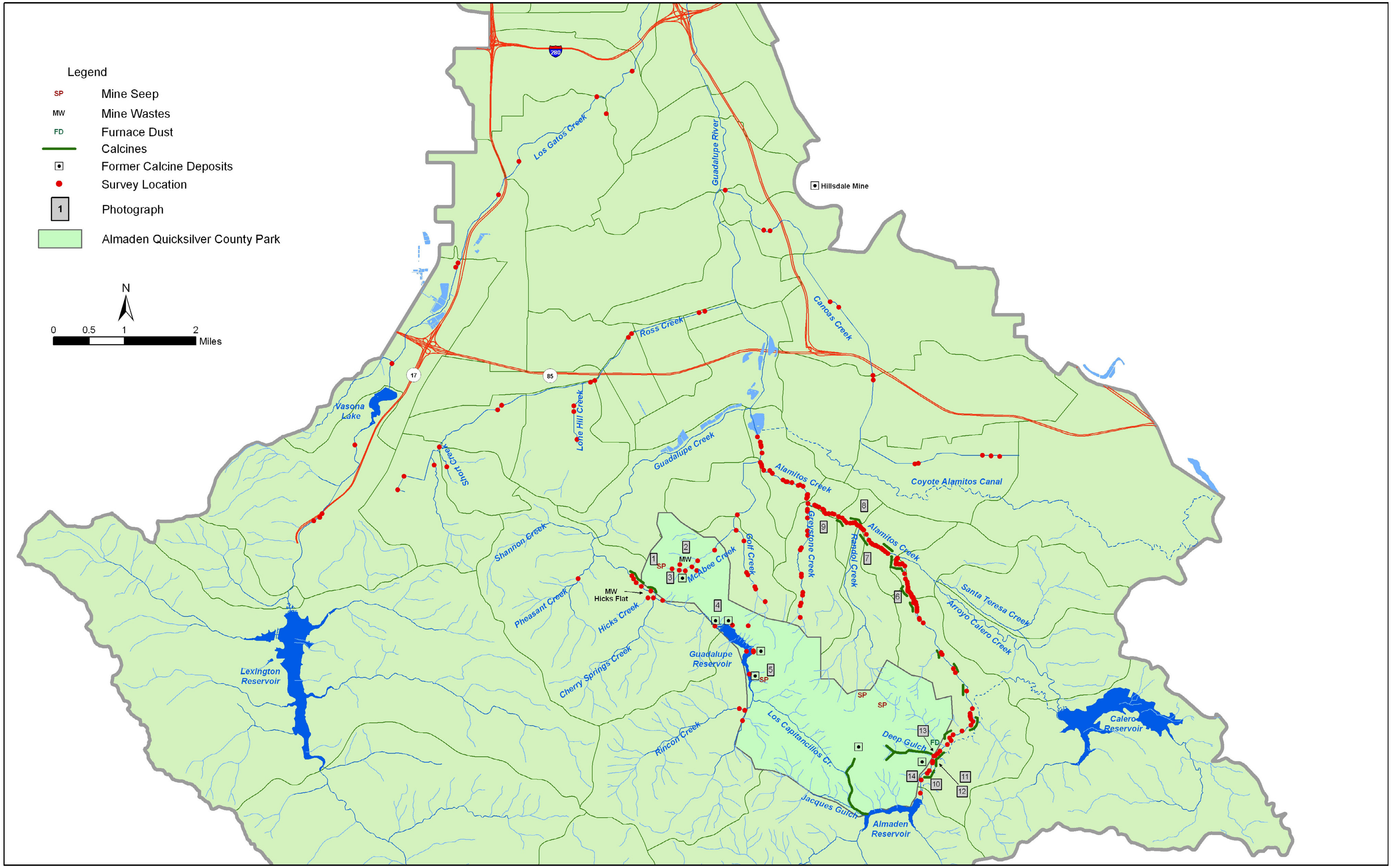


Figure 2-8. Location of exposed mine wastes and seeps along the tributaries to the Guadalupe River.

The locations of reaches of the creeks where calcines were observed during the field surveys in summer 2003 are identified in Figure 2-8. Example photographs of the creek reaches with cemented and loose calcines and other mine waste deposits are shown in Figure 2-9. For example, above the Hacienda Furnace Yard along Alamitos Creek, there are large non-cemented deposits of calcines on the slopes above the creek. Both early calcines composed of cobble-sized material and later calcines from the Scott furnaces composed of minus 3-inch material are present. A site visit indicated that the gabion wall along the creek is now failing (Austin, 2005). Below the Hacienda Furnace Yard, in the reach of Alamitos Creek between Bertram Road and Harry Road there are small calcine deposits along the banks, of which some are cemented and some are loose. Many of these deposits are above the low flow channel. A small area of furnace dust is present under the Almaden Road bridge. On Alamitos Creek downstream of Harry Road, there are calcine areas, which are often cemented and limited in extent, such as six sites between Harry Road and Greystone Lane. Calcines are observed in the gravel bars along the entire reach of Alamitos Creek.

Along Guadalupe Creek outside of the Almaden Quicksilver County Park, possible calcine deposits were observed along the banks of upper Guadalupe Creek near the former Guadalupe Mine. A partly vegetated mine waste pile is present at Hicks Flat on the opposite side of Guadalupe Creek from the main mine.

There are two much smaller mines in the Canoas Creek watershed, the Santa Teresa and Bernal Mines. The Santa Teresa mine was operated as an underground mine from 3 main adits. In 1903, a 40-ton Scott furnace was installed, which produced 9 flasks of mercury (Bailey and Everhart, 1964). The Bernal Mine was an underground mine with 2 shafts and an adit by 1902. In 1942, two new holes were drilled, and in 1946, the adit was extended, and a retort was installed. The mine was idle by 1947, and no evidence of mercury production was found in the abandoned retort. The Hillsdale Mine is outside the watershed boundary of the Canoas Creek watershed, but due to quarrying and regrading operations it may have affected Canoas Creek. The Hillsdale Mine produced 30 to 40 flasks in spring 1871, and small amounts up to 1874; it was idle from 1875 to 1892 and from 1907 to 1915 (Cox, 2000). A few flasks of mercury were produced in 1915; the mine was reworked from 1939 to 1946. The gravel quarry started after 1947 and excavated part of the mine in the early 1980's. The lower portion of Canoas Creek was rerouted in the 1960's to enter the Guadalupe River further upstream, and it was channelized with concrete partway up the side slopes.

2.1.7 WATER AND SEDIMENT DATA FROM ALMADEN COUNTY QUICKSILVER PARK

From 1994 to 2003, water samples have been collected in the wet season from creeks that drain the Almaden Quicksilver County Park by the Santa Clara Parks and Recreation Department (SCPRD). The sites are shown in Figure 2-11. The total mercury in the 2000-2003 water samples was analyzed using EPA Method 1631, as summarized in Table 2-6. The Senador Mine site drains to McAbee Creek, which joins Golf Creek, then Alamitos Creek. The Mine Hill tributary to Jacques Gulch site drains into Jacques Gulch, then into Almaden Reservoir. Deep Gulch drains to

Photographs of Exposed Mine Wastes, Seeps, etc.

Photo 1 **Mine Seep at Senador mine**

Photo 2 **Mine Waste Piles at Senador Mine**

Photo 3 **Senador Mine Reduction Works**

Photo 4 **Silica carbonate outcrop at San Mateo Mine**

Photo 5 **Mine wastes and seeps near Enriquita Mine and seeps**

Photo 6 **Cemented calcine on Alamitos Creek**

Photo 7 **Cemented layers on Alamitos Creek**

Photo 8 **Undercut calcines on Alamitos Creek**

Photo 9 **Cemented calcines on Alamitos Creek**

Photo 10 **Calcines along the edge of Alamitos Creek**

Photo 11 **Calcines on the upper flood plain above Alamitos Creek**

Photo 12 **Close-up of calcines above Alamitos Creek**

Photo 13 **Furnace dust beneath an Alamitos Creek bridge on New Almaden Road below Hacienda Furnace Yard**

Photo 14 **Calcine deposits on hill below road slip above Alamitos Creek**

Figure 2-9. Examples of calcine deposits and other mine wastes in or near creeks.

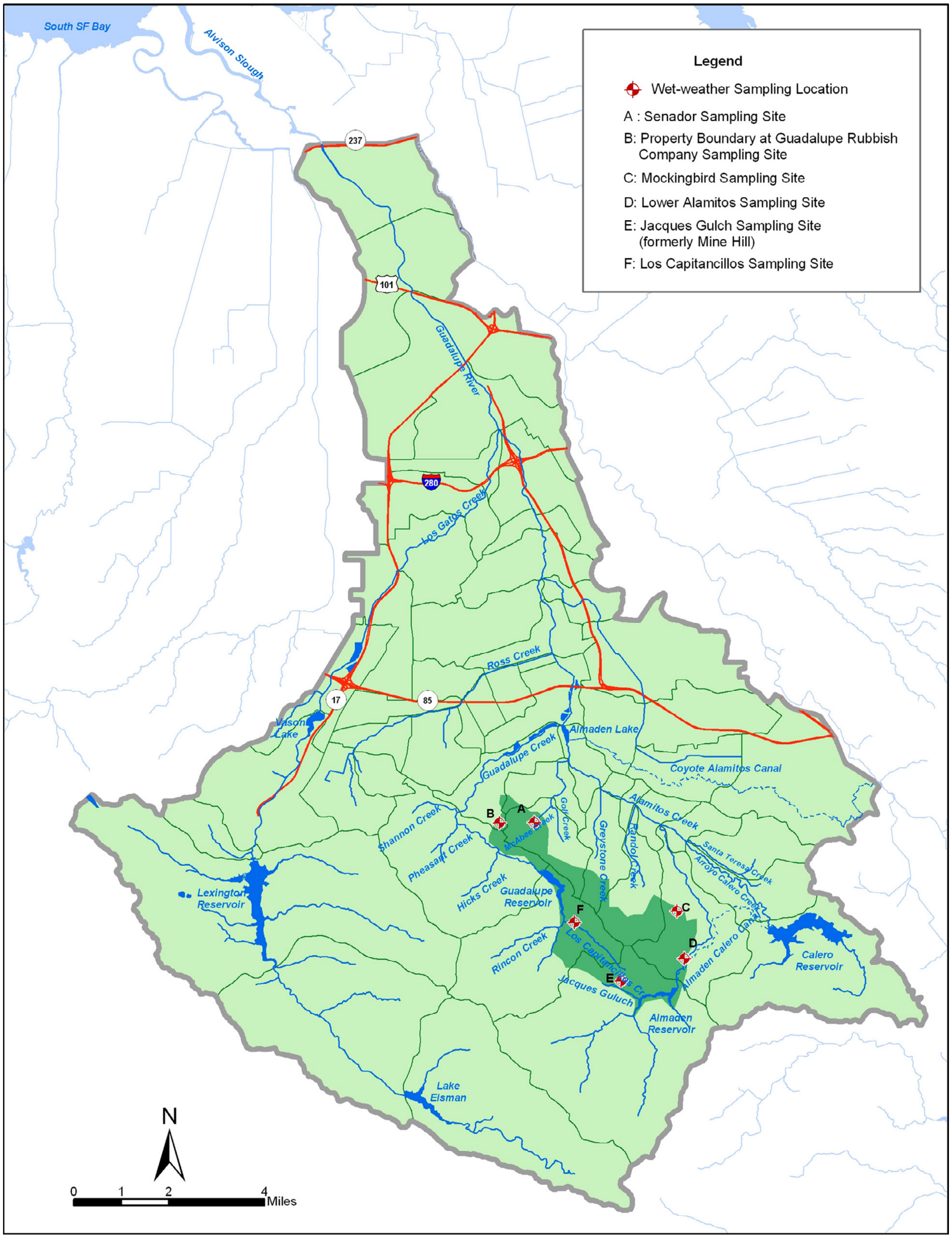


Figure 2-10. Wet-weather sampling locations used in 2003 for Almaden Quicksilver County Park by SCPRD.

Alamitos Creek near site D during large storms in the wet season, but percolates underground for the remainder of the year. This site is not shown on Figure 2-10, as it was not sampled in 2003. In 2003, two sites were added: one site at North Los Capitancillos Creek above Guadalupe Reservoir, and a second site at a gully draining part of the Guadalupe Landfill above McAbee Creek. The Deep Gulch and Upper Alamitos Creek sites were dropped, and the Mockingbird site on upper Randol Creek was not sampled. The highest mercury concentrations occurred in January 2000 at most sites when the suspended solids were high during a large storm event (total rainfall was 2.52 in. the day before sampling and 3.11 in. the day of sampling - SCPRD, 2003). High total mercury concentrations also occurred in samples collected on Feb. 25, 2004, when rainfall was 0.12 in. the day before sampling and 2.6 in. the day of sampling, which had especially high suspended solids.

Sediment samples were collected in 1989 at several locations in or near the former mining areas prior to the remediation efforts on Mine Hill and in the lower portions of Deep Gulch Creek within the Hacienda Furnace Yard. Sediment samples from Deep Gulch Creek had total mercury ranging from 2 to 590 mg/kg on a wet weight basis (Dames & Moore, 1989). Sediment samples from Alamitos Creek collected below the reservoir had total mercury ranging from 1.5 to 95 mg/kg on a dry basis (WCC, 1992). A tributary of Randol Creek sampled in 1992 had total mercury of 5.1 to 230 mg/kg on a wet weight basis (WCC, 1992). Guadalupe Creek above Camden Avenue was sampled from 1980 to 1989 by the USGS; total mercury ranged from 0.04 to 70 mg/kg dry (WCC, 1992). These data illustrate the high mercury concentrations present in the mining area prior to the remediation efforts.

Table 2-6
Mercury Concentrations in Stream Water Samples Draining Almaden Quicksilver County Park

Sampling Site and Map Identifier	Dates Sampled (Number of Dates)	Total Suspended Solids (mg/L)	Total Mercury (ng/L)
Deep Gulch Creek	2000-2002 (6)	<1-11	23–2,180
Upper Alamitos Creek	2000-2002 (6)	5.1-19	10.6-71.7
Lower Alamitos Creek (D)	2000-2004 (9)	2.2-26	18-2,900
	2/25/2004	1,790	110,000
Senador Mine (A)	2000-2004 (9)	<0.5-360	21.9-3,692
	2/25/2004	3,230	2,000
Mine Hill Tributary to Jacques Gulch (E)	2000-2004 (9)	<1-680	4.3-6,667
	2/25/2004	440	440
N. Los Capitancillos (F)	2003 (2)	5.4	5.8-26
	2/25/2004	8,890	5,300
Landfill Gully (B)	2003 (2)	1.9-21	79-60
	2/25/2004	3,410	2,500
Mockingbird C	2/2/2004	40	140
	2/25/2004	220	390

Data are from SCPRD, 2003 and 2004. Note samples collected on 2/25/04 were not analyzed using the low level method EPA 1631.

2.2 COMPARISON TO OTHER MERCURY AND GOLD MINES IN CALIFORNIA

Numerous mercury mines are located in the 400 km-long mercury mineral belt of the Coast Range of California. There are 51 mercury mines that each produced more than 1,000 flasks of mercury (34,475 kg) (Rytuba, 2000), while the NAMD alone produced 38.4 Million kg of mercury. Mercury production began in 1846; 70 percent of the NAMD production occurred before 1875 and 80 percent before 1935 (Bailey and Everhardt, 1964). Limited production of open cuts was conducted after 1940. The two major types of deposits are silica-carbonate deposits and hot springs. Cinnabar is the dominant mercury form in both types, but secondary mercury compounds are more prevalent in hot spring areas. Most of the mercury produced was used in the amalgamation process to obtain gold from placer deposits using hydraulic, drift, and dredging methods and crushed hardrock ore deposits. The peak mercury production in the California mercury mines was in 1877 (2,776 M kg), of which most was used in the Sierra Nevada and Klamath-Trinity Mountains (Hunerlach, et al, 1999). The New Almaden Mining District was the largest mercury producer in North America. Characteristics of example mercury and gold mines for comparison to the New Almaden Mining District are presented in Table 2-7a for mercury mines and in Table 2-7b for gold mines. The mines listed are those with ultra-clean mercury measurements in water and/or sediment samples. Data for other mercury and gold mines provides perspective showing the importance of the New Almaden Mining District relative to mercury production in the state. Mercury and methylmercury concentrations in water and sediment samples from nearby waterbodies have been compiled to determine how the data from the Guadalupe River watershed compare to other areas. The data also provide information on other mercury sources to San Francisco Bay, besides the Guadalupe River.

Table 2-7a.
Summary of Mercury Mines in California Used in Analysis

Mine or Mining Area	Type of Mine Deposit and Form of Ore	Years of Production	Mercury Production	Nearest Waterbody Affected
Mercury Mines				
New Almaden Mining District	Silica carbonate - cinnabar	1846 to 1975	38.4 M kg	Almaden/ Guadalupe Reservoirs/Guad River
Gambonini	Hot Springs deposit - cinnabar	1960 to 1970	0.17 M kg	Walker Creek and/Tomales Bay
New Idria	Silica carbonate – cinnabar, metacinnabar	1854 to 1972	17.2 M kg	San Carlos Creek/San Joaquin River*
Knoxville District (Manhattan, Reed and others)	Silica carbonate – cinnabar/metacinnabar; also has gold deposits	1862 to 1970s	Total for district 5.4 M kg	Davis Creek and Reservoir and Cache Creek*
Sulfur Bank	Hot Springs Deposit – cinnabar and secondary mercury of sulfates, chlorides, and oxychlorates	1872 to 1957	4.5 M kg	Clear Lake/Cache Creek*
Sulfur Creek and Manzanita	Geothermal complex	NA	NA	Sulfur Creek/Cache Creek*
Turkey Run and Abbot	Hot springs Deposit	NA	NA	Harley Gulch and Cache Creek*

*These waterbodies ultimately discharge into the Sacramento River and San Francisco Bay. References: Rytuba, 2000/2005; Ganguli et al, 2000; Suchanek et al, 1998; Rytuba and Enderlin, 1999, and Whyte and Kirchner, 2000.

Table 2-7b.
Summary of Gold Mines in California Used in Analysis

Mine or Mining Area	Type of Mine Deposit	Years of Production	Mercury Use	Nearest Waterbody Affected
Gold Mines				
Bodie Mine	Gold hardrock, placer	Peak 1860 to 1880	30-stamp amalgamation plant on creek	East Fork Walker River
Boston/Sailor Flat	Gold placer deposit	NA	Used mercury	Upper Greenhorn Creek/Bear River*
Lower Clear Creek Area	Gold placer deposits	1850 to 1942	Used mercury	Flat, Spring Creek and Lower Clear Creek*
Dutch Flat Mining District	Gold placer deposits	1857 to 1900	>185 M yd3 gravels mined using mercury	Bear River*
McLaughlin	Hot spring gold-mercury (previously Manhattan Hg mine)	1985 to 1996; ore production until 2001	Mercury used to obtain 3 M troy ounces of gold	Clear Lake*

*These waterbodies ultimately discharge into the Sacramento River and San Francisco Bay.
References for table: Rytuba, 2000; Rytuba et al, 2000, Alpers and Hunerlach, 2000, Hunerlach et al, 1999, Ganguli et al, 2000; Suchanek et al, 1998; Rytuba and Enderlin, 1999, and Ashley et al, 2002.

2.2.1 Aqueous Mercury Concentrations in Water Samples near Mines

Total and methylmercury data for water samples of mine drainage and creeks or other waterbodies near mercury and gold mines in California were compiled to compare with data in the Guadalupe River watershed. A summary of mercury concentrations in water samples collected in 2003 and 2004 for the Guadalupe River watershed is provided in Table 2-8. Mercury concentrations in the mine-influenced creeks are considerably higher than the urban creeks and creeks in non-mining areas of the watershed. However, due to the increased suspended sediment load in the Guadalupe River, mercury concentrations are more similar to the mine-influenced creeks than to the urban creeks, and higher than in the reservoir samples. The comparison for methylmercury differs in that the highest concentrations are found in the two reservoirs in the former mining area and Almaden Lake. The median methylmercury concentration in the Guadalupe River samples was higher than for urban creeks, although the maximum concentration was higher for the urban creeks.

A similar table with data for other mercury and gold mines is presented in Table 2-9. The latter table indicates that total mercury and methylmercury are higher in creeks near mercury mines than gold mines, except at some mines where acid drainage occurs. Median concentrations of total mercury in water samples from acid mine drainage at gold mines were higher than at mercury mines. The maximum and mean total mercury concentrations were higher in the mercury mines than the acid mine drainage from gold mines. Acid mine drainage is not as prevalent at mercury mines as gold mines, since gold deposits are typically associated with larger quantities of iron sulfide minerals. The highest methylmercury concentrations were observed in creeks near mercury mines. The increased methylmercury concentrations observed in wetlands near gold mines highlight the importance of waterbody conditions that can favor in-situ methylation.

Table 2-8.
Summary of Mercury and Methylmercury Data for Water Samples from the Guadalupe River Watershed

Statistic	Runoff Samples from Creeks in the Almaden County Quicksilver Park (2000 through 2003)	Guadalupe River Samples	Mine Area Creeks	Mine-Influenced Downstream Creeks[b]	Urban Creeks	Other Upper Watershed Creeks	Reservoirs in Mining Areas (Almaden and Guadalupe)	Other Reservoirs
Unfiltered Total Hg (ng/L)[a]								
Minimum	1.70	14.48	13.40	3.64	2.04	1.92	2.93	1.37
Maximum	6667.00	464.60	191.10	570.40	29.83	13.54	77.40	19.80
Mean	477.93	161.24	62.61	60.67	13.35	4.44	17.91	7.01
Median	60.00	78.60	42.20	32.99	12.28	3.40	14.30	4.65
Std. Deviation	1268.57	141.86	57.29	106.36	10.20	3.13	14.54	6.31
Count	39	21	9	29	17	16	67	12
Filtered Total Hg (ng/L)[a]								
Minimum	0.90	1.63	1.66	1.38	0.64	0.79	1.00	0.29
Maximum	24.00	22.22	32.91	34.39	18.99	3.94	12.20	5.04
Mean	12.43	10.26	13.53	9.30	5.06	1.59	3.39	2.14
Median	14.00	9.17	8.30	6.34	2.83	1.26	2.65	1.70
Std. Deviation	8.81	6.87	10.65	7.94	5.09	0.98	2.37	1.54
Count	9	21	9	29	17	16	67	12
Unfiltered MeHg (ng/L)[a]								
Minimum	-	0.164	0.031	0.119	0.004	0.014	0.204	0.057
Maximum	-	0.915	0.201	8.266	1.351	0.151	12.800	2.022
Mean	-	0.500	0.111	1.096	0.264	0.057	2.004	0.381
Median	-	0.533	0.086	0.409	0.184	0.039	0.695	0.183
Std. Deviation	-	0.193	0.070	1.833	0.335	0.046	2.822	0.551
Count	-	21	9	29	17	16	67	12
Filtered MeHg (ng/L)[a]								
Minimum	-	0.061	0.101	0.134	0.002	-	0.042	0.010
Maximum	-	0.154	0.169	6.073	1.102	-	8.270	1.253
Mean	-	0.104	0.135	0.942	0.204	-	1.189	0.247
Median	-	0.097	0.135	0.268	0.041	-	0.333	0.094
Std. Deviation	-	0.033	0.048	1.558	0.352	-	1.870	0.372
Count	-	10	2	18	12	-	67	12

[a]Samples were collected for the Guadalupe River Mercury TMDL watershed project and analyzed using ultra-clean methods.
[b]Almaden Lake sample not included in statistical analyses (Tot. Hg - 25.36 ng/L; MeHg - 17.85 ng/L; Filt. Tot. Hg - 4.4 ng/L; Filt. MeHg 1.72 ng/L).

Table 2-9.
Summary of Mercury and Methylmercury Data in Water Samples from Waterbodies near Gold and Mercury Mines in California

Statistic[a]	Creeks Gold Mining	Creeks[c] Mercury Mining	Acid Mine Drainage Gold Mining	Acid Mine Drainage Mercury Mining	Wetlands Gold Mining	Lakes and Reservoirs Gold Mining
Unfiltered Total Hg (ng/L)[b]						
Minimum	0.62	0.30	1.30	5.20	2.10	0.90
Maximum	231.00	38304.00	1330.00	405.00	254.00	2.88
Mean	23.69	502.41	214.24	150.23	41.54	1.76
Median	3.50	16.60	45.00	40.50	7.79	1.02
Std. Deviation	54.03	3183.84	357.65	221.34	93.75	1.00
Count	20	161	23	3	7	7
Filtered Total Hg (ng/L)[b]						
Minimum	<0.40	0.20	0.70	1.64	0.81	0.44
Maximum	196.00	399.00	63.00	1.64	3.96	3.50
Mean	8.16	32.95	14.80	1.64	2.05	1.26
Median	1.09	2.20	7.00	1.64	1.86	0.90
Std. Deviation	33.03	73.36	20.36	-	1.36	0.96
Count	36	159	20	1	6	19
Unfiltered MeHg (ng/L)[b]						
Minimum	<0.04	<0.013	<0.04	0.210	0.040	0.227
Maximum	0.037	20.600	2.330	0.360	6.720	0.479
Mean	0.028	0.723	0.303	0.303	1.841	0.378
Median	0.027	0.180	0.100	0.340	0.454	0.429
Std. Deviation	0.009	2.393	0.645	0.081	2.722	0.133
Count	3	161	12	3	7	3
Filtered MeHg (ng/L)[b]						
Minimum	<0.04	0.011	0.040	0.270	0.033	<0.04
Maximum	0.038	7.130	0.890	0.270	2.280	0.096
Mean	0.025	0.219	0.240	0.270	0.672	0.041
Median	0.020	0.074	0.050	0.270	0.107	0.020
Std. Deviation	0.011	0.619	0.368	-	0.970	0.030
Count	3	159	5	1	5	7

[a]Statistics were calculated using 1/2 the method detection limit.
[b]Samples were collected and analyzed using ultra-clean methods.
[C]Additional creek water samples were collected for mine drainage from the Gambonini Mercury Mine. The range of total mercury concentrations were from 485 to 1,040,000 ng/L (Whyte and Kirchner, 2000).

Many of these creeks eventually flow into the Sacramento River where total mercury samples ranged up to 105 ng/L during a winter storm, and methylmercury concentrations ranged up to 2 ng/L (Domalgalski, 2001). The measured total mercury concentrations in the Guadalupe River are higher than the Sacramento River, which has a much larger watershed and multiple tributaries. Winter methylmercury concentrations were less (maximum of 0.92 ng/L) in the Guadalupe River; summer concentrations in the two mining area reservoirs and downstream creeks were much higher (maximum of 12.8 ng/L and 8.3 ng/L, respectively).

2.2.2 MERCURY IN SEDIMENT SAMPLES NEAR MINES

Total and methylmercury data for sediment samples in mine wastes and waterbodies near mercury and gold mines in California were also compiled. A summary of mercury concentrations in sediment samples collected in 2003 and 2004 for the Guadalupe River watershed is provided in Table 2-10. Due to the former practice of disposing of mine wastes in Alamitos and Guadalupe Creeks and in their tributaries, the total mercury concentrations in these two creeks are similar to the present-day samples from creeks in the mining area (following remediation efforts). A similar table with data for gold and mercury mines is presented in Table 2-11. This table shows that total mercury concentrations in sediment near gold mines and other mercury mines are generally less than those in the Guadalupe River sediments and mine-influenced creeks. The sediments from the urban creeks had low concentrations of total mercury, compared to the other samples in the Guadalupe River watershed or the creek samples from near other mines. While maximum methylmercury concentrations were higher in the mine-influenced creeks, due to the reservoir inflows, the median concentrations were similar between the Guadalupe River, mine-influenced creeks, and the mine area creeks. The median concentration in the urban creeks was considerably less (0.2 ng/g dry weight), compared to 1.6 ng/g dry weight in the Guadalupe River sediments. The mine area creeks in the Guadalupe system had similar methylmercury concentrations to creeks at other mercury mines, while higher methylmercury concentrations occurred at some of the mine drainage sites from both gold and mercury mines.

Table 2-10.
Summary of Mercury and Methylmercury Data for Sediment from Guadalupe River Watershed

Statistic	Guadalupe River	Mine-Influenced Downstream Creeks	Mine Area Creeks	Urban Creeks
Total Hg (mg/kg dry wt.)[a]				
Minimum	0.065	0.223	1.13	0.042
Maximum	69.51	168.54	143.69	0.112
Mean	10.77	43.51	31.30	0.074
Median	3.0580	19.71	18.12	0.071
Std. Deviation	18.08	55.55	50.10	0.030
Count	18	11	7	4
MeHg (ng/g dry wt.)[a]				
Minimum	0.043	0.065	0.053	0.039
Maximum	3.23	35.85	4.56	1.94
Mean	1.39	5.30	1.52	0.60
Median	1.64	1.76	1.37	0.22
Std. Deviation	0.92	10.46	1.82	0.89
Count	18	11	5	4

[a]Samples were collected for the Guadalupe River Mercury TMDL project and analyzed using ultra-clean methods.

Table 2-11.
Summary of Mercury Data in Sediment from Waterbodies near California Gold and Mercury Mines

Statistic[a]	Creeks Gold Mining Bulk	Creeks[d] Mercury Mining Bulk	Lake/ Reservoir Gold Mining Bulk	Mine Drainage[c] Gold Mining Bulk	Tailings/ Fill Gold Mining Bulk	Tailings/ Fill Gold Mining >2 mm	Tailings/ Fill Gold Mining <2 mm	Wetland/ Pond Gold Mining Bulk	Wetland/ Pond Gold Mining Fines
Total Hg (mg/kg dry wt.)[b]									
Minimum	0.020	0.05	0.0060	0.0044	0.0300	0.0200	0.0400	0.0229	0.1900
Maximum	21.00	50.91	0.0530	6.71	0.2020	0.0400	0.1400	0.1600	0.2950
Mean	3.05	4.50	0.0295	2.65	0.0988	0.0275	0.0728	0.0829	0.2573
Median	0.04	0.58	0.0295	2.40	0.0995	0.0250	0.0556	0.0914	0.2720
Std. Deviation	7.91	11.29	0.0332	2.78	0.0549	0.0096	0.0456	0.0523	0.0462
Count	7	25	2	7	9	4	4	8	4
MeHg (ng/g dry wt.)[b]									
Minimum	0.020	0.056	0.016	<0.015	<0.015	-	0.101	0.225	1.02
Maximum	0.699	7.760	6.11	111.83	0.299	-	0.387	31.10	3.00
Mean	0.302	2.333	3.06	17.94	0.075	-	0.244	5.25	1.82
Median	0.188	1.020	3.06	0.050	0.036	-	0.244	0.588	1.63
Std. Deviation	0.354	2.486	4.31	41.693	0.112	-	0.202	11.45	0.914
Count	3	25	2	7	6	-	2	7	4

aStatistics were calculated using 1/2 the method detection limit.
[b]Samples were collected and analyzed using ultra-clean methods.
[c]Higher mercury concentrations can occur when elemental mercury is present such as the Polar Star Mine in the Dutch Flat area (Hunerlach et al., 1999).
[d]The range of mercury in creek sediment from the New Idria Mine were 4.5 mg/kg to 21.3 mg/kg (Marvin-Dipasquale et al, 2000.

3.0 DATA SUMMARY

Sampling was conducted in 2003 and 2004 under the Guadalupe River Watershed Mercury TMDL project to provide additional data for use in development of the TMDL. The Synoptic Survey provided an initial overview of the creeks and reservoirs; water and sediment sampling was conducted at 24 locations on July 30-31, 2003. Additional data were obtained between February 26 and April 23, 2004 to assess the magnitude of mercury loading to the Guadalupe Watershed during the wet season when water samples were collected at 55 locations and sediment samples were collected from nine locations. Detailed dry season sampling was conducted at Almaden and Guadalupe Reservoirs from May 11 to August 31, 2004 to estimate methylmercury production and transport from the reservoirs to the downstream creeks. Fish sampling was also conducted during the dry-season sampling to measure fish-tissue mercury concentrations throughout the watershed. This section summarizes the data from these sampling efforts. Detailed descriptions of the results are provided in “Technical Memorandum 5.3.2 Data Collection Report” (Tetra Tech, 2005a). Historical data are also summarized in that report.

3.1 WET SEASON CREEKS AND RIVER SAMPLING

3.1.1 UPPER WATERSHED CREEKS

Three sampling events were conducted in the Almaden, Calero, Guadalupe, and Lexington Reservoir watersheds between March 2 and April 20, 2004. The sample locations are shown on a map of the upper Guadalupe River watershed (Figure 3-1). Measurements were made of suspended sediments, flow rates at ungauged locations, total and dissolved mercury, and methylmercury in each creek upstream of where it enters a reservoir, the reservoir outlets, and the Almaden-Calero Canal. The reservoir outlets and the Almaden-Calero Canal were also analyzed for dissolved methylmercury. The daily rainfall at the watershed gauges during the sampling events is shown in Figure 3-2.

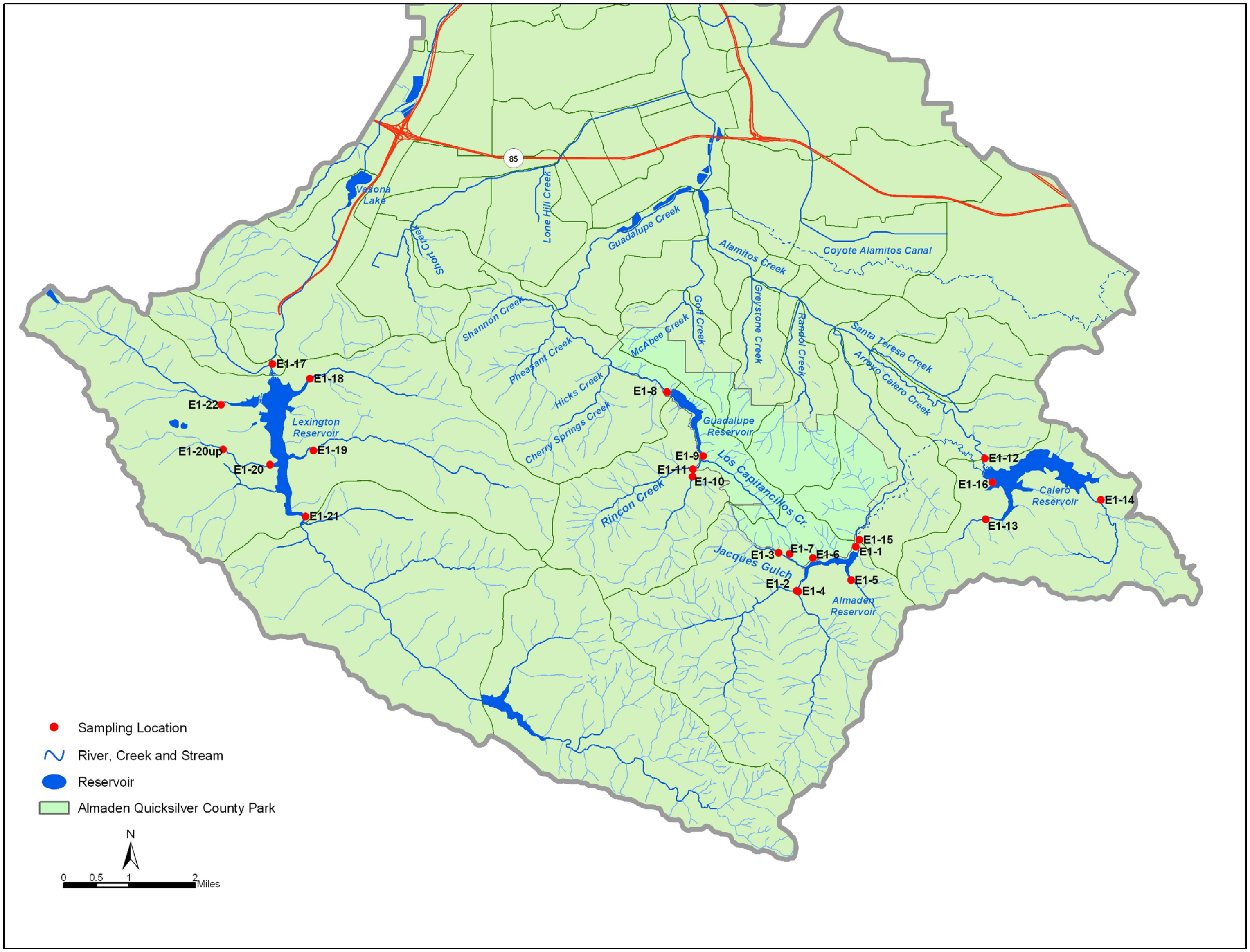


Figure 3-1. Sampling Locations for Upper Watershed Creeks and Reservoir Outlets

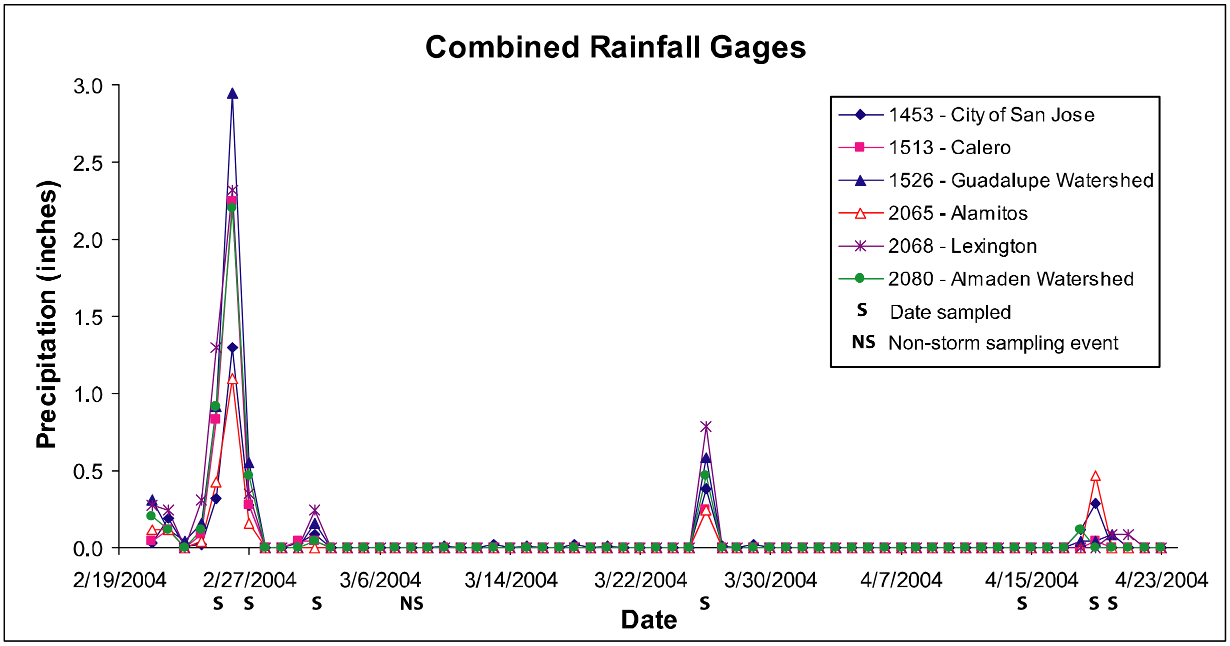


Figure 3-2. Rainfall measured at selected gages during the sampling period for this study ("S" indicates date sampled. "NS" indicates date when sampled on non-storm day.)

The flows for the tributaries and outlets for the three sampling events are provided in Table 3-1. The chemical data are presented in the Data Collection Report (Tetra Tech, 2005a). Each reservoir watershed had one dominant inflow, therefore both flow and mercury concentrations are needed for load estimates. For Calero Reservoir, the dominant inflow for these sampling events was the Almaden-Calero Canal, although releases to the canal are variable. The wet season data are summarized below:

- **Suspended solids.** The suspended solids concentrations ranged from 0.4 mg/L in the Mine Hill tributary to Jacques Gulch, a tributary to Almaden Reservoir, to 54 mg/L in Lyndon Canyon, a tributary to Lexington Reservoir. The suspended solids in the reservoir outlets ranged from 6.3 mg/L (Calero – 4/14/04) to 97.6 mg/L (Lexington – 3/2/04). The suspended solids in the canal varied from 7.7 mg/L to 17.9 mg/L.

- **Total Mercury.** The total mercury concentrations in the tributary samples ranged from 1.9 ng/L in Briggs Creek at Bear Creek Road, a tributary to Lexington Reservoir, to 82 ng/L, in the West tributary from Mine Hill to Almaden Reservoir. The total mercury concentrations in the reservoir outlet samples ranged from 5.9 ng/L (Lexington – 4/20/2004) to 77.4 ng/L (Guadalupe – 3/2/2004). The total mercury in the canal samples ranged from 24.7 ng/L to 90.5 ng/L. As seen in Figure 3-3, the tributaries to Guadalupe and Almaden Reservoirs influenced by mining had higher total mercury concentrations (13.4 ng/L to 82.2 ng/L) than the other tributaries to those reservoirs (2.0 ng/l to 8.7 ng/L (Jacques Gulch above the Mine Hill tributary)). The total mercury in the Lexington tributaries ranged from

1.9 ng/L (Briggs Creek) to 13.5 ng/L (Lyndon Canyon). The dissolved fraction was variable, but lowest in the Lexington Reservoir tributaries.

