

GUADALUPE RIVER WATERSHED MERCURY TMDL PROJECT
AGREEMENT NO. A2643G

TECHNICAL MEMORANDUM 4.3
DRAFT FINAL CONCEPTUAL MODEL REPORT

Prepared for

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TABLE OF CONTENTS

1.0	Introduction.....	1-1
1.1	Role of the Conceptual Model in the Development of the Mercury TMDL.....	1-2
1.2	Guide to the Conceptual Model – Report Organization	1-4
2.0	Watershed Characterizations and Description of Mercury Sources	2-1
2.1	Watershed Description and System Characteristics.....	2-1
2.2	Description of Existing Mercury Data and Other Relevant Data.....	2-20
2.2	Wetland Vegetation	2-36
3.0	Summary of the Synoptic Survey Results – An Initial Step in Conceptual Model Development	3-1
3.1	Background Water Chemistry.....	3-1
3.2	Elevated Mercury Levels.....	3-3
3.3	Mercury Water Chemistry	3-4
3.4	Almaden Lake	3-5
4.0	Conceptual Model of Mercury Behavior in the Guadalupe River Watershed.....	4-1
4.1	Overview of Mercury Transport Processes.....	4-1
4.2	Overview of Mercury Transformation and Biological Uptake	4-2
4.3	Mercury Behavior in Guadalupe River Watershed Reservoirs: Knowns and Unknowns	4-6
4.4	Mercury Behavior in Creeks: Knowns and Unknowns.....	4-13
4.5	Mercury Behavior in Guadalupe River: Knowns and Unknowns	4-17
4.6	Mercury Bioaccumulation and Numeric TMDL Targets.....	4-20
5.0	Preliminary Source and Loading Estimates	5-1
5.1	Dry Weather Estimates	5-7
5.2	Wet Weather Estimates	5-8
5.3	Annual Variability of Mercury Loads at the USGS Gauge Station at St. Johns Street, San Jose	5-9

5.4	Uncertainty	5-9
5.5	Summary of Findings from Load Estimates.....	5-11
6.0	Summary and Strategy for Developing the Data Collection Plan	6-1
6.1	Mercury Sources and Loading	6-1
6.2	Mercury Production, Fate and Transport Process.....	6-2
6.3	Bioaccumulation	6-3
6.4	Data Collection Plans.....	6-4
7.0	References	7-1
Appendix A Responses to Guadalupe Mercury TMDL Work Group Comments on Technical Memorandum 4.1 Conceptual Model Report.....A-1		
Appendix B Responses to Guadalupe Mercury TMDL Technical Review Committee Comments on Technical Memorandum 4.1 Conceptual Model Report B-1		

LIST OF TABLES

Table 2-1	Reservoir Capacity and Drainage Area of Reservoirs of Guadalupe River System.....	2-6
Table 2-2	Size of Subwatersheds in Guadalupe River Watershed	2-7
Table 2-3	Past Sediment Removal Operations in Guadalupe River Watershed ...	2-13
Table 2-4	Production of Mercury from Major Mines in New Almaden Mining District.....	2-16
Table 2-5	Acreage of Existing Land Uses for the Guadalupe River Watershed	2-21
Table 2-6	Comparison of Dry and Wet Weather Water Samples for Mercury	2-21
Table 2-7	Mercury Concentrations in Stream Water Samples Draining Almaden Quicksilver County Park.....	2-24
Table 2-8	Sampling Locations and Rationale.....	2-27
Table 2-9	Summary of Fish Mercury Measurements from Guadalupe River Watershed.....	2-35
Table 3-1	Mercury Species Concentrations	3-6
Table 4-1	Range of Total Mercury Concentrations.....	4-8
Table 4-2	Range of Unfiltered Methylmercury Concentrations	4-8

LIST OF FIGURES

Figure 2-1.	General topography of Guadalupe River watershed.	2-2
Figure 2-2.	Major waterbodies and subwatersheds of Guadalupe River system.	2-3
Figure 2-3.	Schematic showing major flows in wet season along Guadalupe River system.....	2-9
Figure 2-4.	Schematic showing major flows during dry season along Guadalupe River system.....	2-10
Figure 2-5.	Location of potential erosion site along the tributaries to the Guadalupe River.	2-11
Figure 2-6.	Example of sediment erosion and bank undercutting sites	2-12
Figure 2-7.	Map of major mine-related features.	2-15
Figure 2-8.	Location of exposed mine-wastes and seeps along the tributaries to the Guadalupe River	2-17
Figure 2-9.	Example of calcine deposits and other mine wastes in or near creeks.....	2-18
Figure 2-10.	Wet-weather sampling locations used in 2003 for Almaden Quicksilver County Park by SCPRD.	2-22
Figure 2-11.	Schematic diagram of sampling locations.....	2-26
Figure 2-12.	Total mercury in reservoirs a) deep water and b) shallow water.....	2-28
Figure 2-13.	Methylmercury in reservoirs a) deep water and b) shallow water.	2-29
Figure 2-14.	Total mercury in creek water samples.	2-31
Figure 2-15.	Methylmercury in creek water samples.	2-32
Figure 2-16.	Examples of wetland vegetation.	2-36

Figure 3-1.	Dissolved oxygen profiles in a) Almaden, b) Guadalupe, c) Calero, and d) Lexington Reservoirs.	3-2
Figure 3-2a.	Concentrations of total methylmercury and total mercury in the four reservoir-stream systems.....	3-7
Figure 3-2b.	Concentrations of dissolved methylmercury and total dissolved mercury in the four reservoir-stream systems.	3-8
Figure 3-2c.	Concentrations of alkalinity and pH in the four reservoir-stream systems.	3-9
Figure 3-2d.	Concentrations of dissolved oxygen and carbon dioxide in the four reservoir-stream systems.....	3-10
Figure 3-2e.	Concentrations of dissolved organic carbon and sulfate in the four reservoir-stream systems.....	3-11
Figure 3-2f.	Concentrations of total phosphorous and conductivity in the four reservoir-stream systems.....	3-12
Figure 3-2g.	Water temperature and concentration of chloride in the four reservoir-stream systems.....	3-13
Figure 4-1.	Transport to reservoirs.....	4-2
Figure 4-2.	Creek/river processes at high flow.....	4-3
Figure 4-3.	Creek/river processes at low flow.....	4-3
Figure 4-4.	Accelerated weathering of mercury solids.....	4-4
Figure 4-5.	Mercury methylation reducing bacteria.....	4-5
Figure 4-6.	Uptake of sulfate-methylmercury.....	4-5
Figure 4-7.	Food chain biomagnification of methylmercury.....	4-6
Figure 4-8.	Hypothesized relationship between sediment mercury and methylmercury concentrations in water.....	4-12
Figure 4-9.	Dissolved methylmercury in creeks downstream of the reservoirs	4-16
Figure 4-10.	Flow and Hg on Guadalupe River downstream of confluence with Los Gatos Creek	4-18
Figure 4-11.	Example relationship between fish size (total length) and mercury concentration in muscle tissue.....	4-22
Figure 5-1	Daily summer loads and concentrations (July 28 - August 1, 2003)	5-5
Figure 5-2	Estimated daily loads and concentrations during a large winter storm (December 15-16, 2002)	5-6
Figure 5-3	Histograms	5-10

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.

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.

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. Sediment mercury concentrations in the creeks exhibit a significant and consistent decline with distance downstream of the mining area. Using a variety of historical data from 1950 to 2001 the estimated suspended sediment load of mercury transported by the river ranged from 1.6 to 890 kg/yr. The high variability associated with the load estimate 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 are as high as 109 – 191 ng/L. The range of total mercury concentrations measured in four reservoirs during the dry season of 2003 is 1.4 – 20 ng/L. Total mercury concentrations are in the range of 25 ng/L near the confluence with the Bay in the dry

season. Methylmercury concentrations in the reservoirs within the mining area are exceptionally high. Epilimnetic mercury concentrations range from 1 – 4.6 ng/L. Maximum methylmercury concentrations in the samples from near the reservoir outlets, representing the deeper portion of the hypolimnion, were 8 – 10 ng/L. 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 process 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 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 synoptic survey 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 seconds (cfs) in less than 24 hours. The high flows recede over 1-2 days. Upstream the reservoirs typically limit the variability of flow in their discharge streams.

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 to a significant extent in impoundments created by drop structures and in-stream zones of aggregation. Above the reservoirs, only suspended sediment is transported downstream, since spilling is extremely rare.

The wet season appears to be largely a season of transport. Methylmercury concentrations are much lower than during the warm dry season. But reagents for methylation are being moved into locations where under warmer conditions methylation proceeds.

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 °F. From the Synoptic Survey of July 28-31, 2003 an interesting picture evolves. By this time the reservoirs have become moderately stratified. Settling of particulate organic matter in summer has depleted the lower waters of dissolved oxygen. The reservoirs now appear to be net methylators of mercury. The methylmercury concentrations in the discharges of Almaden and Guadalupe approach values of up to 10 ng/l. Methylmercury concentrations in the epilimnetic and upper hypolimnetic waters are less than in the discharge. Surprisingly, the reservoir concentrations showed little difference over a depth range of 40 feet.

The reservoirs' volumetric discharges were about 4-6 cfs (Lexington 15-20 cfs) to the downstream creeks. Unlike the reservoirs, the creeks 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 in the creeks, the amount of methylmercury produced is not enough to offset the loss of methylmercury.

Mass Balance Analysis: Mass balance calculations, based upon measurements and estimates of flow and concentration of total mercury, indicate the following:

1. Wet season high flows deliver practically all of the total mercury transported in the watershed.
2. The four major reservoirs, Lexington, Almaden, Guadalupe and Calero are sinks for total mercury; they all 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. Atmospheric deposition appears to account for a significant fraction of the mercury input to both Calero and Lexington Reservoirs.

Fish Mercury Levels: Fish mercury levels have been a concern in the watershed for several years. Analysis of fish samples taken from Guadalupe Reservoir on May 28, 2003, by U.S.EPA, shows Largemouth Bass (average length 37 cm) having an average mercury concentration of 4.0 mg/kg (wet weight basis). Black Crappie (average length 16 cm) had an average mercury concentration of 1.9 mg/kg. Both values are above U.S. EPA's standard for fish tissue mercury, 0.3 mg/kg (wet weight).

Evolving Questions: Major questions deriving from the analysis of historical and synoptic survey data need to be addressed to provide input to the development of a scientifically defensible quantitative linkage. Answers to key questions will improve our understanding of mercury behavior in the watershed and help identify feasible remedial measures. Example questions include:

- Does the mercury that is being methylated in the impoundments originate from dissolved mercury entering the impoundments, or from solubilization of mercury solids in the inflow and sediments? Or does the methylmercury originate from some combination of these two sources?
- The methylmercury concentrations in the upper and lower waters of the Guadalupe and Almaden Reservoirs are similar. Is mercury methylation in the epilimnetic sediments quantitatively important, or is the source of methylmercury the hypolimnion and its sediments?

The planned sampling program (Task 5) will address these and additional questions identified during ongoing conceptual model refinement. Additional data are needed not only to answer such questions but also to develop, test, and refine a quantitative linkage that predicts decreases in fish mercury levels, given various potential remedial measures.

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 and identifies additional data that are needed for the development of the TMDL (Total Maximum Daily Loads) Technical Report and the Implementation Plan. Three important roles are ascribed to the conceptual model: data synthesis, communication, and project planning.

The conceptual model is the third of five products being developed in Phase 1 of the TMDL for Mercury in the Guadalupe River Watershed (Tetra Tech, 2003a). The other four products are:

- **Preliminary Problem Statement.** *Technical Memorandum 1.2 Preliminary Problem Statement* (Tetra Tech, 2003b) describes the current understanding of the processes or factors that are most relevant to controlling mercury in the watershed. The Problem Statement provides 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 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, 2004) 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 results of the data collection task will be summarized in a report that describes how these data reduce uncertainty and increase our knowledge of the estimates of mercury loads and the significance of processes controlling mercury methylation. The Data Collection Report will also describe the use of this information in the preparation of the TMDL and Implementation Plan.

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.

In complex natural systems, there are many vantage points from which to view and describe the relationships among the important physical, water quality, and biological variables that define the behavior of mercury in the watershed system. The challenge is to identify the most important variables and processes without creating a complex abstraction that, while definable and defensible, does not provide practical guidance that is relevant to the regulatory decision-making process. On the other hand, an oversimplification of the system is of limited value if it does not provide a meaningful representation of the system that is appropriate for designing regulatory actions.

1.1 ROLE OF THE CONCEPTUAL MODEL IN THE DEVELOPMENT OF THE MERCURY TMDL

It is with the recognition of the need to provide a scientific basis for the TMDL and with the acknowledgment of the uncertainties associated with model development that three main goals were identified for the Mercury Conceptual Model for the Guadalupe River Watershed (the mercury conceptual model): data synthesis, communication, and project planning.

1.1.1 DATA SYNTHESIS

The mercury conceptual model 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 recently conducted synoptic survey (Tetra Tech, 2003d), which provides 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. For although there are five waterbodies within the watershed listed as impaired due to the presence of mercury (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).

1.1.2 COMMUNICATION

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 throughout this project to facilitate the discussion of important issues and individual elements of the TMDL.

1.1.3 PROJECT PLANNING

By explicitly identifying the important processes that control mercury cycling and summarizing our understanding of these processes, the conceptual model provides a technical basis for TMDL project planning. The information presented in this report will be used to guide the scope and direction of the other tasks, as well as the overall technical approach for the development of the TMDL.

The mercury conceptual model extends the description of our knowledge of existing conditions and the processes affecting the existing conditions. The first attempt is made at quantifying the linkage between mercury sources, loadings between different segments of the system, and bioaccumulation. The system is divided into five groups of water bodies: 1) reservoirs, 2) streams and creeks in the upper watershed (above Ross Creek) draining the historic mercury mine areas, 3) creeks in the upper watershed draining areas not known to contain mines, 4) Guadalupe River downstream of Almaden Lake to St. Johns Street and 5) Guadalupe River from St. Johns Street to Alviso Slough. For each segment, quantitative estimates are made of the mercury sources and concentrations within water, sediment, and fish tissue. These analyses are used to identify additional data needed to develop the TMDL. A series of testable hypotheses are developed, and data collection strategies are described to

address these hypotheses and to reduce uncertainty associated with conclusions based on existing data.

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, existing information on recent mercury measurements in the watershed, including the results of the recently completed Synoptic Survey (Tetra Tech, 2003d), and fish bioaccumulation data are also summarized in this section.

3.0 Summary of the Synoptic Survey Results – An Initial Step in Conceptual Model Development

A side-by-side comparison of Lexington, Almaden, Guadalupe, and Calero Reservoirs, and their downstream creeks, provides insight into the behavior of mercury in the Guadalupe River Watershed. This presentation serves as a starting point for the development of the Conceptual Model.

4.0 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.

5.0 Preliminary Source and Loading Estimates

Preliminary source descriptions and mercury loading estimates are presented for dry and wet seasons. Using historical streamflow data from 1950 to 2001, annual total mercury loads for the Guadalupe River are estimated. This exercise provides another indication of where additional data are needed to prepare the mercury TMDL.

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 data collection plans 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.

This Draft Final Conceptual Model Report is a revision of *Technical Memorandum 4.1 Conceptual Model Report*. The preparation of the Draft Final Conceptual Model Report involved the review of comments on the preliminary document from the Guadalupe Mercury TMDL Work Group and the Technical Review Committee. A listing of these comments and the technical responses are presented in Appendices A and B of this report. These comments and continuing discussions with members of the Work Group and Technical Review Committee have resulted in several changes in the Draft Final Conceptual Model Report. Tetra Tech will recommend that a Final Conceptual Model Report be prepared following the completion of the sampling efforts described in *Technical Memorandum 5.2.3 Data Collection Plan* (Tetra Tech, 2004).

6.0 SUMMARY AND STRATEGY FOR DEVELOPING THE DATA COLLECTION PLAN

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 the Synoptic Survey. The conceptual model also provides new perspectives and identifies several fundamental hypotheses and questions that need to be addressed in developing the watershed-wide mercury TMDL.

The hypotheses and questions identified in the development of the conceptual model provide the starting point for the data collection plan that will be developed and implemented in Task 5 of the Guadalupe River Watershed Mercury TMDL (SCVWD, 2002). The stated purpose of the data collection effort in Task 5 is to “reduce uncertainty with respect to the estimated significance of processes, the estimated magnitudes of mercury loads ...”. But the data collection effort must also provide the necessary information to establish a link between the sources of Hg in the watershed and the maximum amount of mercury that can exist within the waterbody while still meeting water quality standards.

The following discussion of the TMDL data requirements serves as 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 during winter storms are needed at several locations. The data requirements vary according to waterbody type:

- **Reservoirs.** Mercury loading to the reservoirs from atmospheric deposition has been estimated using existing wet and dry deposition data collected at various locations around San Francisco Bay (see Chapter 5). Atmospheric sources and runoff from waste materials may both be important within the sub-watersheds of Almaden and Guadalupe Reservoirs. At Calero and Lexington Reservoirs the potential exists for mercury contributions from the bedrock and soils. Measurement of total mercury and methylmercury (particulate and dissolved), TSS, and flow rates will be required throughout the course of selected storm events.
- **Streams and creeks in the upper watershed, above Ross Creek.** Measurements of TSS, total mercury, and flow rates are required at multiple locations on Alamitos Creek and Guadalupe Creek. Emphasis needs to be on sampling near known or suspected sites of enhanced erosion and scour and at locations receiving runoff from waste piles. Sampling should also be conducted above and below drop structures or impoundments to assess effects of these structures on sediment transport. Data on quantities removed at each structure will be obtained to evaluate the effectiveness of District sediment removal efforts.
- **Creeks in the watershed draining areas not known to contain mines.** Measurements of TSS, total mercury, and flow rates are required at multiple locations along Los Gatos Creek, Ross Creek and Canoas Creek.
- **Guadalupe River downstream of Almaden Lake to Coleman Avenue.** Measurements of TSS, total mercury, and flow rates are required at multiple locations. Emphasis should be on sampling above and below drop structures to assess effects of these structures on sediment transport. During the sampling design phase, the importance of and the ability to accurately compare suspended solids transport versus bed load transport will be assessed.
- **Guadalupe River from Coleman Avenue to Alviso Slough.** Measurements of TSS, total mercury, and flow rates are required at multiple locations. This sampling should be coordinated with Clean Estuary Partnership sampling program at the USGS gauging station.

6.2 MERCURY PRODUCTION, FATE & TRANSPORT PROCESSES

The results of the Synoptic Survey 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 high level of methylmercury at the outlets of the reservoirs offers strong evidence that the anoxia that occurs in the lower waters during summer stratification facilitates mercury methylation. However, the location of mercury methylation in the reservoirs was not pinpointed in the Synoptic Survey. Spatially and temporally detailed measurements of total and methylmercury (dissolved and particulate) are required in the reservoirs before, during, and after thermal stratification becomes established in the summer.

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 still be significant and may be preventing a further decrease in methylmercury concentration. This hypothesis needs to be confirmed through paired mercury and methylation-rate measurements in the sediment and overlying waters of the creeks and river.

- 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 crucial mercury source (e.g., crystalline and amorphous HgS and absorbed mercury in sediments, or dissolved mercury in the water column). Also the local dependencies of the production of methylmercury by sulfate reducing bacteria need to be clarified. Field and/or laboratory measurements of net methylation rates at several locations in the water column and sediments under a variety of conditions (e.g., relative degree of anoxia, sediment mercury concentrations, temperature) and locations (littoral wetlands, backwaters, etc.) are required.

6.3 BIOACCUMULATION

The TMDL requires the ability to link reductions in methylmercury production to reductions in the selected assessment endpoints. It appears that fish tissue mercury concentrations are a logical choice as an assessment endpoint for which a numeric target for the TMDL can be developed. Waterbody-specific relationships between aqueous methylmercury concentration (C_{water}) and fish tissue concentrations ($F_{i,j,l}$) are expected to be of the following form:

$$F_{i,j,l} = K_{i,j,l} C_{\text{water}}$$

where:

K = the water-fish partition coefficient

i = selected fish species

- j = fish size class
- l = reservoir or water body segment

This type of function would be used in conjunction with a methylmercury production function to complete the linkage analysis. However, the ability to predict the response of mercury concentrations in fish tissue to reductions in aqueous methylmercury concentrations is independently important because it can be used to address questions regarding the effectiveness of potential intervention strategies or devices. For example, will the reduction of dissolved or methylmercury concentrations in reservoirs, achieved by artificially aerating the reservoir or its hypolimnion, result in reductions in mercury concentration in fish tissue?

Establishing a quantitative relationship between sediment mercury concentrations, mercury concentrations in the water, and fish tissue levels is important. Armed with such information, the determination of the sediment-concentration reductions required to achieve selected target concentrations of mercury in fish tissue (e.g., 0.3 mg/kg) can be specified. Achievement of this level of prediction will be challenging, yet will be necessary to support the quantitative linkage essential to developing credibility in the TMDL process.

6.4 DATA COLLECTION PLANS

The next step in the Guadalupe Rive Watershed Mercury TMDL process is the development of the data collection plan. The data collection program will include controlled, in-lake or in-stream, experiments and field sampling. The primary challenge will be to develop information that is useful for constructing the required predictive relationships between mercury concentrations in sediment, water, and fish. An encouraging aspect of the problem is that the four reservoir-stream systems (Chapter 3) present characteristics that are conducive to these requirements. The “laboratory” conditions are relatively consistent: the waterbodies exhibit similar basic water quality/chemistry characteristics (e.g., alkalinity, pH, productivity, DOC, SO₄, and temperature). At the same time, there is a wide range and non-uniformly distributed set of values for mercury speciation, concentration and levels in biomass. This bodes well for the ability to examine the response of elements of the system to a wide range of changes in mercury ambient concentration and loading.

7.0 REFERENCES

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APPENDIX A
RESPONSES TO GUADALUPE MERCURY TMDL WORK
GROUP COMMENTS ON TECHNICAL MEMORANDUM
4.1 CONCEPTUAL MODEL REPORT

- A1) General comment: This conceptual model succinctly summarizes the available information and thereby provides a springboard to future activities such as monitoring. The stakeholder participation is also appreciated, and documents such as the conceptual model provide direction and a focus for receiving comments such as these.

Page #	Comment
2-5	<p>The header “Meteorology” is misspelled. Response: <i>Has been corrected.</i></p>
2-5	<p>Although I would agree that it is not necessary to collect more atmospheric Hg deposition data, I would recommend continuing to consider the effects of that source. In particular, the effects of forest fires (denuding land to make it more erosive, flux to local atmosphere) should be considered in any observations of long-term datasets in which spikes could be accounted for by this mechanism. Response: <i>Atmospheric deposition is a source and is considered in Section 5. There have not been known, large forest fires in the watershed, so we do not think this is important here, but will consider this source in future documents developed as part of this study.</i></p>
2-6	<p>It would be informative in the text to note that about 65% of the watershed (containing most all of the mines) lies above the 6 reservoirs. Response: <i>The 65% percent figure above includes the Lexington Reservoir subwatershed, which does not include known mines. The percent of the watershed in Guadalupe and Almaden is presented as a percent of the total watershed on p 2-7. Not all the mining area drains to the reservoirs, so the above combined value was not included in the revision.</i></p>
2-19	<p>The last full paragraph (“While the mine production...”) notes that mine site contributions are unknown. I’d suggest using the USLE model to do so. It’s quick, standardized, and fairly easy to present to readers (tabulate input values). Ron Churchill of the Cal Dept of Conservation did this for mercury mines in the Cache Creek watershed and got reasonable results. Response: <i>The intent of this paragraph was to explain why we propose collecting new data from tributaries that drain the mining area. This is a more direct way of obtaining information on the mercury load under present conditions. The paragraph has been changed to make the data gaps clear. Modeling may be conducted to refine the loading estimates during development of the TMDL.</i></p>
2-20	<p>Although it is probably done in the “problem statement”, the mercury problem deserves to be described in this document as well. There’s no indication in this report to say why the TMDL is being done, where loads must be reduced. A map indicating listed waterbodies should be included, for example. If you choose not to add this information in the report itself, perhaps you could append and reference the “problem statement”. Response: <i>The waterbodies needing a TDML were listed on page 1-3 of this report. A sentence has been added on page 1-1 to explain that the Preliminary Problem Statement provides a summary of why the waterbodies were listed on the Mercury TMDL list.</i></p>
3-6	<p>There’s an unnecessary paragraph break in the text. Response: <i>There is no more text; the remaining pages in this Section are large figures.</i></p>
3-7	<p>I don’t find any explanation of how/why Hg measurements just downstream of the reservoirs was up to an order of magnitude higher than in the bottom of the reservoirs (Figure 3-2a and b). If that is analytical error, you need to</p>