Table 3-1.
Flows for Reservoir Tributaries and Outlets, Wet Season Sampling 2004

Station No.	Station Name	Date	Time	Gauged Flow, cfs	Est Flow, cfs
E1-1	Almaden Reservoir Outlet	3/2/2004	12:00	30.2	
E1-1	Almaden Reservoir Outlet	3/8/2004	14:00	21.4	
E1-1	Almaden Reservoir Outlet	4/14/2004	10:10	5.4	
E1-2	Herbert Creek	3/2/2004	15:10		43.4
E1-3	Jacques Gulch above Mine Hill Tributary	3/2/2004	15:00		0.75
E1-3A	Jacques Gulch above Mine Hill Tributary	3/26/2004	9:30		0.91
E1-4	Barret Canyon	3/2/2004	15:35		31.2
E1-5	Larrabee Gulch	3/2/2004	13:35		1.50
E1-6	W. Tributary from Mine Hill to Almaden Reservoir	3/2/2004	14:30		0.03
E1-7	Mine Hill Tributary to Jacques Gulch	3/2/2004	15:30		0.4
E1-7	Mine Hill Tributary to Jacques Gulch	3/26/2004	10:31		0.5
E1-8	Guadalupe Reservoir Outlet	3/2/2004	13:35	5.2	
E1-8	Guadalupe Reservoir Outlet	3/8/2004	14:50	5.2	
E1-8	Guadalupe Reservoir Outlet	4/14/2004	9:18	6.25	
E1-9	N. Los Capitancillos Creek	3/26/2004	9:00		1.58
E1-9A	N. Los Capitancillos Creek	3/3/2004	9:55		0.17
E1-10	Upper Guadalupe Creek	3/2/2004	14:15		3.76
E1-11	Rincon Creek	3/2/2004	13:55		4.94
E1-12	Calero Reservoir Outlet	3/2/2004	9:55	3	
E1-12	Calero Reservoir Outlet	3/8/2004	13:10	2.9	
E1-12	Calero Reservoir Outlet	4/14/2004	9:15	3	
E1-13	Cherry Canyon	3/2/2004	9:25		1.13
E1-14	Pine Tree Canyon	3/2/2004	10:30		1.89
E1-15	Inlet to Almaden-Calero Canal	3/2/2004	11:30	NA	
E1-15	Inlet to Almaden-Calero Canal	3/3/2004	11:03	NA	
E1-16	Outlet to Almaden-Calero Canal	3/2/2004	8:25	3.8	
E1-16	Outlet to Almaden-Calero Canal	3/3/2004	11:34	59.4	
E1-17	Lexington Reservoir Outlet	3/2/2004	9:10	6.1	
E1-17	Lexington Reservoir Outlet	3/8/2004	9:45	2.7	
E1-17	Lexington Reservoir Outlet	4/20/2004	7:30	31.8	
E1-18	Limekiln Canyon	3/2/2004	9:45		2.4
E1-19	Soda Spring	3/2/2004	10:15		10.5
E1-20	Briggs Creek at CDF	3/2/2004	12:25		<0.1*
E1-20up	Briggs Creek at Bear Creek Road	3/8/2004	8:30		1.88
E1-21	Upper Los Gatos Creek	3/2/2004	11:50		45.6
E1-22	Lyndon Canyon	3/2/2004	11:00		13.2

*Considered to be affected by backwater from reservoir, so sampled upstream.

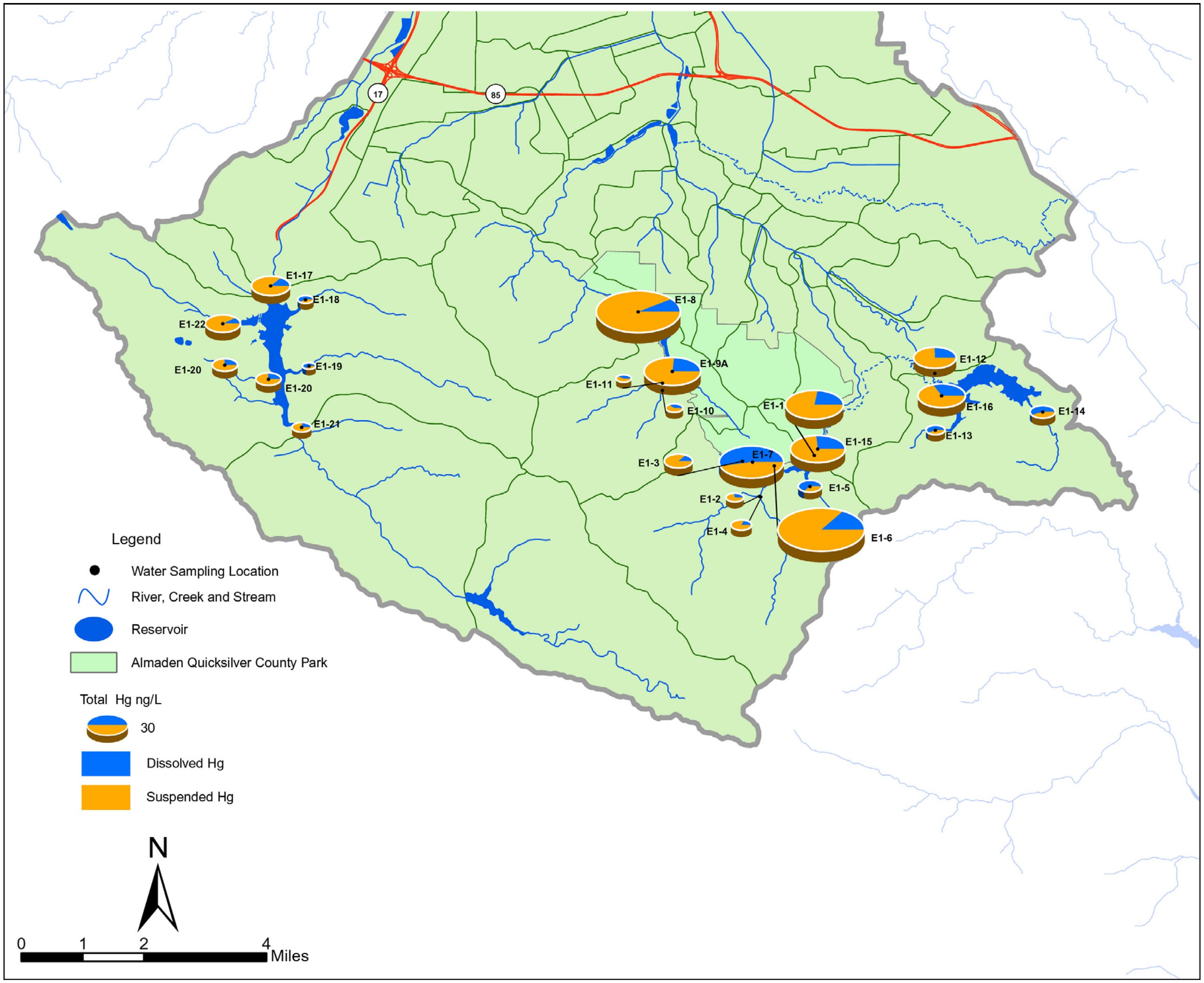


Figure 3-3. Total and dissolved mercury in reservoir watershed water samples.

- **Methylmercury**. The methylmercury in the tributaries ranged from 0.01 ng/L in Briggs Creek at Bear Creek Road, a tributary to Lexington Reservoir, to 0.20 ng/L in N. Los Capitancillos Creek, a tributary to Guadalupe Reservoir. The reservoir outlets had a wider range of methylmercury concentrations (0.06 ng/L in Lexington to 0.70 ng/L in Guadalupe). Methylmercury concentrations in the canal ranged from 0.22 ng/L to 0.29 ng/L. The reservoir outlets from Almaden and Guadalupe Reservoirs had higher methylmercury (0.23 ng/L to 0.70 ng/L) than the tributaries (0.03 ng/L to 0.20 ng/L). Methylmercury in the tributaries to Lexington ranged from 0.01 ng/L to 0.14 ng/L. The dissolved fraction was significant, even when the methylmercury concentrations were low.

- **Mercury in Particulate Fraction.** The mercury content on the suspended particulates was calculated from the total and dissolved mercury concentrations and the suspended solids, as follows:

$$P = (T - D)/SS \times 1000$$

where

P = particulate fraction of mercury in ng/g
T = total mercury in ng/L
D = dissolved mercury in ng/L
SS = suspended solids in mg/L.

The results are expressed on a mass basis, i.e., ng of mercury per gram of suspended matter. The mercury content in the suspended fraction can indicate the mercury concentration of future sediment if it settles at a downstream location.

The Guadalupe Workgroup asked whether the mercury concentration of the particulates was less than 0.2 mg/kg, the proposed annual median suspended sediment target for the San Francisco Bay TMDL. While the samples from the tributaries to Lexington Reservoir had low mercury concentrations in the particulate fraction (0.11 to 0.58 mg/kg), only one tributary, Briggs Creek, had particulate mercury concentrations less than 0.2 mg/kg. In comparison, the samples from mine-influenced tributaries had mercury concentrations in the particulate fractions ranging from 0.63 mg/kg to 61.26 mg/kg. The particulate-fraction concentrations measured in other tributaries from the upper watershed were also greater than 0.2 mg/kg. The outlet from Lexington Reservoir was the only outlet with particulate mercury concentrations less than 0.2 mg/kg (0.14 mg/kg to 0.19 mg/kg).

The highest total mercury concentrations measured were found in the three tributaries draining the mining area:

Mine Hill tributary to Jacques Gulch then Almaden – 42.2 ng/L to 45.6 ng/L
West tributary to Almaden Reservoir – 82.2 ng/L
N. Los Capitancillos Creek to Guadalupe Reservoir – 13.4 ng/L to 35.1 ng/L.

Total mercury concentrations in the other creeks ranged from 2.0 ng/L in Jacques Gulch above the Mine Hill tributary to 13.5 ng/L in Lyndon Canyon. Lyndon Canyon had suspended solids of 54.1 mg/L; the higher total mercury concentration is due to the higher suspended solids; the particulate mercury was low (0.23 mg/kg). The dissolved mercury was also highest in the three mining area creeks. The highest methylmercury concentration (0.29 ng/L) was in the outlet of the Almaden-Calero Canal, compared to 0.06 to 0.20 ng/L in the above mining area creeks.

The concentrations of the total and methylmercury in the upper watershed creeks are compared in Figure 3-4. The tributaries to Lexington Reservoir had the lowest concentrations of both mercury species, while the Almaden-Calero Canal had the highest maximum concentrations of both species. The canal sample with the highest total mercury had moderate suspended solids (17.9 mg/L) and elevated particulate mercury (4.7 mg/kg). The next highest concentration was from the west tributary to Almaden Reservoir, which had low suspended solids (2.4 mg/L) but high particulate mercury (29.56 mg/kg).

3.1.2 Creeks Below Impoundments Affected by Mercury Mining

Runoff from former mining areas and in-stream processes are contributing mercury to Guadalupe, Alamitos and Calero Creeks, three of the major tributaries to the Guadalupe River. Three sampling events were conducted between March 8 and April 23, 2004 at 18 sites on Alamitos, Guadalupe, and Calero Creeks and their tributaries. The locations were selected to distinguish the mercury load coming from tributaries from erosion and sediment resuspension. The sampling locations are shown on a map of the upper Guadalupe River watershed on Figure 3-5. Measurements were made of suspended sediments, flow rates at ungauged locations, total and dissolved mercury, and methylmercury at each location. Dissolved methylmercury was measured at five of the locations, two on Guadalupe Creek and three on Alamitos Creek. Results were used to compare tributary loads to the major creeks and the internally-generated loads from bank erosion and sediment resuspension within the creeks.

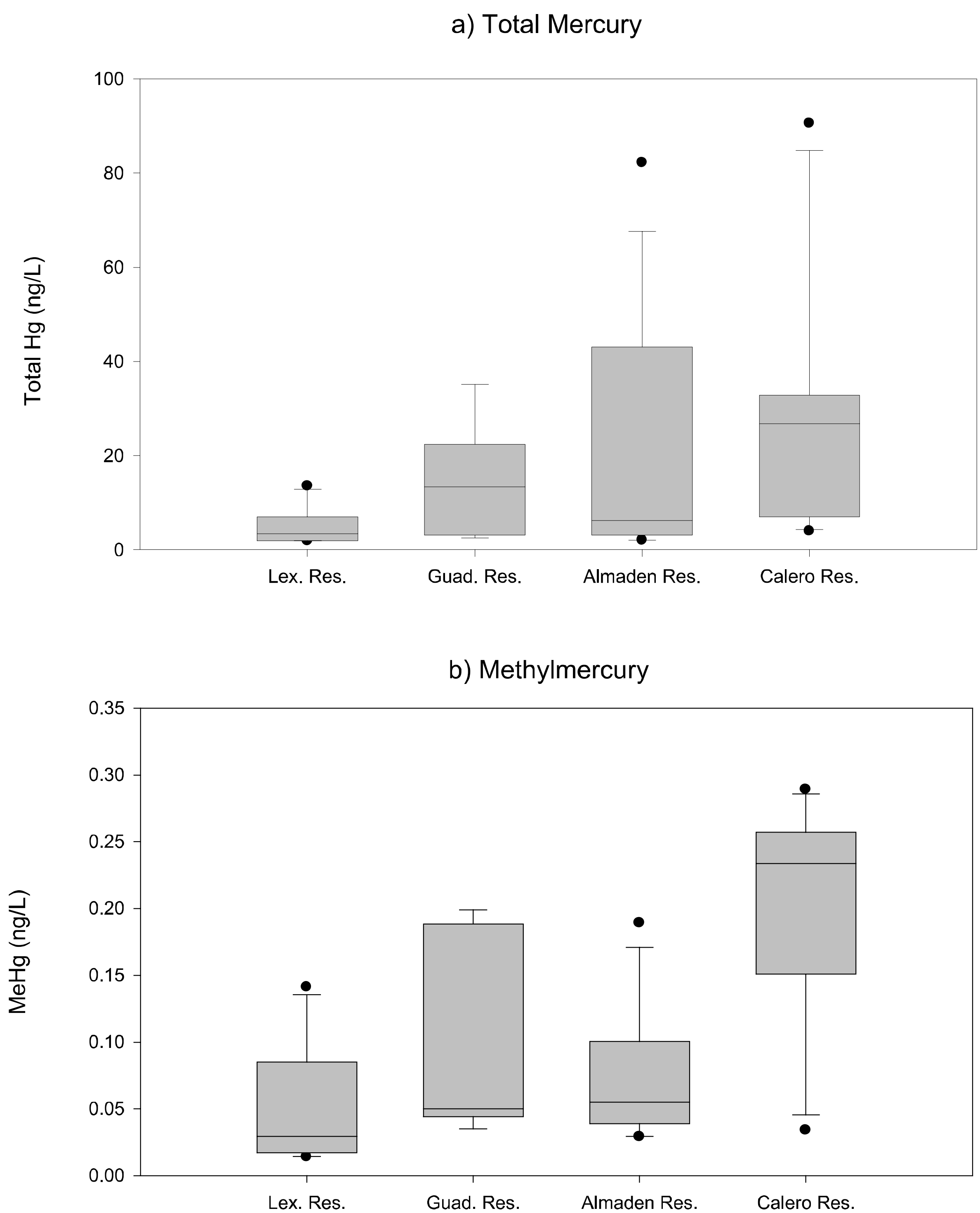


Figure 3-4. Box Plots for reservoir tributaries a) total mercury and b) methylmercury

(Box plots show the 25th and 75th percentiles as the top and bottom of the box; the median is the line inside the box. The line below the box is the 10th percentile and the line above the box is the 90th percentile. The black circles above or below the box show values outside of the 10th or 90th percentiles.)

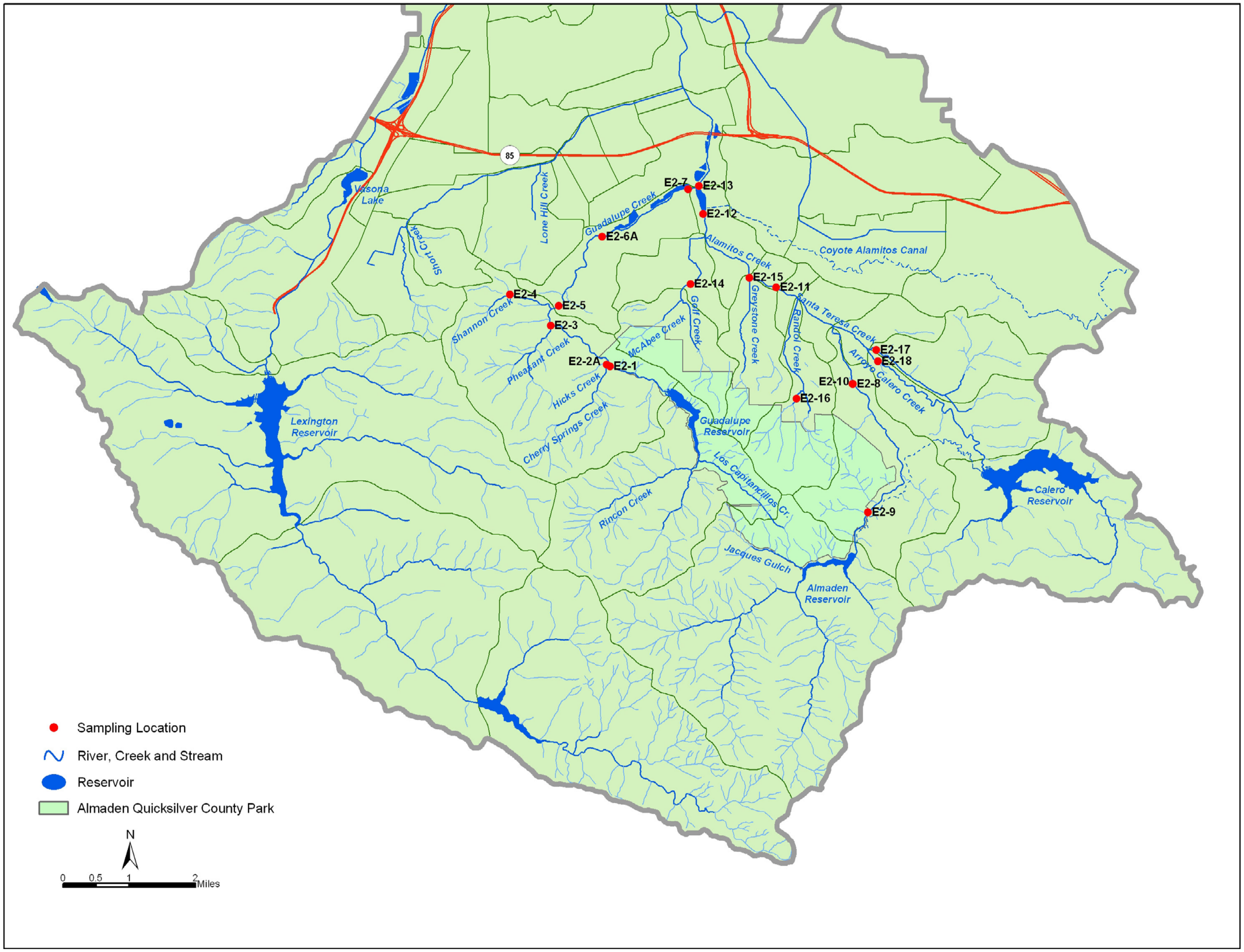


Figure 3-5. Sampling Locations of Creeks, Affected by Mining Below Impoundments

Flows at the sampling locations are provided in Table 3-2. Water quality and mercury results are presented in the Data Collection Report (Tetra Tech, 2005a). There was limited rainfall at the time of sampling in this part of the watershed, so low flows were sampled.

Table 3-2.
Flow Measurements for Element 2 Sampling Locations, Wet Season 2004

Station No.	Station Name	Date	Time	Est Flow, cfs
E2-1	Guadalupe Creek upstream of Cherry Springs Creek	4/14/2004	8:59	6.08
E2-2A	Cherry Springs Creek	4/14/2004	8:48	3.61
E2-2B	Cherry Springs Creek (replicate)	4/14/2004	8:48	rep
E2-3	Pheasant Creek	4/14/2004	8:22	0.75
E2-4	Shannon Creek	4/14/2004	7:58	0.2
E2-5	Guadalupe Creek @ Old Gauge	4/14/2004	7:37	12.6
E2-5	Guadalupe Creek @ Old Gauge	4/20/2004	10:59	17.6
E2-6	Guadalupe Creek below Masson Dam	4/20/2004	7:45	NA
E2-6A	Guadalupe Creek below Masson Dam	4/19/2004	12:30	NA
E2-6B	Guadalupe Creek below Masson Dam (replicate)	4/19/2004	12:30	rep
E2-7	Guadalupe Creek above Almaden Expressway	3/8/2004	11:50	7.05
E2-7	Guadalupe Creek above Almaden Expwy	4/19/2004	0.45	1.01
E2-7A	Guadalupe River above Almaden Expwy	4/20/2004	9:49	2.22
E2-7B	Guadalupe River above Almaden Expwy (replicate)	4/20/2004	9:49	rep
E2-8	Deep Gulch at previously-used site	3/26/2004	11:00	0.21
E2-9	Alamitos Creek @ Almaden Road Bridge near AQC Park	4/20/2004	13:30	4.54
E2-10	Alamitos Creek @ Harry Road	4/19/2004	14:29	13.36
E2-10	Alamitos Creek @ Harry Road	4/20/2004	12:50	2.6
E2-11	Alamitos Creek at Greystone Lane	4/19/2004	13:15	7.06
E2-11	Alamitos Creek @ Greystone Lane	4/20/2004	12:20	2.16
E2-12	Alamitos Creek above Almaden Lake	3/8/2004	12:25	31.68
E2-12	Alamitos Creek above Almaden Lake	4/19/2004	11:50	8.57
E2-12	Alamitos Creek above Almaden Lake	4/20/2004	10:31	11.78
E2-13	Almaden Lake Outlet	4/19/2004	11:27	15.7
E2-13	Almaden Lake Outlet	4/20/2004	10:09	14.96
E2-14	Golf Creek upstream of Alamitos Cr (below Camden Ave)	4/23/2004	1:00	NA
E2-15	Greystone Creek upstream of Alamitos Creek	4/19/2004	13:35	1.31
E2-16	Randol Creek upstream of Alamitos Creek	4/19/2004	14:00	0.2
E2-17	Santa Teresa Creek upstream of Calero Creek	4/14/2004	8:45	0.51
E2-18	Calero Creek @ Harry Road	4/14/2004	7:45	2.56

All flows were estimated from field measurements, since permanent gauges are not present.

The major water quality results for the wet season are outlined below:

- **Suspended solids.** The ranges for the tributaries and creeks are summarized below:
  - Tributaries to Alamitos Creek: 1.1 mg/L (Greystone Creek and upstream site on Randol Creek) to 16.9 mg/L (Calero Creek)
  - Alamitos Creek: 2.2 mg/L to 9.1 mg/L
  - Almaden Lake Outlet: 11.2 mg/L to 12.3 mg/L
  - Tributaries to Guadalupe Creek: 0.9 mg/L (Pheasant Creek) to 1.8 mg/L (Shannon Creek)
  - Guadalupe Creek: 2.0 mg/L to 13.4 mg/L

- **Mercury.** The total mercury concentrations in the samples are summarized below:
  - Tributaries to Alamitos Creek: 3.6 ng/L (upstream site on Randol Creek) to 37.1 ng/L (Golf Creek)
  - Alamitos Creek: 34.3 ng/L to 139.5 ng/L
  - Almaden Lake Outlet: 36.5 ng/L to 49.5 ng/L
  - Tributaries to Guadalupe Creek: 2.0 ng/L (Pheasant Creek) to 2.7 ng/L (Shannon Creek)
  - Guadalupe Creek: 13.8 ng/L to 40.3 ng/L

- **Methylmercury.** The total mercury concentrations in the samples are summarized below:
  - Tributaries to Alamitos Creek: 0.06 ng/L (Deep Gulch) to 0.43 ng/L (Golf Creek)
  - Alamitos Creek: 0.26 ng/L to 0.55 ng/L
  - Almaden Lake Outlet: 0.28 ng/L to 0.32 ng/L
  - Tributaries to Guadalupe Creek: 0.02 ng/L (Cherry Springs Creek) to 0.06 ng/L (Pheasant Creek)
  - Guadalupe Creek 0.24 ng/L to 0.57 ng/L.

Total and dissolved mercury concentrations are shown in Figure 3-6 for both Alamitos and Guadalupe creeks. Alamitos Creek was highest on April 20th at the bridge below Hacienda Yard (139.5 ng/L at E2-9), remained high at the Harry Road location (97.3 ng/L at E2-10), but decreased to 39.2 ng/L before entering Almaden Lake. The tributaries entering Alamitos Creek below Harry Road (Golf, Greystone, and Randol) had lower mercury concentrations than the main stem, and lower flows. The highest total mercury concentration in Guadalupe Creek was measured below Masson Dam on April 20th (40.3 ng/L at E2-6), when the upstream sample at the Old Gauge (E2-5) was less (28.1 ng/L). Mercury was almost as high in the main stem of Guadalupe Creek above Cherry Springs Creek (33 ng/L), even though the tributaries

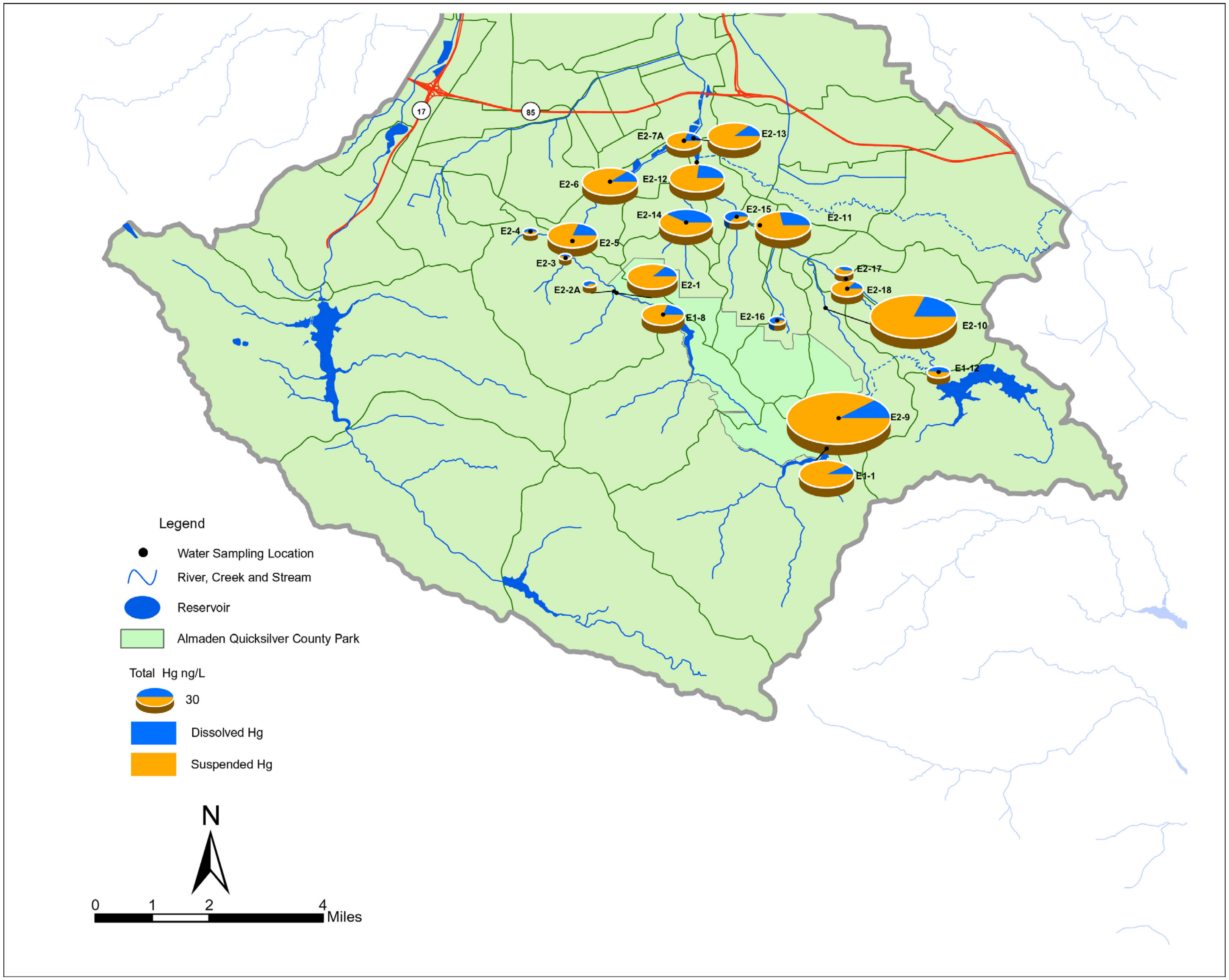


Figure 3-6. Total and dissolved mercury concentrations in Alamitos and Guadalupe Creeks and tributaries.

between this location and the dam were low (2.0 ng/L in Pheasant Creek and 2.7 ng/L in Shannon Creek). These results suggest that mercury is coming from resuspended sediments. Guadalupe Creek above its confluence with Alamitos Creek had variable mercury concentrations (13.8 ng/L on the non-storm day when the flow was about 7 cfs and 16.1 to 32.7 ng/L for the April sampling events when the flow was 1-2 cfs). The decreased suspended solids and total mercury at the confluence are consistent with deposition behind Masson Dam.

Particulate mercury concentrations were greater than 0.2 mg/kg in all the samples collected from Alamitos and Guadalupe Creeks and their tributaries. The total mercury in particulates of Alamitos Creek were greater than 10.0 mg/kg, between the bridge below Hacienda Yard and its confluence with Almaden Lake. The tributaries to Alamitos Creek have lower particulate mercury (0.68 mg/kg in Calero Creek to 7.8 mg/kg in Golf Creek) than the main stem (10.3 mg/kg to 23.8 mg/kg). The lake outlet samples had lower mercury content (2.6 to 4.0 mg/kg) than the upstream main stem, showing that some deposition of the high mercury suspended solids is occurring in the lake. The tributaries to Guadalupe Creek had lower particulate mercury (0.8 mg/kg in Shannon Creek to 1.2 mg/kg in Pheasant Creek) than the main stem (1.1 mg/kg to 14.8 mg/kg).

Methylmercury in the tributaries to Alamitos Creek below Harry Road (0.12 ng/L in Randol Creek to 0.43 ng/L in Golf Creek) were higher than the tributaries to Guadalupe Creek (0.02 to 0.06 ng/L). Methylmercury concentrations on Alamitos Creek were similar below the bridge near the AQC Park (0.51 ng/g) to Harry Road (0.55 ng/L), and then decreased downstream to the inlet to Almaden Lake (0.28 to 0.31 ng/L), as seen in Figure 3-7. The Almaden Reservoir outlet, when sampled on April 14, had a lower methylmercury concentration (0.29 ng/L). A methylmercury maximum was observed in Guadalupe Creek below Masson Dam (0.57 ng/L on April 20th). The methylmercury at the Guadalupe Reservoir outlet on April 14 was higher (0.7 ng/L) than the above downstream location. The methylmercury concentration was lower in the upstream reach of Guadalupe Creek at the Old Gauge (0.35 ng/L) than at Masson Dam on April 20th. This trend indicates that some in-situ methylation or resuspension of methylmercury-bearing sediment is occurring above Masson Dam. Methylmercury concentrations decrease from below the dam to the mouth of the creek at Almaden Expressway.

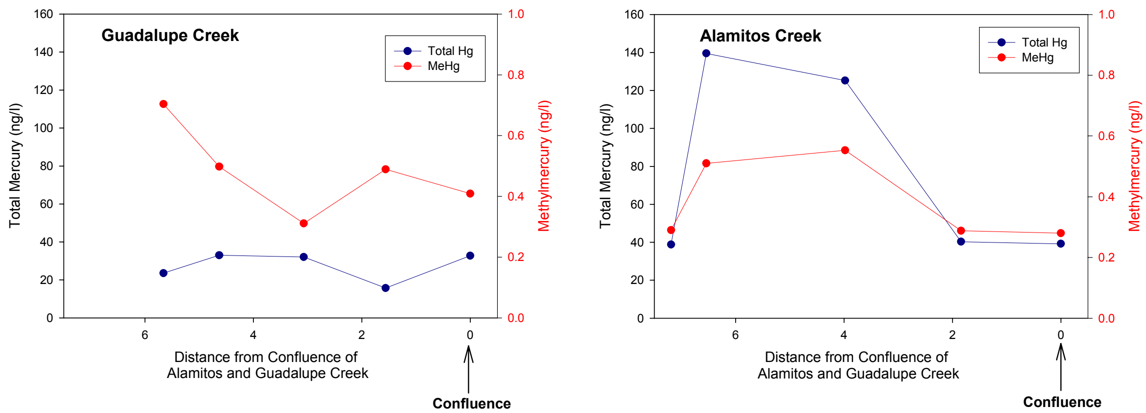


Figure 3-7. Mercury species along Guadalupe and Alamitos Creeks in April 2004

Mercury and other parameters were measured at some of the same locations sampled in the Synoptic Survey and the wet season. Results for locations sampled for Alamitos and Guadalupe Creeks are presented in Table 3-3. Total mercury at the reservoir outlets was higher in the wet season than the dry season samples from July 2003, while methylmercury exhibited the opposite trend. Total mercury concentrations increased in the wet season samples at the mouth of Alamitos Creek. Methylmercury was higher in the summer for both Alamitos and Guadalupe Creeks, due to reservoir releases. The higher total mercury concentration in Alamitos Creek at Harry Road in July 2003 is due to higher suspended solids (14 mg/L), compared to the April sample (4.6 mg/L). The decrease in methylmercury with distance from the reservoirs in the July 2003 samples was due to demethylation, uptake, and some sediment deposition.

Increased sediments during storm events can be introduced from sediment pick-up by overland runoff, urban runoff and pick-up of sediment present in stormdrains, bank erosion and resuspension of bedded sediment in a creek channel or tributaries. The main stem receives the sediment contributions from its tributaries , direct urban runoff, and stormdrains, in addition to bank erosion and resuspension of sediment in the channel of the main stem. A survey of creek reaches where erosion was occurring or likely such as along undercut banks was conducted in 2003; these locations are shown in Figure 3- 8. Example photographs of the sites are shown in Figure 3-9. At several locations along Alamitos Creek, erosion may cause mine wastes to be discharged into the creek. At other locations such as along Ross Creek, sediment from an urban area would be discharged to the creek, which also contributes to the total mercury load in the Guadalupe River.

Table 3-3.
Comparison of Dry and Wet Season Results for Alamitos and Guadalupe Creeks

Location	2004 Sample ID	Total Mercury, ng/L			
		February-00	July-03	March-04	April-04
Almaden Reservoir Outlet	E1-1	NS	7.49	36.6	38.79
Deep Gulch Creek	E2-8	NS	108.6	13.41	NS
Alamitos Creek at Harry Road	E2-10	NS	435.9		125.2
Alamitos Creek above Almaden Lake	E2-12	NS	25.88	86.49	39.32
Guadalupe Reservoir Outlet	E1-8	NS	18.89	77.4	23.56
Guadalupe Creek at Old Gauge	E2-5	82.8	33.15	NS	28.07
Guadalupe Creek above Almaden Expressway	E2-7	74.1	38.9	13.82	32.75
Location	**2004 Sample ID**	**Methylmercury, ng/L**			
		February-00	**July-03**	**March-04**	**April-04**
Almaden Reservoir Outlet	E1-1	NS	4.34	0.328	0.29
Deep Gulch Creek	E2-8	NS	0.2	0.057	NS
Alamitos Creek at Harry Road	E2-10	NS	0.96	NS	0.553
Alamitos Creek above Almaden Lake	E2-12	NS	0.306	0.275	0.31
Guadalupe Reservoir Outlet	E1-8	NS	8.27	0.319	0.704
Guadalupe Creek at Old Gauge	E2-5	0.25	5.21	NS	0.355
Guadalupe Creek above Almaden Expressway	E2-7	0.51	0.99	0.242	0.409

The data obtained for Alamitos and Guadalupe Creeks show that in general total mercury increases as flow increases. High flows above 1,000 cfs can occur on both creeks for short durations based on an evaluation of historical flow data and 2003 and 2004 data, which would have greater suspended solids, and hence would contribute larger total mercury loads to the downstream Guadalupe River. For Guadalupe Creek, bank erosion and resuspension of sediment are important, since the tributaries have low mercury for all three forms. For Alamitos Creek, the tributaries also contribute less mercury than the upstream reaches of the creek, particularly from the bridge near AQC Park to Harry Road. Golf Creek, which includes McAbee Creek draining the former Senador mine area has the highest mercury concentrations (of all three forms) of any of the tributaries to Alamitos or Guadalupe Creeks. However, flow from Golf Creek only reaches Alamitos Creek under high flow conditions due to a series of upstream drop structures, which also retain sediment.

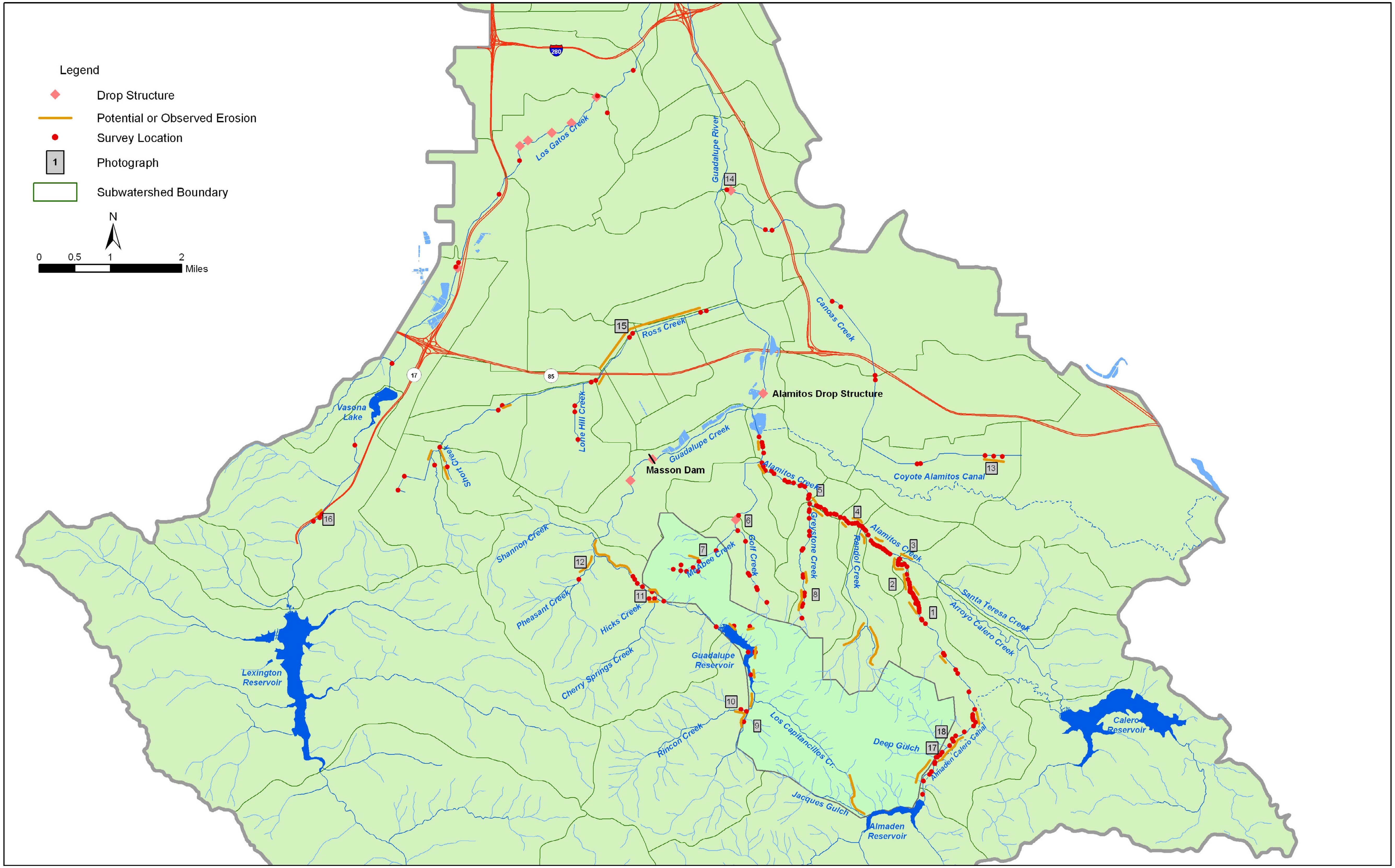


Figure 3-8. Location of potential erosion sites along the tributaries to the Guadalupe River.

Photographs of Potential Sediment Erosion Sites

Photo 1 **Eroding bank along Alamitos Creek**

Photo 2 **Undercut bank on Alamitos Creek**

Photo 3 **Gravel bar and undercut bank on Santa Teresa Creek**

Photo 4 **Potential erosion on Alamitos Creek**

Photo 5 **Steep bank on Alamitos Creek**

Photo 6 **Drop structure on McAbee Creek**

Photo 7 **Eroded bank on McAbee Creek below Senador Mine**

Photo 8 **Underbank on Greystone Creek**

Photo 9 **Potential bank erosion on Rincon Creek**

Photo 10 **Potential bank erosion on Rincon Creek**

Photo 11 **Potential bank erosion on Hicks Creek**

Photo 12 **Potential erosion on Pheasant Creek**

Photo 13 **Eroding bank on Canoas Creek**

Photo 14 **Drop structure on Canoas Creek**

Photo 15 **Eroded bank on Ross Creek**

Photo 16 **Potential erosion on Los Gatos Creek**

Photo 17 **Eroded bank on Alamitos Creek**

Photo 18 **Steep bank on Alamitos Creek**

Figure 3-9. Examples of sediment erosion and bank undercutting sites.

3.1.3 URBAN CREEKS

Limited data for mercury were previously available for the urban watersheds contributing to the Guadalupe River. The three urban creeks (Ross, Canoas, and Los Gatos) were sampled between February 27 and April 23, 2004. The locations (Figure 3-10) were selected to estimate the mercury load coming from urban areas and to determine if there are differences along the creeks. Measurements were made of suspended sediments, flow rates at ungauged locations, total and dissolved mercury, and methylmercury at each location. Dissolved methylmercury was measured at four of the locations (E3-1, E3-4, E3-5, and E3-7).

Water samples were collected at seven locations along Ross Creek, Canoas Creek, and Los Gatos Creek. The flows at the time of sampling are provided in Table 3-4. The chemical data are presented in the Data Collection Report (Tetra Tech, 2005a). The mercury results are summarized below:

- **Suspended Solids.** The suspended solids concentrations in the urban creeks and Guadalupe River are summarized below:
  - Ross Creek: 1.1 mg/L to 24.5 mg/L
  - Canoas Creek: 2.7 mg/L to 45.6 mg/L
  - Los Gatos Creek: 2.5 mg/L to 90.4 mg/L
  - Guadalupe River main stem: 5.0 mg/L to 118.6 mg/L.