	<p>severely discount the use of these data for decision-making.</p> <p>Response: <i>The samples within the reservoir were not collected at the bottom, but were below the thermocline at a depth of 40 ft from the surface, as described on page 2-25. The outlet draws water from greater depths close to the bottom of the reservoirs –see profiles on page 3-2. A sentence has been added to page 3-4 to provide the depths of the reservoir samples and to explain where the outlets are located.</i></p>
4-6	<p>Although conventional wisdom would say that reservoirs are THg sinks, you haven't shown that here. I didn't see any inflow or outflow loads reported. Some reservoirs (Englebright in the Sierras) seem to be sources of THg, from scour of finer particles or bypass of Hg-laden floodwaters. MeHg production is also not shown here (no inflow data) to indicate that the reservoirs are sources. Some are not, at least for large portions of the year, because of biodilution, photo degradation, and other effects.</p> <p>Response: <i>There were data for one tributary Jacques Gulch to Almaden Reservoir showing that high mercury concentrations do occur in the wet season from mine wastes. Additional data are being collected from tributaries to all four reservoirs under Task 5, because no data are currently available to make this assessment.</i></p>
4-10	<p>Although it makes life tough, I appreciate the recognition that Calero and Lexington reservoirs (no real sources) also have high Hg in fish. If you decide to model Calero, I know that Dr Geoff Schladow of UC Davis (530-752-6932) has done some research on that lake and has a hydrodynamic model set up for it.</p> <p>Response: <i>Comment noted and will be addressed in future documents produced as part of this study.</i></p>
4-12	<p>The figure is very useful for discussion purposes. Anyone who thinks the watershed is at point B rather than A is fooling themselves.</p> <p>Response: <i>Comment noted.</i></p>
4-13	<p>There are other studies of spatial variability in Hg concentrations. And many of them found anomalous conditions as well (higher near the surface than deeper). Some of this was presented at the CALFED Mercury Strategic Planning workshop (first of two) at Moss Landing in 2002.</p> <p>Response: <i>Comment noted.</i></p>
4-21 to 4-23 and 6-3	<p>My sense is that you're going down a slippery slope when you try to calculate BCFs for Hg. What averaging period for concentrations in water do you use? Which fish species in which environments do you measure and use as surrogates for other locations (recognizing that food web effects are significant)? Given that we're likely at Point A (Figure 4-8), how could you use a BCF to calculate necessary water column concentrations?</p> <p>Response: <i>Methylmercury measurements have not previously been made for both water and fish tissue samples. We will propose sampling to develop the first data set to evaluate the relationship between water-column methylmercury concentrations and fish tissue. We will propose the sampling of young-of-the-year or age-1 fish of the same species (most likely largemouth bass or black crappie) at several locations to assess relatively short-term responses to changes in the aquatic environment. Multiple measurements will be made of methylmercury concentrations in reservoirs and other water quality parameters over the dry season to obtain better information on an appropriate averaging period. The information that we propose to collect will be used to better characterize the curve presented in Figure 4-8 and the location on that curve represented by existing conditions.</i></p>

5-2	<p>The box diagrams are nice, but not all of the information is presented there. I see four arrows with no loads. Response: <i>The intent is to show what information is currently available. Arrows with no loads imply that no data are available. This is now made clear in Figures 5-1 and 5-2.</i></p>
5-3	<p>The assumed mercury concentration for CVP water is low. Concentrations in the lower Sacramento River measured over the past decade average around 7 ng/L. Response: <i>Comment noted. Additional data will be obtained to revise this source estimate and the loading diagrams that will be presented in the Data Collection Report.</i></p>
6-1	<p>Although dredging and bank stabilization projects have been and will be undertaken in local waterways and bank failure is noted to be the likely dominant sources below the reservoirs, this section says nothing about collecting information to determine those loads. One could take bank and streambed sediment samples and measure the volume of erodible sediments. Ron Churchill of the Cal Dept of Conservation is starting up a project to do this in the Cache Creek watershed. Response: <i>Comment noted. Grain size will be measured in bank and bottom samples from the river, which will be used to estimate erodible sediment in the Data Collection Report.</i></p>
6-3	<p>Although the text notes that bioavailability of various sources is important, there's no recommendation here to measure their relative bioavailability. Response: <i>Under Task 5, bank and bottom sediments are being collected and will be analyzed for Hg and its bioavailability using chemical extraction methods.</i></p>

Com-ment #	Page	Paragraph	Line	Comment
1	3-3	1	1-3	<p>Elevated dissolved-sulfide concentrations can suppress methylation. It would be useful to measure dissolved sulfide concentrations, at least in hypolimnetic waters. Response: <i>Sulfide was measured in the Synoptic Survey in water samples from the hypolimnion and will be measured in two reservoirs under Task 5.</i></p>
2	3-4	1	9-12	<p>Alternatively, could those elevated MeHg:total Hg ratios also reflect dissolution or desorption by dissolved organics (~3 mg-C/L)? Response: <i>It is unclear what the reviewer meant here. The presence of organics in water and the dissolution of mercury by organics does not affect the methylmercury measurements.</i></p>
3	3-5	2	1-2	<p>In this sentence and through the report, it would be useful to specify whether the reference is being made to the dissolved or particulate fractions. Response: <i>The distinction has been made clear. In general, when we speak of total mercury, we refer to both the dissolved and particulate fractions.</i></p>

4	3-5	4	2	<p>With emergent macrophytes in the littoral zones, is it possible that the organically rich sediments in these zones are contributing to the elevated epilimnetic concentrations for Me-Hg? In addition, the time scales of stratification (not just the extent of stratification), affect vertical exchange. I would not dismiss the potential contribution of vertical mixing on the basis of the synoptic sampling.</p> <p>Response: <i>Comment noted. Organic-rich sediment is not present in Guadalupe Reservoir and occurs only in part of Almaden Reservoir. Additional information will be obtained in the Task 5 sampling as stratification develops.</i></p>
5	3-6	1	1-4	<p>The hypothesis of a benthic Me-Hg source is reasonable and should be measured.</p> <p>Response: <i>Elevated Hg is present in sediments in Lake Almaden. The gravel bars that are exposed during the low elevation period of the lake in the winter were sampled as part of the Task 5 sampling, and will provide new information on total and MeHg in this waterbody.</i></p>
6	4-3	1	1	<p>Based on the initial statement in this paragraph, it would seem useful to measure sulfides in these reservoirs in support of this hypothesis about supply of Hg to the water column. It may also be worthwhile running some speciation calculations with the thermodata for aqueous mercury-sulfide complexes and Hg-Humate complexes included.</p> <p>Response: <i>Sulfide was measured, and was present in the reservoir outlets. It will also be analyzed in the reservoir samples collected under Task 5 in the summer of 2004. Depending on the results, Hg speciation calculations could be performed.</i></p>
7	4-5	1	2-3	<p>It is my understanding that there is a limit to the extent that the presence of sulfides stimulate Hg methylation.</p> <p>Response: <i>This is an area of active research; experimental results and field results have shown high variability depending on conditions. The reviewer's comment is correct, there is some speculation that very high sulfides inhibit methylation. But data for this are preliminary and come from only a small number of sites.</i></p>
8	4-6	5	1	<p>In the third bullet, suggest rewording to read, "Complexation and dissolution of mercury by dissolved organic substances, retard adsorption and removal by settling particles."</p> <p>Response: <i>Sentence revised as suggested.</i></p>
9	4-12	2	7-10	<p>Is there any reason to expect that any of the reservoirs (including Lexington) represent condition C where sediment Hg limits Hg methylation?</p> <p>Response: <i>This seems unlikely based on experience at other mining areas and industrial sites.</i></p>

10	4-13	3	3-4	In view of the elevated Me-Hg concentrations in the epilimnion, please consider measuring the flux of dissolved total and methyl between the bottom sediment and overlying water in littoral and profundal zones. Response: <i>This may be conducted during the implementation phase of the TMDL.</i>
11	4-13	5	1-2	One might also hypothesize that microbial transformation rates would be elevated with temperature and hence fluxes from the sediments would be seasonally dependent. Response: <i>Comment noted.</i>
12	4-17	2	3-5	There are at least three potentially important processes here: (1) benthic demethylation greater than methylation, (2) water-column demethylation greater than methylation (photolytic and microbial), and (3) that the combination of benthic and water-column transformation rates generates a net demethylation. As a first cut, you might do a back of the envelope calculation on whether photolytic degradation can come close to generating those concentrations gradients along the stream reaches. Response: <i>Processes noted.</i>
13	4-21	1 and 2	All	These two bullet statements represent multiple process jumps (i.e., repartitioning of particulate mercury, methylation of dissolved mercury, uptake and trophic transfer). The relationship mentioned may be very much spatially and temporally dependent (Where do the Hg loads end up). Response: <i>Comment noted. These were key questions that need to be addressed.</i>
14	5-7	2	1-3	Section 5 provides considerable new information. In the Data Collection phase, it would be useful to confirm the assumption that dry versus wet season concentrations for particulate and dissolve Hg (e.g., that dissolved Hg is not affected by flow). Response: <i>Both dissolved and total mercury and MeHg are being measured in the Task 5 sampling and sampling locations with dry and wet data will be compared.</i>
15	5-8	3-4	All	A quantitative measure of uncertainty is needed here for the load calculations. If that cannot be provided, please state what needs to be accomplished in the Data Collection phase to remedy this. Response: <i>Estimates of uncertainty will be provided with future loading estimates in the Data Collection Report.</i>

16	6-3	2, 4	All	<p>The synoptic survey provides very useful, new information about the distribution of Hg in the watershed, but the questions indicated in these two bullet statements about fate and transport processes are “kicked up a notch”. Both require critical information during the Data Collection phase about biogeochemical processes that regulate the repartitioning, transformation and transport of Hg species. The new information on Brent Topping’s State of the Estuary poster may help with the discussion of “establishing TMDL linkages”. Measurements of microbial methylation and demethylation rates, as well as abiotic (photolytic) demethylation rates in the water column would seem to be required for Data Collection phase as an extension of the synoptic-survey results and conceptual-model hypotheses.</p> <p>Response: <i>Comment noted. Some of the recommended studies may be carried out during the implementation phase of the TMDL.</i></p>
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- B1) The report does a great job describing watershed characteristics and summarizing existing mercury data and other relevant data in different media (Chapter 2). It also does a great job of summarizing the results of the recent synoptic survey and describing current conditions in the different segments of the watershed (reservoirs v. streams) (Chapter 3).
Response: *Comment noted.*
- B2) Further, the report did an outstanding job of describing a complex situation and breaking it down into logical, definable and workable components, while simultaneously summarizing in detail what is known and unknown in each of the components. The hypotheses for each of the components appear logical and well-thought out, and the resulting data requirements to further the hypotheses, appear appropriate (Chapter 4). The preliminary source and loading estimates in Chapter 5 appear reasonable, given the amount of uncertainty which is appropriately acknowledged. Chapter 6 does a good job in broadly defining future data needs.
Response: *Comment noted.*
- B3) It would be helpful to have a gauge of the level of certainty or uncertainty that exists between making assumptions on methylmercury based on data of total mercury samples, i.e. how much extrapolation would we be comfortable with?
Response: *MeHg needs to be measured; it is not scientifically valid to make estimates of MeHg from total mercury in an area such as this with a wide variety of conditions and sources. Both total and methyl mercury will be measured in the Task 5 sampling in the water and sediment samples.*
- B4) Finally, and we believe there will be much discussion of this, we recognize that not only is mercury a particularly complex pollutant, but that the river system we are attempting to build a TMDL around and its relation to the SF Bay, is also complicated. However, as most people are probably aware, TMDLs are frequently developed where there are a great deal of unknowns, where large assumptions have been made, and where the expectation exists that when the science has caught up in particular areas, adaptive management will require another review. We would like to support the careful review of the data gaps associated with the various hypotheses in the conceptual model. We

hope that we (the stakeholder group and the TRC) can come to agreement on what the key information that could be derived from further study would be that would enable us to move forward with the TMDL while acknowledging that there is not enough time or money to resolve all the unknowns that are presented in the conceptual model.

Response: *Comment noted.*

- C1) In general, the report appears to adequately represent the important transport and transformation processes of mercury in the Guadalupe River Watershed. The report does have one significant oversight: it ignored the significance of data that show mercury levels in Lexington Reservoir significantly exceeding water quality standard. This finding that designated uses are not being supported in what is characterized as a “control” system, and its effect on the TMDL, should be addressed immediately by the Guadalupe River Watershed Mercury TMDL Work Group (Work Group).

Response: *The reservoir water data presented in Section 3 for Lexington Reservoir were less than 25 ng/L, the current Basin Plan numeric objective for freshwater as a 4-day average (San Francisco Bay RWQCB 1995). In fact, none of the reservoir samples collected for the Synoptic Survey exceeded the water quality criteria of 25 ng/L. Fish exceed the new EPA draft guideline of 0.3 mg/kg, but this criterion has not been incorporated into the SF Bay Basin Plan as yet. Lexington data will be compared to the other watersheds to determine the effect of atmospheric deposition and the natural geologic formations.*

- C2) The Lexington Reservoir-Los Gatos Creek system is characterized in the report as a “control” system, due to the limited mercury in its bedrock and the absence of direct mining influences. The synoptic survey data presented in the report, however, show high mercury concentrations in Lexington Reservoir. The average mercury concentration in largemouth bass sampled from Lexington Reservoir was reported in Table 2-10 as 0.7 parts per million (ppm). This concentration is more than double the EPA human health mercury fish criterion of 0.3 ppm. Total mercury in the deeper hypolimnion of Lexington Reservoir was reported at 12.8 nanograms per liter (ng/l) in Table 4-1. This concentration exceeds the threshold of 10 ng/l representing “high concentrations” provided in Footnote 2 on Page 3-4 of the report. In addition, unfiltered methylmercury was reported in Table 4-2 at 1.3 ng/l in the hypolimnion 10 feet below the thermocline of Lexington Reservoir, exceeding the threshold of 1 ng/l representing “high concentrations” provided in Footnote 2 on Page 3-4 of the report. The presence of fish tissue mercury concentrations in the Lexington Reservoir “control” system that are more than double the human health mercury fish criterion (along with high water column mercury concentrations) is an extremely important finding relative to the TMDL development. This finding implies that either: (1) background sources are so large that existing fish tissue criterion can never be attained; and/or (2) there are external sources of mercury to the system that are not being considered.

Response: *As noted above, the values listed in the footnotes on page 3-4 of the report were intended for relative comparisons; they are not regulatory criteria; the footnote in the report will be changed to explain this. The report has been changed to indicate that the Lexington data will be compared to the other watersheds to determine the effect of atmospheric deposition and the natural geologic formations, not as a “control”. The tributary sampling under Task 5 will provide information on the mercury concentrations due to atmospheric deposition and natural formations. These data will also provide information on whether there is an effect on the soils in the Lexington Reservoir watershed due to deposition from the furnaces used in the historical mercury mining or whether there appear to be unknown mercury mines.*

- C3) If the mercury is coming from an uncontrollable background source, TMDL development based upon an assumption of achievability of “fishable/swimmable” water quality standards will, as a practical matter, be impossible. Under these circumstances, efforts should be directed towards conducting a Use Attainability Analysis (UAA) to determine appropriate water quality standards. A UAA is a structured scientific assessment of the factors affecting the attainment of a designated use, including physical, chemical, biological and economic factors (see 40 CFR § 131.3(g)). A UAA, therefore, consists of a water body survey and assessment and an economic analysis, if appropriate. Federal regulations require States to conduct UAAs should they seek to designate a use for a water body other than uses specified in Section 101(a)(2) of the Clean Water Act, which sets forth a national goal of water quality that provides for protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water (see 40 CFR § 113.10(j)). Additional information about the linkage between water quality standards and UAAs can be found in EPA 1999, as cited in References section below. If, as the report implies, mercury concentrations in the Lexington Reservoir and in the fish population found there reflect background or otherwise uncontrollable conditions, then the State has no practical choice other than to conduct a UAA, if such an analysis has not already been conducted.

Response: See C4

- C4) The Animas River in Colorado is an example of where a TMDL was delayed to allow for completion of a UAA (CDPHE 2002). The Animas River is included on Colorado’s 303(d) list for metals that originate from historic mining, mineral milling, prospecting activities, and natural geologic conditions. The Colorado Department of Public Health and the Environment (CDPHE) delayed the TMDL development process to allow the Animas River Stakeholder’s Group to complete a UAA, which was used to determine the aquatic life use attainability, appropriate numerical standards to protect the potential aquatic life uses, and the sources to be controlled to meet those goals.

Response: *Comment noted. This information is important to consider in the development of the TMDL for the Guadalupe River Watershed. However, the discussion of these regulatory issues is beyond the scope of the conceptual model.*

References:

Colorado Department of Public Health and the Environment (CDPHE). 2002. Total Maximum Daily Load Assessment: A Watershed Based Approach for the Upper Animas River Basin. Water Quality Control Division, Denver, CO. <http://www.cdphe.state.co.us/wq/Assessment/TMDL/pdf/tmdl/TMDLUpperAnimasDEC02.pdf>

EPA. 1999. Introduction to Water Quality Standards. EPA-823-F-99-020. Office of Water. Washington, DC. <http://epa.gov/waterscience/tribes/intro.pdf>

D1) **Clarity of Purpose and Appropriate Contents**

The Report states that the purpose of Technical Memorandum 4.1 is to describe our understanding of the biogeochemical processes controlling mercury in the watershed, and to identify additional data that are needed for the development of the TMDL Technical Report and the Implementation Plan. Regional Board staff strongly concur with this purpose for the Report; it is our goal to move forward with the TMDL decision-making process. However, we have observed that many in the target audience would like this Report to thoroughly address all aspects of the TMDL project. Therefore, we encourage you to remain committed to the stated purpose, and to incorporate changes

in the report only if they would help us move forward with the TMDL decision-making process.

D2) Major Comments

1. Executive Summary for General Audience

The vast majority of this document is written for a fairly sophisticated and technical audience, which is appropriate. However, the utility of the Conceptual Model is limited without an Executive Summary written to a general audience. We would prefer it to be available in two formats – one in the full report, and a second as a stand-alone document including a few figures. Also, see the editorial comments below.

Response: *An Executive Summary has been prepared for the final report.*

2. Prioritize unknowns

This Report does not clearly answer which data gaps we can live with as gaps, and which gaps must be filled to move forward. This Report should conclude with a clear summary of what we need to do to move forward with the TMDL decision-making process.

Response: *Prioritization of data gaps was done as part of the Task 5 Data Collection Report and guided the implementation of the sampling program.*

3. Lacks overview of conceptual model

Section 4 is broken into 6 subsections, but does not present a summary Conceptual Model that combines the watershed setting and key watershed characteristics with the relevant fate, transport and effects. The Conceptual Model should provide the linkage analysis, about half of which is presented in Section 6.3. It would be helpful to present a "macro" model that illustrates the overall processes before discussion of the model(s) of transport processes.

Response: *The overall processes are discussed in Section 4.1 (transport) and Section 4.2 (transformation and uptake) before more watershed-specific information is discussed. Sections 4.1 and 4.2 are our rendition of the "macro" model as indicated by the reviewer. No further changes have been made to the structure of this chapter.*

4. Wildlife should be discussed in more detail; Food web missing

Wildlife living in the watershed should be discussed in greater detail. If you are not able to provide a description of all the wildlife in the Final Draft, please inform us what your plan is to answer this question. A robust linkage analysis is necessary to select wildlife targets. There is only a general discussion of the food web. No discussion of key species, relative importance of species for which we have data, and no discussion of human consumption and relative risk.

Response: *The Tetra Tech contract did not include sufficient funding for a detailed food web analysis.*

5. Control actions (implementation options) missing

The Report should provide sufficient information to guide our future monitoring efforts (e.g., location, HgT or HgDiss). We recommend a general discussion in a tabular format. One table entry for example, might be whether additional work is required in the New Almaden Mining District, or whether the previous work at Almaden Quicksilver County Park was sufficient.

Response: *This discussion should be deferred until after the Task 5 Data Collection Report has been completed; such decisions will be made as part of the implementation phase of the TMDL.*

6. Confusion on Loads

The broader audience requires more context on the Bay mercury TMDL Load Allocation to the Guadalupe River. In addition, they perceived that within the Guadalupe watershed, the HgT load is downplayed relative to MeHg. On Page 5-2 the estimated urban runoff load should be consistent with the Bay mercury TMDL which was calculated using 0.38 mg/kg.

Response: *The urban runoff contribution, currently, is a relatively uncertain estimate. We used the 0.5 mg/kg value for sediment Hg concentration, following Abu-Saba and Tang (2000) (Table 16 in that report). This reflects the midpoint of a range between 0.2 mg/kg to 0.8 mg/kg.*

7. Background (pre-mining) [Hg]

Background is not defined in the report, state knowns, unknowns, hypotheses. Consider and discuss that localized atmospheric deposition from retorts may have impacted water bodies not in the immediate mining or processing area (i.e. Lexington Reservoir). Reference the Bay sediment cores collected near Alviso Slough (Flegal's report is cited in the Bay mercury TMDL report).

Response: *This possibility will be investigated using the wet weather mercury results from sampling of the tributaries to the reservoirs as part of Task 5.*

8. What is [HgT]sed of concern?

Not 20 ppm haz waste threshold; How about 0.2 ppm from SFBay Hg TMDL? In Regional Board staff opinion, mercury in Bay Area soils ranges from 0.08 up to 0.2 ppm in soils in mercury-rich areas. Consequently, we recommend a threshold of 0.2 (not 0.5) see footnote P3-4.

Response: *Footnote 2 on Page 3-4 has been revised to remove any suggestion that the proposed values represent regulatory criteria. The selected values were used to partition the reported data for the Guadalupe River Watershed into high and low concentrations.*

D3) **Additional Technical Comments**

1. Page 2-14, not all calcines are cemented; provide more information on the geochemistry since you are using them as an identification feature.

Response: *The report stated that calcines were "often" cemented. Our field surveys have noted where cemented calcines and non-cemented calcines occur along the various creeks. A note about uncemented calcines was added to the report.*

2. Page 2-16, "recent site visits" is unclear, remind the readers they took place during the synoptic survey.

Response: *The text was changed to indicate that the visits occurred in the summer and fall of 2004 as part of the Synoptic Survey under Task 2.*

3. Page 2-19, perhaps "long term fate not well understood" should be presented in a later portion of the report with an explanation of your recommended action item.

Response: *This paragraph was revised to identify the data gaps.*

4. Table 2-6, provide more information on sampling (no range of data, no averages). Or were these single-point samples?

Response: *These were single-point samples, except where two samples were measured on 2 occasions at 3 locations.*

5. Historical Sediment data pages 2-23 to 2-25 and Tables 2-7, 2-8
This is data, but not information. Very awkward that data in paragraphs is not listed in the tables. Recommend that this text and tables be scrapped, instead provide a brief overall summary statement on the data, and present two or three figures of many box plots.
- Box plot of sediment data, grouped from left to right from top of watershed, then Almaden Reservoir & Canal and Alamitos Creek; then Guadalupe Reservoir and Creek; then Guadalupe River from top to bottom.
 - Either two separate figures for wet and dry sediment data, or one figure with color-coded wet and dry data
 - First set of data to plot is from Dames & Moore 1989. If there is sufficient data, break it up into several box plots (Mine Hill, Senador Mine, Hacienda Furnace Yard, etc.)
 - Separate figure of box plots for water samples
 - Box plots should show min, max (not 10th & 90th percentiles) – define box plot schematic in the report
- Response:** *The format of the data will be revised to make it easier to understand. Table 2-8 has been replaced by a summary in the text.*
6. Sediment Samples from Creeks (page 2-30)
Add to Fe, sulfide, phosphorus data discussion and illustrations the threshold concentrations for these parameters relative to methylation.
- Response:** *Iron and phosphorus influence the redox and productivity of waterbodies, respectively, but there are not specific thresholds that relate to mercury or methylation. High iron and sulfide indicate anoxic conditions, which favor methylation, but there are not specific threshold concentrations for sulfide in sediment, either.*
7. Fish tissue data
Put these high values in context. How about a California context – compare to 3 highest values from the 2000 & 2001 Toxic Substances Monitoring Program data?
- Response:** *The EPA criterion for human health (0.3 mg/kg) was used to provide context for the reported values. The data identified in the comment will be obtained and evaluated to assess the availability of fish mercury data for the same species and size classes. The results of this comparison will be presented in the Data Collection Report. The referenced data could be used for future comparisons of new data collected in the Guadalupe River Watershed.*
8. Page 2-6, carry over paragraph from page 2-5. It is not clear whether percentages are just for the main stem of the Guadalupe River or include the tributaries. A map would be desirable.
- Response:** *Text will be changed to indicate that the percentages refer to the river main stem plus tributaries.*
9. Page 2-7, discussion of hydrology abruptly changes into a discussion of bedload transport. This should be under a new subheading.
- Response:** *A new subheading will be added.*
10. Pages 2-8 and 2-13, it is confusing to have the discussion of District sediment removal activities intermixed with sediment transport discussion, all under the subheader "hydrology".
- Response:** *A new subheading will be added.*

11. Pages 2-16 and 2-19, a table of observations and transport potential of the calcine deposits would be easier to read.