- **Mercury.** Total mercury in the urban creeks and Guadalupe River are summarized below:
  - Ross Creek: 5.30 ng/L to 18.47 ng/L
  - Canoas Creek: 4.14 ng/L to 27.97 ng/L
  - Los Gatos Creek: 2.04 ng/L to 29.83 ng/L

    Guadalupe River main stem: 14.48 ng/L to 464.6 ng/L

Los Gatos Creek contributed higher suspended solids to the river than Ross or Canoas Creek, particularly when Vasona Reservoir spilled, as it did on February 27th. Los Gatos Creek contributed less total mercury and methylmercury than the tributaries influenced by mining, Alamitos and Guadalupe Creeks (Figure 3-11). Los Gatos and Canoas Creeks had similar maximum total mercury concentrations during the large flow event in February 2004, with the highest measured concentration below the Vasona Reservoir in Los Gatos Creek (29.8 ng/L) when the suspended solids was 90.4 ng/L. Los Gatos Creek had higher methylmercury below Vasona Reservoir and upstream of this reservoir than in the downstream locations on the same sampling day.

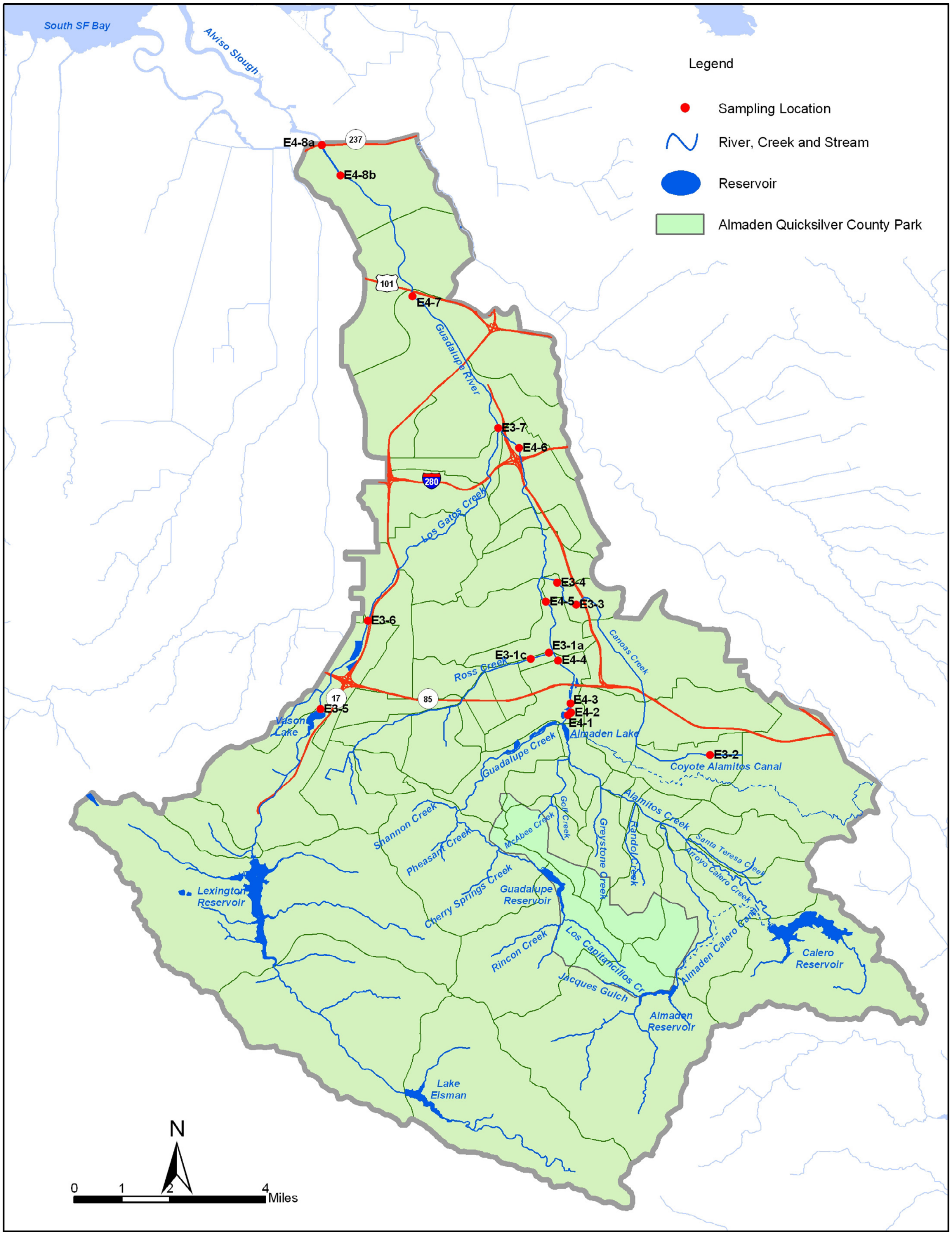


Figure 3-10. Sampling Locations for Urban Creeks and the Guadalupe River.

Table 3-4.
Flow Measurements at Elements 3 and 4 Sampling Locations, Wet Season 2004

Station No.	Station Name	Date	Time	Gauged Flows, cfs	Est. Flows, cfs
E3-1A	Ross Creek upstream of Guadalupe River	2/27/2004	14:00	12.5	
E3-1B	Ross Creek upstream of Guadalupe River (replicate)	2/27/2004	14:00	rep	
E3-1	Ross Creek upstream of Guadalupe River	3/8/2004	10:45	1.2	
E3-1	Ross Creek upstream of River (below Cherry Ave.)	4/23/2004	11:30	0.30	
E3-2	Canoas Creek at Lean Avenue	2/27/2004	14:45		1.5
E3-2	Canoas Creek at Lean Ave	4/20/2004	11:40		0.06
E3-3	Canoas Creek at Dow Drive	2/27/2004	13:00		4.12
E3-4	Canoas Creek upstream of Guadalupe River	2/27/2004	12:05	7.4	
E3-4	Canoas Creek upstream of Guadalupe River	3/8/2004	9:19	0.7	
E3-4	Canoas Creek upstream of Guadalupe River	4/20/2004	9:25	1	
E3-5	Los Gatos Creek below Vasona Reservoir Outlet	2/27/2004	8:35	spilling	79.2
E3-5	Los Gatos Creek below Vasona Reservoir Outlet	4/20/2004	8:10		18.72
E3-6	Los Gatos Creek at Camden Avenue	2/27/2004	9:30		9.92
E3-7	Los Gatos Creek above Guadalupe River	2/27/2004	10:20	18.1	
E3-7	Los Gatos Creek above Guadalupe River	3/8/2004	8:45	2.7	
E3-7	Los Gatos Creek upstream of Guadalupe River	4/20/2004	8:50	31.8	
E4-1	Guadalupe River above Alamitos Drop Structure	2/26/2004	8:50		NA
E4-1	Guadalupe River above Alamitos Drop Structure	4/20/2004	8:40		NA
E4-2	Guadalupe River below Alamitos Drop Structure	2/26/2004	9:25		spilling
E4-2	Guadalupe River below Alamitos Drop Structure	3/8/2004	11:30	20.87	NA
E4-2	Guadalupe River below Alamitos Drop Structure	4/20/2004	9:08	9.51	NA
E4-3	Guadalupe River at Blossom Hill Road	2/27/2004	9:15	57	
E4-3	Guadalupe River at Blossom Hill Road	4/20/2014	8:20	9.6	
E4-4	Guadalupe River upstream of Ross Creek Inflow	2/27/2004	10:10		NA
E4-4	Guadalupe River upstream of Ross Creek Inflow	3/8/2004	11:10		30.96
E4-4	Guadalupe River upstream of Ross Creek Inflow	4/20/2004	10:40		9.18
E4-5	Guadalupe River upstream of Canoas Creek Inflow	2/27/2004	10:30	174.6	
E4-5	Guadalupe River upstream of Canoas Creek Inflow	3/8/2004	9:42	31.5	NA
E4-5	Guadalupe River upstream of Canoas Creek Inflow	4/20/2004	9:55	9.9	
E4-6	Guadalupe River at San Carlos Street	2/27/2004	11:10		NA
E4-6	Guadalupe River at San Carlos Street	4/20/2004	11:55		NA
E4-7	Guadalupe River at Highway 101	2/26/2004	10:25	807	
E4-7	Guadalupe River at Hwy 101	4/20/2004	12:25	29.00	
E4-7A	Guadalupe River at Highway 101	3/8/2004	15:10	45	
E4-7B	Guadalupe River at Highway 101 (replicate)	3/8/2004	15:10		rep
E4-8	Guadalupe River at HWY 237	2/27/2004	12:00		NA
E4-8	Guadalupe River at Hwy 237	4/20/2004	13:00		NA

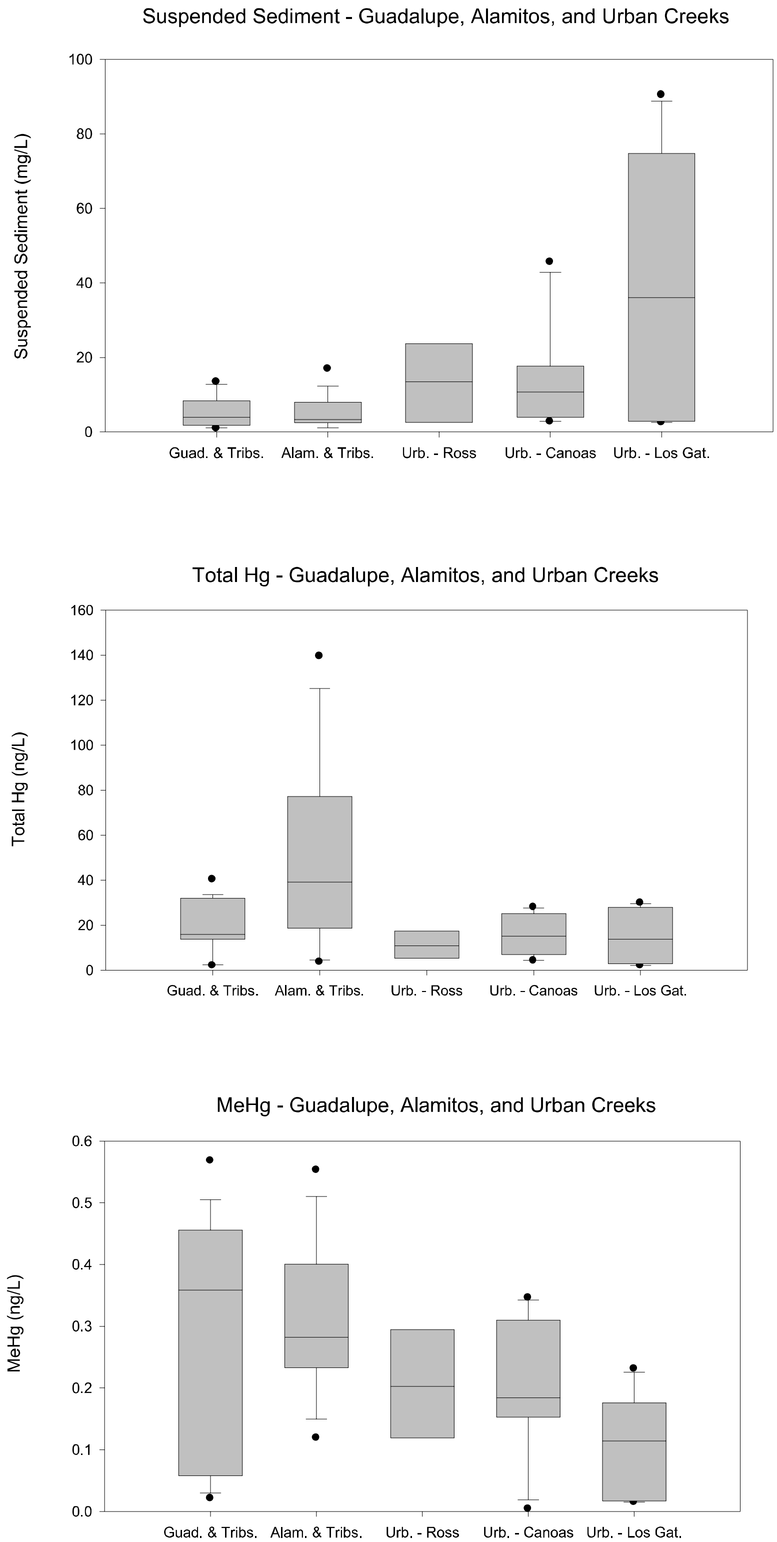


Figure 3-11. Box Plots Comparing Suspended Sediment, Total and Methylmercury for Urban Creeks and Upstream Tributaries to Guadalupe River.

3.1.4 GUADALUPE RIVER

The main stem of the Guadalupe River was sampled on three dates between February 26 and April 20, 2004 at eight locations on the Guadalupe River to characterize the wet season runoff. The sampling locations are shown on the map with the urban creeks (see Figure 3-10). The flows at the time of sampling were included in Table 3-4. Measurements were made of suspended sediments, total and dissolved mercury, and methylmercury at each location. Dissolved mercury and dissolved methylmercury were measured at two of the locations (E4-7 and E4-8).

Mercury along the Guadalupe River and urban creeks are compared for a moderate and small storm in Figure 3-12. In all three events, total mercury was higher in the upper part of the river near the Alamitos Drop Structure, compared to the lower part by Highways 101 and 237. The 2004 wet season sampling of the Guadalupe River at the Highway 101 gauge showed the highest total mercury (363.9 ng/L) on the day with the highest flow (807 cfs) and the lowest total mercury (14.5 ng/L) on the day with the lowest flow (29 cfs). The total mercury at Highway 237 ranged from 32.8 ng/L to 182.5 ng/L. The range of total mercury in the urban creeks before the confluence with the river was considerably less: 2.0 to 21.8 ng/L in Los Gatos Creek, 5.3 to 18.5 ng/L in Ross Creek, and 4.1 ng/L to 12.3 ng/L in Canoas Creek. The contribution from the mining-influenced creeks, Alamitos and Guadalupe Creeks, was higher (65.8 ng/L to 464.6 ng/L) as measured below the Alamitos Drop structure.

The suspended solids were higher in the large storm event (46.1 to 118.6 mg/L) than the small storm (7.1 to 17.7 mg/L). With the exception of the sampling location at Blossom Hill Road, all forms of mercury along the river were highest in the large storm event, including methylmercury. A possible explanation for the increase in total mercury concentration at Blossom Hill Road in the April 20th sample is that sediment can spill over the Alamitos Drop Structure during high flow events. The mercury-bearing sediment can then be resuspended and transported downstream by succeeding storms.

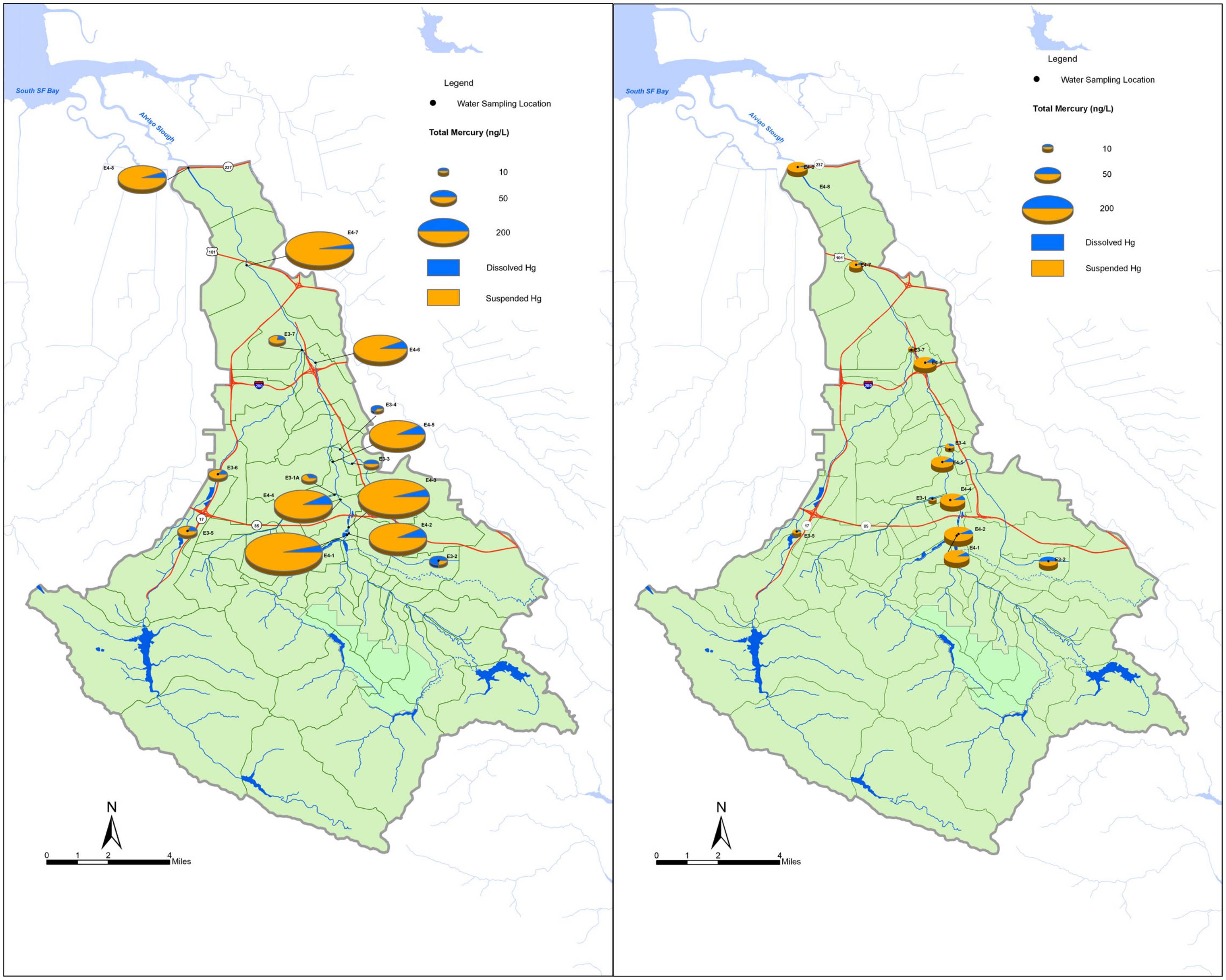


Figure 3-12. a)Total and Dissolved Mercury for Moderate Flow Event February 26-27, 2004 and b)Total and Dissolved Mercury for Small Storms – April 2004.

The methylmercury in the three urban creeks ranged from 0.004 to 0.23 ng/L, compared to the river locations that ranged from 0.16 to 0.9 ng/L. The highest methylmercury in the river samples on the highest flow day (2/26/04) was above and below the Alamitos drop structure (0.92 ng/L); the concentrations decreased below the drop structure (0.74 ng/L) and remained at a similar concentration at Highway 101 (0.75 ng/L). The following day, there was an increase in methylmercury concentrations from the Blossom Hill site (0.56 ng/L) to the reach above Ross Creek (0.65 ng/L) and San Carlos Street (0.59 ng/L), which may be due to resuspension of sediment from the river bottom. On the low flow events, methylmercury concentrations decreased at both Highway 101 and 237, compared to the concentrations upstream at San Carlos Street. Most of the methylmercury was associated with the particulate phase, rather than the dissolved phase.

Particulate mercury concentrations are compared in Figure 3-13. The three urban creeks had low concentrations compared to the main stem of the Guadalupe River. The urban creeks are similar to the upper watershed creeks not affected by mining, representing background conditions. The highest particulate mercury concentrations were observed in the creeks affected by mining, particularly Alamitos Creek. (Figure 3-14). The river samples have less variability, but are in the range of Guadalupe and Alamitos Creeks. The particulate mercury concentrations were similar along the main stem of the Guadalupe River from the confluence of Alamitos and Guadalupe Creeks to above Canoas Creek, then decreased toward the Bay. All particulate data are presented in the Data Collection Report (Tetra Tech, 2005a).

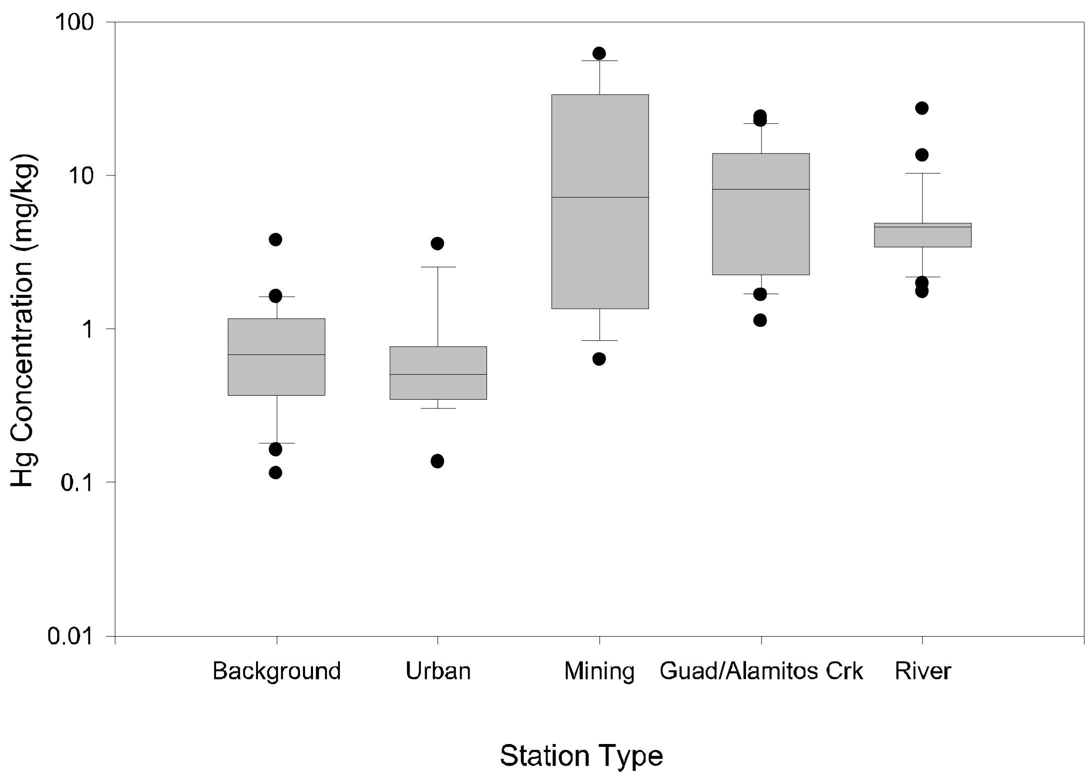


Figure 3-13. Particulate Mercury Concentrations by Waterbody Group.

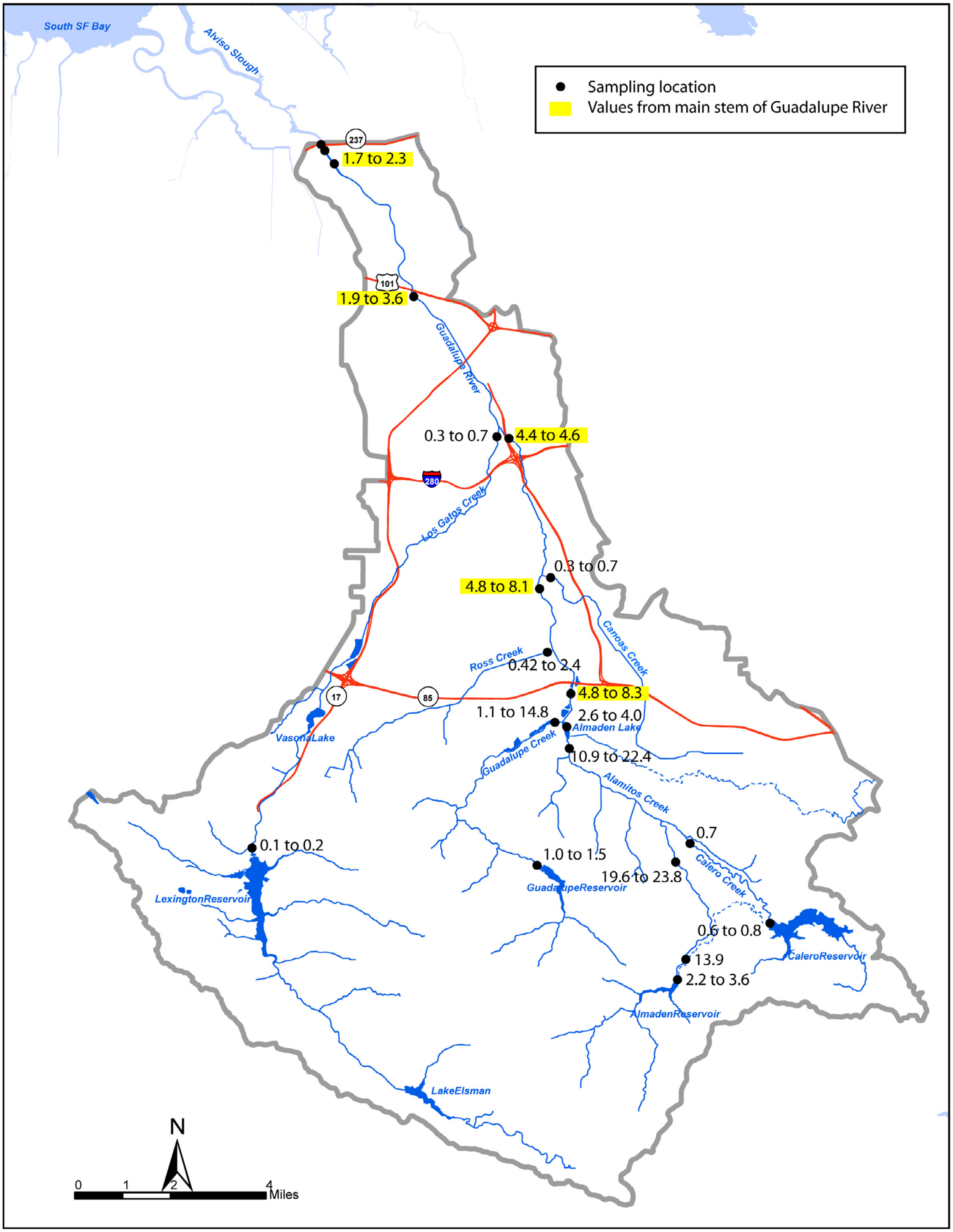


Figure 3-14. Particulate Mercury (mg/kg) at key locations in Guadalupe River Watershed from 2004

The measured concentrations of total and methylmercury and suspended solids are compared for the urban creeks, creeks affected by mining, and the reservoir outlets in Figure 3-15. The maximum total mercury and methylmercury concentrations were highest in the Guadalupe main stem. These plots show that the urban creeks contribute more suspended solids, but less total and methyl mercury than the two creeks affected by mining. The reservoir outlets had higher methylmercury concentrations in some, but not all the outlets, compared to the urban creeks. The maximum methylmercury concentration (0.92 ng/L) was measured in the sample above the Alamitos Drop Structure; the second highest concentration (0.75 ng/L) was from Highway 101 for the high flow event (both on the high flow sampling day - February 26, 2004 when the flow at the new USGS gauge near Highway 101 was 807 cfs – see Table 3-4).

Large storms result in much higher flows below the confluence with Los Gatos Creek than sampled for the TMDL project. In the 2002–2003 water year, mercury samples for such large storms were analyzed for SFEI. The total mercury concentrations ranged from 0.18 µg/L to 18.67 µg/L between November 7, 2002 and May 29, 2003 for 27 samples (McKee et. al., 2004). The maximum mercury concentration was sampled on December 16, 2002 when the flow at the old USGS gauge on St John's Street was about 4,500 cfs and the suspended solids was 967 mg/L. The total mercury concentration at the gauge was 4.96 µg/L on May 29, 2003 when the flow was less than 100 cfs and suspended solids was18.1 mg/L. These results are much higher than the results from the 2004 results, the USGS study discussed above by Thomas, and recent sampling by the Army Corps of Engineers (ACOE, 2004). The higher mercury concentrations for extreme flood conditions are expected, but the measured mercury concentrations were also higher for low flow conditions.

3.2 WET SEASON SEDIMENT SAMPLING

3.2.1 UPSTREAM TRIBUTARIES

Sampling was conducted to compare total mercury and methyl mercury in sediment from creeks in the mining area and from Alamitos and Guadalupe Creeks to bank soil and bottom sediment from the Guadalupe River. The sediment in the mining area creeks was collected to determine the potential for resuspension and transport of mercury-bearing sediment. Sampling was conducted once at each location. Mining area bottom sediment samples were collected from the Mine Hill tributary to Jacques Gulch (E1-7S) and N. Los Capitancillos Creek (E1-9S) (see Figure 3-16). These samples were analyzed for total and methylmercury, grain size distribution, and moisture. A sampling location on McAbee Creek, a tributary to Golf Creek, was added (E2-19S), since a large debris dam was found in the creek below the Senador Mine entrance to the Almaden Quicksilver County Park (AQCP). Both bottom and bank samples were collected and analyzed for total mercury. Sediment samples, primarily gravels, were also collected from two deposition areas: where Alamitos Creek enters Almaden Lake and at the confluence where Guadalupe Creek meets Alamitos Creek below the lake. These samples were analyzed for total and methylmercury, grain size distribution, and moisture.

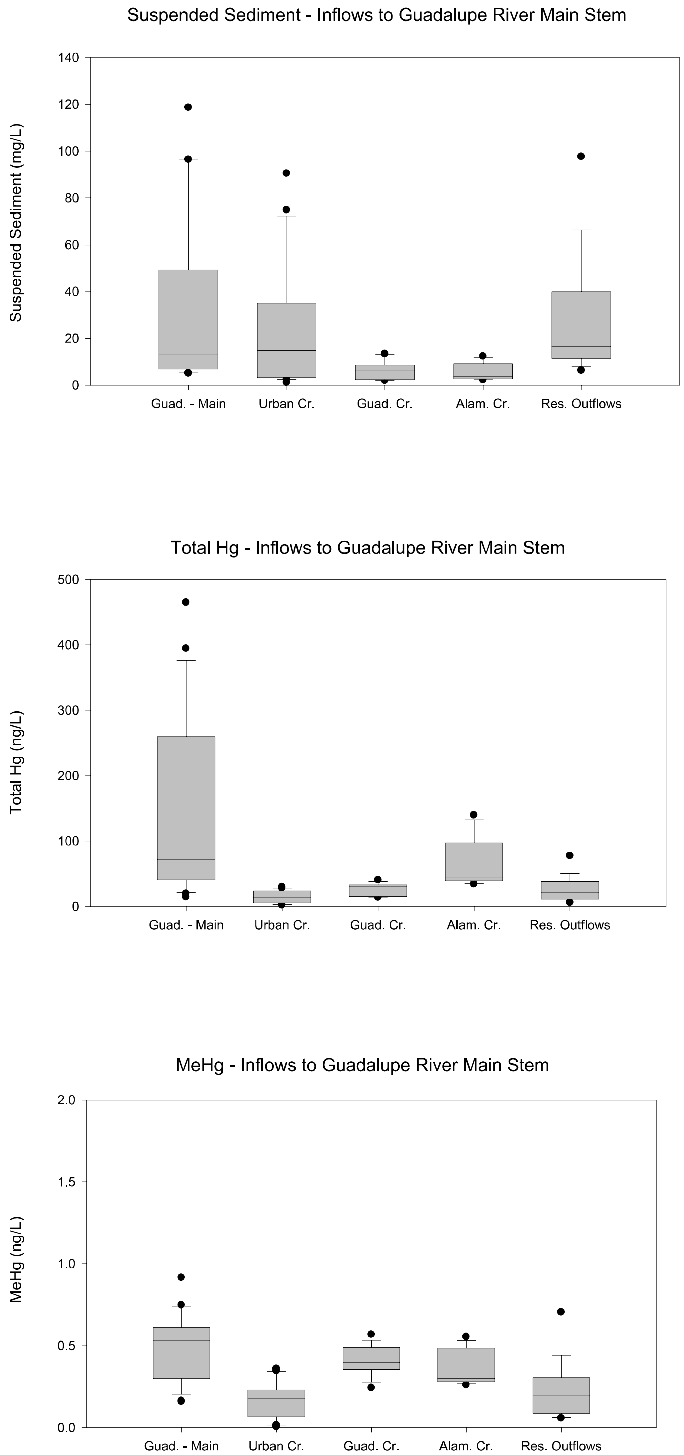


Figure 3-15. Box Plots Comparing Suspended Sediment, Total and Methyl Mercury for Guadalupe River Main Stem to Inputs.

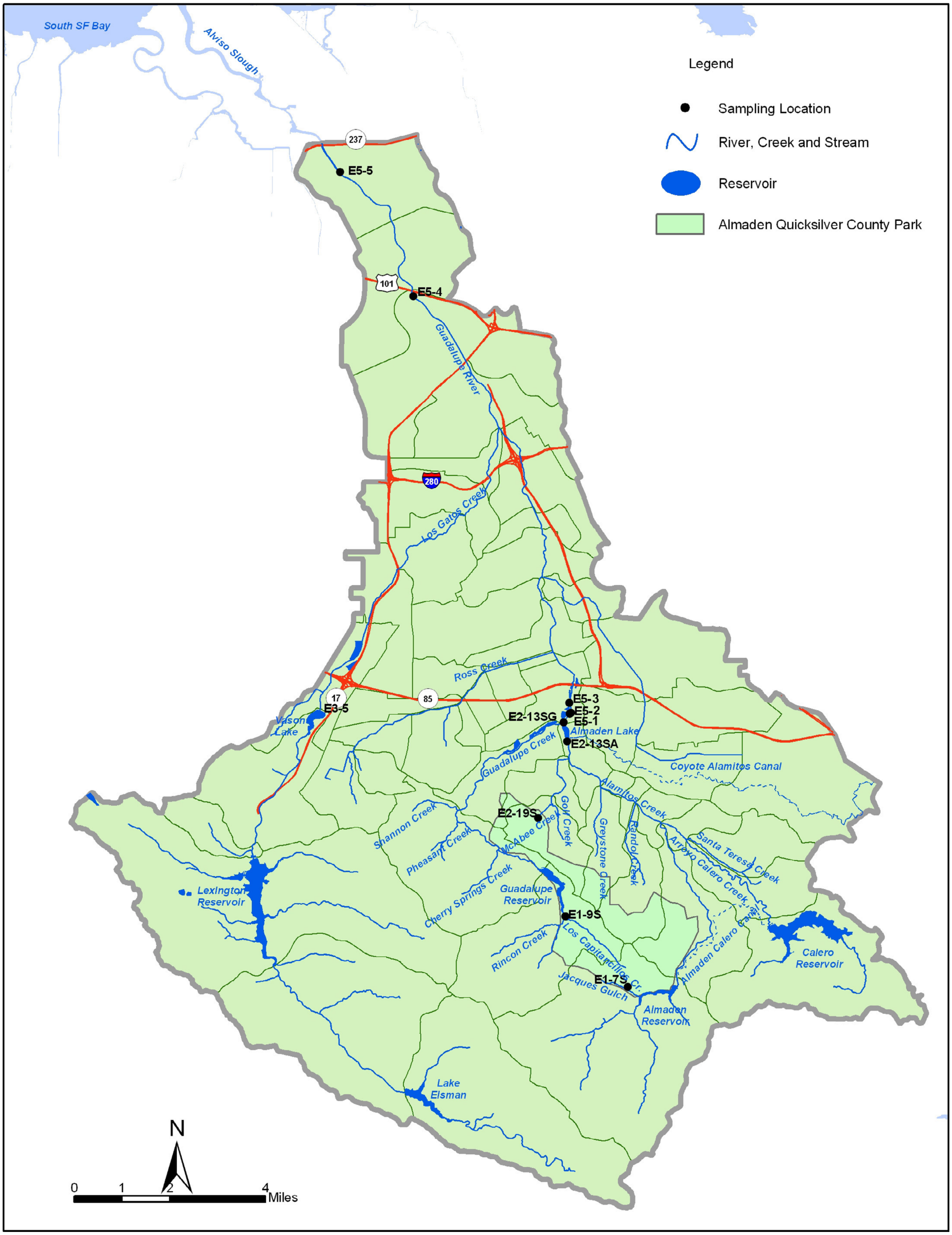


Figure 3-16. Sediment Sampling Locations for Wet Season 2004

3.2.2 GUADALUPE RIVER

Sediment transport is an important factor in the release of mercury to San Francisco Bay. Sediment samples were collected from the Guadalupe River at five locations as shown on the map (Figure 3-16) on March 8, 2004. At each of four locations along the Guadalupe River, four samples were collected: two bottom sediment samples and two bank samples. At one of these locations (E5-4), an additional set of four samples was collected to provide an estimate of variability. One additional sediment sample was collected from above the Alamitos Drop Structure on the Guadalupe River in the built-up sediment above the upstream wall. The sediment samples were analyzed for total mercury, methylmercury, moisture content, and grain size. In addition, samples were collected at three locations (E5-2, E5-4, and E5-5) from the river bottom for analysis of sulfate and sulfide.

Additional analyses were conducted to evaluate relationships between mercury and grain size and the potential leachability, and hence bioavailability, of the mercury. In general, the leachability was less in coarse sediment samples from the mining area creeks, than in the fine-grained sediment from the river bottom near the Bay. The predominant form of the mercury based on the sequential extraction tests (Bloom et al, 2003) was cinnabar, consistent with the source of the ores from silica carbonate deposits.

The sediment results are presented in the Data Collection Report (Tetra Tech, 2005a). The concentrations presented on maps, plots, and discussed in the text are presented on a dry weight basis. Notable findings from the sediment samples are:

- **Mercury**. The total mercury concentrations in the sediment samples (dry-wt basis) are summarized below:
  - mercury in sediment from creeks in the mining area ranged from 0.18 mg/kg to 18.65 mg/kg.
  - mercury in sediment in the deposition areas at the end of Alamitos and Guadalupe Creeks ranged from 16.45 mg/kg to 18.78 mg/kg.
  - mercury in sediment from the Guadalupe River ranged from 0.065 mg/kg to 39.28 mg/kg.

- **Methylmercury**. The methylmercury concentrations in the sediment samples are summarized below:
  - 0.05 ng/g to 0.14 ng/g in sediment from creeks in the mining area; 0.06 ng/g to 0.29 ng/g in sediment from the deposition areas at the end of Alamitos and Guadalupe Creeks;
  - 0.05 ng/g to 3.2 ng/g in sediment from the Guadalupe River.

The total mercury concentrations at key locations are shown in Figure 3-17 from both the wet season and the synoptic survey. The river samples from Highways 101 and 237 were less than the upper river samples. For most sediment samples, the total mercury concentrations were higher in the bank sediments than the bottom sediments. The urban creeks had low mercury concentrations, compared to the main stem and the

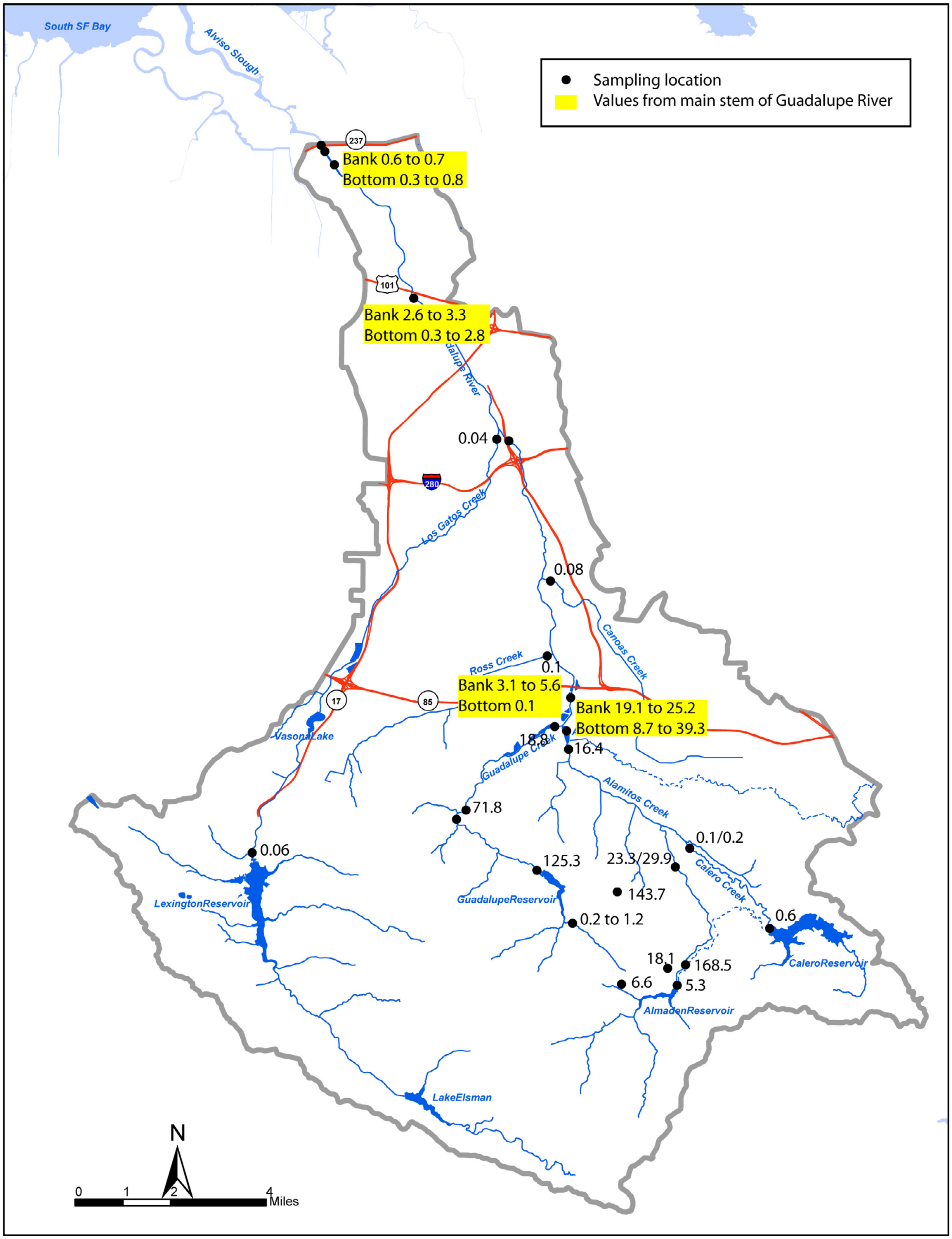


Figure 3-17. Total mercury concentrations (mg/kg) in Sediment Samples at Key Locations in the Guadalupe Watershed in 2004

tributaries affected by mining. The sediment mercury concentrations on Alamitos and Guadalupe Creeks are high due to past transport of mine wastes.

In the upper reaches of the river, the bottom samples had higher methylmercury concentrations than the bank samples. While the sediment data are variable, the general trend of the bottom samples was that total mercury was highest below the drop structure, then low at Blossom Hill Road, higher at Highway 101, then decreasing at Highway 237. The importance of the higher mercury in the bank samples is that during high flow events, erosion or sloughing of the bank soils can occur, which introduces higher mercury-bearing sediment to the river.

3.3 DRY SEASON RESERVOIRS

Methylmercury is the chemical form of mercury most directly linked to uptake by biota. An understanding of methylation processes in reservoirs is needed to develop the linkage between water column and fish mercury. Almaden and Guadalupe Reservoirs were sampled on six dates between May 11 and August 31, 2004. Measurements of total and dissolved mercury and methylmercury in water, and associated parameters (dissolved oxygen, sulfate, sulfide, dissolved organic carbon, and nutrients) were made in these two reservoirs to follow the development of stratification and its effect on net methylmercury production. The mercury samples were collected from the reservoirs from the epilimnion and below the thermocline at mid-depth of the hypolimnion, and at the outlets of the two reservoirs. Depth profiles for temperature, specific conductivity, pH, dissolved oxygen, and turbidity were developed using *in situ* measurements.

3.3.1 SAMPLE RESULTS: RESERVOIRS

The outflows from both reservoirs were low during the dry season, between 1.7 and 10.3 cfs from Guadalupe Reservoir and between 5.2 and 5.6 cfs from Almaden Reservoir with a few short-duration high flow events (lasting a few hours) of up to 167 cfs. There was only one small rain event on May 28th during the sampling period with 0.08 inches of rain at the rain gauges within both reservoir watersheds. There were no transfers from Almaden Reservoir to Calero Reservoir during this period with the possible exception of two brief, hour-long events in mid-July of 16 and 18 cfs, based on the automated gauge readings.

All dry-season data on mercury and related water chemistry in the reservoirs are presented in the Data Collection Report (Tetra Tech, 2005a). Key findings from data on mercury speciation are summarized below. The outlet samples represent a deeper depth in the reservoir than the mid-depth hypolimnion samples.

- **Suspended solids.** The suspended solids concentrations were higher in Guadalupe Reservoir, as shown below:
  - Almaden Reservoir: 0.8 mg/L to 4 mg/L
  - Almaden Reservoir outlet: 1.4 mg/L to 3.5 mg/L
  - Guadalupe Reservoir: 1.9 mg/L to 10 mg/L

– Guadalupe Reservoir outlet: 4.5 mg/L to 11.5 mg/L

- **Total mercury.** Total mercury concentrations were somewhat higher in Guadalupe Reservoir compared to Almaden Reservoir as shown below:

  Almaden Reservoir
  - epilimnion 3.54 ng/L to 4.9 ng/L
  - hypolimnion 4.10 ng/L to 19.8 ng/L
  - outlet 7.25 ng/L to 20.8 ng/L, and

  Guadalupe Reservoir
  - epilimnion 11.0 ng/L to 42.8 ng/L
  - hypolimnion 6.5 ng/L to 39.4 ng/L
  - outlet 14.7 ng/L to 49.2 ng/L.

- **Methylmercury.** Methylmercury concentrations were a significant fraction of the total mercury (sometimes more than 20% of total mercury). Methylmercury concentrations were higher in Guadalupe Reservoir as shown below:

  Almaden Reservoir
  - epilimnion 0.34 ng/L to 0.64 ng/L
  - hypolimnion 0.43 ng/L to 5.49 ng/L
  - outlet 2.91ng/L to 7.20 ng/L, and

  Guadalupe Reservoir
  - epilimnion 0.20 ng/L to 0.57 ng/L
  - hypolimnion 0.41 ng/L to 11.5 ng/L
  - outlet 0.85 ng/L to 12.8 ng/L.

- **Mercury in Particulate Fraction.** The total mercury in the particulate fraction from the Almaden Reservoir outlet varied from 1.98 mg/kg to 6.63 mg/kg, compared to 1.60 mg/kg to 3.85 mg/kg from the Guadalupe Reservoir outlet.

Both reservoirs were stratified with respect to temperature and dissolved oxygen beginning in May, as seen in Figure 3-18. Almaden Reservoir stratified sooner than Guadalupe. The dissolved oxygen decreased with depth in the hypolimnion and was less than 1 mg/L at a depth of 25 feet in Guadalupe Reservoir by July and at a depth of less than 35 feet in Almaden Reservoir by June 10th. Between mid to late August, the temperature difference decreased with depth as the reservoir started to turn over. There was still a gradient with respect to dissolved oxygen at the end of August. Guadalupe Reservoir was still stratified with respect to temperature and dissolved oxygen at the end of August. An average depth of 25 feet for the epilimnion was used for the loading analysis in Chapter 4 of this report.

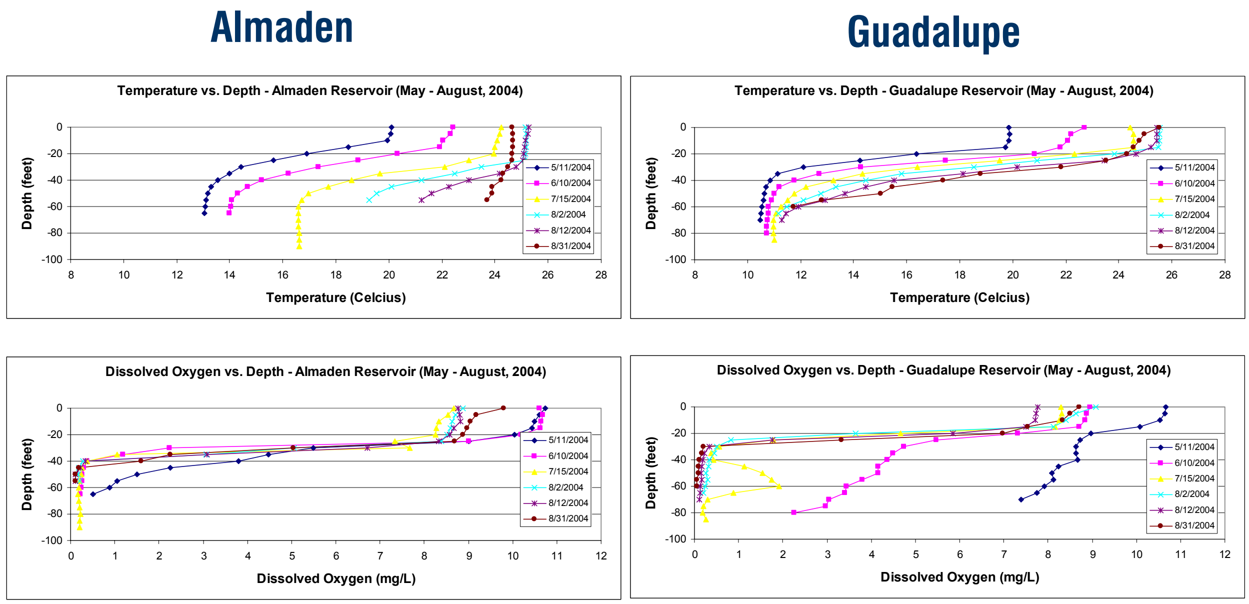
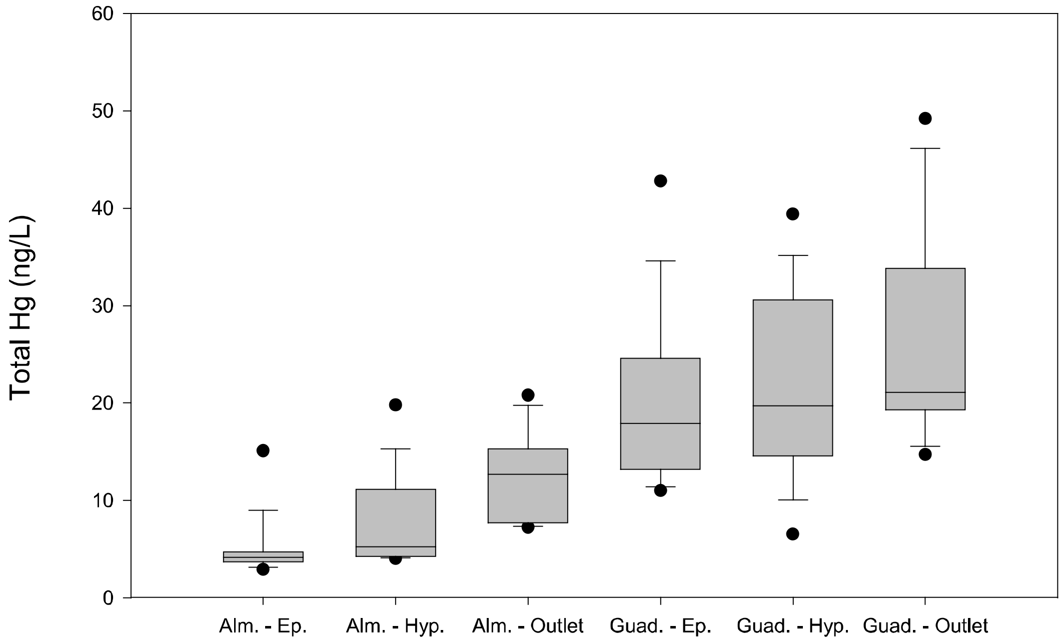


Figure 3-18. Depth Profiles of Temperature and Dissolved Oxygen for Almaden and Guadalupe Reservoirs

3.3.2 Comparison of Mercury Results for Reservoirs

The concentrations of total and methylmercury species and suspended solids in the reservoirs and outlets are compared in Figure 3-19. The mercury and methylmercury concentrations in both reservoirs increased from epilimnion to hypolimnion to the outlets. The highest concentrations of total and dissolved mercury and methylmercury were found in the outlet from Guadalupe Reservoir on August 31, 2004, partly due to the higher suspended solids of 11.5 mg/L. Figure 3-20 shows a clear increase in methylmercury concentrations over the summer in both reservoirs, following the onset of thermal and dissolved oxygen stratification. Methylmercury concentrations were also significantly higher in the late summer than in the wet season when the oxycline is absent or not well-defined in the water column.

Data on total and methylmercury collected during the dry season, 6 times over a fourteen-week period, demonstrated the gradual buildup of methylmercury in Almaden and Guadalupe Reservoirs. Much of the methylmercury generated in the reservoirs was produced in the hypolimnion, which is where the withdrawals for downstream supply take place. The most significant production of methylmercury occurred when the hypolimnion was largely anoxic (dissolved oxygen levels less than 1 mg/l), as expected for microbial transformations by sulfate reducers that require anoxia.



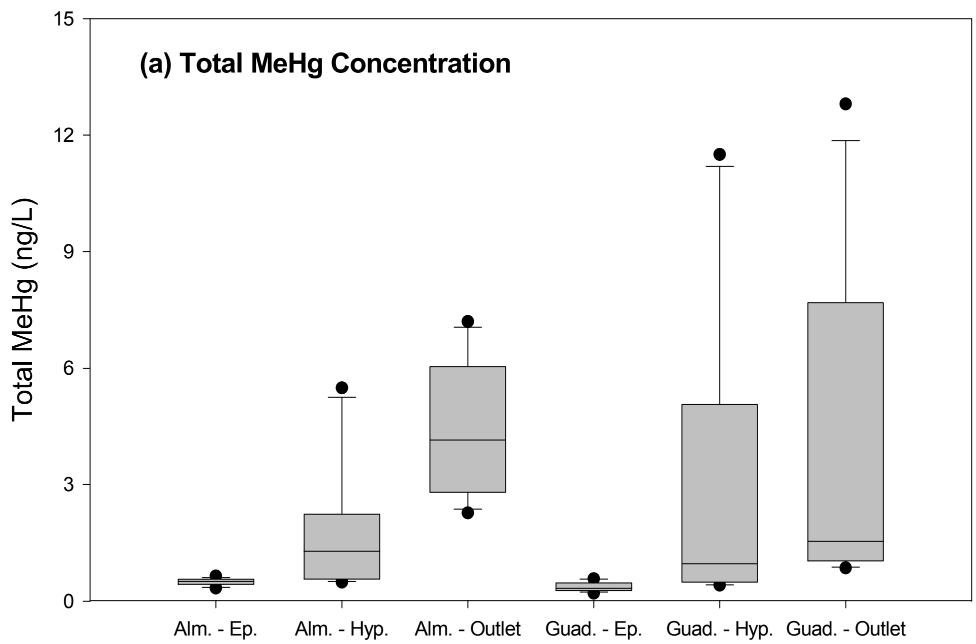


Figure 3-19. Comparison of a) Total Mercury and (b) Total (unfiltered) Methylmercury in Almaden and Guadalupe Reservoirs.

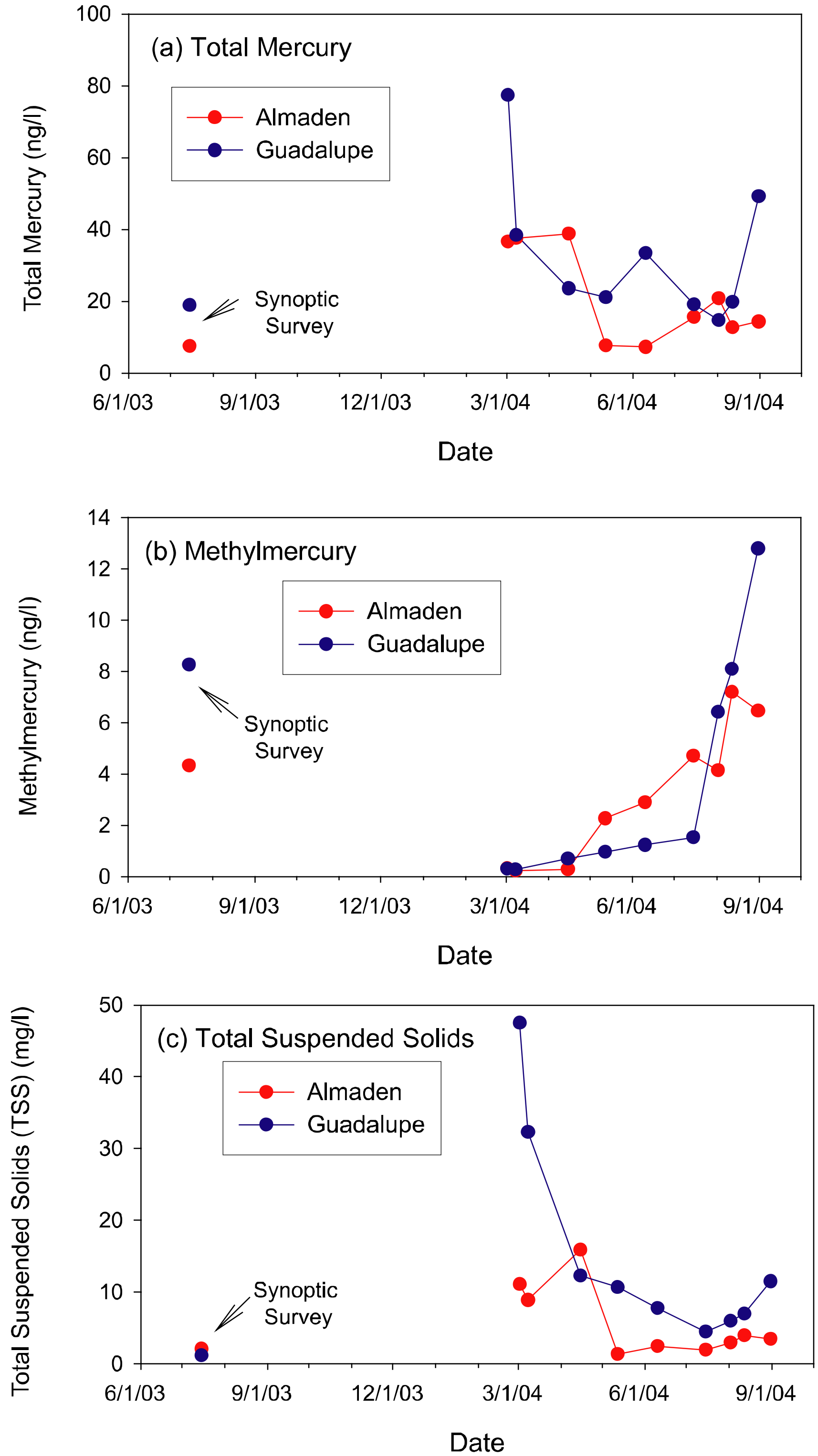


Figure 3-20. (a) Total mercury, (b) methylmercury, and (c) TSS in Almaden and Guadalupe Reservoir Outlets as measured during the Synoptic Survey in 2003 and during the wet and dry season sampling in 2004.

3.4 FISH TISSUE MERCURY DATA

Three sets of fish tissue mercury data exist. The historical fish mercury data consist of 263 measurements in 16 different species of fish collected from multiple locations in the Guadalupe River Watershed. These data were presented in the Guadalupe River Mercury TMDL Workgroup's Recommended Interim Sampling and Monitoring Plan (EOA, 2000). The majority of these data were collected from 1971 – 1987.

Tetra Tech collected largemouth bass (*Micropterus salmoides*) and black crappie (*Pomoxis nigromaculatus*) from Guadalupe Reservoir on May 28, 2003, in conjunction with the U.S. EPA's National Lakes Survey. Tetra Tech collected 15 largemouth bass between 27.3 and 50.5 cm. in total length (TL), and 10 black crappie between 13 and 17 cm. TL. Muscle tissue was collected from each sample for mercury analysis.

A summary of the existing mercury measurements for the most abundant species from these first two data sets is presented in Table 3-5. Because of the differences in size and number of fish at each location, these data are of limited value for making comparisons between locations. However, these data show that the mercury concentrations in fish muscle tissue in the Guadalupe River Watershed exceed the U.S. EPA human health mercury fish criterion (0.3 mg/kg [ppm], U.S. EPA, 2001) at all locations sampled. The historical record shows that mercury concentrations in fish tissue have been very high, and recently collected data, presented below, show that the mercury concentrations remain very high.

Table 3-5
Summary of Fish Mercury Measurements from Guadalupe River Watershed

Location	Sample Size	Avg. Hg (ppm)	Avg. Length (cm)	Avg. Weight (g)
Rainbow Trout				
Alamitos Creek	27	2.9	13.5	108
Guadalupe River	21	1.0	14.4	41.2
Almaden Reservoir	8	0.5	–	–
Guadalupe Reservoir	6	1.3	25	263
Largemouth Bass				
Guadalupe Perc. Pond	21	0.9	14.5	51.2
Guadalupe Reservoir	15	4.0	37.4	700.0
Calero Reservoir	11	2.2	78.6	1179.7
Lexington Reservoir	5	0.7	26.2	436.6
Bluegill				
Guadalupe River, Perc Ponds	19	0.4	–	–
Guadalupe Reservoir	21	2.8	18.6	169.1
Lexington Reservoir	3	0.05	17.3	135.3
Sucker				
Guadalupe Perc. Pond	15	0.6	–	–
Guadalupe River, Highway 17	20	0.4	–	–
Black Crappie				
Calero Reservoir	14	1.3	20.7	164.5
Guadalupe Reservoir	10	1.9	15.5	52.0

In the spring and summer of 2004 an important sampling program was conducted by the USEPA and the Santa Clara Valley Water District to develop new information on the concentration of mercury in fish tissue in the impoundments (Guadalupe Reservoir, Almaden Reservoir, Calero Reservoir, Lexington Reservoir, and Lake Almaden) and creeks throughout the watershed. Adult and age-1 largemouth bass were collected in five impoundments within the watershed. Santa Clara Valley Water District biologists collected samples of the California roach (*Lavinia symmetricus*) at six creek and river locations in the watershed (SCVWD, 2004). These data were collected specifically to establish a baseline to compare changes in fish mercury concentrations over time and in response to mercury source reductions in the water column. A detailed description of the 2004 sampling effort and results is presented in the Data Collection Report (Tetra Tech, 2005a). A summary of these data is presented below, and use of these data in the TMDL is discussed in Section 5.6 of this report.

3.4.1 2004 Adult Largemouth Bass Samples

Total mercury concentrations were measured in muscle tissue samples from adult largemouth bass collected at five impoundments (four reservoirs and Lake Almaden) in the watershed. The results are summarized in Table 3-6. The target sample size was 20 fish from each impoundment, and although fewer samples were collected at Guadalupe (n = 18) and Lexington (n=11) Reservoirs, these large numbers of samples at each impoundment provide an excellent summary of mercury concentrations in large predatory fish (Trophic Level 4) in the watershed. Both the average and range of mercury concentrations exhibit large differences between impoundments. There is an order of magnitude difference in the average total mercury concentrations between Guadalupe Reservoir (6.1 mg/kg wet wt.) and Lexington Reservoir (0.6 mg/kg wet wt.). The coefficients of variation (CV) for the mercury measurements at each impoundment (0.16 – 0.40) are relatively low for environmental measurements. These low CV values indicate the narrow distribution of mercury concentrations in the fish as well as the likelihood of detecting statistically significant differences in mercury concentrations between impoundments.

Table 3-6
Summary of Adult Largemouth Bass Mercury Data

		Total Mercury Concentrations (mg/kg wet)				Total Length (cm)			
Waterbody	Sample Size	Average	Min.	Max.	Coefficient of Variation	Average	Min.	Max.	Coefficient of Variation
Guadalupe Reservoir	18	6.1	3.1	13	0.40	41.8	30.7	53.2	0.18
Almaden Reservoir	20	4.3	2.2	7.4	0.30	43.9	33.8	51.2	0.11
Lake Almaden	20	2.3	1.1	3.8	0.34	41.8	31.2	53.2	0.16
Calero Reservoir	20	1.1	0.8	1.6	0.16	36.7	29.7	47.7	0.12
Lexington Reservoir	11	0.6	0.4	1.0	0.27	40.8	35.8	50.2	0.12

Figure 3-21 presents the average and 95% confidence intervals for total mercury concentration in a 40 cm largemouth bass at the five impoundments sampled. Regression equations were used to calculate the expected mercury concentrations corresponding to a specified (standardized) fish length (Bhattacharyya and Johnson, 1977; Tremblay et al, 1998) to account for the difference in the size of fish collected in the five impoundments. The concentration of mercury in 40 cm largemouth bass exhibits a wide range (0.6 – 5.8 mg/kg) in the waterbodies sampled, and the measured concentrations appear to correlate well with the proximity to the mining district. Because the average total lengths for the adult largemouth bass samples at the five impoundments were similar; the differences between the total mercury concentrations in the fish samples were tested using ANOVA and the SNK multiple comparison tests (Tremblay et al, 1998). The results of these tests indicate the existence of statistically significant differences in the mercury concentrations in adult largemouth bass between all pairs of impoundments, except Calero and Lexington Reservoirs.

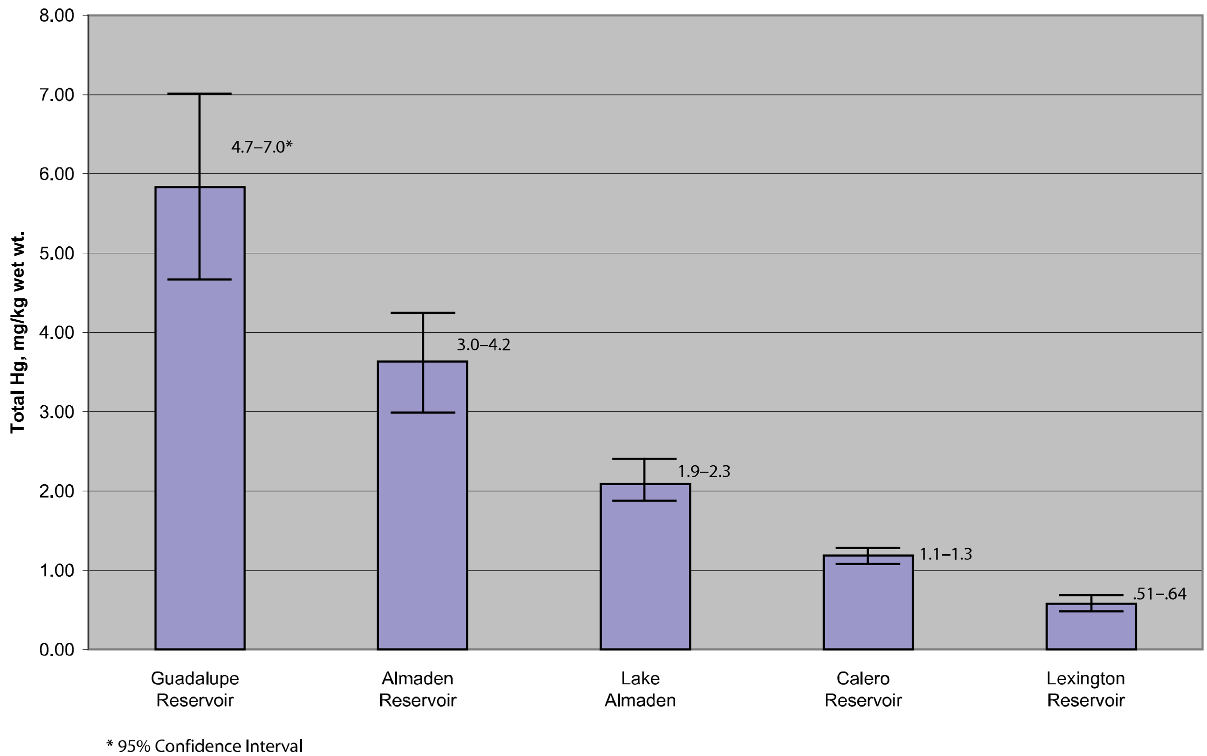


Figure 3-21. Mercury concentrations for standardized 40 cm largemouth bass.

3.4.2 2004 Age-1 Largemouth Bass Samples

Total mercury concentrations were measured in whole-body samples of age-1 largemouth bass collected at the same five impoundments in the Guadalupe Watershed. The results are summarized in Table 3-7. Twenty fish of similar size were obtained from each impoundment, and the variability of the measurements, as indicated by the low coefficients of variation, was low within each impoundment. While the variability of the mercury measurements was low within impoundments, large differences were observed in the fish mercury concentrations between the impoundments. The total mercury concentrations measured ranged from 0.06 mg/kg wet wt at Lexington Reservoir to 1.53 mg/kg wet wt at Almaden Reservoir. All forty samples from Almaden and Guadalupe Reservoirs had mercury tissue concentrations that exceed the U.S. EPA water quality criterion of 0.3 ppm (mg/kg wet wt.). Figure 3-22 presents the average and 95% confidence intervals for total mercury concentrations in an 8 cm largemouth bass at the five impoundments sampled.

Table 3-7.
Summary Of Age-1 Largemouth Bass Mercury Data

		Total Mercury Concentrations (mg/kg wet)				Total Length (cm)			
Waterbody	Sample Size	Average	Min.	Max.	Coefficient of Variation	Average	Min.	Max.	Coefficient of Variation
Guadalupe Reservoir	20	0.83	0.64	1.11	0.17	9.0	7.7	9.7	0.07
Almaden Reservoir	20	0.96	0.58	1.53	0.29	6.9	5.6	8.2	0.10
Lake Almaden	20	0.39	0.21	0.53	0.22	9.3	8.0	10.2	0.08
Calero Reservoir	20	0.21	0.10	0.58	0.53	7.4	5.5	10.2	0.22
Lexington Reservoir	20	0.09	0.06	0.14	0.22	8.9	7.1	10.2	0.10

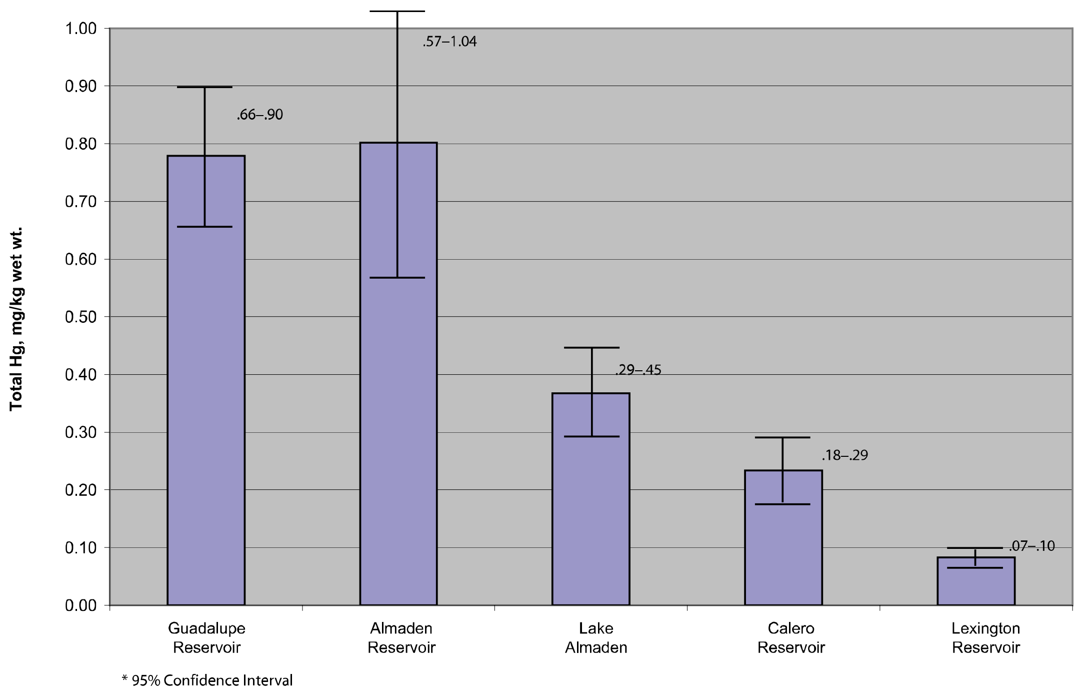


Figure 3-22. Mercury concentrations for standardized 8 cm largemouth bass.

3.4.3 2004 California Roach Samples

Santa Clara Valley Water District biologists collected samples of the California roach (*Lavinia symmetricus*) from six locations in creeks and the Guadalupe River (SCVWD, 2004). Nine locations, representing a wide range of expected aqueous mercury concentrations, were initially selected for sampling (Figure 3-23), but only a few or no roach were present at some of the sampling locations. Whole fish samples, with the gastrointestinal tract removed to prevent contamination with mercury from ingested sediment, were collected to quantify the mercury concentrations in fish species that represent potential prey items to wildlife species.

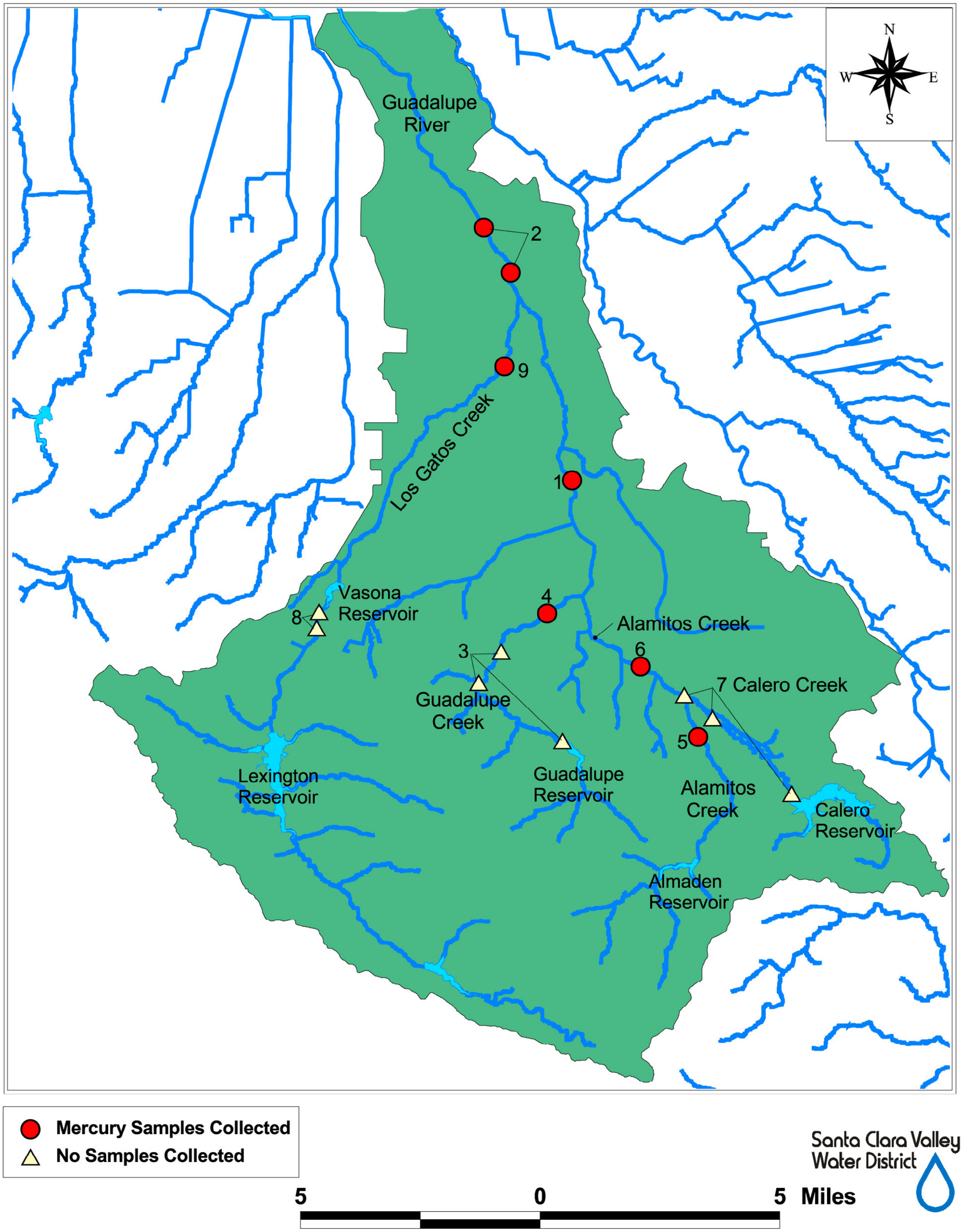


Figure 3-23. Stream sampling sites in the Guadalupe Watershed (SCVWD, 2004).

The results of the California roach sampling effort and the mercury analyses are presented in Table 3-8. All samples were similar in size, between 40 to 55 mm fork length, and based on the examination of scales, age-1 or younger (SCVWD, 2004). The measured mercury concentrations ranged from an average value of 0.03 mg/kg wet wt in Los Gatos Creek (Site 9, Figure 3-23) to an average value of 0.39 mg/kg wet wt on Guadalupe Creek (Site 4, Figure 3-23). Los Gatos Creek is fed by Lexington Reservoir, and the Los Gatos Creek site was selected as a reference to compare non-mining-influenced fish-tissue samples to mining-influenced fish-tissue samples. The Guadalupe Creek sampling site at Meridian Avenue was selected because of its proximity to the mining district and the fact that it is fed by Guadalupe Reservoir. At the Guadalupe Creek sampling site at Meridian Avenue, the mercury concentrations in the tissue of all 20 California roach were greater than the U.S. EPA water quality criterion of 0.3 mg/kg wt wet.

Table 3-8.
Summary of California Roach Mercury Data

			Total Mercury Concentrations (mg/kg wet)			
Site Number	**Waterbody and Location**	**Sample Size**	**Average**	**Min.**	**Max.**	**Coefficient of Variation**
1	Guadalupe R., at Foxworthy Ave.	9	0.15	0.12	0.19	0.17
2	Guadalupe R., at Coleman Ave.	25	0.08	0.04	0.12	0.32
4	Guadalupe Creek, at Meridian Ave.	20	0.39	0.31	0.48	0.11
5	Alamitos Creek, at Harry Road	20	0.28	0.20	0.41	0.21
6	Alamitos Creek, at Greystone Lane	20	0.15	0.10	0.26	0.26
9	Los Gatos Creek, at Lincoln Ave.	20	0.03	0.02	0.04	0.24

ANOVA and SNK multiple range tests were used to examine the statistical significance of observed differences in the average mercury concentrations of these whole-body fish samples between locations (Tremblay et al, 1998). The average mercury concentrations at the Guadalupe River at Foxworthy Avenue and Alamitos Creek at Greystone Avenue (Sites 1 and 6, Figure 3-23) were equal (0.15 mg/kg wet wt), but the differences between the measured mercury concentrations at the other four sites were each significantly different from one another. The range of values at each sampling location and the magnitude of the differences between these locations is shown in the box plots in Figure 3-24. These plots show the 10th, 25th, 50th (median), 75th and 90th percentiles of the fish mercury concentrations. Values above the 90th and below the 10th percentile are plotted as points.

These results clearly demonstrate the ability to quantify the mercury concentrations in fish that are potential prey items to wildlife in the watershed. California roach are omnivores and filamentous algae is the primary staple in their diet, but they can also feed on small insects and crustaceans (Moyle 2002). The California roach are intermediate between Trophic Level 2 (TL2) or TL3 species. The low variability in the mercury concentrations measured at each location, indicated by the small values of the coefficients of variation, suggest that the California roach, like the age-1 largemouth bass, will also make a good biosentinels to detect changes in response to interventions that reduce methylmercury concentrations in the aquatic food web.

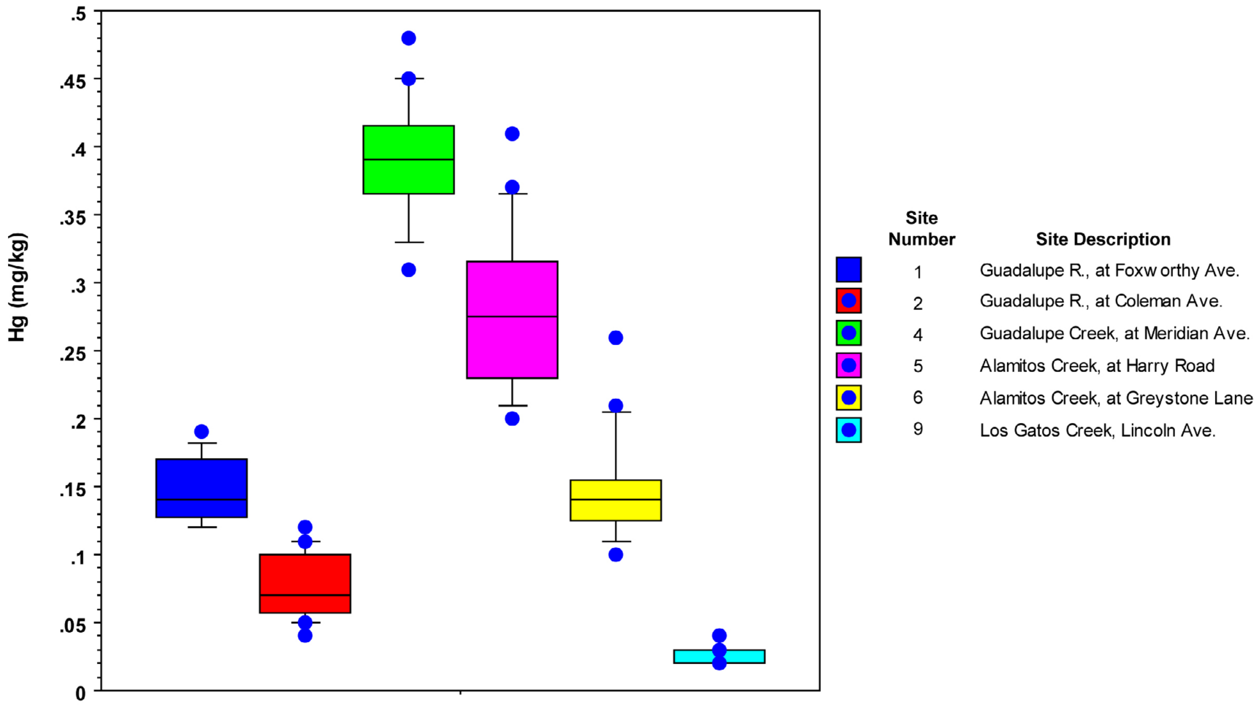


Figure 3-24. Mercury concentration in California roach collected at six sites in the Guadalupe River Watershed. (see Figure 3-23 for location of sampling sites)

3.4.4 Summary of Bioaccumulation Data

A summary of the 2004 fish sampling results is shown on a schematic diagram of the Guadalupe River Watershed in Figure 3-25. The range of measured concentrations of mercury in the fish tissue is shown for each sampling location. The shading of the fish symbols indicates the relative magnitude of the concentrations measured. For example, the maximum concentrations of mercury in adult largemouth bass were measured at Guadalupe Reservoir, where the range of values was 3.1 to 13.0 mg/kg wet wt. The lowest mercury concentrations in both the adult and age-1 largemouth bass were measured at Lexington Reservoir, where the ranges of mercury values were 0.4 – 1.0 mg/kg wet wt for adults and 0.06 – 0.14 mg/kg wet wt for age-1 fish. The stream sampling sites, where the California roach tissue samples were collected, are also shown on the watershed schematic. The highest concentrations in the whole-body California roach samples were measured at Guadalupe Creek sampling site (Site 4), where the range of mercury concentrations was 0.31 – 0.48 mg/kg wet wt. The lowest concentrations in the California roach were measured on Los Gatos Creek (Site 9), where the ranges of values was 0.02 to 0.04 mg/kg wet wt.