Response: *Additional references to the map were included.*

12. Page 2-19, what happened in February of 1938?

Response: *The reference to the February 1938 landslide has been removed, since this section of the report was only intended to provide a general description of factors that could affect the movement of calcine deposits. The original reference was to a landslide that occurred in late February 1938 above the town of New Almaden on the road to the reservoir. This landslide moved large blocks of soil and mine wastes 75 feet down slope toward Alamitos Creek*

13. Figure 2-9, photo no. 13, does furnace dust contain a high concentration of mercury relative to other mining wastes? Would that explain presence of liquid mercury in this location?

Response: *Yes, furnace dust does have higher Hg. The elemental mercury is related to the furnaces that were located upstream of this location.*

14. Page 2-19, the discussion of land uses is very brief, and not connected to the purposes of this report or the TMDL project. A detailed land-use map is warranted. A discussion of (directly connected) impervious area, degree of urban area by reach, etc. would also benefit later discussion of loadings.

Response: *A table describing the land uses by area is presented in Technical Memorandum 1.2 Preliminary Problem Statement.*

15. Page 2-20, the finding of highest observed mercury was associated with the highest flow at USGS station conflicts with data in Table 2-6 (second highest mercury concentration was under dry conditions). If suspended sediment concentration data are available, they should be presented with the total mercury data.

Response: *There were two measurements in October 2000. The highest mercury concentration of 139 ng/L on 10/26/04 was associated with the higher flow of 147 cfs. The other flow was 23.9 cfs when the Hg was 18 ng/L on 10/27/04. The dry weather flow was 14 cfs, which is similar to that of the second day above. The TSS data will be added to Table 2-6. None of these flows are high for this river, when the flow exceeds 2,000 cfs and the mercury can be over 1,000 ng/L (SFEI, 2003). Mercury does not correlate well to either flow or suspended solids. This is new information that was not available when the report was prepared.*

16. Page 2-23, Historical Sediment Data, second sentence, what exactly do you mean by “has identified areas with mercury concentrations of concern”?

Response: *The statement meant “high mercury concentrations”; it was intended as an introductory statement to the detailed paragraph below. The phrase “of concern” will be dropped and “elevated” will be substituted.*

17. Pages 2-25 through 2-32, and Section 3 both present synoptic survey data. It is confusing to the reader to have it presented in two sections.

Response: *Section 2 presents the new water and sediment data compared to historical, while Section 3 presents only the water column data for the reservoirs and downstream creeks in the context of mercury behavior, as stated in the first sentence of the section on page 3-1.*

18. Page 2-33 paragraph 3, make a connection to the later discussion of methylation in small emergent wetlands. The Conceptual Model appears weak in discussing methylation in the riparian zone. Do you already have a working hypothesis?
Response: *Our hypothesis is that limited methylation in the creeks occurs in the small wetland areas and in-stream pockets of well-vegetated zones with anoxic sediments, but not in other reaches of the creeks. Most of the pools are not deep enough to generate anoxic conditions in the coarse, sand and gravel sediments that are present in the creek reaches. Methylation is occurring in Lake Almaden, which has anoxic conditions.*
19. Page 2-34, the second paragraph is poorly worded; re-word to something like, “other local atmospheric sources, such as landfill emissions (from the Guadalupe landfill)”. “Runoff” – from where or what? Groundwater seeps are not typically significant sources of mercury because the mercury binds to subsurface soils, except in hydrothermal areas. Explain the link to TMDL actions, or propose no actions.
Response: *The word “local” will be added. The “runoff” meant urban runoff in the lower part of the watershed, which is a significant component of wet season flows; the word “urban” will be added to make this clear. While groundwater is not considered a major source here due to adsorption of mercury by soils, and because there is limited groundwater recharge to the creeks and rivers in this watershed, it could be a source and has been requested by other reviewers and the regulatory agencies to be kept in the list of possible sources.*
20. Page 2-37, Is it indeed bamboo, and not *Arundo donax*?
Response: *The plant is Arundo donax, and that will be changed in the report.*
21. Page 3-3, Section 3.2 first sentence – what does this sentence mean? Are you referencing the eastern Canadian lakes? If so, the geochemistry may be very different than in the Guadalupe.
Response: *This sentence refers to the present understanding from mercury research in many areas that if atmospheric deposition were the only source of mercury to the watershed, reservoirs with the water chemistry of this area would not be likely to have high mercury concentrations in fish, due to the high alkalinity and pH and lack of high DOC concentrations. The presence of a large source, mercury mines, changes the response of these waterbodies. The sentence was revised.*
22. Page 3-3, Section 3.2 second paragraph – Is Lexington Reservoir an appropriate ‘control’? Does it have no legacy atmospheric inputs? (see Major Comment #7).
Response: *The report will be changed to delete the reference to Lexington as a “control”. Additional sampling of the tributaries to Lexington Reservoir was conducted under the Task 5 sampling to determine whether elevated mercury is present due to the natural geologic formations, unknown small mines, or due to elevated mercury deposition from the past furnaces in the mining district. The data from Lexington will be compared to the other reservoirs to help estimate the effect of atmospheric deposition. The furnace deposition source is considered unlikely due to the elevations of the intervening hills and the prevailing wind patterns in this area. The importance of the first two sources are unknown, but will be determined from the sampling results.*
23. Page 3-4, Reservoirs, first paragraph, the wording is confusing. What is fact and what is hypothesis? “That is, much of Hg entering”, state clearly this is hypothesis 1, because later you have a second hypothesis. Provide a reference on sulfide reducing bacteria or state it is a hypothesis.

Response: *The text has been modified to make a forward reference to Chapter 4 where the known facts about methylation and specifically sulfate reducing bacteria are discussed in detail. That is also the section where different hypothesis and the means for testing them are proposed. Chapter 3 serves merely as a summary of the measured data from the synoptic survey.*

24. Page 3-5, dilution (mainly) and dispersion may also cause the concentration of MeHg to decrease. Provide more information on the seasonality of MeHg; seasonality must be addressed in the TMDL Report.

Response: *The Task 5 sampling includes wet season sampling, and will provide MeHg concentrations that can be compared to the dry season. Seasonality of MeHg concentrations will be addressed in the Data Collection Report discussing the Task 5 sampling results.*

25. Section 4.1, specify which report sections you mean by “first part”, and which sections for “second part”.

Response: *The numeric sections that are associated with the first and second parts are specified.*

26. Page 4-1, It is not clear why weathering of local minerals is not important in the Guadalupe and Almaden Reservoir watersheds.

Response: *Weathering of minerals, aside from cinnabar, is a minor source of mercury that would occur in all the watersheds. In the Guadalupe and Almaden Reservoir watersheds, the mine source overwhelms this contribution.*

27. Section 4.2.1, wording of “total mercury flows” is confusing. How about “total mercury concentrations”, or “total mercury loads”?

Response: *The word “flows” will be changed to “loads”.*

28. Section 4.5, opening paragraph, reference the Figure which shows Blossom Hill Road.

Response: *The name “Alamitos Drop Structure” will be added to Figure 2-5 at its location, already shown, and the name in the text in Section 4.5 will be changed.*

29. Page 4-5, in discussion of bioconcentration, no citation is provided for the statement that a large degree of biomagnification “is thought” to result from MeHg’s affinity for thiols.

Response: *Reference was added.*

30. Section 4.3, first paragraph, presents the hypothesis that reservoirs are sinks. This hypothesis should be developed in subsequent sections of the report, or supported with additional existing data. For example, is there existing turbidity or TSS data on discharges and spills from the reservoirs? Are these measurements essentially unchanging throughout the year?

Response: *The Guadalupe and Almaden Reservoirs rarely spill. Turbidity data from the outlet at Almaden Reservoir has been measured monthly in 2003, and will be added to the Data Collection Report showing the turbidity and TSS data. The stormwater data from Mine Hill (Jacques Gulch) was discussed in Section 2 (See Table 2-7). The maximum TSS in this tributary to Almaden Reservoir was 680 mg/L, compared to 31 mg/L for the outlet.*

31. Page 4-6, processes relevant to mercury in reservoirs also include the food chain (web) and transport out.

Response: *Outflow of mercury in reservoirs was discussed in the first paragraph on page 4-6. The emphasis of the section was on the chemical behavior of mercury. Uptake by biota through the food chain is discussed in Section 4.6.*

32. Page 4-14, recent SFEI data and analyses should be considered in the discussion.

Response: *The SFEI 2003 results were not available at the time of preparation of this report and are still being reviewed. The SFEI 2003 results will be described in the Data Collection Report.*

33. Page 4-19, Section 4.5.2, remind the reader where to look up “ongoing changes to the Lower Guadalupe River”

Response: *A note to refer to the Hydrology under Section 2.1 will be added.*

34. Page 4-20 River Hypothesis 2, the use of the word ‘originate’ is confusing. Is it not likely that these sediments did originate in the upper watershed, and are mining waste? Could they have been transported before the dams were constructed? A reminder to the reader of where to find a brief history of dam construction may be warranted.

Response: *This hypothesis will be modified in future documents produced for this study with additional information that is now becoming available. Because the large reservoirs rarely spill, only suspended solids can now be transported downstream. Previously-deposited mine wastes before the reservoirs were built in the 1930’s are present in the creek floodplains of Alamitos Creek. The date of reservoir construction will be added to Table 2-1. These materials can be transported downstream and may reach Lake Almaden. When the flashboards at the Alamitos Drop Structure have been removed, sediment including sand can be transported past this structure during flood flows (often >2,000 cfs). This represents a mechanism for mine wastes to reach the lower river under present conditions. This hypothesis will be modified to explain that mostly suspended solids are transported below the reservoirs, and the section on reservoir construction will be modified in Section 2.*

35. Page 4-23, fish tissue data needs should include consideration of species, trophic levels, and other food web factors.

Response: *Comment noted.*

36. Section 5.0 should be supported with an appendix of calculation details; Stress in report that (some or all of) these loads are calculated based on single data points – these are not robust load calculations. Provide estimates for mercury loads not resulting from mining legacies and urban runoff, or explain if there is not sufficient data to support this calculation. Figures 5-1 and 5-2 are excellent; One would wish, of course, that one could easily find these data in the text, but the relationship between the text and these figures is unclear. Why 20% - is 20% of the Park area covered with mines? If this 20% figure is in a previous section, reference it (Section 2, perhaps?). Why about 380 ng/L to Guadalupe but about 910 ng/L to Almaden? Back this up in the calculation section. Follow through in the discussion by relating to effectiveness of previous remedial actions, and your recommended sampling activities (if any).