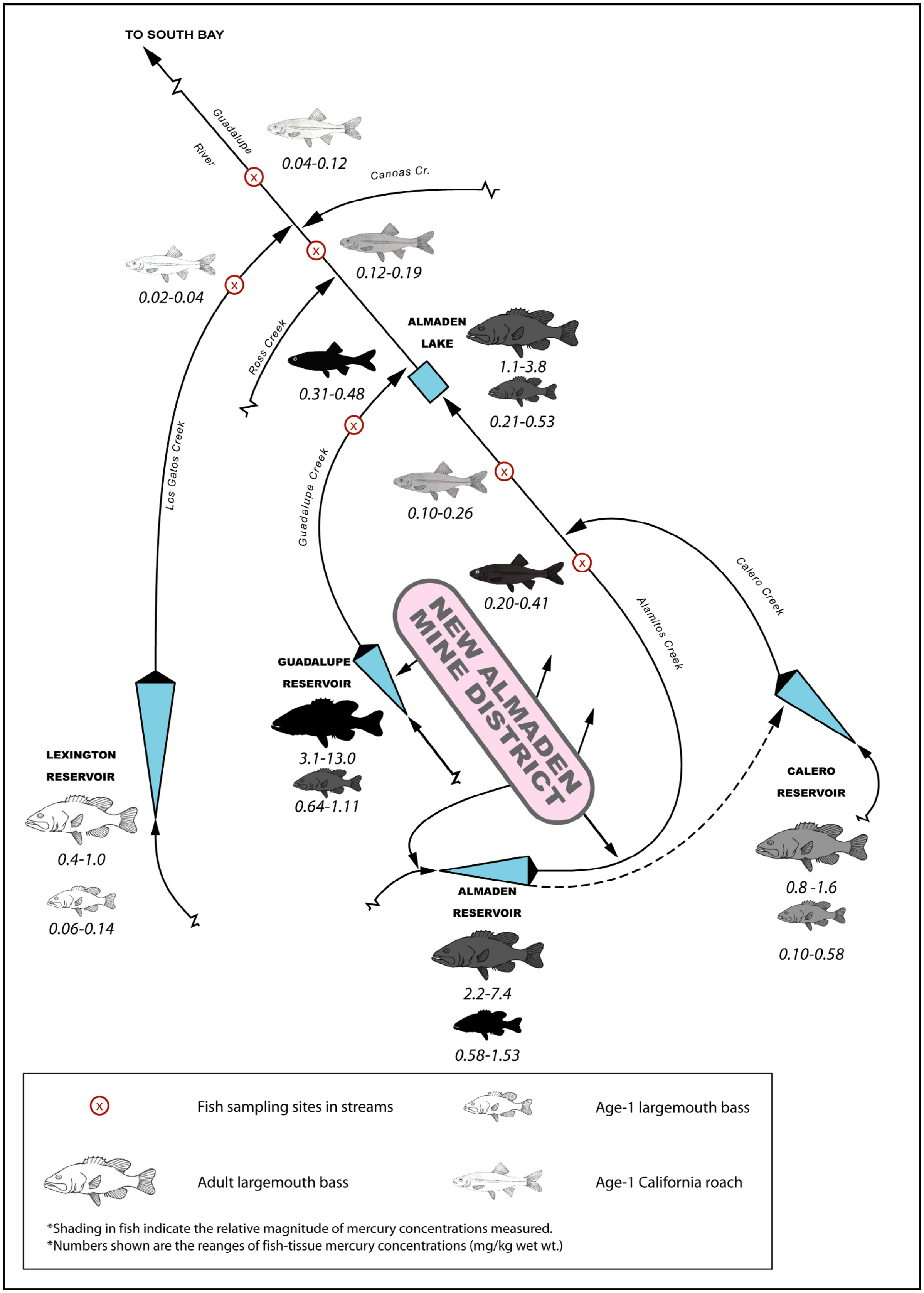


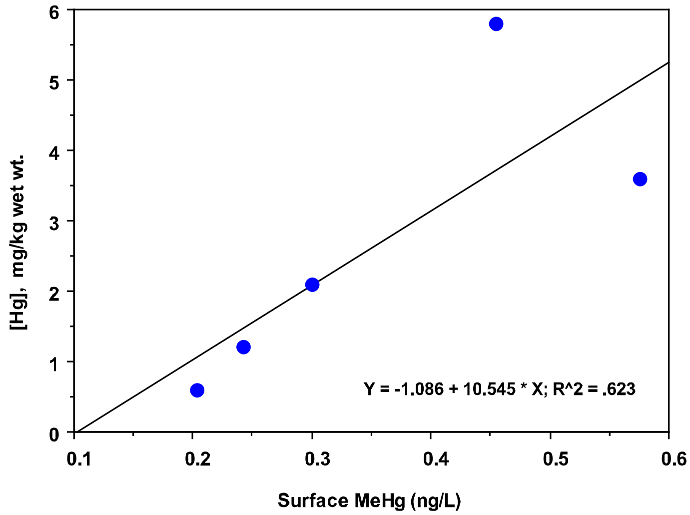
Figure 3-25. Summary of 2004 fish sampling results.

The differences in the fish tissue mercury concentrations exhibited in Figure 3-25 were examined further to determine if a linkage could be established between fish tissue concentrations and aqueous mercury concentrations. Table 3-9 presents measurements of total mercury concentrations in adult largemouth bass at the five locations sampled and unfiltered aqueous methylmercury concentrations in the surface and hypolimnion of the impoundments. The fish tissue concentrations are the average total mercury measurements for a 40 cm adult largemouth bass. The water concentrations in Table 3-9 are averages of measurements at Almaden and Guadalupe Reservoirs on one date in July 2003 and six dates between May 11 and August 31, 2004. These measurements were taken at both the surface and at the reservoir outlet (referred to in the table as the hypolimnetic samples since water is released from the bottom of the reservoirs below the thermocline). The July 2003 samples were collected for the Synoptic Survey (Tetra Tech, 2003d), while 2004 samples were collected during the 2004 dry season sampling conducted as part of the Data Collection Program (Tetra Tech, 2005a). The mercury concentrations at Almaden and Guadalupe Reservoirs are well characterized. A single value is used for the surface-water methylmercury concentration at Lake Almaden. This value is the average of two samples collected at the outlet in April 2004 as part of the Wet Weather Sampling under Part 1 of the Data Collection Plan (Tetra Tech, 2005a). There is no measurement for the hypolimnion at Lake Almaden. The surface-water and hypolimnion values for Calero and Lexington Reservoirs are from samples collected on one date in July 2003.

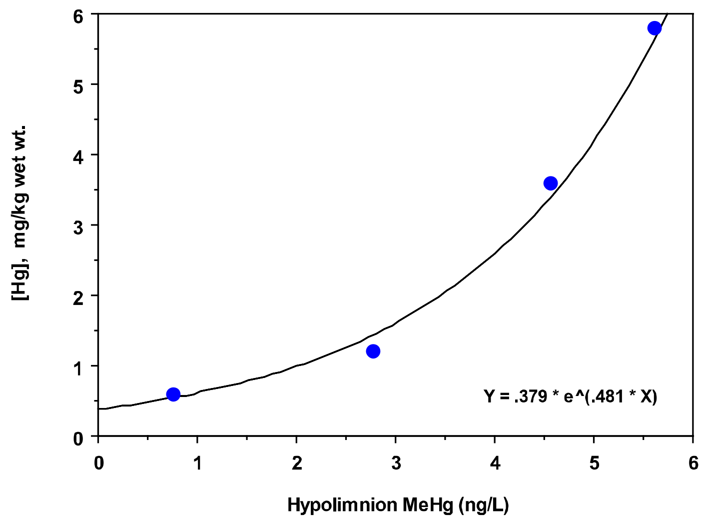
Table 3-9.
Paired Mercury Measurements In Adult Largemouth Bass And Impoundment Water Samples.

Waterbody	Average Fish Tissue Total Hg *mg/kg wet*	MeHg, ng/l unfiltered		Log(BAF, L kg-1)	
		Surface	Hypolimnion	Surface	Hypolimnion
Guadalupe Reservoir	5.80	0.46	5.61	7.1	6.0
Almaden Reservoir	3.60	0.58	4.57	6.8	5.9
Lake Almaden	2.10	0.30	-	6.8	-
Calero Reservoir	1.20	0.24	2.77	6.7	5.6
Lexington Reservoir	0.60	0.20	0.76	6.5	5.9

The relationship between the mercury concentration in the adult largemouth bass and the water samples is shown in Figure 3-26. Fish mercury concentrations are positively correlated with the methylmercury concentrations measured in both the surface water and the hypolimnion. The exponential relationship between the methylmercury concentration in the hypolimnion and the mercury concentration in the adult largemouth bass may be related to the fact that the average methylmercury concentrations in Guadalupe and Almaden Reservoirs used in the regression analysis underestimate methylmercury production in the systems. The average values were calculated using measurements collected throughout the period of reservoir stratification, but methymercury production rates increase with time (and oxygen depletion) during the summer stratification period. Conversely, mercury methylation may not increase significantly or as rapidly during the summer stratification period in an uncontaminated waterbody like Lexington Reservoir.



(A)



(B)

Figure 3-26. Relationship between mercury concentrations in adult largemouth bass and methylmercury concentrations in surface (A) and hypolimnetic (B) waters samples.

The log transformed values of the bioaccumulation factors (BAFs) are also shown in Table 3-9. The BAF is the ratio of the tissue concentration to the water column concentration of mercury in units of L kg-1:

$$BAF = CT/CW * 10^6$$

where:

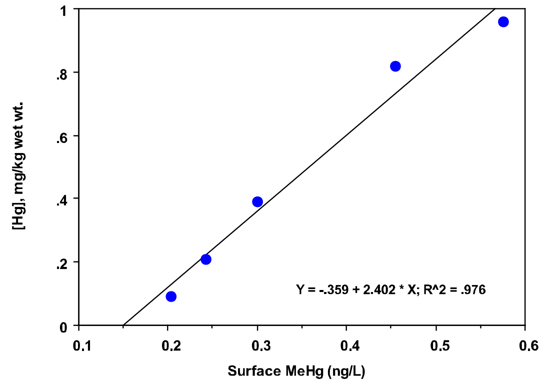
CT = MeHg concentration in the fish tissue, mg/kg
CW= MeHg concentration in the water, ng/L

These log-transformed values correspond and are within the expected range of bioaccumulation factors for large piscivorous fish.

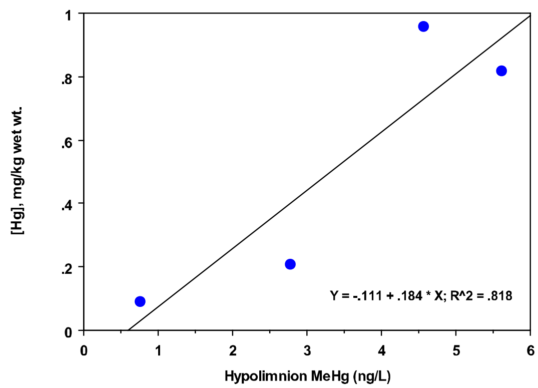
Table 3-10 presents paired measurements of total mercury in the age-1 largemouth bass (Trophic Level 2) and unfiltered methylmercury in the surface and hypolimnion of the impoundments in the Guadalupe Watershed. The fish tissue concentrations are the values calculated for an 8 cm age-1 largemouth bass. The water concentrations in Table 3-10 are the same concentrations that were presented in Table 3-9. As shown in Figure 3-27, the paired concentrations are positively correlated. The fit of the data is expecially good for the relationship between the surface-water methylmuercury concentration and the concentration of mercury in the age-1 largemouth bass ($r^2 = 0.98$).

Table 3-10.
Paired Mercury Measurements In Age-1 Largemouth Bass And Impoundment Water Samples.

		MeHg, ng/l unfiltered		Log(BAF, L kg-1)	
Waterbody	**Average Fish Tissue Total Hg *mg/kg wet***	**Surface**	**Hypolimnion**	**Surface**	**Hypolimnion**
Guadalupe Reservoir	0.82	0.46	5.61	6.3	5.2
Almaden Reservoir	0.96	0.58	4.57	6.2	5.3
Lake Almaden	0.39	0.30	-	6.1	-
Calero Reservoir	0.21	0.24	2.77	5.9	4.9
Lexington Reservoir	0.09	0.20	0.76	5.6	5.1



(A)



(B)

Figure 3-27. Relationship between mercury concentrations in average age-1 largemouth bass and methylmercury concentrations in surface (A) and hypolimnetic (B) waters samples.

A summary of mercury concentrations measured in California roach (Trophic Level 2-3) and surface water at the six locations sampled by the SCVWD in 2004 is presented in Table 3-11. The fish tissue concentrations are the average total mercury concentrations. The water samples were collected at five sites near the fish sampling locations in July 2003 as part of the Synoptic Survey (Tetra Tech, 2003d). Most water samples were collected at or close to the fish sampling locations. The calculated BAF values are consistent with observations in other systems where methylmercury is taken-up rapidly in the water column by algae and transferred by ingestion to zooplankton and planktivorous fish. The concentration of methylmercury in the California roach is approximately 300,000 to 600,000 times the methylmercury levels in the water column. A strong positive relationship is exhibited between the unfiltered methylmercury concentrations in the streams and Guadalupe River and the measurements of mercury in the fish tissue (Figure 3-28).

Table 3-11.
Summary of Stream Sampling Mercury Data

Site	Waterbody	Fish Total Hg mg/kg wet	Total Hg, ng/l unfiltered	Me Hg, ng/l unfiltered	Log(BAF) (L kg^{-1})
1	Guadalupe R., Foxworthy	0.15	105	0.323	5.66
2	Guadalupe R., Coleman Ave.	0.08	-	-	-
4	Guadalupe Crk, Meridian Ave.	0.39	38.9	0.990	5.60
5	Alamitos Crk, Harry Road	0.28	503.2	0.886	5.50
6	Alamitos Crk, Greystone	0.15	25.88	0.306	5.68
9	Los Gatos Crk, Lincoln	0.03	3.2	0.037	5.83

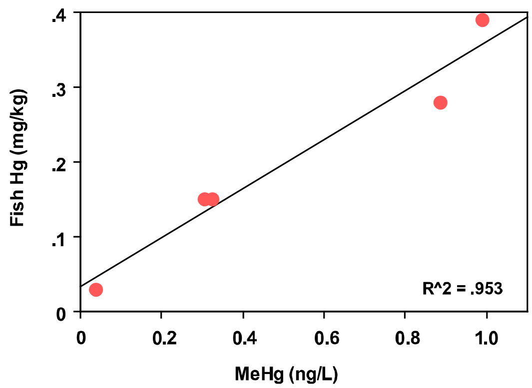


Figure 3-28. Relationship between mercury concentrations in California roach and unfiltered methylmercury concentrations in water samples.

The fish sampling program conducted in 2004 builds on the historical data and combines the results from several field and laboratory efforts where different species, size ranges, and locations were sampled. The results of the fish sampling and measurements of mercury in tissue samples provides valuable new information to support the use of fish tissue as a numeric target for the TMDL. Fish tissue mercury concentrations have been shown to be elevated within the watershed, and the reported concentrations represent a potential risk to human consumption and wildlife predators. A baseline for fish mercury concentrations in the watershed has been established. Age-1 largemouth bass and California roach have been shown to be sensitive biosentinels that can be used to monitor recovery in the streams and impoundments of the watershed. This information is combined with other mercury measurements in the watershed in Section 5.6 to assess the feasibility of developing an aqueous methylmercury target in addition to a fish-tissue target for this TMDL.

4.0 ESTIMATED MERCURY LOADS

4.1 DESCRIPTION OF HOW EACH SOURCE IS ASSESSED

The watershed includes six groups of waterbodies with distinct mercury loading characteristics:

- Creeks in New Almaden Mining District (NAMD)
- Upper watershed creeks (outside of NAMD)
- Impoundments
- Creeks below impoundments affected by mercury mining activities
- Urban Creeks
- Guadalupe River

The characteristics of these waterbody groups are discussed in terms of the magnitude of the mercury sources, the importance of these sources to the overall effects on the watershed, and the physical factors that affect either the magnitude of the mercury source or the bioavailability of the mercury. An emphasis is placed on identifying the uncertainties that exist in the load calculations. Data needs that can be incorporated into future adaptive management plans are also identified.

Major non-point sources of total mercury in the waterbodies of the Guadalupe River Watershed include natural background loads (of which atmospheric deposition is a major part), erosion of historic mine wastes, urban runoff, and erosion within stream banks. Methylmercury sources, particularly for this watershed, differ from total mercury sources in that significant production usually occurs within waterbodies during the warm summer months, and the most important sources are primarily internal. In addition to the non-point sources to creeks, reservoirs have distinctive characteristics and thus were considered separately for source assessment.

In general, mine-derived mercury loads are the most distinctive feature of the Guadalupe River watershed, although other sources, such as urban runoff, and background loads, including atmospheric deposition, are also present. Historic mines exist in the upper watershed and are a source of mercury to Almaden and Guadalupe

Reservoirs and also to the creeks below them. Downstream of the four major reservoirs, urban runoff loads are more significant in the creeks as well as in the river. Besides these loads, the other known source of mercury includes atmospheric deposition and water transfers to Calero Reservoir from the Central Valley. Load diagrams presented later in this chapter illustrate the sources and flow of mercury through the watershed. Mercury loads are related to impairment within the Guadalupe River and also to impairment in San Francisco Bay where the river discharges.

Loads were assessed separately for the wet and dry season based on the knowledge that most mercury transport occurs during the wet season, and most methylmercury production occurs in the warm, dry season. A large part of the wet season data collection for the mercury TMDL was focused on measurements of flow and mercury speciation at different locations and different times in the watershed. The data analysis approach used was to infer the loads from non-point sources indirectly from the measured concentrations and flows in the streams of the watershed. Using representative sub-watersheds that were affected principally by one type of mercury source, we estimated the areal contribution of background, historic mines, and urban areas. These loads were expressed in units of $\mu g/m^2$ over the wet season. This source analysis was limited to the wet season. For the dry season, the sampling was focused on the measurements of mercury species at different depths in the two reservoirs most affected by mining (Almaden and Guadalupe) and these data were used to infer methylmercury production. In this section, we explain the approach used to determine the contribution of each of these sources to the loads flowing through the watershed.

For the purpose of this discussion, all loads are estimated as net loads, which includes the potential effects of losses that may occur. Thus, within streams, sediment erosion is a source of mercury, and settling is a loss. However, when we speak of loads, we imply net loads (sources minus losses) at the point of interest.

4.1.1 BACKGROUND LOAD

Soda Spring in the watershed of Lexington Reservoir was used to estimate the background load. The watershed for this creek has practically no development and no mercury mines. Wet weather daily flows were estimated using the SWAT hydrologic model, using the topography, precipitation, and vegetation specific to this watershed. Using the flow estimates, total suspended solids, total mercury, methylmercury, and dissolved mercury concentrations in flowing water were estimated from regressions for the non-mining creeks in the upper watershed (see Figure 6-1 of the Final Data Collection Report, Tetra Tech, 2005a, which shows the curve for creeks upstream of the reservoirs). The load calculation approach, and the data used are discussed more fully in Section 6 of Tetra Tech (2005a). Loads were estimated from the flows and concentrations, and were found to be 1.16 $\mu g/m^2/yr$ for total mercury, 0.33 $\mu g/m^2/yr$ for dissolved mercury, and 0.012 $\mu g/m^2/yr$ for methylmercury over the wet season. This background load consists of wet and dry deposition, transport of past dry deposition, and loads from the erosion of natural geologic materials of the area. Given the data, however, it is not possible to decompose the total background loads into these specific constituents. However, the loads may be compared with total mercury atmospheric deposition estimates. The atmospheric deposition input was estimated as a daily load using wet and dry deposition data collected by SFEI at various locations around San Francisco Bay. Wet deposition was estimated using a rainfall concentration of 9.7 ng/l (SFEI, 2001) and a rainfall amount of 48 inches in the watersheds tributary to the reservoirs, and a rainfall amount of 14 inches for the rest of the watershed. Annual wet deposition was estimated as 11.6 $\mu g/m^2/yr$ in the upper watershed and 3.4 $\mu g/m^2/yr$ in the lower watershed. The annual dry deposition was estimated as 19 $\mu g/m^2/yr$ (SFEI, 2001) throughout the system. Thus, the total deposition is approximately 30 $\mu g/m^2/yr$ and about 3% is exported from land into waterbodies. This is generally consistent with a recent review that reports total export fractions in stream runoff of approximately 5%, with the remainder being sequestered in the watershed or volatilized (Grigal, 2002).

The rainfall received in the vicinity of Lexington reservoir was 30 inches over October 2003 to May 2004. When these background loading rates were applied to other parts of the Guadalupe Watershed, which had more or less rain, they were scaled proportionally to the amount of rainfall. This is because the transport of these background loads occurs via runoff, which is expected to be roughly proportional to rainfall.

4.1.2 Loads from Historic Mines

North Los Capitancillos Creek was used to estimate the load from historic mining areas. This creek was selected for the historic mine load estimate because, unlike other creeks upstream of Almaden and Guadalupe Reservoirs, the watershed for this creek is almost entirely within Almaden Quicksilver County Park, the area with significant historic mining activity.

Wet weather daily flows were estimated from the hydrologic model described in the Final Data Collection Report (Tetra Tech, 2005a). Using the flow estimates, TSS concentrations were estimated in the watershed. Total mercury concentrations were calculated by multiplying the TSS load by the particulate mercury concentration (average of 17.5 mg/kg for all mine sites), and methylmercury and dissolved mercury concentrations were estimated from regressions for the mining creeks in the upper watershed. Loads were estimated from the flows and concentrations, and were found to be 54.5 $\mu g/m^2$ for total mercury, 14.8 $\mu g/m^2$ for dissolved mercury, 0.11 $\mu g/m^2$ for methylmercury over the wet season. These loads are more than 40 times greater than the background for total and dissolved mercury, and about 10 times greater than background for methylmercury. It should be pointed out, however, that concentrations observed at the North Los Capitancillos Creek station were not the highest among those observed for all the mining creeks. It is indicative of an average value for all the mine areas, although it is possible that the mine loading rates are significantly higher from certain locations within the Almaden Quicksilver County Park.

An important source of error and uncertainty in the calculated loads are the limited range of the TSS values that were encountered during wet weather sampling in 2004 (see Figure 6-1 of the Final Data Collection Report, Tetra Tech, 2005a, which shows the curve for creeks upstream of reservoirs). The highest TSS values encountered in this calculation, including modeled flows in the 2003-2004 wet season, are not much higher than 10 mg/l, largely driven by the flow-TSS relationship shown in the figure cited above. In particular, the slope of the flow-TSS relationship is relatively flat because of the absence of TSS data corresponding to higher flows. These values may be too low for representing the entire wet season because a set of data analyzed by the Park staff indicate TSS levels more than two orders of magnitude larger. However, the Park data indicate lower mercury concentrations on particulates. If, on the other hand, the particulate Hg concentrations are as high as 17.5 mg/kg as used in this calculation, and the peak TSS values are 10 to 100 times greater than what we observed, the calculated loads may be much higher. At this time, because of the absence of flow data associated with the Park mercury and TSS measurements, detailed load calculations cannot be performed using these concentration data. However, the low TSS values in our data set are known to be a major source of uncertainty and must be quantified in future work. An example of the significance of large winter storm loads is provided in Section 4.9.

Of particular significance to the mercury TMDL, although the *relative* loads from different sources and water bodies are well-represented in these calculations, the absolute magnitudes of these loads may have been underestimated because of the absence of large rain storms during the our sampling. Thus, sampling in wetter years or during large storm events may result in greater transported loads than those reported in the sections below.

4.1.3 Urban Loads

The watershed for Ross Creek was used to estimate the load from urban areas. The watershed for this creek is almost entirely urbanized with no mining activity. Wet weather daily flows were obtained from the flow gauge near the downstream end of the creek. Using the flow data, total suspended solids, total mercury, methylmercury, and dissolved mercury concentrations in flowing water were estimated from regressions for urban creeks (see Figure 6-1 of the Final Data Collection Report, Tetra Tech, 2005a, which shows the curve for urban creeks). The load calculation approach, and the data used are discussed more fully in Section 6 of Tetra Tech (2005). Loads were estimated from the flows and concentrations, and were found to be 1.6 $\mu g/m^2$ for total mercury, 0.61 $\mu g/m^2$ for dissolved mercury, and 0.02 $\mu g/m^2$ for methylmercury over the wet season. The rainfall in the vicinity of the Ross Creek Watershed was 12.9 inches in 2003-2004. The loads are considerably higher than the background loads, especially when those loads are scaled to the lower rainfall in this watershed. These loads are also roughly an order of magnitude lower than the historic mine loads.

4.1.4 Loads to Reservoirs

Based on the watershed area for each reservoir, and the fraction of the area that was comprised of either undeveloped land or historic mines, loads were added according to the values discussed above. An exception was made for Calero Reservoir, which in addition to watershed loads, also receives occasional flows from Almaden Reservoir and from the Central Valley Project. Wet weather flows from Almaden Reservoir were estimated to average 7.5 cfs during the wet season, based on SCVWD data for 2001 and 2002. This average flow was multiplied by the average concentration measured at the outlet of the Almaden-Calero Canal to obtain an estimate of the load from Almaden Reservoir. For Calero Reservoir, which receives inflows from the Central Valley Project and Almaden Reservoirs, the inflow volumes were based on data provided by the District. The Central Valley flow was assumed to be 3,700 acre-feet (average of 2001 and 2002 values) and was applied only during the summer months. The mercury concentration in this source was assumed to be 1 ng/l.

4.1.5 Reservoir Loads to Downstream Creeks

Because reservoirs contain a substantial amount of storage, and because their outflows are controlled, it is thought that mercury concentrations in their outlets are less variable than in creeks, especially during the wet season. For this reason, the reservoir loads were computed in a manner simpler than that applied to streams: outflows were multiplied by the average mercury concentrations obtained in the wet weather sampling.

4.1.6 Dry Season Methylmercury Production and Export from Reservoirs

The primary data source for these calculations was the monthly to biweekly sampling of Almaden and Guadalupe Reservoirs conducted between May and August of 2004. Load calculations for mercury considered the measured mercury concentrations and the reservoir stored-water volumes, both of which changed over time. Besides the mercury concentration data, other data required for the load calculations are the volumes of water stored in the reservoir in the hypolimnion and the epilimnion, and the outflows from the reservoirs. The depth to the hypolimnion was estimated from the temperature and DO profiles that were taken during the mercury sampling. The calculation of the hypolimnion and epilimnion volume was based on detailed bathymetric maps of the reservoirs. The reservoir stored water volumes were obtained from automated gauges that are associated with SCVWD's online ALERT system (http://alert.valleywater.org). The concentrations over the sampling period were multiplied by the volume of the hypolimnion or the epilimnion to determine the mass of total or methylmercury in either compartment. Because concentration data were obtained less frequently than depth data, concentrations at dates without measurements were estimated by interpolation from the two nearest values with measurements.

The loads of mercury exported to Guadalupe Creek and Alamitos Creek were calculated as the product of mercury concentrations in the reservoir outflows, and the flow rate data routinely collected by SCVWD and reported on the ALERT system. Daily average flow data were used (computed from 24-hourly values). Actual measured total and methylmercury concentration data were used when available; for dates without mercury data, values were interpolated from the nearest two dates of sampling.

4.2 APPROACH TO ESTIMATING LOADS AND UNCERTAINTIES

Using gauged flow data over the entire 2003-2004 wet season, and relationships between flow and concentrations of total suspended solids, total mercury, and methylmercury, loads were computed across the entire watershed. When the inflows originated on land, they were estimated from land-based loading rates described above, and using GIS-based information on the distribution of land uses within the appropriate sub-watershed. Reservoir loads were estimated separately from creek loads as described above. The outflow loads from the creeks were calculated based on the flow (either modeled or gauged), and using the relevant correlations for TSS, total mercury, dissolved mercury, and methylmercury. Loads were identified separately for total and dissolved mercury, and for methylmercury.

In the discussion that follows, we first address the issue of uncertainty in all load calculations presented, followed by an overview of the estimated loads throughout the watershed. Finally, we discuss the estimated loads for each group of waterbodies in the Guadalupe River Watershed: the creeks draining the watershed upstream of the reservoirs, the major reservoirs/impoundments, the creeks downstream of the impoundments, the urban creeks, and the main stem of the Guadalupe River to San Francisco Bay.

Loads of constituents over defined time periods are obtained as a product of the flow volumes and the concentrations. When both flow and concentrations are highly variable over short durations, as is the case for most creeks in the Guadalupe River Watershed, accurate load estimates are strongly dependent on the availability of temporally detailed data. Although the mercury sampling for the TMDL consisted of a large effort to obtain mercury species and flow data through the watershed in the wet season, the data are still not sufficient to fully quantify the loads at all locations sampled, i.e., define the average loads and the variability associated with each load. Therefore, the numerical values of the loads presented in this section must be considered as estimates that can be used for comparing the relative magnitudes of different sources in the watershed.

To facilitate interpretation of the data, we have classified the uncertainty in the estimated loads into three categories:

- **High:** when flow data were limited to the mercury sampling time and location, and calculations were based on modeled flow
- **Medium:** when continuously gauged flow data were available

- **Low:** When continuously gauged flow *and* supporting information, such as total suspended solids data were available.

Guadalupe River fell in the low-medium uncertainty category above because of the presence of a multi-decade continuous flow record and an independent station monitored for total suspended solids and mercury by San Francisco Estuary Institute.

4.3 Transported Loads Throughout the Watershed (Wet Season)

Total mercury, methylmercury, and dissolved methylmercury loads for the major waterbodies in the Guadalupe River Watershed are shown in graphical form in Figures 4-1 through 4-3. For total mercury loads, shown in Figure 4-1, all reservoir outflows appear to be of roughly the same magnitude except Calero Reservoir. Although concentrations flowing out of Lexington Reservoir are lower than from Guadalupe and Almaden Reservoirs, this is compensated by the substantially larger volume of outflows. Further downstream, the largest loads to Guadalupe River originate from Alamitos Creek, followed by Los Gatos and Guadalupe Creek. Alamitos Creek loads, upstream of Calero Creek, are substantially higher than Almaden Reservoir outflow loads, indicating the mobilization of internal sediment loads. Although Los Gatos Creek does not contain any mines, the relatively high loads are a consequence of its larger watershed compared to Guadalupe Creek. The loads exiting Guadalupe River to San Francisco Bay are far higher than the total loads entering from all the tributary creeks and from its watershed. This is a strong indication of uncertainties in the upstream contributing loads, loads from the highly urbanized area, and the mobilization of internal sediment loads.

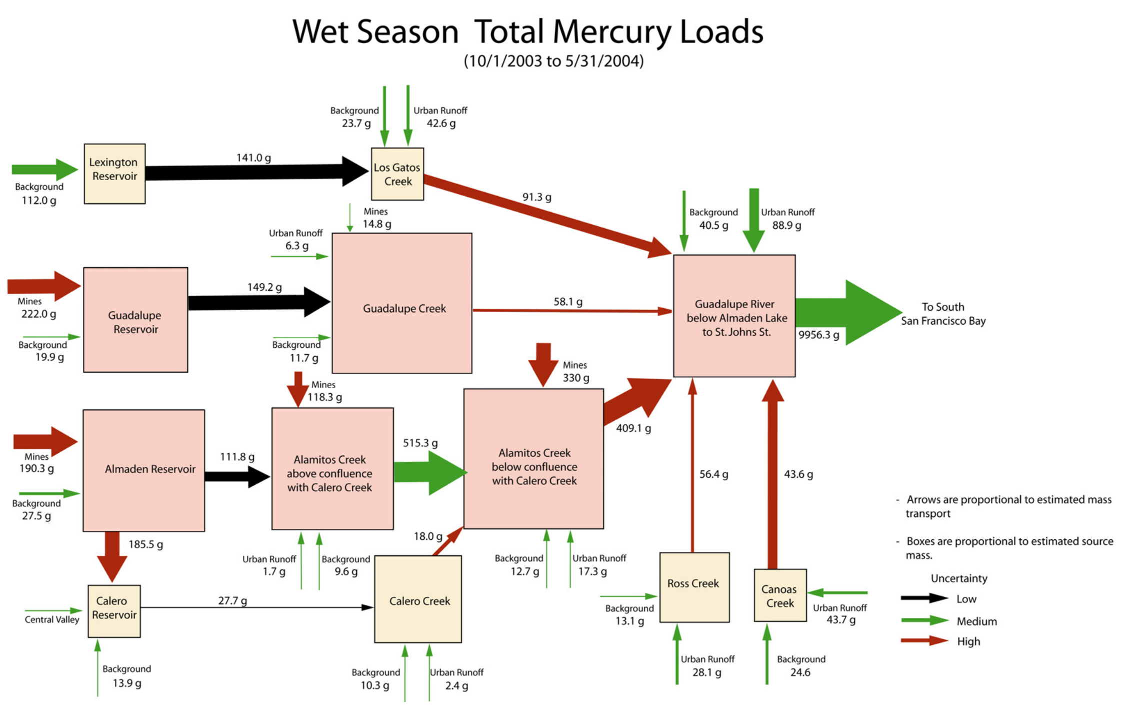


Figure 4-1. Estimates of total mercury loads in the Guadalupe River Watershed. All loads are in grams. See text for discussion of uncertainty of numerical estimates.

For methylmercury loads, shown in Figure 4-2, Guadalupe Reservoir is the largest contributor in the wet season, followed by Lexington and Almaden Reservoirs at somewhat lower levels, with Calero Reservoir being the lowest. Further downstream, with the exception of Alamitos Creek, the methylmercury loads to Guadalupe River from the different creeks are not too dissimilar, indicating that even small amounts of total mercury can produce enough methylmercury if the right aquatic chemistry conditions are present. As with total mercury, the methylmercury loads exiting Guadalupe River to San Francisco Bay are somewhat higher than the total loads entering from all the tributary creeks and from its watershed.

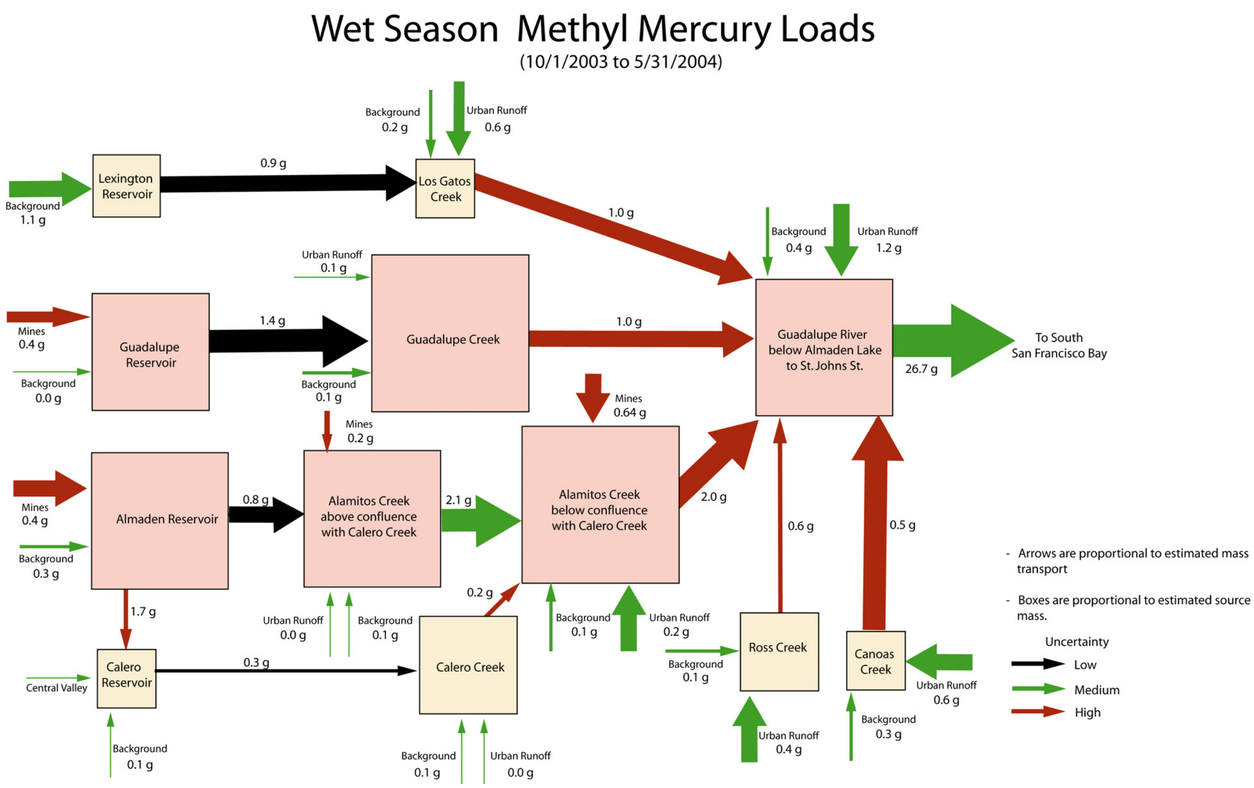


Figure 4-2. Estimates of methylmercury loads in the Guadalupe River Watershed. All loads are in grams. See text for discussion of uncertainty of numerical estimates.

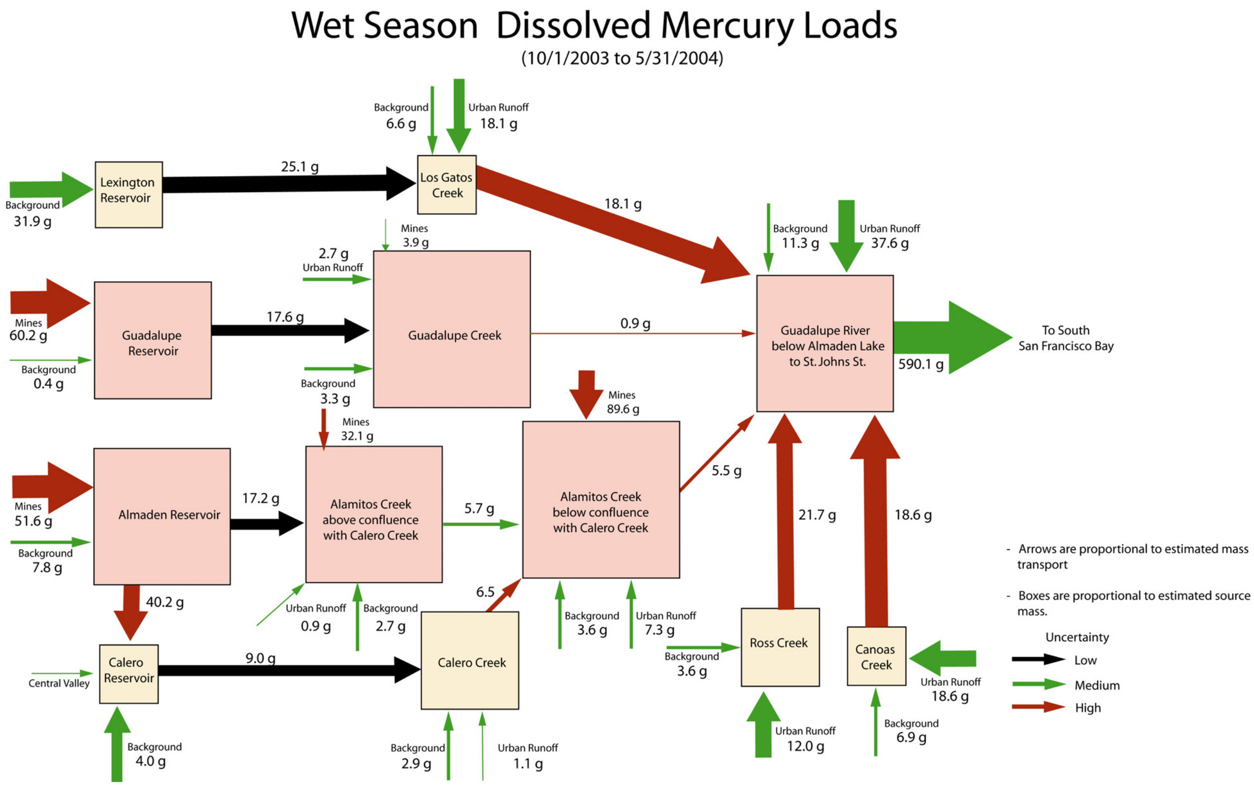


Figure 4-3. Estimates of dissolved mercury loads in the Guadalupe River Watershed. All loads are in grams. See text for discussion of uncertainty of numerical estimates.

4.4 RESERVOIR PRODUCTION AND EXPORT OF METHYLMERCURY (DRY SEASON)

The internal methylmercury loads and the methylmercury exports for Guadalupe and Almaden Reservoirs are shown in Figures 4-4 and 4-5. Depending on the reservoir, there is 3 to 10 times as much methylmercury accumulated in the hypolimnion than in the epilimnion. There is a substantial increase in methylmercury beginning in July, particularly for Guadalupe Reservoir. Methylmercury exports from Almaden Reservoir were similar to that from Guadalupe Reservoir (7.2 g vs. 5 g). In both instances more of the methylmercury produced was exported than retained in the reservoirs. More methylmercury is exported during the dry than during the wet season (Figure 4-2 and Table 4-6).

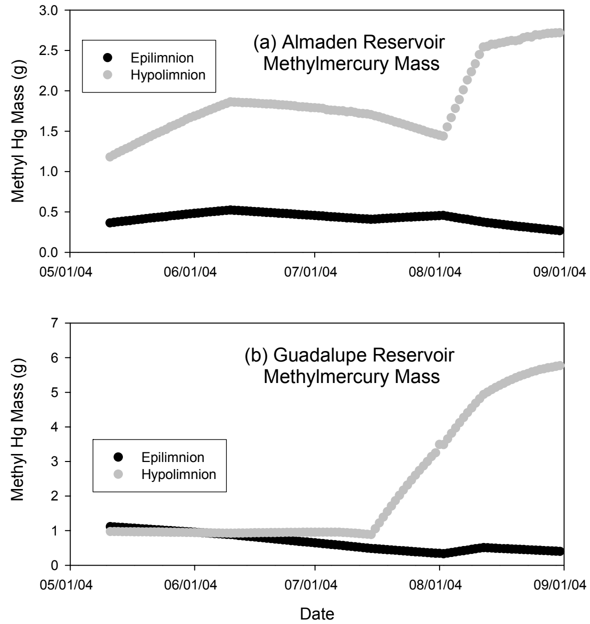


Figure 4-4. Estimates of internal methylmercury production in Almaden and Guadalupe Reservoir during the 2004 dry season.

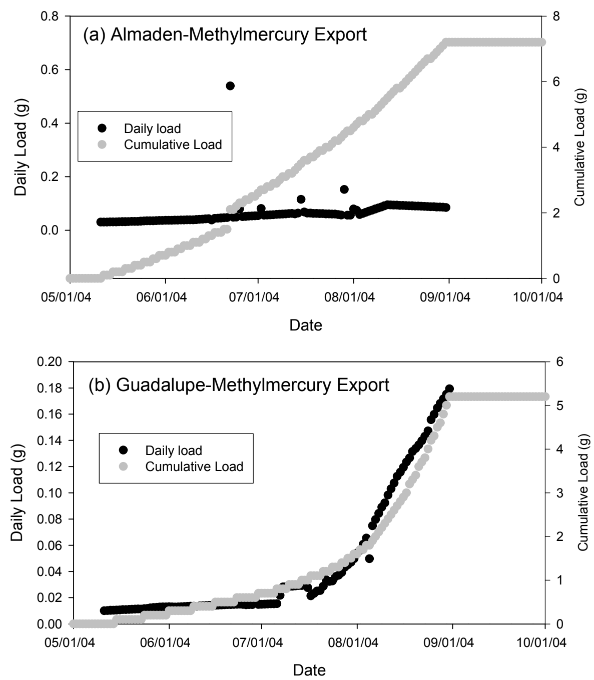


Figure 4-5. Estimates of downstream exports of methylmercury from Almaden and Guadalupe Reservoir during the 2004 dry season.

4.5 UPPER WATERSHED CREEKS

The creeks draining into the reservoirs in the upper Guadalupe River watershed can be divided into two groups: those affected by past mercury mining and those not affected (Table 4-1). Most of the subwatersheds are undeveloped open-space, parks, or areas with minimal development, except for one subwatershed to Lexington Reservoir, Upper Los Gatos, which has more development along Highway 17. Atmospheric wet and dry deposition, transport of past dry deposition, and erosion and transport of natural geologic materials represent mercury sources to all the subwatersheds. The susceptibility of the creeks to erosion and sediment transport varies depending on whether the slopes are forested or grass covered, the extent of landslides, and faults. Faults are common in the upper watersheds, which can trigger landslides. Mercury deposits may be associated with fault zones.

Table 4-1.
Creeks Affected by Mining in Upper Watershed

Reservoirs	Creeks Affected by Mining
Almaden	Jacques Gulch and West Tributary to Reservoir
Calero	Only Almaden-Calero Canal
Guadalupe	N. Los Capitancillos
Lexington	None*

*Limekiln Canyon has limited silica carbonate outcrops but no historic mines.

Estimated total mercury loads to the four larger reservoirs are shown in Table 4-2 as described in Technical Memorandum 5.3.2 Data Collection Report. The loads have been divided into two components: 1) background loads from atmospheric wet and dry deposition, transport of past dry deposition, and erosion and transport of natural geologic materials; and 2) mining loads from transport of exposed mine wastes and mine seeps. Mine-related loads were estimated to Almaden, Calero, and Guadalupe Reservoirs. For each of these reservoirs, the contribution from transport of mine wastes was larger than the background load.

Table 4-2.
Estimated Wet-Season Total Mercury Loads from Upper Watershed Creeks

Loads to Reservoir	Background Load, g	Mine-related Load, g	Uncertainty
Almaden	27.5	190.3	High
Calero	13.9	185.5	High
Guadalupe	19.9	222.0	High
Lexington	112.0	none	High

Uncertainties in the total mercury loads derive from the variable rainfall over annual and inter-annual cycles and from use of limited data to estimate the mercury content of the particulate and total load (one or two sampling events of low runoff events in the wet-season of 2004). Most of the upper watershed creeks, including those draining former mining areas, are dry in the summer. Additional sampling of the mine-related creeks during high flow events in the wet-season could reduce the uncertainty. The upper watershed creeks contribute to the downstream waterbodies only from the reservoir outlets. Thus, quantification of these outlets only is necessary for development of mercury loadings to the downstream waterbodies.

The estimated methylmercury loads from the upper watershed creeks to the reservoirs are small in the wet-season, as shown in Table 4-3. The loads from the creeks influenced by mining contributed more methylmercury than the non-mining creeks. Because most of the creeks are dry in the summer, higher methylmercury loads are not expected. Three creeks that continue flowing in the summer (Rincon and Herbert Creek and Barret Canyon) are fed by springs at low flows, and the conditions for methylation are not expected. Upper Los Gatos Creek has flow during the summer from Lake Elsman, but because of the distance from the lake to Lexington Reservoir, and the demethylation that occurs in the creeks in the watershed, Lake Elsman is not expected to contribute significant methylmercury in the summer. Thus, the upper watershed creeks do not represent a major source of methylmercury to the reservoirs, which is primarily due to internal sources such as methylation in the anoxic water column and/or sediment in the reservoirs.

Table 4-3.
Estimated Wet-Season Methylmercury Loads from Upper Watershed Creeks

Loads to Reservoir	Background Load, g	Mine-related Load, g	Uncertainty
Almaden	0.3	0.4	High
Calero	0.1	1.7	High
Guadalupe	0.0	0.4	High
Lexington	1.1	None	High

4.6 Creeks Below Impoundments

4.6.1 Creeks Affected by Mercury Mining Activities

Mercury loads were estimated for two creeks affected by mining: Alamitos and Guadalupe Creeks. Alamitos Creek begins at the outlet of Almaden Reservoir and ends at Lake Almaden, where deposition of gravel and coarse sediment occurs. As seen in Figure 4-6, Alamitos Creek and Guadalupe Creek join below Lake Almaden, and then flow downstream forming the Guadalupe River. Following the wet season, flashboards are installed at the Alamitos Drop Structure, shown in Figure 4-6, to raise the level of both Lake Almaden and an impounded section between the lake outlet and the drop structure. A fish ladder allows for fish passage across the drop structure. Sediment can build-up behind the flashboards over the dry season, and in the wet season when the boards are removed, sediment can be transported downstream. Where Guadalupe Creek joins Alamitos Creek below the lake, there is also a significant deposition zone, as seen in Figure 4-6. Sediment samples from both of these deposition areas had high mercury concentrations (16.4 to 18.8 mg/kg) Tetra Tech, 2005a).

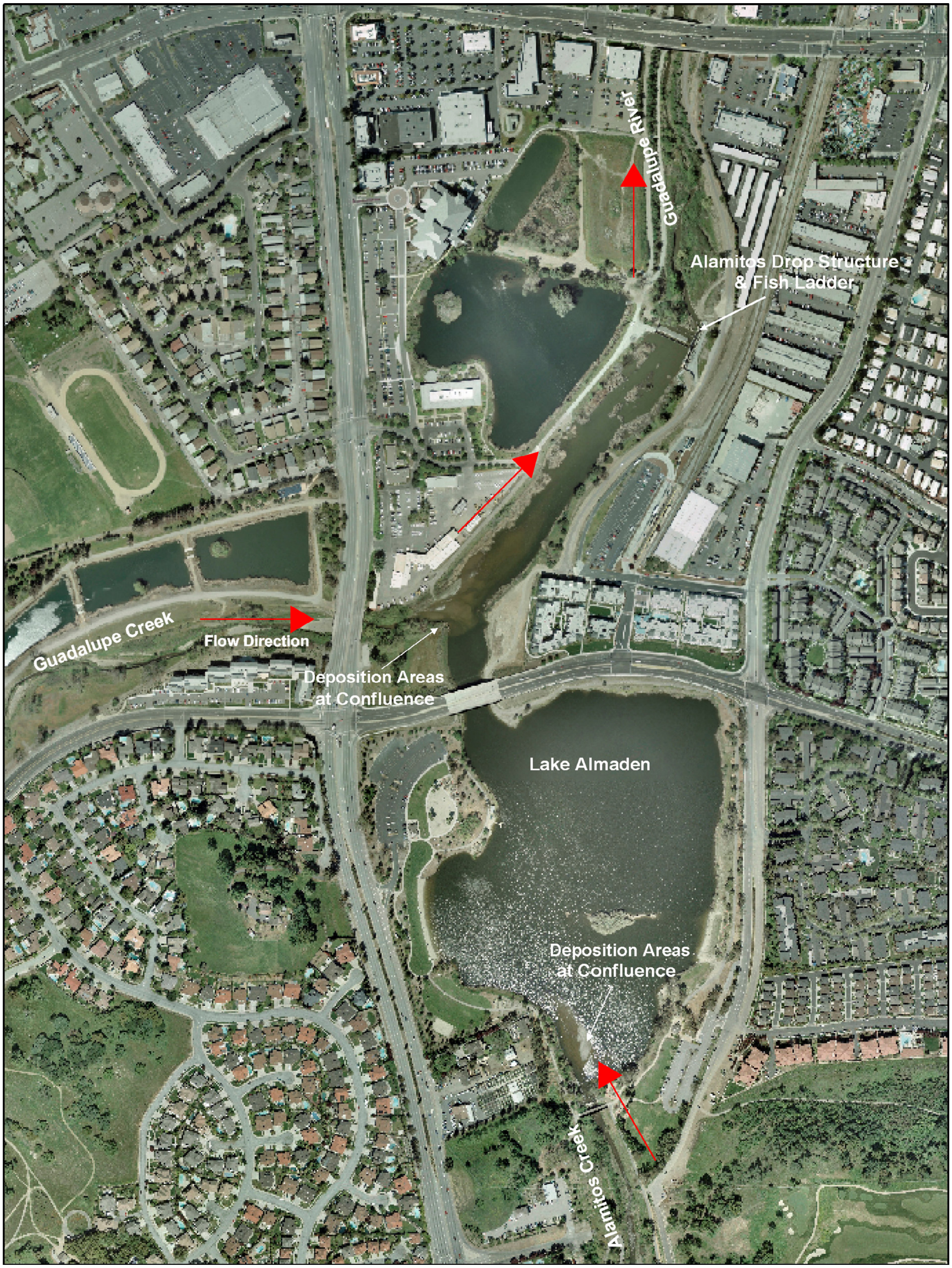


Figure 4-6. Aerial photograph of Lake Almaden and vicinity showing deposition areas at mouths of Guadalupe and Alamitos Creeks

Both Alamitos and Guadalupe Creeks have inflows from reservoirs and tributaries with varying land uses including past mining activities. Alamitos Creek has three tributaries that drain part of the Almaden County Quicksilver (AQC) Park, McAbee Creek (a tributary of Golf Creek), Randol Creek, and Greystone Creek. A series of small drop structures and a debris dam reduces the mercury load from these creeks that ultimately reaches the main stem of Alamitos Creek. Other tributaries to Alamitos Creek are Calero Creek and its tributary, Santa Teresa Creek. Guadalupe Creek has limited mining activities on a tributary to Cherry Springs Creek and flows along part of the former Guadalupe Mine, which is outside of the AQC Park boundary. Mine wastes were disposed to both Alamitos and Guadalupe Creeks, but especially to Alamitos, because extensive furnaces and retorts were located along its bank near the Hacienda Furnace Yard above the town of New Almaden.

The estimated total mercury loads to both creeks are shown in Table 4-4. The load to both creeks from the upstream reservoirs is significant. However, the importance of erosion of past mine wastes along the creek is seen in the internal load generated from the upper part of Alamitos Creek above its confluence with Calero Creek. The wet-season inflows from the reservoirs were the major source of methylmercury to the two creeks, which is also true for the dry season. Uncertainties in these loads are due to the variability of rainfall, which in turn results in changing levels of erosion, and differences in extent of the mine contribution to various parts of the watershed.

4.7 Urban Creeks

There are three urban creeks, Los Gatos, Ross, and Canoas, which discharge into the Guadalupe River. Los Gatos Creek has the largest flows, because it has a larger watershed and receives inflow from Lexington Reservoir. Ross Creek is a short creek with minimal to no flow in the summer. Canoas Creek is longer than Ross Creek but also has minimal flows in the summer. Sources to these creeks include atmospheric deposition, stormwater runoff, and erosion of stream bank materials.

The estimated total mercury and methylmercury loads into these creeks are shown in Table 4-5. These loads were calculated on an areal basis, where GIS data were used to define the fraction of each subwatershed that was covered by urban land. The areal loading rate for urban lands was based on the calculation described in section 4.1.3. The largest total mercury and methylmercury loads from the urban creeks to the Guadalupe River were from Los Gatos Creek. Los Gatos Creek is dominated by the reservoir outflow, particularly for methylmercury. For all three creeks, the urban contribution was larger than the background.

Table 4-4
Estimated Mercury Loads in Alamitos and Guadalupe Creek
(in grams over the wet season, (10/1/2003 to 5/31/2004)

Alamitos Creek (up to confluence with Calero Creek)

	Loads In				Total Inflows	Loads to Alamitos Creek
	Background	Urban	Almaden Reservoir	Historic Mine Loads		
Total Hg	9.6	1.7	111.8	118.3	**241.4**	**515.3**
Methyl Hg	0.1	0	0.8	0.16	**1.1**	**2.1**
Uncertainty in loads	Medium	Medium	Low	High	**High**	**High**

Calero Creek, a tributary to Alamitos Creek

	Loads In			Total Inflows	Loads to Alamitos Creek
	Background	Urban	Calero Reservoir		
Total Hg	10.3	2.4	27.7	**40.4**	**18**
Methyl Hg	0.1	0	0.3	**0.4**	**0.2**
Uncertainty in loads	Medium	Medium	Low	**High**	**High**

Alamitos Creek (below confluence with Calero Creek)

	Loads In					Total Inflows	Loads to Guadalupe River
	Background	Urban	Upper Alamitos Creek	Calero Creek	Historic Mine Loads		
Total Hg	12.7	17.3	515.3	18	330	**893.3**	**409.1**
Methyl Hg	0.1	0.2	2.1	0.2	0.64	**3.3**	**2**
Uncertainty in loads	Medium	Medium	High	High	High	**High**	**High**

Guadalupe Creek

	Loads In				Total Inflows	Loads to Guadalupe River
	Background	Urban	Guadalupe Reservoir	Historic Mine Loads		
Total Hg	11.7	6.3	149.2	14.8	**182**	**58.1**
Methyl Hg	0.1	0.1	1.4	0	**1.6**	**1**
Uncertainty in loads	Medium	Medium	Low	High	**High**	**High**

Table 4-5.
Mercury Loads in Urban Creeks in the Guadalupe River Watershed
(in grams over the wet season, (10/1/2003 to 5/31/2004)

Los Gatos Creek

	Loads In			Total Inflows	Loads to Guadalupe River
	Background	Urban	Lexington Reservoir		
Total Hg	23.7	42.6	141.0	**207.3**	**91.3**
Methyl Hg	0.2	0.6	0.9	**1.7**	**1.0**
Uncertainty in loads	Medium	Medium	Medium	**Medium**	**High**

Ross Creek

	Loads In		Total Inflows	Loads to Guadalupe River
	Background	Urban		
Total Hg	13.1	28.1	**41.2**	**56.4**
Methyl Hg	0.1	0.4	**0.5**	**0.6**
Uncertainty in loads	Medium	Medium	**Medium**	**High**

Canoas Creek

	Loads In		Total Inflows	Loads to Guadalupe River
	Background	Urban		
Total Hg	24.6	43.7	**68.3**	**43.6**
Methyl Hg	0.3	0.6	**0.9**	**0.5**
Uncertainty in loads	Medium	Medium	**Medium**	**High**

4.8 IMPOUNDMENTS

4.8.1 RESERVOIRS

Mercury loads in four major reservoirs in the Guadalupe River Watershed were assessed as part of this TMDL: Almaden, Calero, Guadalupe and Lexington Reservoirs. Two of these reservoirs, Almaden and Guadalupe, are significantly affected by mining sources. Lexington Reservoir is considered to be unimpacted by mercury mining activities, and may be considered a background reservoir from the standpoint of mercury contamination. Calero Reservoir has mercury impacts in-between the background and the mining-impacted reservoirs, because of water transfers from Almaden Reservoir and mercury-enriched geology in this subwatershed. The reservoirs are all in the upstream portion of the watershed and receive water, and mercury loads, from creeks primarily during the wet season. Mercury in the reservoirs accumulates as sediment (not measured as part of this study) and is also exported downstream. Mercury in the reservoir sediments and water column is methylated and exported downstream during the dry season.

Estimated total and methylmercury exports from the reservoirs during the dry and wet season are shown in Table 4-6. On a mass basis, Almaden, Guadalupe, and Lexington Reservoirs are all significant sources of total mercury in the wet season, the first two as a result of high concentrations and Lexington because it is much larger and has higher outflows on average. The total mercury exports in the dry season are substantially lower than in the wet season, for the two reservoirs where such a comparison could be made. Methylmercury exports in the wet season are relatively low (~1% of total mercury load) and follow the same pattern as the total mercury load. In the dry season however, the picture changes: the methylmercury loads are between 3 and 10 times larger than in the wet season, and furthermore, methylmercury constitutes a much larger fraction of the total mercury load (between 13 and 34 %).

Table 4-6.
Estimated wet and dry season exports of total and methylmercury from the reservoirs.

Reservoir	Total Mercury Export (wet), g	Methylmercury Export (wet), g	Total Mercury Export (dry), g	Methylmercury Export (dry), g	Uncertainty
Almaden	287.3	0.8	21.0	7.2	Low
Calero	27.7	0.3	No data	No data	Low
Guadalupe	149.2	1.4	37.0	5.0	Low
Lexington	141.0	0.9	No data	No data	Low

Of all the loads estimated in this TMDL, it is thought that the uncertainties in the reservoir exports are low. This is because the flows at all outlets are gauged continuously, and more importantly because both flows and total mercury concentrations are relatively uniform. Methylmercury concentrations are variable, but they exhibit a clear seasonal pattern (a buildup over the summer months) that was captured reasonably well during the data collection sampling program in 2004. Thus, in general the concentration and flow data needed for reasonably accurate load estimates are available at the reservoir outlets.

4.8.2 Other Impoundments

Mercury loads for other impoundments in the Guadalupe River watershed were not estimated. Major impoundments downstream of the above four reservoirs are Lake Almaden upstream of the confluence of Alamitos Creek and Guadalupe Creek, Vasona Reservoir on Los Gatos Creek downstream of Lexington Reservoir, and a much smaller impoundment on Guadalupe Creek above Masson Dam. There are also off-stream percolation ponds along some creeks and the Guadalupe River, where flows can be diverted for groundwater recharge.

Lake Almaden has shallow and moderately deep areas, up to about 40 feet, and contains sediment and gravel deposited at the confluence of Alamitos Creek and the lake. The wet-season sampling in 2004 indicated that total mercury concentrations downstream of the lake were less than upstream in the creek, although the suspended solids were higher in the outlet samples. The particulate mercury concentrations were higher in the upstream samples. Methylmercury concentrations were similar in the wet-season samples for both up and downstream samples. Additional sampling of Lake Almaden in the summer would be needed to determine if the elevated methylmercury concentrations found during the Synoptic Survey in July 2003 are representative of summer concentrations. The fish data collected in 2004 suggest that internal methylation in the lake is occurring.

Vasona Reservoir is a small reservoir on Los Gatos Creek and often spills during large storm events, as occurred when sampled on February 27, 2004 as part of the data collection program. The total mercury and suspended solids concentrations during spilling were higher than for a non-spill event when both the Lexington Reservoir and a site downstream of Vasona Reservoir were sampled on the same date. The methylmercury concentrations were similar for the non-storm event. Because this reservoir is shallow, it is less important than the larger upstream reservoirs.

Masson Dam on Guadalupe Creek forms a small, shallow impoundment. A fish ladder allows for fish passage. Previous sampling suggests that methylmercury may increase due to this impoundment, but this source is less important than the large reservoirs.

4.9 Uncertainty in Upper Watershed Loads

Loads described in the sections above are primarily based on sampling conducted during the 2003-2004 wet season, with most samples being collected in late February and beyond. Limited large storms during this period precluded sampling at high flows in much of the upper watershed. Further, given the remoteness and inaccessibility of some of the sampling stations, it is unlikely that they can be adequately sampled, on a grab-basis, for the short-duration peak flows that occur in the watershed. The loads presented above must be discussed in light of these constraints in the existing data set. As a general rule, increased flows result in higher suspended solids and therefore, higher mercury transport. This process was accounted for by using flow-TSS correlations to estimate TSS levels at flows higher than those physically sampled. However, because of the absence of high flow data in the upper watershed, it is possible that these correlations were not accurate, and were perhaps underestimated especially at higher flows.

Calculations using data from the Almaden Quicksilver County Park illustrate the significance of high TSS events. Measurements made by the Park on Los Capitancillos Creek on February 25, 2004 indicated TSS values of 8,890 mg/l and mercury values of 5,300 ng/l (reported in Table 2-6 of this report). Flow measurements were not made during this sample collection event. However, based on modeled flow data we have computed using rainfall in the 2003-2004 wet season, the average estimated flow on this date is 57.6 cfs. Assuming that the peak flow is approximately 4 times the average daily flow, and that this flow lasts for 4 hours, the transported load from the Los Capitancillos Creek during this period is estimated to be 490 g, a value much higher than the estimated annual load of mercury from mines to the Guadalupe Reservoir. Although approximate, this calculation highlights the significance of the storm event loads in the upper watershed, and indicates a major source of uncertainty in the estimated loads presented here: the contribution of large winter storms. The absence of adequate flow and TSS data in the upper watershed precludes a more detailed analysis of this uncertainty. Based on this assessment it appears that the calculated loads presented here are more likely to be underestimates rather than overestimates. Further quantification of the upper watershed loads through additional wet weather data collection in future stages of this project is strongly recommended.

4.10 GUADALUPE RIVER

The Guadalupe River begins below Lake Almaden at the confluence of Alamitos and Guadalupe Creeks and discharges into San Francisco Bay. Tributaries to the river include Alamitos and Guadalupe Creeks, the two creeks affected by past mining, and three urban creeks, Ross, Canoas, and Los Gatos. The flow from Alamitos and Guadalupe Creeks is controlled by the Alamitos drop structure and associated fish ladder. However, sediment can build-up behind this drop structure over the dry season, which can then be transported downstream during large storm events in the wet season. Other sources to the river include atmospheric deposition, urban runoff routed to large storm drains that discharge directly into the river, and resuspension and erosion of stream bank material. The flow regime of the lower Guadalupe River will change as a result of the new flood control projects currently under construction. For example, flows above 3,000 cfs will soon be routed to a new underground bypass channel, which will re-enter the river above Alviso Slough. At the junction of the routed flows, channel widening and hardening is expected to limit erosion. Thus, the sediment transport regime may also change due to less bank erosion.

The estimated total mercury and methylmercury loads for the wet-season to the Guadalupe River are shown in Table 4-7. The largest loads for both total mercury and methylmercury were estimated to be from Alamitos Creek. The increased total mercury load to the Bay compared to the inflows is due partly to internally-generated load from resuspension of sediment and bank erosion and from transport of deposited sediment behind gates in the larger storm drains, which discharge to the river. There is also uncertainty in the upstream loads.

Table 4-7.
Estimated Mercury Loads in the Guadalupe River
(in grams over the wet season, (10/1/2003 to 5/31/2004)

	Loads In							
	Background	Urban	Guadalupe Creek	Alamitos Creek	Ross Creek	Los Gatos Creek	Canoas Creek	**Total Inflows**
Total Hg	40.5	88.9	58.1	409.1	56.4	91.3	43.6	**787.9**
Methyl Hg	0.4	1.2	1.0	1.9	0.6	1.0	0.5	**6.6**

4.11 UNCERTAINTY IN GUADALUPE RIVER LOADS TO SAN FRANCISCO BAY

We sought to quantify the uncertainty in Guadalupe River loads by accounting for the residual error in the regressions using Monte Carlo Analysis. The Monte Carlo approach is used to estimate likely ranges of loads, given imperfect knowledge about the needed inputs, particularly flow-concentration relationships and inter-year variability in flows. This is done by assuming probability distributions for the key inputs, and performing the load calculations multiple times where values of inputs are drawn from a specified probability distribution. Each Monte Carlo trial results in an estimate of the load. When this process is repeated several times (typically several hundred or thousand times), one obtains a distribution of the loads that is consistent with the uncertainty in input parameters.

For the specific case of developing the uncertainty-based load estimates of mercury for the Guadalupe River Watershed, where flows are related to TSS, and the TSS to mercury concentrations, we need a method that, given a specific value of flow, provides a probabilistic estimate of TSS, and a probabilistic estimate of the total mercury concentrations. These can be used to generate a probabilistic estimate of the mercury load, and, if the process is repeated a large number of times, can provide a distribution of the load. The statistical approach for doing this is to use the residual errors in the regressions to develop Monte Carlo estimates of key input parameters.[1] This approach was implemented in Microsoft Excel, using the Crystal Ball program. Crystal Ball is a specialized simulation tool for performing Monte Carlo simulations.

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[1] The statistical approach for doing this is to assume that the linear regression models developed by Tetra Tech are expressed as $y = \alpha + \beta x$, where y is the dependent variable and x is the independent variable, and α and β are the intercept and slope. Using N pairs of observed data (X_i, Y_i), a least-squared error estimator was used to determine α and β. Our goal is to develop a Monte Carlo procedure that will generate random values of the dependent variable y for specified values of the independent variable x. The variance of the model error will be computed using the N data samples. An unbiased variance estimator s_m^2 is computed (Bhattacharyya and Johnson, 1977, pages 341-357) as follows:

$$s_m^2 = \frac{SSE}{(N-2)}$$

where *SSE* is the residual sum of squares using *N* data pairs (X_i, Y_i):

$$SSE = \sum_{i=1}^{N} (Y_i - \alpha - \beta X_i)^2 .$$

The Monte Carlo algorithm generates random deviates of the linear model by assuming the dependent y variable of the model has Gaussian distribution $N(\mu_y, \sigma_y)$. The variance of the dependent y variable is assumed to be the same for any value of the independent variable x. The jth deviate y_j of the dependent variable can be generated for the specified dependent value x^* as follows:

$$y^* = \alpha + \beta x^*, \text{ where } y_j \in N(y^*, s_m).$$

The load of total mercury being transported out of the Guadalupe Watershed into San Francisco Bay was used for the uncertainty analysis. The Monte Carlo estimate of wet weather loads was computed using the following steps:

1. The flows, obtained from the USGS flow gauge in the downstream portion of the Guadalupe River, were assumed to be accurately known, i.e., there was no uncertainty associated with them.
2. For a specific day, the flow rate was used to obtain a probabilistic estimate of the TSS using the regression equation for stations on the river, and using the statistical approach above.
3. Using the probabilistic estimate of TSS, a similar probabilistic estimate was obtained for total mercury concentration using the mercury-TSS correlation for the River stations.
4. Multiplying the flow and mercury concentration for each day provided an estimate of the daily load
5. The entire wet weather load was calculated by summing the daily loads from 10/1/2003 to 5/31/2004.
6. Steps 1) through 5) were repeated 1,000 times to obtain a distribution of the wet weather load for 2004.

The distribution of wet season loads for 2003-2004 is shown in Figure 4-7. The distribution shows a somewhat skewed bell curve, with a longer tail on the right-hand side than on the left-hand side, as a consequence of some of the variables being log-transformed in the regressions. Total loads range from approximately 8 to 20 kg. The mid-point of the distribution is about 12 kg.

Although loads for a given year are uncertain, we also know that there is significant year-to-year variability in the flows out of the Guadalupe Watershed. Because flows and mercury loads are related, it is likely that multi-year uncertainty will be significantly greater than the single-year uncertainty estimate. To assess the multi-year uncertainty, we performed a Monte Carlo analysis using daily average flows from 1960-2002, where a single year over this period was randomly sampled to compute total wet weather loads from October through May. The distribution of loads for the multi-year analysis is shown in Figure 4-8. It can be seen that the multi year uncertainty is considerably greater than the single year uncertainty, with values ranging from near zero for the extremely low flow years to almost 100 kg for the high flow years. Although this is not an unexpected result, the Monte Carlo analysis permits quantification of the process, and can be used to relate individual-year loads, and potential load reductions, to the overall distribution of loads.

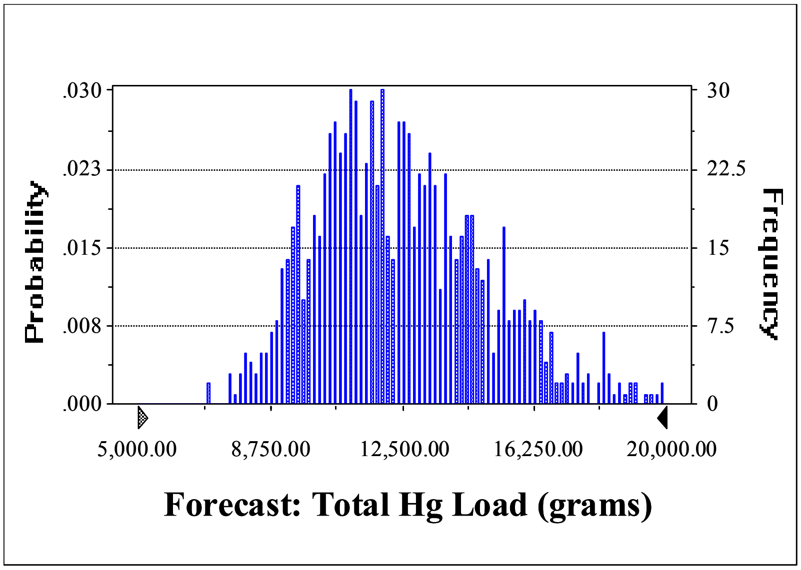


Figure 4-7. Uncertainty in the single-year estimate (2003-2004 wet season) of total mercury loads from Guadalupe River to South San Francisco Bay. The calculations were obtained using the uncertainty in the flow-TSS and the TSS-total Hg relationships using a Monte Carlo simulation with 1000 trials. The average estimated wet weather load for 2003-2004 is about 10 kg.

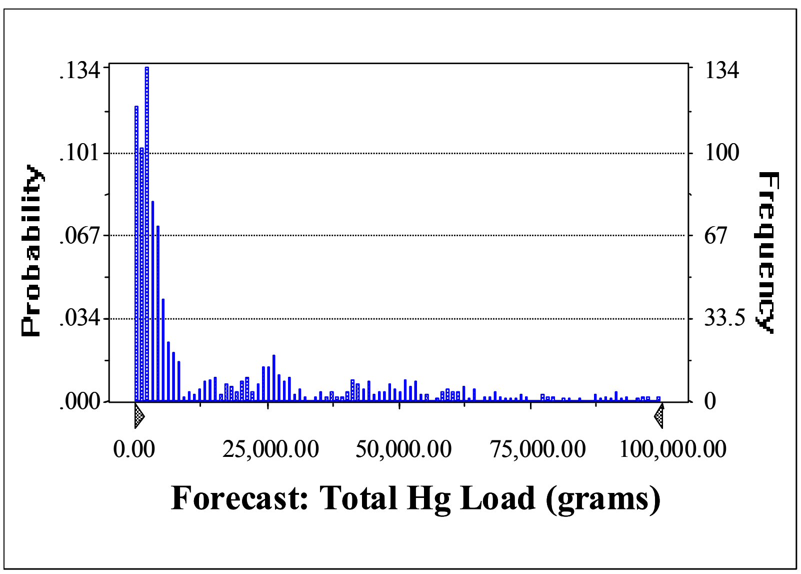


Figure 4-8. Uncertainty in the multi-year estimate (1960-2001 wet seasons) of total mercury loads from Guadalupe River to South San Francisco Bay. The calculations were obtained using the uncertainty in the flow-TSS and the TSS-total Hg relationships and using a Monte Carlo simulation with 1000 trials. The distribution of loads is much wider than for the single year estimate, driven by the large year-to-year variability in flows.

A further cause of uncertainty may be that the Tetra Tech data used to develop the flow-TSS correlations are not based on the full range of flows in the system. As an alternative, a flow-TSS relationship for the Guadalupe River based on the 2002-2003 wet season developed by the San Francisco Estuary Institute (SFEI, McKee et al., 2004) was used to estimate total mercury loads. This has the benefit of being based on a continuous record of flow and TSS for a period of several months. The loads estimated between the 1960 wet season and the 2001 wet season for the Tetra Tech and SFEI relationships are shown in Figure 4-9. It is clear in these plots that the nature of the correlations used to estimate TSS can make a large difference to the estimates of mercury loads in the system. In general, the greatest discrepancies occur in the high flow years, and the loads estimated using the SFEI approach are consistently higher. A comparison of this nature for locations in the upper watershed would be very valuable; however, the absence of enough monitoring data precludes such an assessment.

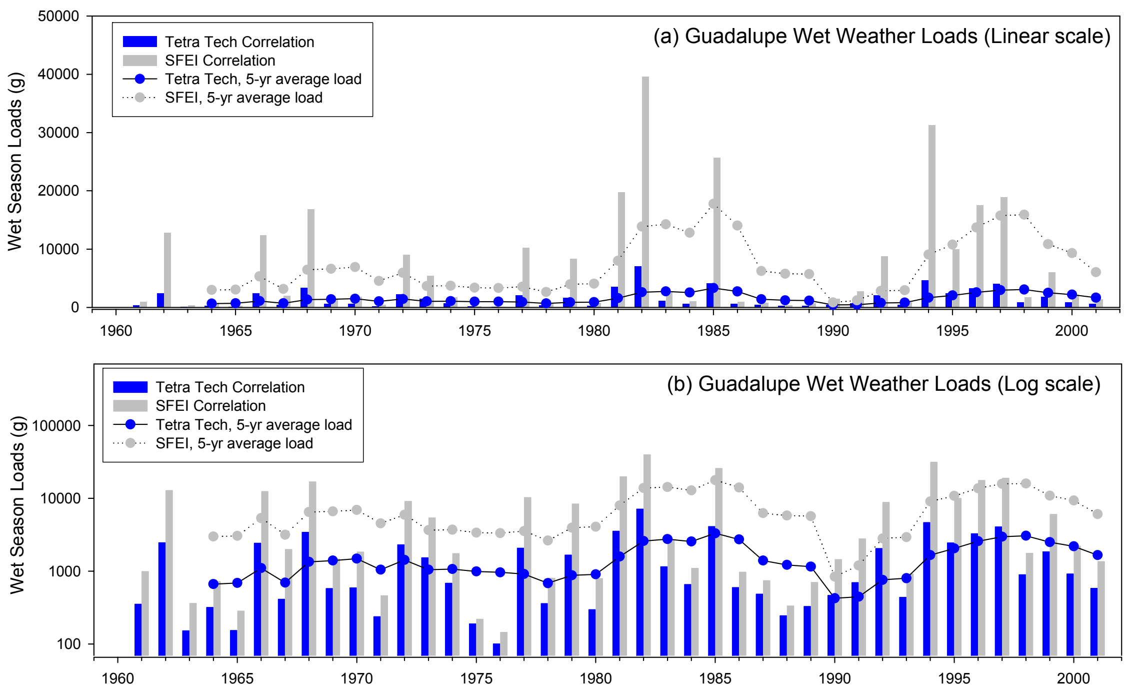


Figure 4-9. Uncertainty in the multi-year estimate (1960-2001 wet seasons) of total mercury loads from Guadalupe River to South San Francisco Bay using two different correlations between flow and suspended solids.

4.12 Recommended Averaging Time for Guadalupe River Loads to San Francisco Bay

Mercury loads exiting the Guadalupe River Watershed vary substantially depending on the volume of flow. Given the historical variability of flows in the river, it is appropriate to define an averaging period to define a baseline for loads against which any future loads must be considered. The averaging period must be chosen based on local site and climate characteristics: an averaging period that is too long will be insufficient to detect trends in changing loads, whereas an averaging period that is too short will be overwhelmed by year-to-year variability.

As a starting point, a five-year averaging period has been proposed by the Water Board. Figure 4-10 shows a comparison of the estimated loads as a function of the averaging period (3 years, 5 years, 7 years, and 10 years) for the Tetra Tech and SFEI correlations used in Figure 4-9. The use of longer averaging periods has the benefit of smoothing out peaks caused by occasional very high flow years, which are typical of this watershed. However a long averaging period (i.e., 10 years) has the effect of elevating the average load for a long period of time. It is conceivable that watershed changes could occur over time frames shorter than 10 years particularly those associated with modification of the flow channel, as proposed in San Jose, or removal of high-mercury containing sediments from dams and river channels. For this reason, a 10-year averaging period is rejected as being too long, and a 5- to 7-year averaging period is considered acceptable.

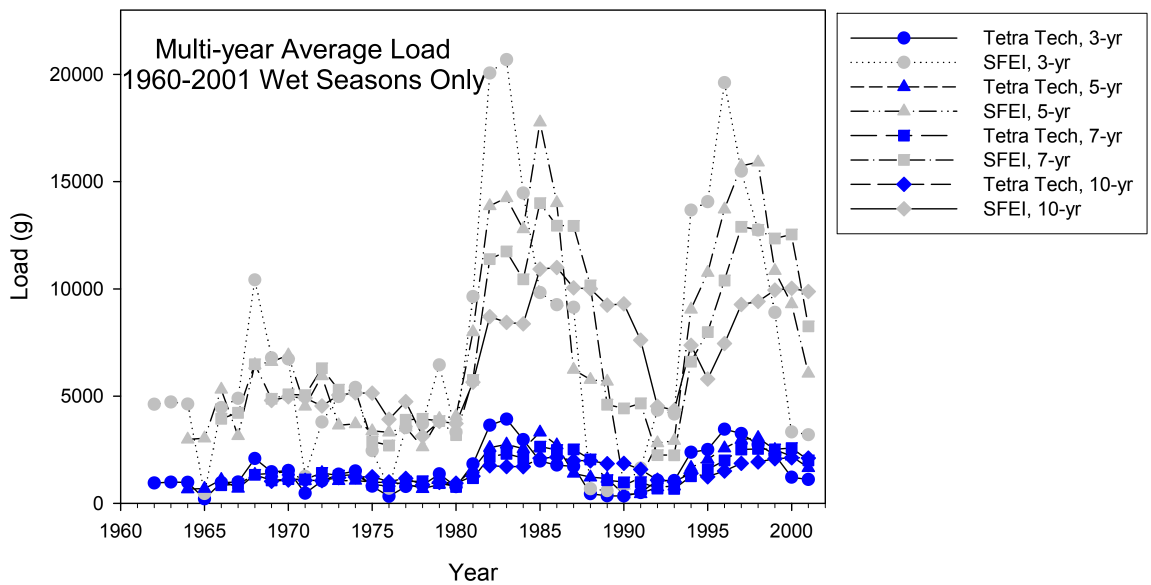


Figure 4-10. Average annual mercury loads as a function of averaging period. Loads were calculated using the Tetra Tech and SFEI correlations between flow and TSS.

4.13 Conclusions

Using mercury concentration and flow data from the data collection effort in 2004, wet and dry season loads were estimated throughout the Guadalupe River Watershed. The wet weather sampling included measurements on all major streams in the watershed and was used to develop an estimate of the movement of mercury. The dry season water column measurements were focused on the two most mercury-contaminated reservoirs and were used to estimate the internally generated methylmercury loads and the downstream exports. The nature of wet season transport, with substantial water, sediment, and mercury moving during specific short-duration storm events introduced some special concerns with respect to the magnitudes of the estimated loads. In particular, during the wet season sampling that forms the basis of this report, there were few instances of large storms during which flows and concentrations could be measured in the upper watershed. Measured wet season concentrations of suspended solids reported here are lower than what others have reported (especially in the Almaden Quicksilver County Park). Given the close association of mercury and suspended sediment transport, the limited high flow and high suspended concentration data in this sampling, it appears, on balance, that the estimated loads in this chapter, although accurately represented on a relative basis, may be lower in magnitude than the actual loads. It is hoped that future wet season sampling as part of the mercury TMDL in the watershed will help reduce these uncertainties.

5.0 CONCEPTUAL MODEL OF MERCURY BEHAVIOR IN THE GUADALUPE RIVER WATERSHED

The conceptual model is presented in two parts. The first part summarizes key aspects of mercury behavior based on general knowledge of the Guadalupe River Watershed and on a review of pertinent scientific literature. The second part of the conceptual model describes, in more detail, the key issues in this watershed and essential information needed to support the development of a TMDL and Implementation Plan. This section has been revised from the Draft Final Conceptual Model (Tetra Tech, 2004a) that was based on the 2003 Synoptic Survey data (Tetra Tech, 2003d) and published scientific literature on mercury behavior. This revision of the conceptual model considers all new data that were collected during the wet and dry season sampling as described in the Data Collection Report (Tetra Tech, 2005a).

5.1 OVERVIEW OF MERCURY TRANSPORT PROCESSES

Most of the mercury in the Guadalupe River Watershed exists as relatively insoluble mercury sulfides in mine wastes that have accumulated in reservoir deltaic deposits and sediments, and in stream bottoms, banks, and flood plains. Mercury also exists adsorbed to sediment within the waterbodies. Mercury in dissolved form is a small fraction of the total mercury, although it may play a proportionally greater role in the formation of methylmercury. Because of the strong association of mercury with solids, the movement of mercury in the watershed is closely tied to the movement of sediments as described below. Because of the seasonal nature of the rainfall in the watershed, i.e., generally between October and April, large flows, and significant sediment and mercury transport occur predominantly in the wet season.

5.1.1 TRANSPORT TO RESERVOIRS

During large runoff events, mercury-containing sediments (from mine wastes) are transported to the Guadalupe and Almaden Reservoirs in the historic mining areas such as from the Mine Hill tributary to Jacques Gulch to Almaden Reservoir and from North Los Capitancillos Creek to Guadalupe Reservoir (Figure 5-1). These creeks are characterized by steep energy gradients and highly variable, intermittent flows. In these reservoirs, atmospherically deposited mercury is quantitatively less significant than the large mine-waste related influxes. Also, in Guadalupe and Almaden Reservoirs, there are mercury-contaminated bottom sediments in the reservoirs from past influx of mine wastes and sediment. In the two other reservoirs, Lexington and Calero, mercury inputs from atmospheric deposition or weathering of local minerals are likely more important. In the case of Calero, two additional sources of mercury, can be cited: the transfers of water from Almaden Reservoir and from the Central Valley Project. For all four reservoirs, the non- atmospheric input of mercury is mostly in particulate form, although the smaller fraction in dissolved form is more chemically reactive and thus on a per unit mass basis more likely to be methylated.