Response: *The first paragraph of Section 5 makes it clear that these loads are preliminary and subject to revision. The chapter provides a framework to identify the types of loads and uses a combination of available data and best professional judgment to estimate loads with the knowledge available today. Indeed, the reviewer is correct that in many instances only single measurements are available. The calculations in this chapter will be updated in the Data Collection Report as new data, particularly wet season data become available.*

37. Pages 5-1 to 5-3, use subheaders for each source category. Assumptions are buried in paragraphs, but would be easier to read if presented in bullet format.
Response: *Comment noted.*
38. On page 5-2, the report cites Abu-Saba and Tang 2000 (not in the reference list) for an urban runoff sediment mercury concentration used in previous draft versions of the SF Bay Hg TMDL. The Joint Stormwater Agencies report is better, or you could cite Johnson and Looker 2003 (not in the reference list – current draft SF Bay Hg TMDL Report), or we can provide you with yet another reference.
Response: *Abu Saba and Tang (2000) has been added to the reference list. Note that Abu Saba and Tang provide a range of values of urban runoff mercury (0.2 to 0.8 mg/kg) of which we take the midpoint. As noted in an earlier response, given the uncertainty in this load, we feel this approach provides an adequate first-cut estimate.*
39. Figures 5-1 and 5-2, explain in the legend that “___ ng/L” indicates data not available.
Response: *A note has been added to the legends.*
40. Section 5-2 provides wet weather estimates for a single storm. What is the recurrence frequency of this storm? It is called "rare" in the text, but does that mean it is a 50-year storm, a 10-year storm, or a storm that happens a few times per year?
Response: *The December 16, 2002 storm had a recurrence interval of 5 years, which has been added to the text.*
41. In Section 5.3, a value of 0.8 ppm is used for sediment mercury at the USGS station (Thomas et al. 2002). After looking at that paper, we do not understand exactly why 0.8 ppm was chosen. The paper seems to include other concentration measurements too. More to the point, it seems that some effort could have been made to estimate an average annual load.
Response: *The range of annual sediment and mercury loads were estimated in Section 5.3 and the histograms of annual loads are presented in Figure 5-3. The annual loads were computed using a mid-point concentration of sediment mercury sampled at the USGS station during an early season winter storm event (a somewhat higher and a somewhat lower value were also reported in the early and later portions of the storm). The data relating mercury concentrations and flows in the Guadalupe River are insufficient, although more new data are being generated by an SFEI study. We felt, given the lack of data, using the midpoint concentration of the storm would be justified for further extrapolation and derivation of a **preliminary** load estimate. Alternatively, we could have used the average of three values, which would have given a nearly identical result.*
42. Page 5-10, the Regional Board SF Bay Hg TMDL estimate of 92 kg/yr is "well within this range," but the reader cannot tell from this report what the range is. What do you estimate the average annual load is?
Response: *The annual loads were estimated in Section 5.3 as 1.6 to 890 kg/year as suspended load and 0.3 to 55 kg/yr as bed load (p. 5-8). Also shown graphically in Figure 5-3.*
43. Section 6-1, measurements are needed – for how long? To what end?
Response: *The remainder of this section describes the data needs to better estimate mercury loads.*

44. Page 6-2, re-word to clearly distinguish findings from data needs. A tabular format would be helpful (e.g., for each data need there is presentation of the relevant question and/or objective for acquiring the data, the data needed, and any relevant comments such as timing, spatial coverage, etc.)

Response: *Comment noted. This information is presented in the separate Data Collection Plan (Tetra Tech, 2004).*

45. Linkage analysis does not have to be quantitative. In fact, although the report suggests in a couple of places that a TMDL linkage analysis should be quantitative, it is not required to be. It is simply preferable. Please word it accordingly in the Guadalupe TMDL reports.

Response: *Comment noted.*

D4) **Comments on Graphics**

1. There are many locations discussed in the report which are not illustrated on either Fig. 2-1 or Fig. 2-2. Figure 2-1 is currently elegant in its simplicity, but there is much more information the readers will benefit from being able to locate on Fig 2-1 (see third and fourth bullets below). It will be challenging to maintain the current clarity on Fig. 2-1. One method is to have small numbers on the figure, with a numbered list in the legend of features and streets in alphabetical order.

- Figure 2-1, additional labels: Almaden Lake, Hwy 237, outline of New Almaden Mining District, explain the pits on Guadalupe Creek just above the River.
- Figure 2-2, additional labels: Canoas Creek, Short Creek
- Additional features to include on Fig 2-1: drop structure below Almaden Lake, USGS gaging station(s), Upper Guadalupe Project, Downtown Guadalupe Project, Lower Guadalupe Project, Alamitos fish ladder, (Page 2-25: below drop structure [Site 10] – where?), Masson Dam
- Additional streets and locations to include on Fig 2-1: St. Johns St., Blossom Hill Road, Bertram Rd., Harry Rd., Graystone Ln., Hicks Flat (MW on Hicks Creek on Fig. 2-8?), Orchard Ln., Almaden Expwy., Camden Ave., Lincoln Ave., (page 2-23: both at Lincoln Ave., and also sampled further upstream – where? Were these single sample locations repeated over many years?), Hillsdale Ave., Mazzone Dr., Pricewood Ct., Callanlan Gulch, Rajikovich Dr., Cherry Ave., Kirk Road, Harwood, McKean Rd., Henwood Rd., Snell Ave., Springer Way, Lark Avenue.

Response: *Figure 2-1 will remain as a schematic. However, additional locations have been added to Figures 2-2 and 2-8. Most sediment samples were collected only for short time periods, while flows have been gauged at select locations for much longer times. The name “the Alamitos Drop Structure” will be added to Figure 2-2 and 2-5, and other references changed to that name with a reference to Figure 2-5. That will eliminate some confusion cited above. The streets were referred to in a table of sediment concentrations that was deleted, so a map of these locations is no longer necessary. Location references have been changed to features shown in the figures.*

2. Figure 2-7, correct the spelling of Deep Gulch; indicate location of bridge (photo 13), define (?), indicate locations of Santa Teresa and Bernal mines.

Response: *The spelling of Deep Gulch on Figure 2-7 was corrected. The Santa Teresa and Bernal mines will be added to Figure 2-7 and the Hillsdale Mine to Figure 2-8. The location of photo13 was modified on Figure 2-8, but it is too big a scale to place it exactly. Instead, the location will be described in more detail in the photo caption for Figure 2-9.*

3. Figure 2-10, do not need "formerly" on item E.

Response: *The intent is to explain that the name for the site used by the SCPRD changed.*

4. Figures 2-12 through 2-15, pie charts are difficult to do well, and they are a good choice for this series of figures. Two-dimensional pies are easier to read than three-dimensional figures.

Figures 2-14 and 2-15: the larger "pies" should be offset from the stream sample sites so that we can see both the results and the sites.

Response: *The stream "pies" have been moved to see the sampling sites.*

5. New figure: a figure to clearly show the links between the mercury sources and the beneficial uses to be protected. In other words, draw the arrows between the mines and other sources to fish, wildlife, and humans (it does not have to be quantitative).

Response: *Comment Noted.*

D5) Editorial Comments

1. The need for an Executive Summary was discussed above in Major Comments.

Response: *The Executive Summary will be added.*

2. A glossary of important technical terms may be helpful to some segments of our audience. For example, define "calcine" and explain how it relates to other forms of mercury.

Response: *The text has been revised to provide more complete descriptions of technical terms.*

3. This report is written at a more technically sophisticated level than our typical TMDL Project Reports, which must be accessible to a broad audience, including lay readers. Please keep this in mind when producing the Data Collection Report, and in the future, when you review Regional Board TMDL Reports.

Response: *Comment noted.*

4. One peculiar spelling caught our eye: "co-located" (see pages 4-12 and 5-3) should be spelled "collocated," or possibly "colocated."

Response: *The spelling will be changed to collocated.*

D6) Comments on References

1. On page 5-2, the report cites Trimble 1997 for sediment loads from urban areas, but it is not in the reference list. Please provide a copy to the Regional Board if you have one readily available.

Response: *The reference has been added.*

Page 5-3 cites Grigal 2002 for the percentage of mercury deposition that is retained in a watershed versus running off. This sounds very interesting, but it is not in the reference list. Please provide a copy to the Regional Board if you have one readily available.

Response: The reference has been added.

2. Page 5-2, who is Mike Burnham?

Response: *He is a Tetra Tech staff person; the text has been changed to "Tetra Tech staff".*

3. Many references were missing in the report; some specific examples were provided above.

Response: *References will be checked and the missing ones added.*

E1) Comments on the Document:

1. Page 1-3, Five waterbodies are listed as impaired. Perhaps a footnote should be added to explain why the Almaden Reservoir is not on the 303(d) list.

Response: *The RWQCB position on listing will be added to Section 1, which explains that the watershed will be treated as a whole for TMDL purposes. The original omitting of Almaden Reservoir was likely due to lack of data.*

2. It is not clear that using the USGS National Pilot Study median values for total, methyl, and sediment mercury concentrations is appropriate. How are the quoted "low" and "high" values used in the Draft CMR derived from the median USGS study values? Also, these values do not appear to be related to impairment of beneficial uses or water quality standards (CTR aquatic life, human health; 1995 Basin Plan). All mercury values, whether high or low, will ultimately have to be linked to the fish-tissue water quality standard of 0.3 mg/kg. It would be helpful to have some discussion of the toxicologically significant numbers (criteria) in the conceptual model in lieu of, or in addition to, reference (survey) numbers.

Response: *The use of values for "high" and "low" was for reference only; they were not intended as regulatory criteria. This point was explained in the text.*

3. Table 3-1, footnote 1 should be after "Particulate Mercury" not after "Total Methyl Mercury"

Response: *The footnote reference will be moved.*

4. Page 3-12, Fig. 3-2f. Are the epilimnion and hypolimnion conductivity values (455 & 425 uS/cm) for Calero Reservoir transposed, or is there actually a small inversion?

Response: *The conductivity values are correct.*

5. Page 4-2 and in other parts of the document: "...methylmercury concentrations decrease with travel distance in most stream reaches." It might be a bit more descriptive to say "with travel distance from reservoirs" to better contrast net reservoir methylation rates with net creek methylation rates.

Response: *This change will be made.*

6. No data were presented on wet weather methylmercury levels in reservoirs. Is there no historical data on this?

Response: *There are now data for the outlets, but not the reservoir itself. Wet weather data will be collected in 2004 and presented in the Data Collection Report.*

7. Identical values for total mercury reported in **Table 4-1** and **Fig. 3-2a** do not always have the same significant figures applied to them. Also, the median values reported in the figure do not always appear to match up with the ranges reported in the table (e.g. is the 5.6 ng/L total mercury reported for Almaden Reservoir epilimnion a median value as shown in the figure or a low value as reported in the table?). See also Table 4-2 significant figures compared to Fig. 3-2a.

Response: *Changes will be made in the text to make it consistent with the tables and figures.*

8. TSS should be added to Figure 3-2. TSS results would have been helpful, for example, to clarify the high total mercury values coming out of Lexington Reservoir. Since Lexington Reservoir also had very high D.O. levels (9.5 mg/L shown in Fig. 3-2d), one might speculate that turbulence resulted in re-suspension of reservoir sediments or sediments at/near the outlet to the reservoir.

Response: *As explained on page 2-30 under the heading, Results for Creeks and Other Locations, the high DO in the Lexington Reservoir outlet is due to the turbulent nature of its discharge structure. The DO levels in the reservoir itself are lower (See Figure 3-1d).*

9. Footnote 2 on page 4-12 compares the MCL drinking water standard of 2,000 ng/L with the California Toxics Rule human health criterion of 51 ng/L. Comparison to the human health criterion of 50 ng/L for MUN (municipal supply) designated waters may be more appropriate. Water and organisms are ingested, not just organisms as indicated in the footnote. Further explanation should be provided. For example, is the MCL, which is 39 times higher than the human health criterion, based on economic considerations (i.e. expense of mercury-removal treatment)?

Response: *This footnote will be changed, since the current Basin Plan criteria of 25 ng/L applies to the waterbodies in this watershed, as determined by the RWQCB (Project Definition 3/2004).*

10. Figure 5-1 and 5-2: The lowest level in the fish concentration data should reflect the national fish tissue criterion of 0.3 ppm.

Response: *The selection of the ranges of fish mercury concentrations was based on the distribution of the data.*

11. There is no estimate of mercury addition from in or near-stream erosion in figure 5-2. This would be useful for comparison to the sediment removal numbers.

Response: *Comment noted.*

12. It is unclear how urban runoff loads in figures 5-2 are calculated. The reference cited (Trimble 1997) is not listed among the references. More discussion should be included on how these numbers were derived and uncertainty surrounding them.

Response: *The urban runoff contribution was calculated using the product of the sediment generated in urban areas and the average concentration of mercury on these sediments, as explained on page 5-2. Both numbers are estimates. The Trimble (1997) reference, now provided, gives an estimate of sediment loading from an urbanized watershed in California that was as close as we could get to a report in the scientific literature. The average mercury concentration was obtained from a Regional Board report (Abu Saba and Tang, 2000). The reviewer's comment that we should discuss the uncertainty of the urban runoff load is valid, and applies to every load presented in Chapter 5. However, at this stage, the data in most areas are insufficient to make valid estimates of uncertainty. As we continue this process, including the addition of significant new wet weather data, we will be better able to characterize the uncertainty of*

the various loads in Chapter 5. The uncertainty will be discussed in the Data Collection Report.

E2) Comments on Process:

1. The City would like to clarify that the Data Collection Plan will include the Guadalupe River downstream to the edge of tidal influence. It is important that the Guadalupe TMDL study fully cover the extent of the Guadalupe River to the Bay so that there are no gaps between the TMDLs.

Response: *The Task 5 sampling will collect water and sediment samples at Highway 101 and 237.*

2. Coordination and sharing of comments needs to be improved. Stakeholder and workgroup comments should be shared with all the members of the technical workgroup.

Response: *Comment noted.*

F1)

- Add a north arrow on Figure 2-1. This is especially important since the next figure, Figure 2-2, is oriented exactly opposite and could cause confusion.

Response: *A north arrow will be added to Figure 2-1.*

- Check the fonts are consistent in Table 2-10.

Response: *Consistent fonts will be used in this table.*

- In Section 2.1, data used to discuss atmospheric deposition is from 1999-2001 (SFEI, 2001). Additional data (2002 and 2003) has been collected via the RMP at the San Jose station. This additional data may be available for determining atmospheric deposition of mercury on the watershed and water bodies.

Response: *Could the reviewer provide a specific reference? We have relied upon literature reports and gray literature reports where available. A web search provided no information for reports describing the data referred to in the comment. Should such data become available, we will incorporate them in future documents produced for this TMDL.*

- In the discussion under Section 2.1 Hydrology (page 2-7, last paragraph), it is stated that during weather flows, "...sediment transport is increased due to scouring of banks and the stream bottom". However, other processes like mass wasting in the watershed, which can also cause an increase in the transport of sediment to the water bodies, are not mentioned.

Response: *Mass-wasting has been added.*

- In Section 2.1, it would be helpful to include a discussion of the reservoirs' stratification and mixing regimes. Are the reservoirs dimictic? If known, this information could help understand the times of year when mercury-latent bottom sediments may be mixed into the epilimnion and potentially transported downstream.

Response: *Limited data are available. Sediments are not transported via the epilimnion, only through the deep outlet, except for exceptionally large floods where spilling occurs. The stratification may be weak such that transfer of mercury from the hypolimnion to the epilimnion can occur. The Task 5 sampling of the reservoirs in the summer of 2004 will help address this question.*

- In Section 2.1, it would be helpful to discuss what is known about the concentrations and volume of mercury currently in bottom sediments and the likelihood for resuspension during the year.

Response: *Sediment data are discussed later in this section on pages 2-7 and 2-8. Resuspension of sediment is limited to the high flow periods in the wet season, since the sediment above the Alamitos Drop Structure is mostly sand or gravel. The potential for resuspension in the lower river was described in an ACOE report (2002).*

- On page 5-2 the estimated total mercury in stormwater sediment, 0.5mg/kg referenced from the San Francisco Bay TMDL report, is incorrect. The estimated total mercury concentration in urban runoff sediments used in the San Francisco Bay Mercury TMDL Project Report, date June 2003, is 0.38 mg/kg. Additionally, it is important to state the assumptions and uncertainties in using the 0.38 mg/kg stormwater sediment estimate from the San Francisco Bay TMDL. Only stating the number and its source may give the reader the impression that this is a widely accepted number, giving the number more credibility than the data may support. Stating the assumptions and data sources, even in a footnote, will provide the reader the opportunity to decide if this number should be refined or is adequate.

Response: *The basis for the 0.5 mg/kg number, the midpoint of a range of values of 0.2 to 0.8 mg/kg as used in Abu Saba and Tang, 2000 is now specified. A reader may consider the effect of using numbers other than 0.5 mg/kg in evaluating the total urban load.*

- Page 5-3, second paragraph, discusses the sediment removal estimates from various water bodies. This should be clarified as natural and/or SCVWD activities sediment removal.

Response: *The sentence was changed to note that sediment is removed by the SCVWD.*

- Section 6.3 discusses the importance of bioaccumulation in the TMDL process and how “prediction will be challenging”, yet necessary. The other sections of this chapter discussed the important data and identified methods of filling the data gaps. The section on bioaccumulation does not specify the proposed methods of filling the data gaps.

Response: *A detailed sampling plan for the collection of fish tissue samples has been laid out in the Data Collection Plan. This plan calls for the development of a data set to evaluate the relationship between water-column methylmercury concentrations and fish tissue. Sampling of young-of-the-year or age-1 fish of the same species is proposed at several locations to assess short-term responses to changes in the aquatic environment. Samples will be collected in both reservoirs and streams, and sampling locations have been selected that exhibit a wide range of methylmercury concentrations.*

- Although we do not concur with allocations proposed for the Guadalupe River watershed in the San Francisco Bay TMDL Project Report, we do believe there should be a better explanation of how the mercury behavior and suggested targets for mercury reduction presented in the Guadalupe River watershed Conceptual Model Report are related to the targets and load allocations proposed for the Guadalupe River watershed in the San Francisco Bay TMDL Project Report.

Response: *Targets for mercury reduction are not specified in the Conceptual Model Report. The identified comparison would be more accurately presented after the new data to be collected under Task 5 are obtained and have been evaluated.*



NEW ALMADEN
QUICKSILVER COUNTY PARK ASSOCIATION

P.O. Box 124, New Almaden, CA 95042

November 14, 2003

Mr. David Drury, P.E.
Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118-3614

Dear Sir:

On behalf of the New Almaden Quicksilver County Park Association (NAQCPA), I am pleased to provide the Santa Clara Valley Water District (SCVWD) my comments regarding the draft Conceptual Model Report Technical Memorandum 4.1, dated October 02, 2003, and prepared by Tetra Tech, Inc. on behalf of the Santa Clara Valley Water District for the Guadalupe River Total Maximum Daily Load (TMDL) Project.

The documents are well prepared and present a good balance of known facts and issues that require further investigation. The extensive use of graphical representation makes the documents much easier for the layperson to understand. My overall recommendation is to further refine the model to answer the fundamental question of whether the approach of tying the TMDL to fish tissue concentration makes sense. There is little chance that mercury removal will return the fish to safe levels in any reasonable timeframe and the California Regional Water Quality Control Board (CRWQCB) needs to reconsider their position regarding using fish tissue concentrations as the goal.

The Guadalupe TMDL Conceptual Model will play a key role in resolving whether it is impracticable and even impossible to restore fish tissue mercury levels to those speculated to exist prior to the California Gold Rush, provided issues such as background concentrations and factors are considered with due weight. A key decision is whether mine waste removal makes any sense relative to the current goal. Historical sediment concentrations can be determined and, in combination with current sediment and water data, are better bases for goal setting and allocating load. A load allocation based on practicable mass removal as opposed to impracticable fish clean up will ensure proper accounting for the positive remedial actions undertaken by the various parties to date.

The report mentions interesting data such as elevated total mercury at Lexington Reservoir and elevated rainfall concentrations measured by the San Francisco Estuary Institute, but only briefly considers the significance in terms of fish tissue concentration and instead the discussion focuses on mine wastes. If fish tissue concentrations remain a driving goal, the nuances of airborne and background mercury and their role in methylation will require considerable further work. Consider the statement at the end of the first paragraph of Section 3.3 in regards to Lexington Reservoir, the background reservoir. If it is relatively free of mining, why are the mercury concentrations sufficient to cause the ambient methylmercury water quality criterion for fish to be exceeded (0.3 mg/kg in tissue)? In light of this, an approach that favors early mass removal must be favored over further studies that will most likely only validate what is already known; it is impracticable to try to restore fish tissue concentrations to a 0.3 mg/kg goal.

Response to Comment: *Under Task 5, sampling of the tributary creeks to Lexington Reservoir is being conducted to determine if the runoff has elevated mercury due to the geologic formations or to atmospheric fallout from past mine furnaces. The tributary mercury concentrations will be used to compare to estimates from present day atmospheric deposition. Under certain conditions, atmospheric deposition is enough to cause fish tissue mercury concentrations in reservoirs, particularly when the levels fluctuate seasonally. The sentence on page 3-3 will be modified to state that Lexington Reservoir data will be used as a comparison.*

Improve the reader's ability to understand exactly where in the reservoirs, and in what number, the synoptic survey samples were collected. It is often difficult to understand whether a sample is from the mouth of

an outfall below a reservoir versus from the underwater opening just upstream of the reservoir dam. There also needs to be more information about the timing and general field conditions at the time of collection. This will allow the reader and scientist to have a better understand of comparative differences and possible issues with making comparisons. Make sure there is enough data to understand relative differences in depth and surface area, their ratio, and the possible effect on methylation rates. For example, an indication of depth will be helpful if included on Figure 3-2a. In addition, there may be some contradiction in the discussion relative to whether or not fish tissue concentrations could be elevated from sources other than mining waste. Consider the elevated total mercury measured in Lexington Reservoir. Characterization and sample populations for this water body are sparse, and further work is needed to resolve this issue, as mentioned above.

Response to Comments: *Details on the synoptic survey sampling are provided in a separate report. The outlet samples were collected from the creek on the downstream side of the dam. Reservoir samples were collected from the epilimnion and shallow hypolimnion. The depth of the mercury samples from the reservoirs will be added to Section 3.3. Further reservoir sampling will be conducted under Task 5 Element 7 in the summer of 2004 in Almaden and Guadalupe Reservoirs.*

The statement on Page 3-3, Section 3.2, that mine wastes are the source of elevated mercury concentrations is inaccurate. Mine wastes are the main source, but not the only source, and it is debatable as to whether there are other sources that lead to elevated mercury concentrations, especially methyl mercury. The report needs to better detail the potential sources identified in the preliminary TMDL report prepared by the CRWQCB and indicate which are or are not subject to evaluation as part of the study. Also, check the mining sites against the table of mines I prepared for the TMDL several years ago. At least one notable mine, the Hillsdale mine (a source to Canoas Creek) is missing. The Hillsdale Mine is the site of an active quarry. Also note that the Guadalupe mine is not part of Almaden Quicksilver County Park and constitutes the eight mine on Capitancillos Ridge. The report, at the bottom of page 2-13, states that the District is a group of seven adjacent mines. This is not correct. The district includes the eight principal mines along Capitancillos Ridge, but other outsider mines as well. I believe the area of the mining district studied by the U.S.G.S. is some sixty or eighty square miles. It covers nearly the area of Figure 2-11, and not just the area of Almaden Quicksilver County Park and the Guadalupe Mine.

Response to Comments: *The sentence about the mine waste sediments on Page 3-3, Section 3.2 will be modified to indicate that the mine waste sediment represent one source of total mercury to Almaden and Guadalupe Reservoirs. Other possible sources are discussed in Section 2 "Other Potential Sources of Mercury in Watershed". The Hillsdale mine, Santa Teresa, Bernal mines and others in the watershed from the previous list will be added to Figures 2-7 or 2-8. The authors are aware of the potential for mine input to Canoas Creek, and will sample the creek in the upper reach under Task 5, as discussed in the Data Collection Report. The sentence at the bottom of page 2-13 about mines in the New Almaden Mining District, will be modified from seven to eight mines. Guadalupe Mine was shown in Figure 2-7. It is known that it is in the Mining District, but outside the Almaden Quicksilver County Park. The Hillsdale mine is outside of the watershed boundary, but due to quarrying and regrading operations, runoff from this area could affect Canoas Creek. Canoas Creek will be sampled under Task 5 to see if there is a mine influence.*

There is frequent mention of seeps as potential sources of concern. This seems overstated given the comparatively small flow of these seeps and the lack of supporting data. Emphasis should not be given other than for the need to resolve the issue of significance. So too, is there significant focus on the reservoirs in the same paragraphs as discussion of the mine wastes. It needs to be further emphasized that the majority of process waste from New Almaden was discharged downstream of Almaden reservoir, and the same situation is the case for the Guadalupe mine and reservoir. Almaden reservoir does receive waste from a rotary furnace that operated from 1941-1945 and 1956-1975 on Mine Hill. The amount of mercury from that operation, however, was on the order of a few tens of thousands of flasks, as compared to over one million flasks from operations at the Hacienda, and over a half-million flasks from operations at the Guadalupe Mill (located below Guadalupe reservoir). Historically, significant process waste was transported downstream, and the report is correct in recommending further consideration of the issue of in-channel versus upland mercury sources. In addition, and not addressed, is the issue of potential airborne fallout from the former processing plants. This fallout may be present in surface soils over a very large area, and its existence and significance needs to be determined.