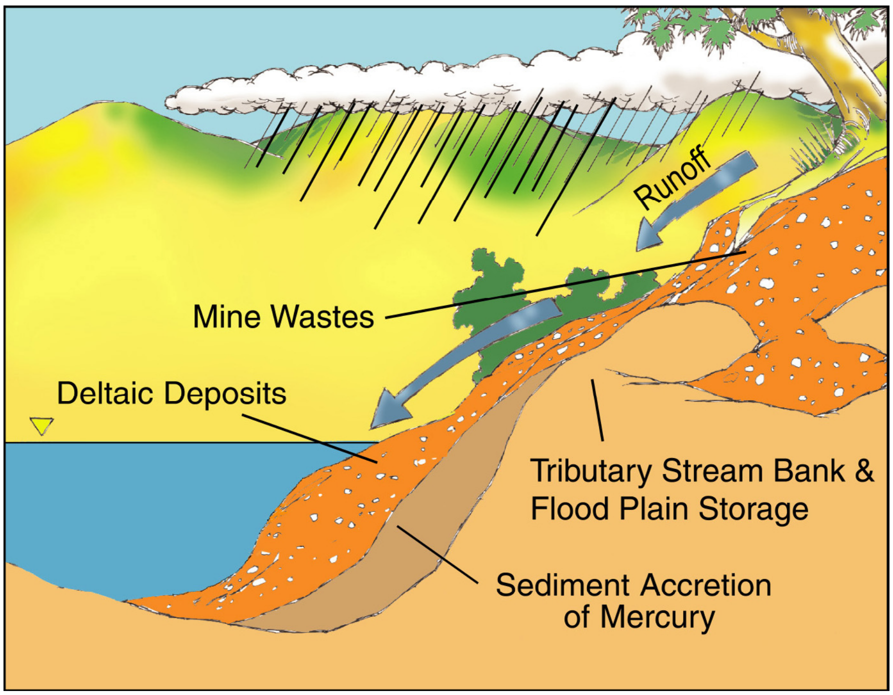


Figure 5-1. Transport to reservoirs.

5.1.2 CREEK/RIVER PROCESSES AT HIGH FLOW

During high flows, large loads of sediment-associated mercury are transported downstream in the creeks and in the Guadalupe River (Figure 5-2). In some reaches, bank erosion occurs to a greater extent than scouring of the bed sediments, and adds significantly to the total transport of mercury. A small percent of the total mercury load is transported as dissolved mercury or methylmercury. Drop structures along some tributary streams and below the confluence of Alamitos and Guadalupe Creeks, the start of the main stem of the Guadalupe River, collect sediments, reducing downstream transport during storms.

5.1.3 Creek/River Processes at Low Flow

During low flow, the total flux of mercury in the creeks and river is much less (Figure 5-3). Transport of dissolved mercury is significant, but quantitatively small compared to the mercury transported as sediment during storms. Sediment mercury transport is important when considering long-term effects of mercury in the watershed, although over the short-term dissolved mercury is more bioavailable. Even though some mercury may be methylated in creeks, the Synoptic Survey data from July 2003 show that methylmercury concentrations decrease with travel distance in most stream reaches. The relationship of total mercury (dissolved plus particulate) with travel distance depends on whether the streams pass through areas with known mine-waste deposits.

5.2 Overview of Mercury Transformation and Biological Uptake

Because the toxicity of mercury to humans and wildlife is closely tied to its uptake through the food chain, it is important to understand the processes that transform mercury in water and sediments into more biologically active forms. Our best current understanding of mercury transformations in the impoundments and creeks of the Guadalupe River Watershed is summarized in the paragraphs that follow.

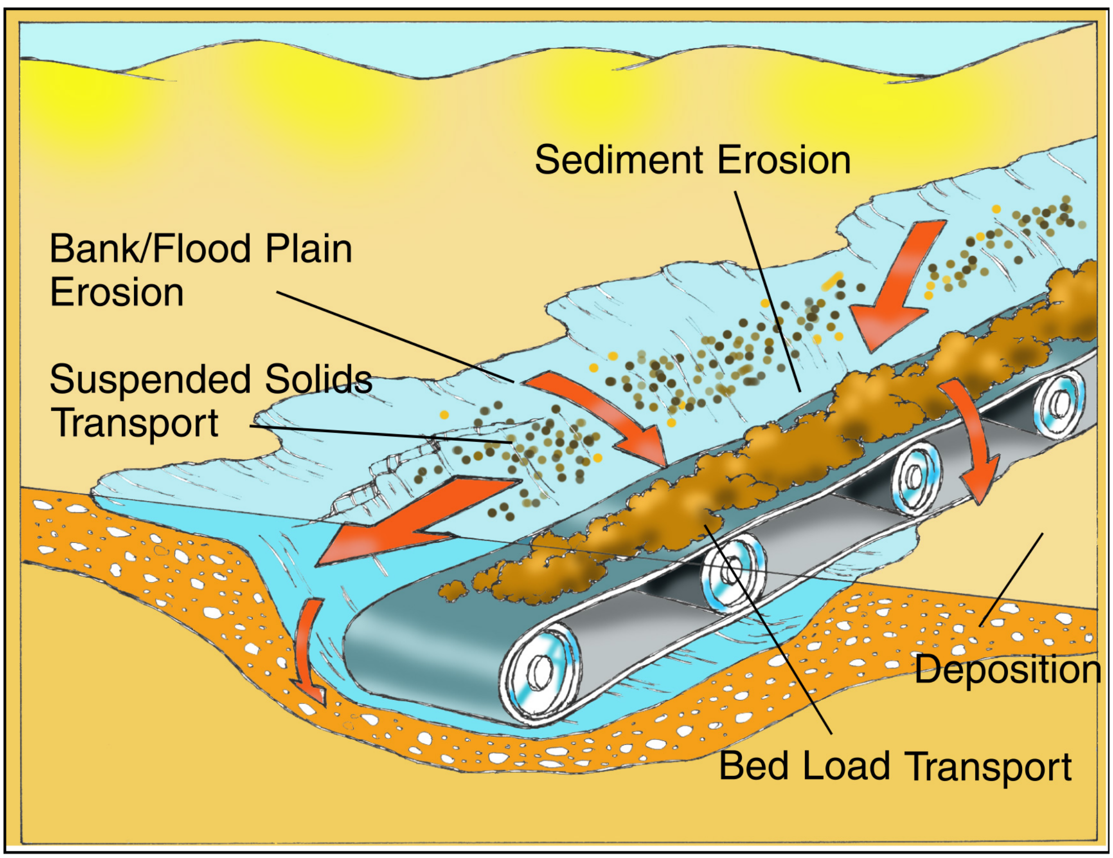


Figure 5-2. Creek/river processes at high flow.

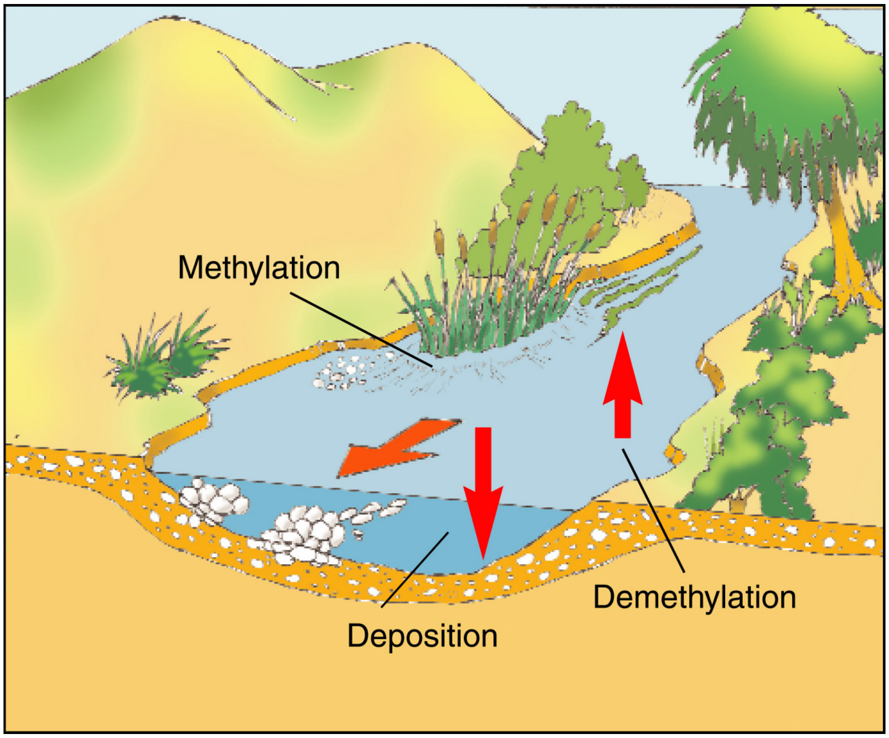


Figure 5-3. Creek/river processes at low flow.

5.2.1 Supply of Hg to the Water Column in Impoundments and Streams

Mercury containing particles may be present in the bottom sediments of impoundments or streams or they may exist in suspension in the water column. Of the chemicals present in these waterbodies, sulfides are most efficient at solubilizing (weathering) mercury associated with particles (crystalline and amorphous HgS, and adsorbed mercury) by forming aqueous mercury sulfide complexes (e.g., HgS^{o}, $Hg(HS)_2^0$ (Paquette and Helz, 1997; Benoit et al., 1999). Evidence also exists that organic ligands can enhance the solubility of solid-phase mercury (e.g., Ravichandran et al., 1998). In addition to solubilization of particulates, dissolved mercury that enters the reservoirs with the wet-season runoff can also be a significant source.

5.2.2 Development of Anoxic Conditions in Deep Waters in Impoundments

During periods of stratification (summers), the lower waters of the reservoirs become depleted of oxygen, and sulfate reducing bacteria (SRB) release sulfides (H_2S, HS^-) into the water as a metabolic by-product (Figure 5-4). Concentrations of sulfides increase in the lower reservoir waters particularly near the sediments. This process also likely occurs in shallower water sediments along the reservoir edges and in streams with abundant aquatic vegetation.

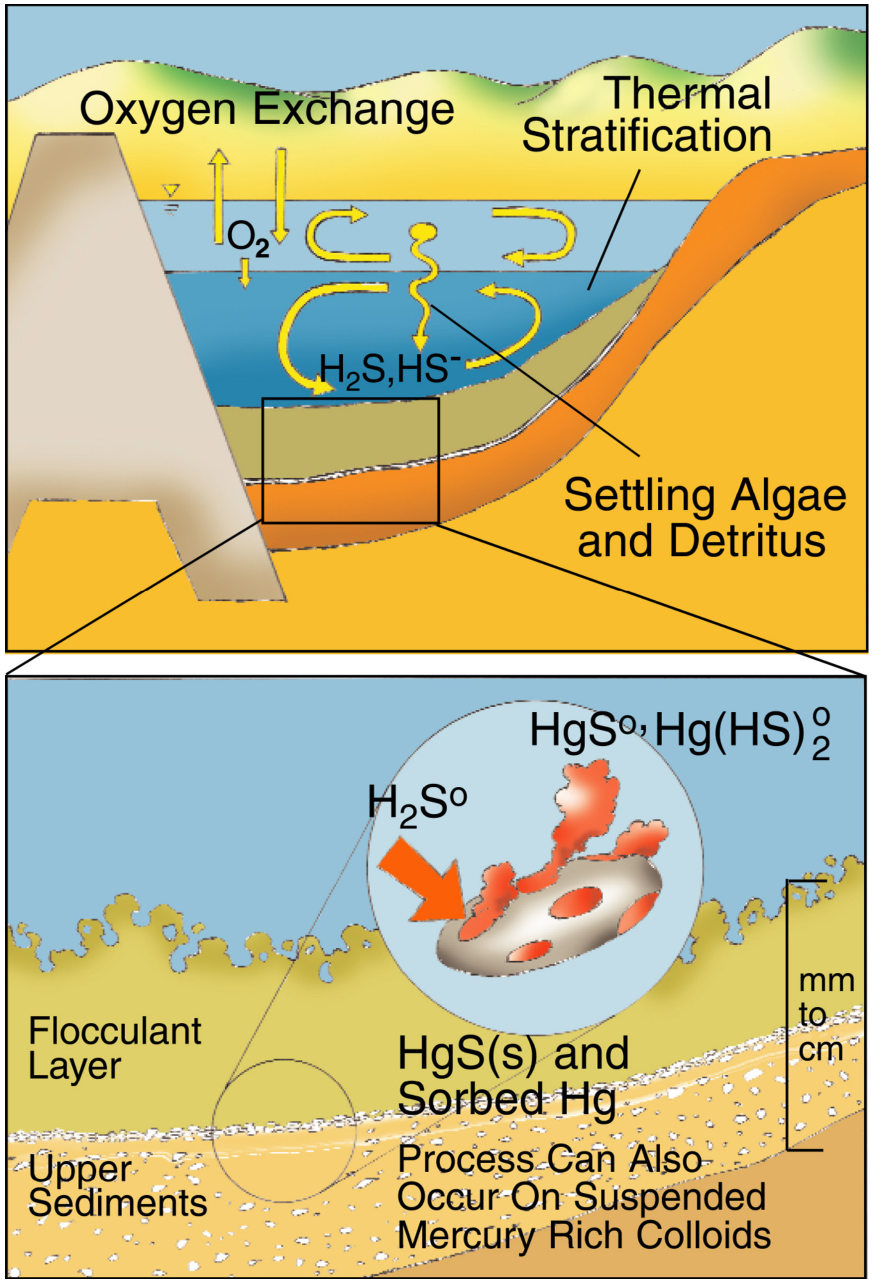


Figure 5-4. A possible pathway for accelerated weathering of mercury solids.

5.2.3 Mercury Methylation

Although all of the processes above are important, by far the greatest research attention has been devoted to the production of methylmercury in the water column and at the sediment-water interface. Methylmercury is a by-product of the activity of sulfate reducing bacteria (Compeau and Bartha, 1985), several different strains of which are found in nature (King et al., 2001). Methylation can occur wherever sulfate reducing bacteria are active, although the hypolimnion and the upper few centimeters of the sediment appear to be the most important zones (e.g., Watras et al., 1995; Gilmour and Riedel, 1995; Bloom et al., 1999; Hines et al., 2000).

For mercury to be methylated, it must first be available in the dissolved form through solubilization from inorganic particles and remineralization from organic particles (Henry et al., 1995, Paquette and Helz, 1997, Benoit et al, 1999). In the water column where sulfate reduction takes place, mercury in the dissolved phase exists primarily as aqueous complexes with ligands such as sulfide and natural organic matter (the solubility of the dissociated Hg^{2+} is negligible compared to the complexed and adsorbed forms). Recent experimental and field studies have led to the hypothesis that the uncharged mercury-sulfide complexes (HgS^0 and $Hg\,(SH)_2{}^0$) are the species most likely to be taken up by bacteria and methylated (Benoit et al., 2001), although the potential uptake of other aqueous complexes of mercury by bacterial cells has also been proposed (e.g., Golding et al.,2002; Kelly et al., 2003). Limited data indicate that there is a range of sulfate concentrations over which methylation is stimulated, and concentrations greater than or less than this range tend to suppress methylation by formation of sulfides (Gilmour et al., 2003).

The sulfate reducing bacteria methylate this mercury in what is generally hypothesized to be a cometabolic (incidental) reaction (Compeau and Bartha, 1985). The accelerated weathering of mercury solids by sulfides and subsequent methylation appears to be a significant means of bringing mercury into solution in these waters. Methylation can occur in the sediment or anywhere in the water column where sulfate reduction occurs and sulfides are thus present (e.g., Henry et al., 1995, Watras et al., 1995). Although bacteria have been extensively documented to methylate mercury, limited early data indicate that abiotic methylation can also be important (Gilmour et al., 2003; Lean and Siciliano, 2003).

In addition to sulfate and sulfide concentrations, the overall behavior of mercury in the water column is also influenced by site-specific conditions including productivity, water temperature, suspended solids, extent of light penetration, pH, alkalinity, dissolved oxygen, dissolved organic carbon, other inorganic anions, and extent of anoxic conditions in the water column or bottom sediments.

5.2.4 Uptake of Methylmercury

The methylmercury produced diffuses from the SRB cells (probably complexed with sulfide) (Figure 5-5). Much of the methylmercury produced is demethylated. However, a portion of the methylmercury enters algal cells at the base of the food chain (Figure 5-6). The methylmercury is thought to enter algal cells, neutrally complexed with small ligands, by passive diffusion. Although some investigators (e.g. Golding et al. 2002) have invoked active transport for uptake, passive diffusion rates appear to be greater than the actual methylation rates, thus indicating passive diffusion as more than adequate and not rate limiting.

5.2.5 Bioconcentration of Mercury

Methylmercury bioconcentrates as it moves up the food chain from algae to zooplankton to prey fish and to predator fish (Figure 5-7). The largest single jump in concentration occurs from the water to algae. Methylmercury's biomagnification is among the largest of all known chemical compounds. Concentrations in fish can be millions of times higher than in water. The large degree of biomagnification is thought to result from methylmercury's strong affinity for thiols (sulfhydryl groups -SH) and sulfide and disulfide linkages ($R-S-R', R-S-S-R'$) associated with proteins in organ and muscle tissue.

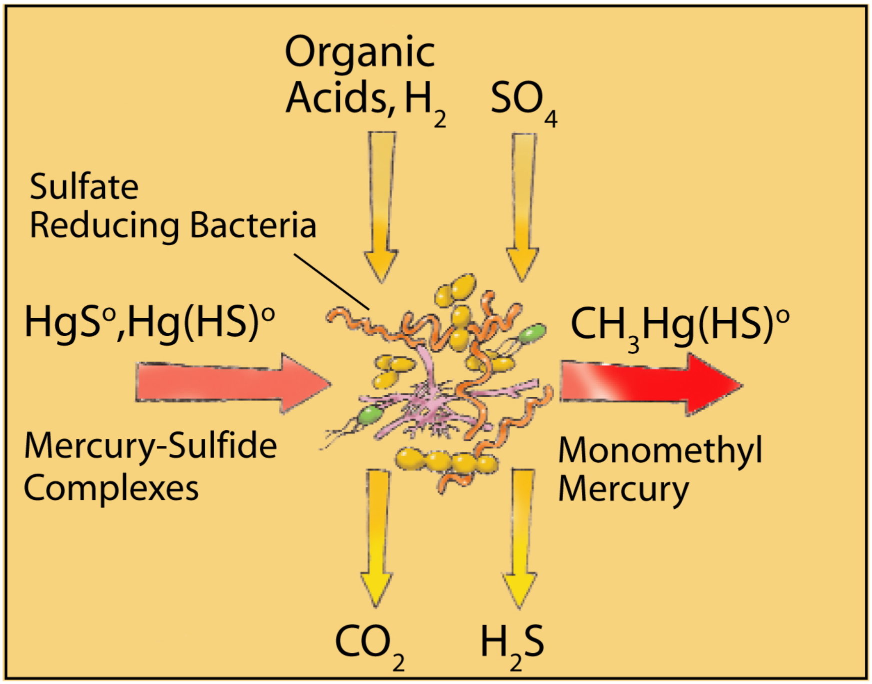


Figure 5-5. Mercury methylation reducing bacteria.

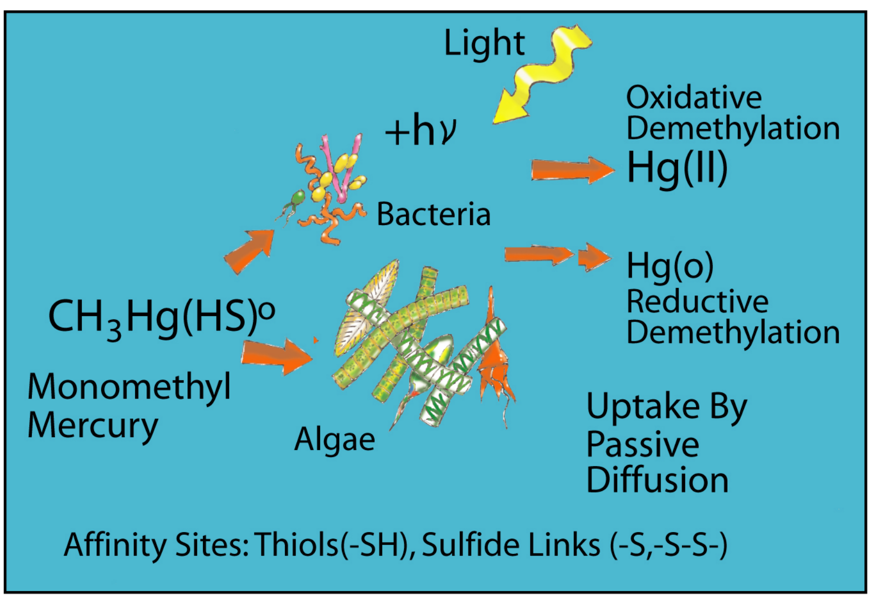


Figure 5-6. Uptake of sulfate-methylmercury

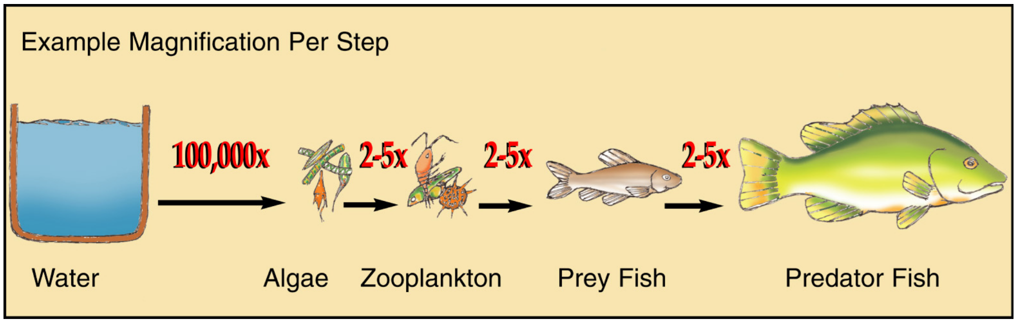


Figure 5-7. Food chain biomagnification of methylmercury.

5.3 Mercury Behavior in Reservoirs: Knowns and Unknowns

Based on data collected during the wet and dry season sampling, a significant advance has been made in understanding mercury biochemical processes in the impoundments in the Guadalupe River Watershed. The discussion that follows considers the new data that were obtained during the wet and dry season sampling conducted as part of the TMDL assessment. The issue of bioaccumulation in fish is discussed under a separate heading (Section 5.6 Bioaccumulation in Fish).

5.3.1 Reservoir Conditions

Reservoirs in the Guadalupe River Watershed are characterized by relatively deep water (50-70 feet), with well-mixed conditions in the wet season and with stratification and low dissolved oxygen in deeper layers in the dry season. Inflows to the reservoirs occur during the wet season (October through May), with large inflows during storm events in the wet season. A few creeks provide minimal flow to the reservoirs during the summer. The outflows during the wet season are a potentially important pathway for removal of inflowing mercury because a large part of it is associated with the particulate phase.

The low dissolved oxygen concentrations in the dry season create conditions that enhance methylmercury production as demonstrated by the sampling results fromAlmaden and Guadalupe Reservoirs. As a result of these conditions and processes, the reservoirs facilitate the production and downstream export of methylmercury, the form that most readily bioaccumulates. Because the reservoir outlets are located near the bottom of the hypolimnion, significant methylmercury concentrations are exported in the dry season to the downstream creeks.

The dry season measurements in the reservoirs in the 2003 and 2004 sampling were designed to capture the differences in mercury methylation with depth. Concentrations were measured in three parts of the reservoirs: 1) near the surface, 2) in the upper portion of the hypolimnion, at a depth of about 10 feet below the thermocline, and 3) the deeper waters of the hypolimnion. The measurements that represent the deeper portion of the hypolimnion were collected at the reservoir outlets. The average total mercury and methylmercury concentrations from these three parts of the reservoirs and the downstream creeks are shown schematically in Figure 5-8. This graphic clearly shows the decrease in methylmercury concentrations with distance downstream during the summer. The methylmercury that forms in the reservoirs is (1) taken up by algae and is transferred to higher trophic levels through the food chain, (2) transported downstream, or (3) gradually demethylated and possibly volatilized via biotic and abiotic pathways.

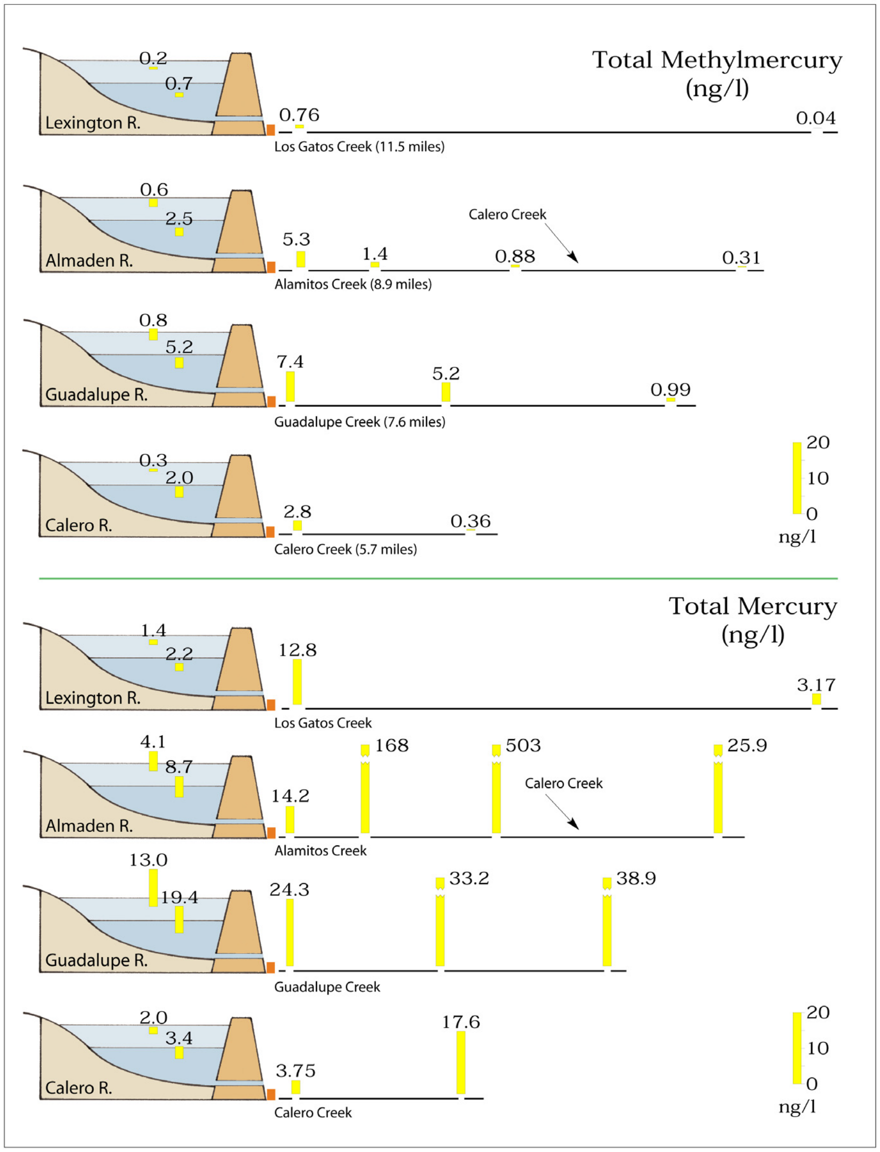


Figure 5-8. Average concentrations of total mercury and methylmercury in the central part of the four reservoir systems in the dry season (Data for the downstream creeks are from July 2003.)

5.3.2 Results of Hypothesis Testing: (Reservoirs)

Methylmercury production in the reservoirs has been shown to be significant. It is therefore important to identify the source for methylmercury production, the primary locations of methylmercury production, and the fate of methylmercury produced in the reservoirs. This information will be critical to establishing the ability to control and predict the changes in reservoir methylmercury concentrations. It was with this goal in mind that the following three hypotheses were developed to guide the data collection efforts.

Reservoir Hypothesis 1

Reduction of total sediment mercury will cause a proportional decline in aqueous methylmercury concentrations.

Discussion – Reservoir Hypothesis 1

A possible source for mercury in the water column of the reservoirs in the dry season, when most of the methylation takes place, and when there are minimal surface-water inflows, is through solubilization and/or suspension of sediments. Mercury that has been solubilized may be methylated. In addition, the upper sediment layer may be a source of methylmercury production. For these reasons, it may be hypothesized that reduction of total sediment mercury may lead to a reduction of methylmercury production.

It is possible that the dissolution of sediment mercury and the methylation of dissolved mercury are both described by plateau-type relationships, such as shown in Figure 5-9. There may be a range of concentrations over which sediment mercury and water column methylmercury are proportional, and a range of concentrations where the methylmercury concentrations are unrelated to the sediment concentrations. This may be a result of a limitation, as yet unknown, in the dissolution or methylation of mercury. The initial conditions, i.e., whether we are at location A or B or C in Figure 5-9, may determine the effect of changing sediment mercury on water column methylmercury concentrations. A similar relationship was found by Krabbenhoft et al. (1999).

An alternative hypothesis is that dissolved mercury in the water column, irrespective of source, is the primary source of mercury being methylated. Then changing sediment concentrations would have little effect on methylmercury production. The water-column concentration of mercury may be more important than the sediment-mercury concentration in the event that newly supplied mercury, in runoff and deposition, is more bioavailable than sediment mercury. There is some evidence in the literature that "new" mercury is more bioavailable than "old" mercury (Gilmour et al., 2003). "New" mercury in the context of the reservoirs is dissolved mercury from atmospheric deposition and wet season runoff; "old" mercury is in the sediments, primarily in the bottom of the reservoirs. While both the dissolved mercury inputs to the reservoirs and the solubilization of sediment mercury are quantitatively important, the higher methylmercury concentrations in the water column of Almaden and Guadalupe Reservoirs, compared to Calero and Lexington Reservoirs, suggest that mercury in the sediment plays an important role.

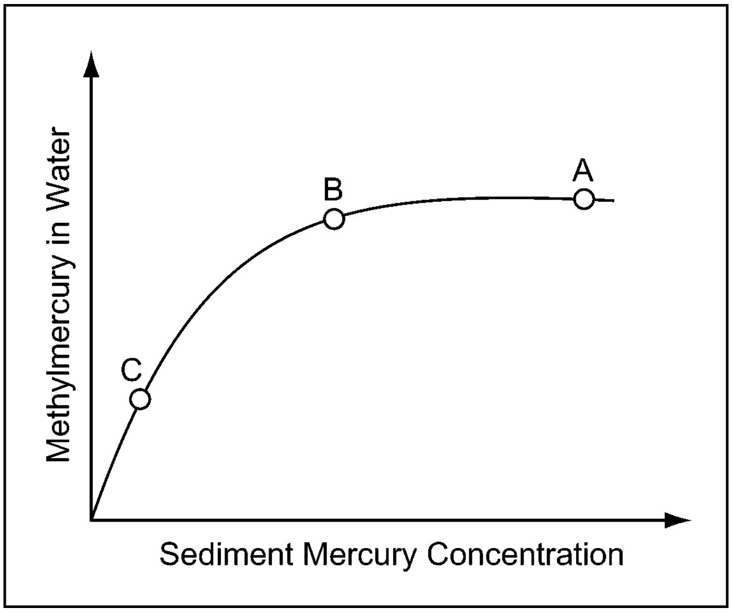


Figure 5-9. Hypothesized relationship between sediment mercury and methylmercury concentrations in water

Additional total mercury data in reservoir sediment were collected in March 2005 for the TMDL in three reservoirs (Lexington, Guadalupe, and Calero) (Tetra Tech, 2005b). The total mercury concentrations in sediment from Guadalupe Reservoir were higher than in sediment from Lexington and Calero Reservoirs (Table 5-1).

Table 5-1.
Statistical Summary of Total Mercury, mg/kg in Reservoir Sediment Samples from March 2005

Reservoir	Number of Samples	Median	Mean	Minimum	Maximum
Guadalupe	16	2.82 (2.95)*	3.32	0.42	7.29 (337.9)*
Calero	18	0.39	0.42	0.10	0.84
Lexington	20	0.10	0.11	0.07	0.18

*One nearshore sediment sample of sand and grit near former mine not included in statistics

The above sediment data provide support to a connection between methylmercury concentrations in water and sediment in that Guadalupe Reservoir had higher aqueous methylmercury concentrations than either of the other two reservoirs. Methylmercury concentrations ranged from 0.20 to 0.76 ng/L in Lexington, 0.23 to 2.77 ng/L in Calero, and 1.05 to 12.8 ng/L in Guadalupe in 2003 and 2004 (Tetra Tech, 2005a).

Conclusion – Reservoir Hypothesis 1

This hypothesis is indirectly confirmed. If methylmercury was formed primarily from the “new mercury”, then the methylmercury concentrations would be greater in the reservoir with the greatest load of background mercury (atmospheric deposition and runoff from non-mine influenced areas). As presented in Section 4.0, the largest background load is to Lexington Reservoir. However, as shown in Table 3-9, methylmercury concentrations in the water column were higher in Almaden and Guadalupe Reservoirs, which are strongly influenced by mining, than in the other reservoirs (Lexington and Calero). In addition, largemouth bass from Lexington Reservoir had lower mercury concentrations than from Guadalupe Reservoir (see Table 3-6 and 3-7). Additional comparisons of fish between reservoirs are presented in Section 3.4.

The recent sediment data from three reservoirs support the hypothesis that total mercury in sediment is related to aqueous methylmercury concentrations, and hence fish mercury concentrations. More detailed sediment mercury data from reservoirs are needed with co-located methylmercury measurements to better understand the linkage.

Reservoir Hypothesis 2

Methylmercury accumulated and/or produced in the epilimnetic zone of the reservoirs during the summer stratification period is significant and makes an important contribution of mercury to the food chain.

Results – Reservoir Hypothesis 2

The dry season sampling in Almaden and Guadalupe Reservoirs in 2004 showed that methylmercury concentrations were greatest in the deep hypolimnion, as represented by the reservoir outlets (2.9 ng/L to 7.2 ng/L in Almaden and 0.8 ng/L to 12.8 ng/L in Guadalupe). Methylmercury concentrations increased over the summer as the reservoir stratified and became anoxic below the thermocline (see Figure 3-20). The increase in methylmercury occurred below the oxycline where the dissolved oxygen decreased to below 2 mg/L. Epilimnion methylmercury concentrations varied over a narrow range in the middle portion of the reservoirs. Previous sampling at a depth of 10 feet in shallow, near-shore zones in July 2003 showed relatively high methylmercury concentrations (2.1 ng/L to 3.0 ng/L), indicating that some methylation may be occurring in vegetated zones. The net mass of methylmercury produced in the epilimnion was one-tenth to one-fourteenth of the net mass produced in the hypolimnion, based on the dry season reservoir mercury load estimates discussed in Section 4. Hence, the epilimnion plays a small role in net methylmercury supply in the reservoirs. Nonetheless, the methylmercury in the epilimnion is important to the trophic transfer of mercury to biota.

Conclusion - Reservoir Hypothesis 2

The original hypothesis was partly disproved, in that more of the methylmercury is produced in the hypolimnion. This finding confirms the seasonal nature of mercury loading: the major concern in the wet season is transport of inorganic mercury and the major concern in the dry season is net methylmercury production and bioaccumulation. With respect to the latter concern, methylmercury production in the epilimnion is important in the nearshore zone where juvenile fish species may live.

Reservoir Hypothesis 3

A significant quantity of the methylmercury produced in the reservoirs during the warm season may be transported to creeks downstream.

Results - Reservoir Hypothesis 3

Methylmercury is produced most rapidly during the warm season (July, August, and September) after the deep hypolimnion has become anoxic. Outflows from the reservoirs during this period have high methylmercury concentrations (see Figure 3-20). Based on the load estimates discussed in Section 4, the downstream exports of methylmercury for both reservoirs were greater than the methylmercury that is accumulated in the hypolimnion in the dry season. After the warm months, the reservoirs become well mixed during fall turnover and methylmercury concentrations decrease.

Conclusion - Reservoir Hypothesis 3

This hypothesis was confirmed: a significant quantity of the methylmercury produced in the reservoirs during the warm season is transported to the downstream creeks. As shown in Table 4-6, the quantity of methylmercury exported from Almaden Reservoir was 7.2 g in the dry season, compared to 0.8 g in the wet season. A similar comparison was made for the Guadalupe Reservoir, which exported 5.0 g in the dry season and 1.4 g in the wet season.

5.4 MERCURY BEHAVIOR IN CREEKS: KNOWNS AND UNKNOWNS

Creeks that flow into the reservoirs are characterized by steep energy gradients and highly variable or intermittent flows. Creeks immediately downstream of the four major reservoirs exhibit lower variability in the flow, especially in summer when reservoir discharges form a major portion of the total flow. Most of the water, and by association, sediment transported by creeks occurs during the wet season (generally November through April). Mercury is strongly associated with particles, and total mercury loads transported by creeks are closely correlated with sediment transport. The role of sediment transport is important in all watersheds, but is particularly important in basins such as the Guadalupe River that have mine wastes and naturally high mercury deposits. High flow events can cause erosion of stream banks and scouring of sediment. Because sediment transport is seasonal, so too are mercury loads delivered to waterbodies. For adequate quantification of loads, there needs to be a relatively high frequency of measurement of mercury and suspended solids concentrations in streams under different flow regimes.

Mercury is transported by streams in particulate and dissolved forms. During the transport, some of the mercury is removed by settling of particles, some of the inorganic mercury is methylated, and methylmercury present in the flowing water may be lost through removal mechanisms, including biological uptake, photocatalyzation, and biotic demethylation. Mercury methylation processes in the wet season are less significant due to the higher flows and lower temperatures. The rates and mechanisms of these processes are not well known in the Guadalupe River Watershed.

The data show that the behavior of creeks in the wet season is very different from that in the dry season. In the wet season, creeks and the river act as transporters of sediment-bound and dissolved mercury. Due to the higher suspended sediment load, the total mercury concentrations are higher on days with large flows, particularly in the main stem of the Guadalupe River. The total mercury concentrations were higher in the creeks influenced by mining than the urban creeks. In the wet season, the highest methylmercury concentrations were measured on the main stem just above the Alamitos drop structure, then decreased with distance downstream. In the dry season, both unfiltered and filtered methylmercury concentrations in the creeks from the reservoirs decrease with distance downstream from the reservoirs, as shown in Figure 5-10 for filtered methylmercury.

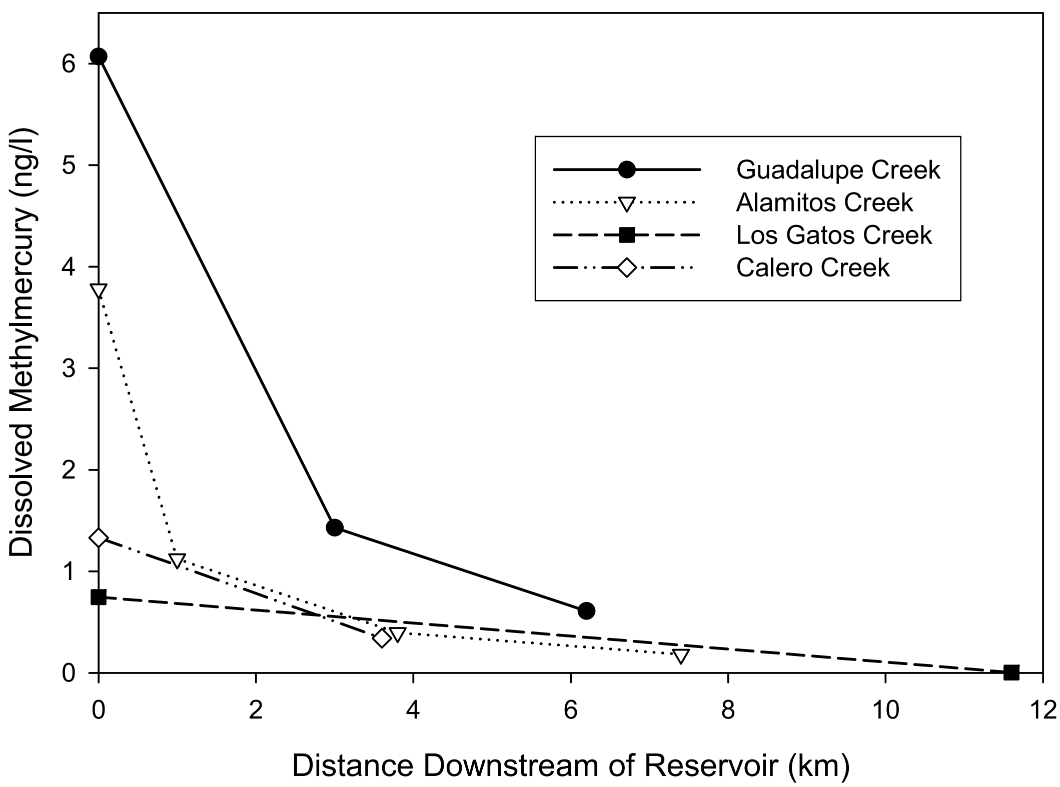


Figure 5-10. Dissolved methylmercury in creeks downstream of the reservoirs, July 2003

5.4.1 RESULTS OF HYPOTHESIS TESTING: CREEKS

Creek Hypothesis 1

Most of the mercury is transported in the wet season.

During the wet season, mercury-containing runoff from mine-waste and mercury-bearing soils enters the creeks in the upper watershed, many of which have flow only during the wet season. For example, Deep Gulch, Jacques Gulch, N. Los Captiancillos, and the eastern tributaries to Randol Creek near the edge of the AQC Park had no flow when visited in July 2003. In the winter, total mercury concentrations in the intermittent creeks in the AQC Park increase when rainfall amounts over an inch extend for 2 or more days, and generate runoff with high suspended solids concentrations (see Section 2.1.7 of this report). Mercury is transported largely in particulate form, so individual storms that produce high suspended solids can be responsible for transporting a large fraction of the annual load. The peak flows in the creeks below the reservoirs can be large (over 1,000 cfs), accompanied by high sediment concentrations and high total mercury concentrations. The flows during the dry season are controlled by the reservoir outflows, which are typically small (less than 10 cfs). Part of the sediment-bound mercury transported by Alamitos Creeks is deposited in Almaden Lake and part transported by both Alamitos and Guadalupe Creeks is deposited behind the Alamitos drop structure. Some of this material can be transported across the drop structure during large storms when the flashboards are not in place.

Wet and dry season total mercury loads were computed for two reservoir outlets, Almaden and Guadalupe. As seen in Table 4-6, the export of total mercury from Almaden Reservoir was 13 times greater in the wet season than the dry season, and four times greater in the wet season from Guadalupe Reservoir.

The relationship between total mercury and flow was best seen in the urban creeks for a low flow and high flow day (Table 5-2). Both total and methylmercury concentrations were greater for the higher flows.

Table 5-2.
Comparison of Wet Season Sampling Results for Urban Creeks

Creek		Flow, cfs	TSS, mg/L	Total Mercury, ng/L	Methylmercury, ng/L
Canoas Creek	Low	0.7	2.7	4.1	0.004
	High	7.4	12.0	12.3	0.18
Los Gatos Creek	Low	2.7	2.5	2.0	0.02
	High	18.1	49.3	21.8	0.16
Ross Creek	Low	1.2	4.0	5.3	0.06
	High	12.5	24.5	18.5	0.23

Creek Hypothesis 2

Methylmercury discharged from reservoirs is significantly removed or demethylated in the creeks.

Results - Creek Hypothesis 2

Synoptic survey data (Tetra Tech, 2003d) show that methylmercury concentrations decrease with travel downstream in Guadalupe, Almaden, Calero, and Los Gatos Creeks in the dry season (see Figure 5-10). The loss of methylmercury along the creeks downstream of the reservoirs is greatest in the summer when biological activity is greater and photodemethylation can occur. In the April 2004 data,there were places where methylmercury increased at a particular location such as below Masson Dam on Guadalupe Creek, near Harry Road on Alamitos Creek, and below Vasona Reservoir on Los Gatos Creek (see Figure 3-7). While local production of methylmercury can occur in small impoundments such as the ponded reach above

Masson Dam on Guadalupe Creek and possibly Almaden Lake, the primary source of methylmercury to the creeks is from the reservoirs in the warm season

Conclusion - Creek Hypothesis 2

This hypothesis was confirmed: *Methylmercury discharged from reservoirs is significantly removed or demethylated in the creeks. Local methylmercury production in the creeks in the summer was not evaluated in detail.*

5.5 MERCURY BEHAVIOR IN GUADALUPE RIVER: KNOWNS AND UNKNOWNS

Flow in the Guadalupe River is greater than in the upstream creeks in the watershed, and has a large range in the wet season. A portion of the river is channelized where the river flows through urbanized areas, and the lowermost portion of the river is tidally influenced. The slope is much lower than in the upper reaches of the watershed, resulting in some reaches with sediment deposition. Flows are variable, and mercury transport, as in the creeks, occurs predominantly in the particulate phase during high flows.

5.5.1 DATA SPECIFIC TO GUADALUPE RIVER

The 2004 wet season sampling of the Guadalupe River at the Highway 101 gauge showed the highest total mercury (363.9 ng/L) on the day with the highest flow (807 cfs) and the lowest total mercury (14.5 ng/L) on the day with the lowest flow (29 cfs). The total mercury at Highway 237 ranged from 32.8 ng/L to 182.5 ng/L. The range of total mercury in the urban creeks before the confluence with the river was considerably less: 2.0 to 21.8 ng/L in Los Gatos Creek, 5.3 to 18.5 ng/L in Ross Creek, and 4.1 ng/L to 12.3 ng/L in Canoas Creek. The contribution from the mining-influenced creeks, Alamitos and Guadalupe Creeks, was higher (65.8 ng/L to 464.6 ng/L) as measured below the Alamitos Drop structure. The total mercury above the drop structure was less, indicating the contribution from built-up sediment that flows over the structure in large storms such as occurred prior to the sampling event, as documented in late January 2004 in the Data Collection Report (Tetra Tech, 2005a). The range before the impoundment section above the drop structure was 13.8 ng/L to 32.8 ng/L for Guadalupe Creek and 39.3 to 86.5 ng/L for Alamitos Creek when lower flows were sampled.

Methylmercury concentrations were higher in the Guadalupe River main stem than the urban creeks: 0.02 to 0.16 ng/L in Los Gatos Creek, 0.06 to 0.36 ng/L in Ross Creek, and 0.004 ng/L to 0.18 ng/L in Canoas Creek. The highest methylmercury concentration of the wet season samples was 0.9 ng/L above the Alamitos drop structure, while the second highest concentration (0.75 ng/L) was from Highway 101 on the high flow day. At Highway 237, methylmercury concentrations ranged from 0.29 ng/L to 0.51 ng/L.

5.5.2 Current Understanding of Mercury Behavior in Guadalupe River Pertinent to TMDL

The behavior of total mercury in Guadalupe River can be conceptualized in two ways: (1) as a receiver of mercury and conveyor of mercury from the upper reaches, with some attenuation and transformation, and/or (2) as having an independent source of mercury because of mine-waste deposits in its sediments and banks. If the first conceptualization is appropriate, then along the Guadalupe River total mercury and methylmercury can be expected to decrease with travel distance in the dry season. Transport of sediment-associated mercury would occur during high flows in the wet season. If the second conceptualization is appropriate, however, then mercury processes in the upper watershed, are isolated by reservoirs and Almaden Lake, and have minimal influence on mercury in the river; what dictates concentrations and downstream transport in the river is the mercury in the stream banks, a result of prior transport.

The new data suggest that actual mercury behavior is best described by a combination of the two conceptualizations. Because sediment and high flows can be transported over the Alamitos drop structure, the river is not isolated from the influence of Guadalupe and Alamitos Creeks. The effects from the creeks above the reservoirs are reduced by loss of methylmercury and sediment deposition. However, there is a source of mercury in the river bank and bottom sediments due to past transport of mine wastes and contaminated sediment. For example, while sediment mercury concentrations decrease downstream along the main stem, because the sediment is finer-grained, it is more easily resuspended. The stream banks had higher mercury concentrations than the bottom samples at a given location, illustrating the importance of reducing bank erosion.

5.5.3 Results of Hypothesis Testing: Guadalupe River

River Hypothesis 1

The Guadalupe River bank and bottom sediments are a significant source of mercury during the wet season.

Results – River Hypothesis 1

With respect to the main stem of the Guadalupe River, resuspension of bottom sediment and erosion of banks is one source of mercury that contributes to the high suspended solids concentrations at high flows, and hence mercury load. The floodplain sediments within the levees may also contribute mercury, but those materials were not sampled for this TMDL. The measured sediment concentrations decreased from the start of the Guadalupe River, at the confluence of Alamitos and Guadalupe Creeks, downstream to Highway 101 and then decreased further at Highway 237 (see Figure 3-17). However, the total mercury loads discharged from the river, estimated using data from the USGS gauge near Highway 101, are greater than the total loads entering from the tributary creeks (see Figure 4-2). This is a strong indication of either the mobilization of internal sediment loads or external loads that are unaccounted for in this reach.

There are other possible sources for the additional mercury load: uncertainties in the loads from Almaden and Guadalupe Creeks, increased urban area load from the downtown area, and stormdrains. The urban creeks contribute about 4 to 30 percent of the flow to the river; storm drains that flow directly into the river can be a significant part of the flow, as seen in Figure 5-11 (represented by the "other" category), and have not been quantified separately. Sediment-mercury concentrations from storm drains in the Guadalupe River Watershed were 0.08 mg/kg to 3.4 mg/kg as total mercury (Kinnetics, 2002), which is greater than the urban creeks (0.04 mg/kg to 0.11 mg/kg) (see Figure 3-17). Sediment samples from the urban creeks were collected in the Synoptic Survey (Tetra Tech, 2003d).

Conclusion – River Hypothesis 1

There are insufficient data to resolve this hypothesis: *The Guadalupe River bank and bottom sediments are a significant source of mercury during the wet season.* However, high flow events are likely to cause erosion of the banks.

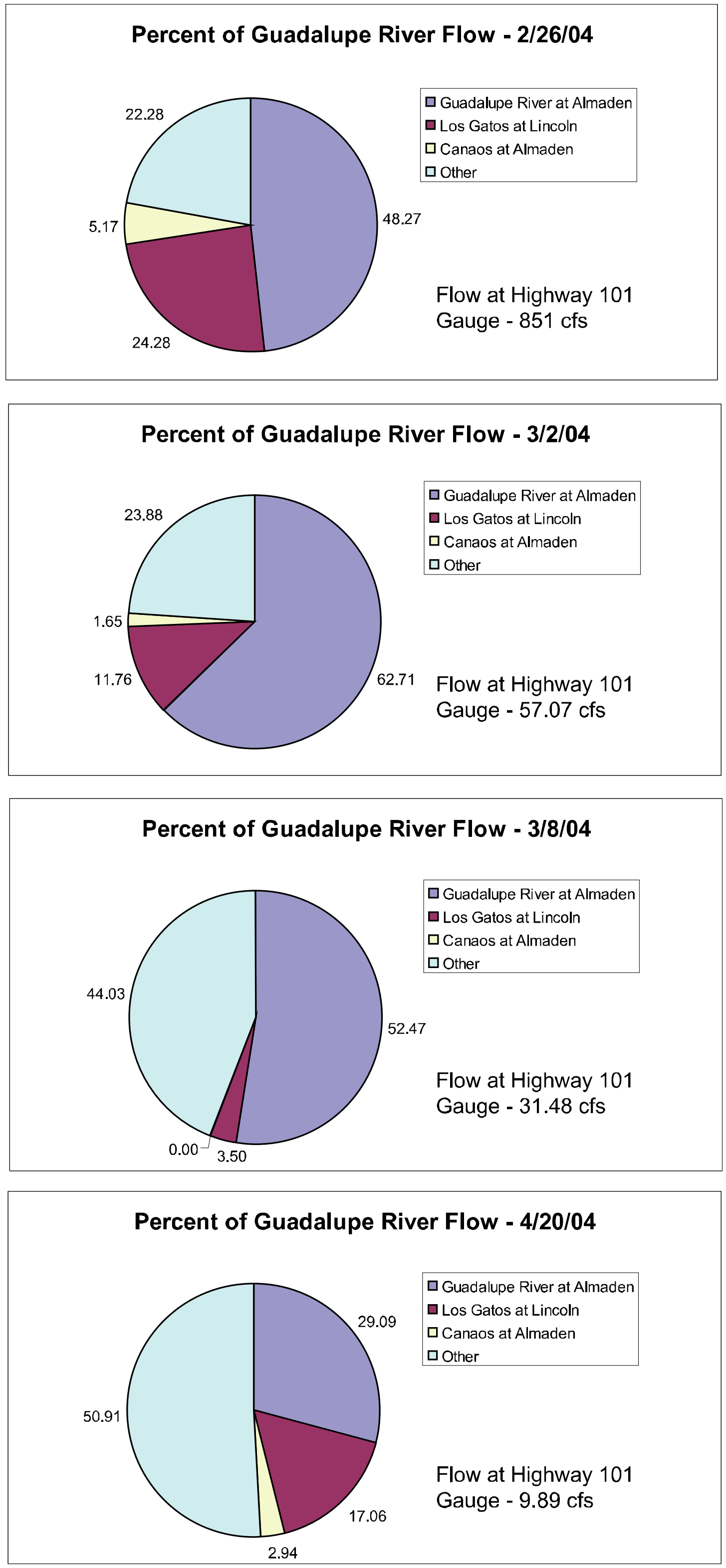
Additional data are needed to refine the sources of mercury to the river. Stormdrain sampling of total, particulate, and dissolved mercury and stormdrain sediment during high flow runoff events would be helpful for several large drains to the lower river. Both the mouths of Guadalupe and Alamitos Creeks and the main stem of the river should be sampled at the same time. Better quantification of mercury loads from Alamitos and Guadalupe Creeks to the river would help resolve the hypothesis. The new mercury load estimated should use data from flow and turbidity gauges at the mouths of both Alamitos and Guadalupe Creeks, in addition to mercury sampling results for total, particulate, and dissolved mercury for a range of flows. Several high flow events need to be sampled. Flow gauges have recently been installed at Graystone Lane on Alamitos Creek and on Guadalupe Creek on Hicks Road, not near the mouth of the creek. These data will still be useful in resolving this hypothesis.

River Hypothesis 2

Under present conditions, mercury-laden sediment is not transported from the upper watershed to the River.

Results – River Hypothesis 2

Prior to 1935 when Almaden and Guadalupe Reservoirs were constructed, mine wastes were discharged to the creeks where winter storms would transport the materials downstream. The new reservoirs retained mine wastes from those creeks that discharged into them, instead of those wastes being transported downstream to Alamitos and Guadalupe Creeks. (Note, however, that some creeks that drain the NAMD discharge directly into either Alamitos and Guadalupe Creeks.) Another impoundment, Almaden Lake, was developed from a former gravel quarry in Alamitos Creek that began in the 1940s and expanded outward. Almaden Lake Park was opened in 1982 (City of San Jose, 2004). Off-stream percolation ponds were constructed near the confluence of Alamitos and Guadalupe Creek in 1976. (Older percolation ponds had been built in 1932 and were modified in 1963.) The Alamitos



Flows used are average daily flows

Figure 5-11. Percent of Flow Contributed by Urban Creeks to Guadalupe River at Highway 101 Gauge (Ross Creek is above the gauge of the river at Almaden Expressway as are Guadalupe and Alamitos Creeks; Ross Creek flows ranged from 0.3 to 12.5 cfs.)

Drop Structure was built to impound water to fill the expanded percolation ponds. A fish ladder at the Alamitos Drop Structure was added in 1999. Flows greater than 57 cfs will overtop this Drop Structure. Flashboards are added after the winter storms to allow more water to be impounded over the summer. Sediment builds up behind the Drop Structure and the flashboards. Past practice was not to remove this sediment, so in large flow events, some sediment could be transported over the drop structure.

In addition, gravel bars have developed at the mouths of both Alamitos and Guadalupe Creeks. Total mercury in these materials ranged from 16.45 mg/kg to 18.78 mg/kg (Tetra Tech, 2005a). Thus, some of the sediment mercury from the upper watershed is retained in impoundments, including Almaden Lake and the impounded reach above the Alamitos Drop Structure. In addition, the tributaries draining the NAMD below the reservoirs have multiple drop structures that retain sediment. Sediment is periodically removed from some of these structures as part of the District’s stream maintenance activities (see Table 2-1). Guadalupe Creek has a small impounded reach behind Masson Dam built in 1962-64, also used to impound water for diversion to off-stream percolation ponds. A fish ladder was added to this dam in 1999. Sediment deposition does occur behind this dam.

While the above structures retain some coarse sediment, suspended solids and thus particulate mercury, can be transported downstream of these structures. Particulate mercury concentrations decrease from the upper watershed in the NAMD to the river below the Alamitos Drop Structure, as shown in Figure 3-14. The concentrations of particulate mercury from the urban creeks are much lower than those in the upper watershed. The particulate mercury concentrations in the Guadalupe River decrease from the confluence with Canoas Creek to Highway 237.

Conclusion - River Hypothesis 2

The behavior of sediment in the Guadalupe River watershed is complicated by the many modifications to the waterbodies that have been made since the 1930’s. The hypothesis testing was inconclusive. Some sediment is retained by the various structures and impoundments along Alamitos and Guadalupe Creeks and the tributaries draining the NAMD below the reservoirs. However, large storm events can cause sediment to overtop the structures such as seen in photographs at the Alamitos Drop Structure taken on January 27, 2004 (Tetra Tech, 2005a). Further reduction in the mercury load transported could be obtained by removing built-up sediment behind the Alamitos Drop Structure prior to the wet season.

Particulate mercury can be transported over the drop structures in large storms, such as sampled in February 2004. A better understanding of particulate mercury transport from the upper watershed to the river is needed. Synoptic sampling during several large storm events would be helpful of the reservoir outlets; creeks draining the NAMD, both near the AQC Park boundary and at their confluence with Alamitos Creek; and up and downstream of Almaden Lake and the Alamitos Drop Structure on Alamitos Creek; and on Guadalupe Creek up and downstream of Masson Dam and at its mouth. Flows and total suspended solids need to be measured at the same time as the samples are collected.

Sufficient data to compute suspended sediment loads to the Guadalupe River from the various creeks are not available. Thus, it is not possible to compare the load from Alamitos and Guadalupe Creeks to the urban creeks, or to internally-generated sediment from erosion and resuspension in the river itself, or to urban runoff and the stormdrains.

River Hypothesis 3

Guadalupe River is a net sink for methylmercury.

Results – River Hypothesis 3

The Guadalupe River was not sampled for methylmercury in the summer. Thus, data are not available to fully evaluate this hypothesis. Data from the wet season showed that more methylmercury was transported out of the Guadalupe River to the Bay than the total loads entering from all the tributary creeks and the reservoirs (see Figure 4-4). While there are several possible reasons for this, the data suggest that resuspension of methylmercury in bottom sediments and sediment transported over the Alamitos Drop Structure may be important sources. However, no wet season samples were collected from stormdrains, which discharge urban runoff to the River.

Although some methylation of mercury may occur, on a net basis, more methylmercury is lost from the creeks of the Guadalupe Watershed in the dry season through demethylation, adsorption and sedimentation, or volatilization, than is generated within them as shown by the data from the Synoptic Survey, which were plotted in Figure 5-10.

Conclusion – River Hypothesis 3

This hypothesis was not confirmed, because no methylmercury data were collected in the dry season for the Guadalupe River. Slightly more methylmercury was exported from the River to the Bay in the wet season than entered from the tributary creeks and estimated background load (see Figure 4-2). Additional data and information would be needed to evaluate this hypothesis such as a survey of possible methylation sites such as deep pools with anoxic zones or riparian wetland zones. The rate of losses may be quite different in the river reaches than the small creeks due to variations in water quality conditions between creeks with low suspended solids and a large river with higher suspended solids, which could result in less photodemethylation.

5.6 MERCURY BIOACCUMULATION IN FISH

The listing of waterbodies within the Guadalupe River watershed as impaired was based, in part, on the Office of Environmental Health Hazard Assessment (OEHHA) posting a public health advisory for Guadalupe Reservoir, Calero Reservoir, Almaden Reservoir, Guadalupe River, Guadalupe Creek, Alamitos Creek, and the associated percolation ponds along the river and creeks (OEHHA, 2003). The OEHHA advisory states that, "because of elevated mercury levels in fish, no one should consume any fish taken from these locations."

The importance of fish mercury concentrations in the impairment decision, and the fact that the ambient water quality criterion for methylmercury is expressed in terms of fish tissue concentrations [0.3 mg/kg (ppm), U.S. EPA, 2001], make tissue concentration a strong candidate for a numeric target for use in the Guadalupe Watershed TMDL. The key questions that must be addressed are:

- What is the relationship between fish tissue concentration and mercury concentrations in the water, and mercury loading to the waterbodies?
- Can a quantitative relationship be developed between fish tissue concentrations and mercury load reductions that would serve as a basis for the TMDL linkage analysis, i.e., determining what specific actions will result in achievement of the relevant water quality standards.

5.6.1 MERCURY BIOCONCENTRATION AND BIOACCUMULATION IN FISH

Methymercury typically constitutes a very small fraction of the total mercury in aquatic ecosystems (typically < 1% in sediments and the water column), but it is the critical form or species of mercury that is incorporated into and magnified in the food chain. In fact, in fish, methymercury accounts for about 95 percent of the total mercury in the muscle tissue (Grieb et al., 1990; Bloom, 1992). The assimilated mercury is distributed throughout the tissues and organs of the fish, but a large portion of the methymercury eventually relocates to skeletal muscle where it becomes bound to sulfhydryl groups and sulfide and disulfide linkages associated with the muscle protein (Harris et al, 2003).

A simplified representation of bioconcentration and biomagnification of methymercury in the aquatic environment is shown in Figure 5-7. Initially, mercury is bioconcentrated from water into planktonic algae cells. Bioconcentration is quantitatively defined as the log of the ratio of the concentration of mercury in the algal biomass to that in the water:

$$BCF_{plankton} = \log(C_{plankton}/C_w)$$

where $BCF_{plankton}$ is the bioconcentration factor for phytoplankton, and $C_{plankton}$ and C_w are Hg concentrations in phytoplankton and water.

The bioconcentration factor for mercury in phytoplankton can be on the order of 5 to 5.5. That is, phytoplankton concentrations are about 100,000 to 300,000 times water concentrations (Lindqvist et al., 1991; Watras and Bloom, 1992; Mason et al., 1996). It has also been shown that the uptake of mercury by phytoplankton is rapid (Mason et al, 1996; Herrin et al, 1998), although the mechanism of uptake and transport of methylmercury across the cell membrane (active transport vs diffusion) is not completely understood (Mason et al., 1996; Moye, et al, 2002).

The corresponding bioaccumulation factors between phytoplankton and zooplankton or benthos and fish are small relative to the large increase in methylmercury concentrations between the water and plankton. As a rule of thumb, the bioconcentration values for methymercury increase by about 0.5 log units (a factor of three times) per trophic level after the initial uptake by phytoplankton. The concentration of methymercury in predatory fish tissue can be more than 3 million times the concentration in water.

Dietary uptake is the dominant pathway for methymercury accumulation in fish. Fish have been estimated to assimilate between 65 to 80 percent of the methymercury present in their food (Wiener et al., 2002). Not only is mercury readily assimilated, it is only slowly eliminated. This results in increasing methylmercury in fish as a function of age, size, and trophic level (Gray, 2002).

Figure 5-12 shows a bioaccumulation model for the trout food wed in New Zealand lakes (Kim and Burggraaf, 1999). Although the bioaccumulation factors for methylmercury between water and zooplankton ($10^{4.72}$) is less than reported for other systems, the overall pattern of increasing methylmercury concentrations for each trophic level, and the bioaccumulation factor between water and the top predator ($10^{6.4}$, a factor of > 2,500,000) are consistent with values reported elsewhere and values that have been measured in the Guadalupe River Watershed.

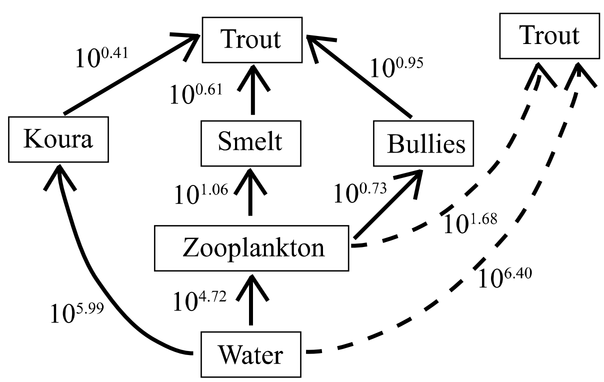


Figure 5-12. Bioaccumulation model for the trout food web in New Zealand Lakes (after Kim and Burggraaf, 1999). Dashed lines do not represent direct linkages but are included to show bioaccumulation factors between food-web elements.

5.6.2 Current Understanding of Bioaccumulation in Impoundments

The U.S. Geological Survey (USGS) made measurements of total and methymercury concentrations in the water column and in phytoplankton and zooplankton in four reservoirs (Almaden, Calero, Guadalupe, and Lexington) and in Lake Almaden on a single sampling event in September 2004 (Kuwabara et al., 2005). The species in the plankton samples were also identified. These new USGS data provide the ability to assess mercury bioaccumulation by lower trophic organisms in the watershed. The total mercury concentrations in phytoplankton samples ranged from 22.8 to 172 ng/g dry wt, and the percent methylmercury in phytoplankton never exceeded 11 percent. The total mercury concentrations in zooplankton samples ranged from 102 ng/g dry wt at Lexington Reservoir to an average value of 904 ng/g dry wt at Guadalupe Reservoir, and the average percent methylmercury in the zooplankton samples throughout the watershed ranged from 44 to 85 percent. Both the concentration of methylmercury in the zooplankton samples and the percent methylmercury was highest at Guadalupe Reservoir. The BCF calculated with the average total methylmercury concentration of water from the epilimnion (0.363 ng/L) and zooplankton (0.904 ng/g dry wt) at Guadalupe Reservoir is greater than 2 million. This number is not directly comparable to the BCF values shown in Table 3-9 and 3-10 for the fish samples from these same waterbodies, because the zooplankton methylmercury concentrations are reported on a dry weight basis, but it demonstrates the high uptake of methylmercury that takes place at the lower trophic levels. The bioaccumulation factors calculated from this study are consistent with previous mercury trophic-transfer factors calculated for other lakes and show the importance of the uptake of methylmercury by the lower trophic levels to the accumulation of mercury in fish tissue in this watershed.

The relationship between mercury in the aquatic environment and fish tissue is widely accepted, but the level of mercury in fish tissue can be affected by numerous biogeochemical factors. The recent data collection efforts in the watershed have been directed at developing site-specific information on the relationship between mercury concentrations in fish-tissue and water. The objective is to develop predictive relationships that can guide the development of numeric targets for the TMDL. The existing information is summarized below. An emphasis is placed on putting the data collected in the Guadalupe River Watershed in the context of the more general understanding of mercury bioaccumulation.

The data collected in the 2004 dry-weather sampling program and summarized in Section 3.4 of this report and in the Data Collection Report (Tetra Tech, 2005a) show a correlation between methylmercury (MeHg) concentrations in the water column and the mercury concentrations measured in fish tissue in the five impoundments in the watershed (Almaden Reservoir, Guadalupe Reservoir, Calero Reservoir, Lexington Reservoir and Lake Almaden). The diagram in Figure 5-13 summarizes the annual hydrologic cycle in the reservoirs and the observed behavior of MeHg cycling in the Guadalupe and Almaden Reservoirs. This information, combined with results from measurements in other lakes and reservoirs described in the literature, provides a basis for the description of the linkage between MeHg concentrations measured in the water column and fish-tissue in the Guadalupe River Watershed. The annual hydrologic cycle is described for the three periods shown in Panels A – C of Figure 5-13.

Panel A: October – May

During most of the year, the reservoirs are well mixed, and fish and other aquatic organisms are found throughout the water column. The temperature decreases as the wet season and winter period commence and increases again in the spring, but the temperature as well as the dissolved oxygen concentrations (at near saturation levels) remain relatively unchanged with depth. During this period, methylmercury concentrations are at low levels (< 1.0 ng/L) for this watershed and are also constant with depth.

Panel B: June – September

Between late spring and early fall (June – September, although the exact timing varies year to year) Almaden and Guadalupe Reservoirs become thermally stratified. The period of stratification is characterized by an upper layer (epilimnion) of uniformly warm (20 – 26 ^{0}C), well-mixed water. The water in the lower layer (hypolimnion) is cold (10 -14 ^{0}C), and the dissolved oxygen becomes depleted by the bacterial decomposition of organic matter in the water column as well as at the sediment-water interface where bacterial decomposition is at its maximum. As shown in Figure 5-13, both the thermal stratification and dissolved oxygen depletion increases over the season. During this period of thermal stratification the fish are restricted to the epilimnion.

A number of studies have shown noteworthy increases in methylmercury concentrations in the hypolimnion during the period of stratification (Herrin et al, 1998; Sellers et al, 2001; Watras and Bloom, 1992). In Guadalupe and Almaden Reservoirs, the increase in the concentration of MeHg in the hypolimnion is pronounced. From concentrations < 1 ng/L in the unstratified period (October – May), the concentrations of MeHg in the hyplimnion near the bottom increase to concentrations > 10 ng/L during the period of stratification.

Panel C: September – October

In the early fall, declining air temperatures result in a loss of heat from the surface waters, and solar radiation can not make up for the heat loss. The surface waters cool and, becoming more dense than the underlying epilimnetic waters, sink. The continual cooling of the surface waters leads to progressive deepening of the epilimnion and increased circulation throughout the water column. The increased circulation leads to a breakdown of stratification and the restoration of oxygen concentrations at near saturated levels throughout the water column.

Several investigators have shown that the introduction of methylmercury produced in the hypolimnion during stratification and its uptake by phytoplankton represents an important internal source of methylmercury in lakes or reservoirs and also a significant entry point of mercury into the food web (Herrin et al, 1998; Gorski et al, 1999; Sellers et al, 2001; Slotton et al, 1995). Herrin et al (1998) showed that the MeHg produced in the hypolimnion during stratification is quickly taken up by phytoplankton during the mixing that takes place at the end of the stratification period. Slotton et al (1995) showed that the uptake of MeHg in zooplankton and fish increased dramatically during the fall mixing of Davis Creek Reservoir, a California reservoir contaminated by mercury mining activities. These studies also show that biotic uptake of mercury is both rapid and short-lived. The decrease in water-column MeHg is equally rapid (within a period of days to weeks). In addition to biological uptake, loss mechanisms for MeHg from the water column include adsorption to particles and settling to the sediments, and photodegradation.

The results of the studies by both Slotton et al (1996) and Gorski et al (1999), from mercury-contaminated and uncontaminated sites, also showed that measuring mercury concentrations in juvenile fish provides an effective tool for monitoring trends of mercury bioavailability within and between lakes and reservoirs.

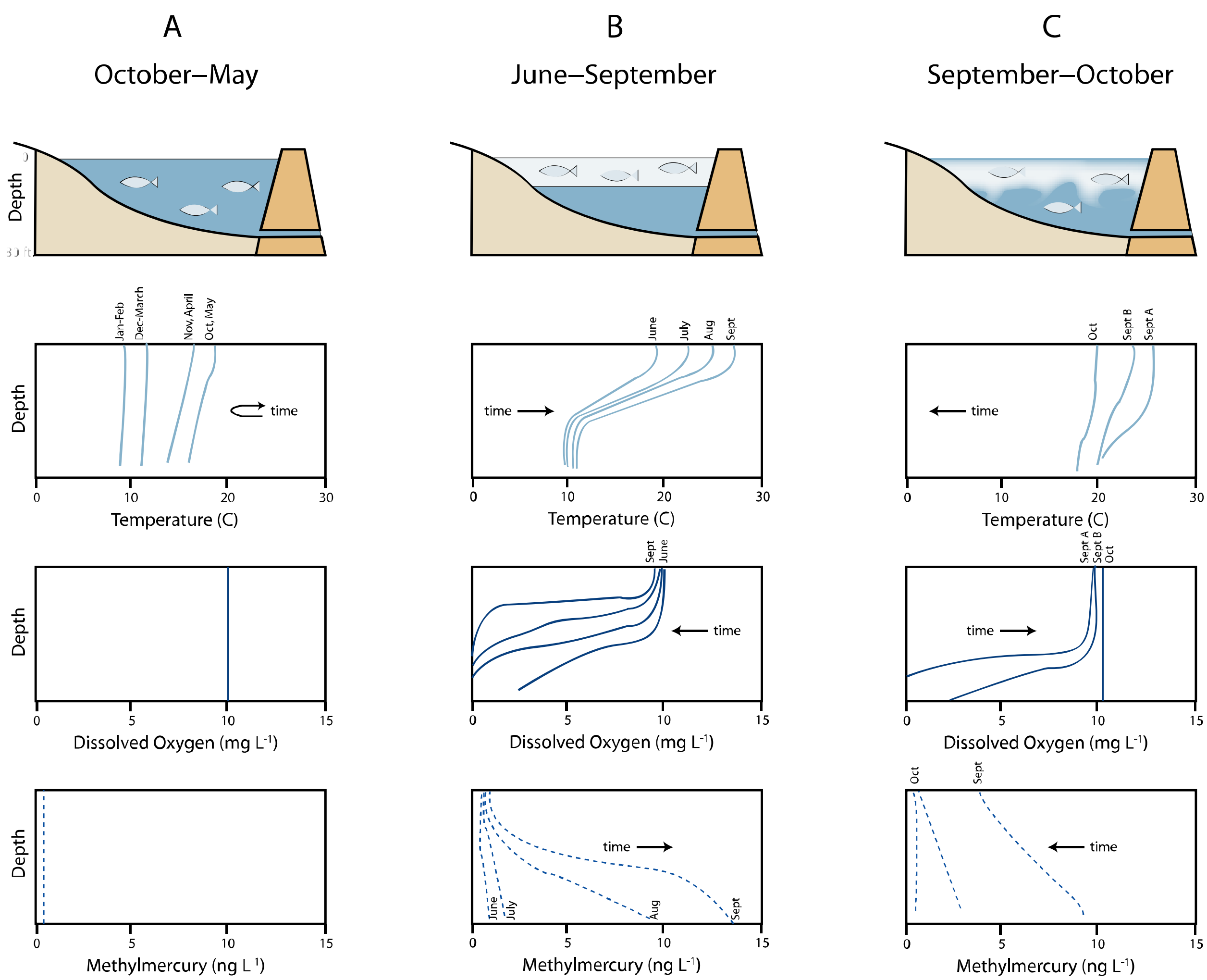


Figure 5-13. Annual hydrologic cycle in reservoirs: temperature, dissolved oxygen, and methylmercury.

This conceptual model of methylmercury production in the reservoirs and uptake by phytoplankton, zooplankton, and small forage fish is consistent with the observations of MeHg production in Guadalupe and Almaden Reservoirs and with mercury measurements in age-1 largemouth bass and the water column in the impoundments sampled throughout the watershed. As discussed in Section 3.4, the mercury concentrations in age-1 largemouth bass samples were highly correlated with MeHg concentrations measured in both the epilimnion and hypolimnion. These results provide strong technical support for the use of the age-1 bass as sentinels for monitoring short-term changes in methylmercury availability in the impoundments of the watershed.

5.6.3 Current Understanding of Bioaccumulation in Streams

The results of the California roach sampling effort and the mercury analyses described in Section 3.4 clearly demonstrated the ability to use these fish-tissue measurements to detect differences in mercury concentrations between locations in the watershed. These samples also demonstrated an important relationship between mercury concentrations in California roach and unfiltered methylmercury concentrations in the water column. Although the source of mercury to these fish is not as well understood as the sources to the impoundments, the elevated concentrations of mercury in these fish sampled in the vicinity of the mining district, coupled with the inability to identify major methylmercury-production sources in the streams (see Section 3), indicates that the hypolimnetic releases from the reservoirs may be the primary source of methylmercury within the watershed.

5.6.4 Hypothesis and Data Requirements: Bioaccumulation

One of the primary goals of the Guadalupe River Watershed Mercury TMDL Project was to address the following hypothesis:

A predictive relationship can be established between aqueous methylmercury concentrations in the basin waterbodies and mercury concentrations in the fish.

Results—Bioaccumulation Hypothesis 1

The results of the fish sampling and measurements of mercury in tissue samples presented above and in Section 3.4 have clearly demonstrated the ability to establish a predictive relationship between aqueous methylmercury concentrations in the watershed and mercury concentrations in fish tissue. A baseline for fish mercury concentrations in the watershed has also been established. Age-1 largemouth bass and California roach have been shown to be sensitive biosentinels that can be used to monitor recovery in the streams and impoundments of the watershed. The relationship between mercury in fish tissue and methylmercury concentrations in the water column has been quantified, and the results indicate the feasibility of developing an aqueous methylmercury target in addition to a fish-tissue target for this TMDL.

Conclusions—Bioaccumulation Hypothesis 1

A predictive relationship can be established between aqueous methylmercury concentrations in the basin waterbodies and mercury concentrations in the fish. However, these results are to a large extent based on a single set of samples, and additional information is needed to quantify and provide uncertainty estimates for the predictive relationships. The relationship between age-1 largemouth bass and methylmercury concentrations in the impoundments is consistent with the data reported in the literature and the conceptual model of the availability of methylmercury in the impoundments (Figure 5-13). The sampling conducted to date has also established a reference value for the fish-tissue concentration at a reservoir in the watershed that appears to be unaffected by mercury mining operations (0.07 – 0.10 mg/kg wet wt for a standardized 8 cm age-1 largemouth bass in Lexington Reservoir). A corresponding range of values for reference aqueous methylmercury concentrations (e.g., 0.05 – 2.2 ng/L unfiltered methylmercury at the outlet of Lexington Reservoir) has also been established.

6.0 SUMMARY

The conceptual model provides a description of mercury behavior in the Guadalupe River Watershed that is based on the analysis of the existing data and the results of extensive field surveys conducted in 2003 and 2004. The conceptual model summarizes this new information and identifies remaining uncertainties that need to be addressed in developing the watershed-wide mercury TMDL.

The following is a summary of the findings of the conceptual model.

6.1 MERCURY SOURCES AND LOADING

Measurements of mercury concentrations at different points in the watershed are required to quantify the loading associated with the different sources. Measurements of mercury, TSS, and flow rates were made to provide new information for estimating mercury loads during the wet season in 2004. Further mercury sampling was conducted in the dry season of 2004 to provide information needed to estimate methylmercury production in the reservoirs.

The major findings of the data collection program were consistent with expectations. Most total mercury is transported in the wet season, particularly at high flows when suspended solids are high. Most of the methylmercury is produced in the dry season in the anoxic portion of the hypolimnion in the reservoirs. Loads were estimated for all three forms of mercury (total, dissolved, and methylmercury) from the upper watershed to the reservoirs, then to the downstream creeks, the Guadalupe River, and finally to South San Francisco Bay. The information obtained and remaining uncertainties are summarized below by waterbody type:

- **Reservoirs**. Mercury loading to the reservoirs from atmospheric deposition was estimated using existing wet and dry deposition data collected at various locations around San Francisco Bay. Measurement of total mercury and methylmercury (particulate and dissolved), TSS, and flow rates were obtained for the wet season at four reservoirs (Almaden, Calero, Guadalupe, and Lexington) and for the dry season at Almaden and Guadalupe Reservoirs.

Most of the methylmercury is produced in the dry season in the anoxic portion of the reservoirs. Remaining uncertainties involve the role of sediment in methylmercury production. Co-located sampling of mercury in the deep hypolimnion and sediment in one or two reservoirs would be needed to evaluate the importance of reservoir sediment.

- **Streams and creeks in the upper watershed above reservoirs**
  Measurements of TSS, total mercury, and flow rates were made at locations on many of the tributaries to the reservoirs. The data showed differences between creeks in the mining area and those outside of it. While additional sampling during high flows would be helpful to refine the mercury contribution of the tributaries to the reservoirs, the new data showed that creeks in the Lexington Reservoir watershed were not affected by mining.

- **Streams and creeks below impoundments affected by mining**
  Measurements of TSS, total mercury, and flow rates were made at multiple locations on Alamitos Creek and Guadalupe Creek. The mercury data show higher total and particulate mercury concentrations in these two creeks than the urban creeks. Mercury loads from these creeks to the Guadalupe River were estimated, but may be low, since the sampling occurred on low flow days.

- **Urban Creeks**
  Measurements of TSS, total mercury, and flow rates were made at multiple locations along Los Gatos Creek, Ross Creek and Canoas Creek. While high suspended solids was contributed on high flow days from Los Gatos Creek, the total mercury concentrations and loads were less than those measured below the Alamitos drop structure. Additional sampling at high flows at the same time as the mouth of Alamitos and Guadalupe Creeks and the main stem of the Guadalupe River would help refine the present load estimates.

- **Guadalupe River**
  Measurements of TSS, total mercury, and flow rates were made at multiple locations along the main stem. Suspended solids and total mercury were greater at high flows, as expected. Methylmercury remained high from below the Alamitos drop structure to the Highway 101 gauge station, suggesting that resuspension of sediments may be occurring. The total mercury load estimate made using data at the Highway 101 gauging station suggest that additional mercury sources are entering the river than were accounted for using the approach and available data. Loads from the river to South San Francisco Bay have a high uncertainty on a year-to-year and inter-annual basis due to widely-varying rainfall. Additional sampling at high flows at the mouth of Alamitos, Guadalupe and the three urban creeks; several large storm drains that directly enter the lower reaches of the river, and the main stem of the Guadalupe River would help refine the present load estimates.

6.2 MERCURY PRODUCTION, FATE & TRANSPORT PROCESSES

The results of the Synoptic Survey and Data Collection effort indicate that a portion of the mercury in solids conveyed to the reservoirs enters the solution phase and represents a significant source of bioavailable methylmercury. However, answers to several questions are crucial to establishing a TMDL linkage and to providing a basis for developing and implementing effective intervention strategies.

- **Where is mercury methylated in the system?** The new dry season data showed that most of the methylmercury leaving the reservoirs was produced in the anoxic portion of the hypolimnion of the reservoirs.

  The Synoptic Survey showed a decrease in methylmercury concentration in the creeks with distance downstream from the reservoirs. The implication is that the creeks are net demethylators. This is not to say that methylation was not occurring in the creeks, but only that in-creek methylation rates did not keep up with the loss rates. In-stream methylation may be significant in specific locations such as in small impoundments on the downstream creeks.

- **What are the mechanisms of mercury methylation?** The TMDL process requires the ability to both predict the reduction in mercury or methylmercury concentration that is required to achieve the selected numeric target(s) and to identify effective interventions. The establishment of this predictive ability requires the identification of the primary mercury source (e.g., crystalline and amorphous HgS and absorbed mercury in sediments, or dissolved mercury in the water column). The new data did not directly answer this question, although the greater methylmercury concentrations in the outlets of Almaden and Guadalupe Reservoirs compared to Calero and Lexington Reservoirs suggest that sediment is important. The recently collected sediment data provide support for this hypothesis, in that Lexington and Calero Reservoirs had lower total mercury concentrations in the bottom sediments than did Guadalupe Reservoir. Almaden Reservoir was not sampled, but historical data show that high concentrations were present. Co-located methylmercury measurements in the deep sediment and hypolimnion would be needed to help answer this question.

6.3 MERCURY BIOCONCENTRATION AND BIOACCUMULATION IN FISH

The results of the 2004 sampling program have established a baseline for fish mercury concentrations in the watershed and have clearly demonstrated the ability to establish a predictive relationship between methylmercury concentrations in water and mercury concentrations in fish tissue. Age-1 largemouth bass and California roach have been shown to be sensitive biosentinels that can be used to monitor recovery in the impoundments and creeks of the watershed. These data are believed to provide a strong foundation on which to build initial fish-tissue and aqueous methylmercury numeric targets.

It is important to note that these results are to a large extent based on a single set of samples, and additional information is needed to quantify and provide uncertainty estimates for the predictive relationships. The fish tissue data exhibit low variability and are the stronger element of the predictive relationships. An emphasis should be placed on the collection of additional water samples to more fully describe the variability of methylmercury concentrations in the water column. Data collected during the implementation phase of the TMDL can be used to reduce the uncertainty and predictability of the relationship between fish tissue and aqueous mercury concentrations.

The fish-tissue mercury measurements that have been developed provide the ability to calculate bioaccumulation factors for each of the fish-species and fish-size groups sampled. In addition, the measurements of mercury concentrations in adult and age-1 largemouth bass provide the ability to calculate the site-specific trophic transfer coefficients that can be used to assess the potential effects of mercury contamination in the watershed on wildlife. Additional analyses are required to bring together mercury data for fish and other aquatic organisms to assess potential risks to wildlife. The focus should be on the development of uncertainty estimates to help bracket the potential risks for wildlife in the watershed.

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