Response to Comments: *One mine seep was sampled during the Synoptic Survey confirming past data indicating that seeps have high mercury. Additional wet season sampling of the creeks draining the Mining District will be conducted under Task 5 to address the potential impacts of remaining upland and in-channel mine wastes and the possibility of past furnace deposition. Downstream sampling will also be conducted to determine the effects of past mine wastes that were discharged downstream.*

Finally, regarding Almaden Lake, please consider that this is likely where most of the calcines from New Almaden were deposited, as well as fines from the placer mercury deposit formation in pre-historic time. Gravel mining in the area may have concentrated mercury in the rejected tailings during the wet-screening process, and this might have some relationship to the elevated methyl mercury levels in Lake Almaden.

Response to Comments: *Two gravel bars in Almaden Lake will be sampled during the wet season, when they are exposed to measure mercury concentrations and particle size distributions. Samples are also being collected of Alamitos and Guadalupe Creeks and above and below the Alamitos Drop Structure.*

In conclusion, the report is well written and the extensive use of graphics is very helpful. I believe the Model, when completed, will be a world-class contribution to understanding the issue of mercury in the watershed. I hope these comments will add value to the goal of arriving at a fair, comprehensive, and feasible TMDL allocation and reduction.

Sincerely,

A handwritten signature in blue ink that reads "Michael F. Cox".

Michael Cox
New Almaden Quicksilver County Park Association

APPENDIX B
RESPONSES TO GUADALUPE MERCURY TMDL
TECHNICAL REVIEW COMMITTEE COMMENTS ON
TECHNICAL MEMORANDUM 4.1 CONCEPTUAL
MODEL REPORT

GUADALUPE RIVER WATERSHED MERCURY TMDL PROJECT

Technical Review Committee Comments on the
Draft Conceptual Model Report

January 6, 2004

Gary A. Gill, Texas A&M University at Galveston
D.B. Porcella, Environmental Science and Management
James Rytuba, U. S. Geological Survey
James G. Wiener, University of Wisconsin-La Crosse

Table of Contents

Reviewer	Page
Gary A. Gill	1
D. B. Porcella.....	7
James Rytuba	11
James G. Wiener.....	13

Comments of Conceptual Model for the Guadalupe TMDL Project

By

Gary A. Gill
Texas A&M University at Galveston

December 19, 2003

Overall Comments

I was very impressed with the current form of the conceptual model that has been developed for the Guadalupe mercury TMDL project. The Tetra Tech team has a wealth of experience in environmental mercury issues and I applaud the work they have done to date on this project. They consistently remain well abreast of the latest insights into mercury biogeochemistry and are leaders in modeling the transport and bioaccumulation of mercury in aquatic systems.

I particularly liked the focus on monomethylmercury (MMHg). Too often projects of this type focus solely on the large abundance of mercury that can exist in sediments and ignore the biogeochemical issues and conditions that lead to elevated mercury levels in top trophic level organisms – i.e. MMHg production and bioaccumulation. This is a significant strength of this project.

The development of the conceptual model as a series of testable hypotheses is also a very good approach; well grounded in science. The approach to the TMDL is also process-oriented and mass-balance oriented. Both of these approaches have proven to be excellent frameworks in other successful environmental mercury studies, including the Mercury in Temperate Lakes (MTL) study in Wisconsin, the Aquatic cycling of Mercury in the Everglades (ACME) and the Florida Atmospheric mercury Study (FAMS) programs in Florida, and the METAALICUS program at the experimental lakes area in Canada. Mass balance and process-oriented approaches were also instrumental in identifying and focusing on the important mercury sources and transport processes at the mercury superfund site in Lavaca Bay, Texas. I am thoroughly convinced that this is why the remediation efforts in Lavaca Bay were so well accepted by EPA, Alcoa, and other stakeholders. Had this approach not been taken in this latter study, it is very likely that the on-going elevated groundwater input of mercury would not have been identified, nor its significance to current conditions recognized.

The conceptual model described in the Guadalupe TMDL project is well linked to our current understanding of how mercury behaves in the environment.

Specific Comments

The following comments will focus particularly on analytical, sampling and mercury cycling issues.

1. Methylmercury in the Reservoirs.

The high concentrations and high percentage of MMHg (methyl to total ratio) in the reservoirs is a very striking feature. Providing some insight into why this is the case seems to me to be an important aspect of understanding the biogeochemical processes influencing mercury in this system. Typically, methylmercury is a small percentage of the total mercury in surface waters. Values in most systems range between 1-5%, with 10% being a high level. While there is clearly a paucity of data, it appears that MMHg in the reservoirs is ~30% of the total levels. This is very unusual, especially for the oxygenated epilimnion waters. It suggests to me that there might be an external source. One possibility that comes to mind is that there is an external source of MMHg, perhaps from something like litterfall. The other possibility might be some form of exchange with the hypolimnion, but the oxygen and temperature structure do not support this. My recommendation would be to do some back of the envelope calculations on possible sources to see if it is possible to rule out their likelihood as a source.

Response: *Additional profiles of temperature, dissolved oxygen, and other water quality parameters will be obtained and mercury will be measured above and below the thermocline during the summer of 2004 to determine how mercury concentrations change as stratification develops. Litterfall does not appear to be as likely a source, since Guadalupe Reservoir has few trees around it, and still had a high percentage of MeHg in the epilimnion. Estimates of the contribution of litterfall to the reservoirs will be made in the Data Collection Report and compared to other mercury sources.*

2. Methylmercury Production Measurements

One of the data needs that is proposed are MMHg production rates (e.g. pages 4-12 and 6-3). I suggest being careful with terminology here and being more specific as to exactly what is intended or desired because it has a number of potential caveats associated with it. MMHg production implies that one is interested (perhaps only) in the rate at which MMHg is being produced. In a system like the Guadalupe River area, what is probably more important is **net** MMHg production (where net = rate of MMHg Production – rate of MMHg destruction or de-methylation). Making this distinction is critical because there are isotopic methods available for monitoring the rate of MMHg production and destruction. On the other hand, if one is more interested in net MMHg production, then this could be achieved by monitoring total and MMHg concentrations in the water column over some specified time interval. I suspect this is what is intended. If there is also an interest in sediments, one approach that is often taken to address MMHg production (intensity), for example in different environmental settings, is to determine MMHg/total Hg ratios. Higher percentages of

MMHg can be assumed to represent environments with enhanced MMHg production. If there is interest in specific MMHg production rates, derived from isotopic methods, be very cautious in using the production rates in any modeling efforts. It is likely that the rates that these techniques provide are not quantitative. Usually they are used on a relative basis only.

Response: *The text will be changed on page 4-12 and 6-3 to indicate that net methylation rates could be measured in the future to provide relative rates in different waterbodies and settings.*

3. Break TMDL into two components or Issues?

In reading the draft conceptual modeling report and listening to the discussions it became very clear to me that the scope of the TMDL can be broken into two components or issues if desired. The two components are the Hg transport issue associated with the watershed and the other is a process based issue – explaining why there are high MMHg levels in the reservoir. The approaches used to address these issues will likely differ. For example, the Hg transport issue can be address with event sampling, focused on the annual period of high flow. Addressing the reservoir issue will require more biogeochemical processes based approaches.

Response: *For the TMDL, both the Hg transport issue and the MeHg issue are important, but as noted different approaches and sampling are needed to fill data gaps. The Task 5 sampling program has been designed to provide additional information for both issues.*

4. Sampling and Analytical Needs and Issues.

To address the hypotheses proposed, I recommend getting as many temporal and spatial measurements as possible. This will help to constrain and support the hypotheses. I recommend that measurements include unfiltered, filtered and (by difference) particulate mercury fractions. Ancillary measurements should include SPM and basic water chemistry parameters (e.g. nutrients, major ions, temperature and oxygen) whenever possible. I think you learn much more by collecting more detailed information at a few sites, rather than collecting just one parameter (e.g. total Hg) at a number of sites.

For the river sampling, be aware that there may be very significant sampling bias due to potential heterogeneity issues. Mine site areas seem to be notorious for having suspended particulate matter that varies in mercury content quite significantly. We observed this to be a very significant issue in collecting samples in the Cache Creek watershed. This problem was partially overcome by collecting as large a sample as possible and using a large stirred collection reservoir from which aliquots could be drawn for the various sub-samples.

Finally, I strongly recommend that attention be paid to quality assurance and quality control issues. As I am sure everyone is aware, mercury contamination during collection and analysis can be severe and not easily overcome. Contamination or bias has plagued many mercury programs despite the best of intentions. Including a field program with good replicate sampling and verification of low mercury blanks from field sampling equipment will help immensely to show that this aspect of the program is under control. Using an analytical laboratory with an established reputation in quality mercury analyses is also mandatory.

Response: *QA/QC measures have been included in the previous sampling program and the Task 5 Data Collection Plan. Frontier Geosciences is conducting all the mercury analyses, which will provide high quality data in a consistent manner. The suspended particulate matter is being measured on the entire volume of the container, not an aliquot, by Frontier. We are collecting replicates to address the variability issue. We will collect equipment rinse samples and field blanks when samples for mercury are not collected directly into the containers. This situation occurs only for the reservoir sampling.*

5. Parameterization of Bioaccumulation

One of the goals of the TMDL is to establish a predictive and quantitative relationship between MMHg in water (or sediment) and fish tissue mercury concentrations. If such a relationship can be established, this would clearly be a major step forward in developing the TMDL. However, I am a little skeptical that a clearly defined relationship will emerge. Also, it is not entirely clear what form the predictive relationship will take or how it will be parameterized. Some expansion on this discussion in the TMDL is warranted. This clearly, in my opinion, is both a major strength and also a major weakness, of the TMDL process as it is currently proposed. If a fully quantitative relationship can be established, then the steps that need to be taken to reduce MMHg production become much easier to manage. If, however, such a relationship does not emerge, then it will not be possible to establish how to reduce mercury flows into the food chain. Is there a back-up plan if this approach does not work?

Response: *Elevated fish mercury concentration was a primary factor in the decision to list waterbodies in the Guadalupe River Watershed as impaired, and the concentration of mercury in fish tissue will be one of the numeric targets in the TMDL. It is essential to vigorously explore the relationship between mercury (total and methyl, particulate and dissolved) in water and sediment and fish mercury concentrations. From previous investigations, it looks like the strongest relationship exists between aqueous methylmercury concentrations and fish tissue. We will propose sampling to develop a data set to evaluate the relationship between water-column methylmercury concentrations and fish tissue. We will propose the sampling of young-of-the-year or age-1 fish of the same species at several locations to assess short-term responses to changes in the aquatic environment. Samples will be collected in both reservoirs and streams, and sampling locations have been selected*

that exhibit a wide range of methylmercury concentrations. Fish tissue concentrations are not the only numeric target. The back-up plan is to rely on placing more emphasis on the use of mercury concentrations in sediment and water as restoration criteria.

Minor Points

1. A number of references cited in the text are missing from the reference list.

Response: *The references will be checked and missing ones added.*

2. Where does the 30% value on page 5-3 come from? Is this just a guess or is there something to back this up?

Response: *Values of export ranging from 0.5% to more than 50% have been reported depending on the land use and the season being studied (review conducted by US EPA (2001)). A more recent review reports total export fractions in stream runoff of approximately 5%, with the remainder being sequestered in the watershed or volatilized (Grigal, 2002). In the absence of watershed-specific information, our choice of an export ratio of 30%, although among the higher end of values reported in US EPA (2001), was intended to provide a conservatively high estimate of atmospheric load to the waterbodies. The paragraph describing this selection has been revised on page 5-3.*

Comments of Conceptual Model for the Guadalupe TMDL Project

By

D. B. Porcella, PhD
Environmental Science and Management

December 1, 2003

Overall Comments

I want to congratulate the Santa Clara Valley Water District for obtaining Tetra Tech Inc. to do this TMDL. Tetra Tech is one of the most highly professional and respected environmental organizations in the world. As I would expect, their conceptual model and associated data are presented clearly, and the writing and graphics are both well done and accurately portray the most recent understanding of mercury dynamics in aquatic ecosystems. In addition the authors show deep understanding of mercury and ecosystems that covers the extensive issues that exist in the Guadalupe River watershed and its receiving waters. Their conceptual model is focused on processes, especially the processes associated with the methylation of inorganic mercury. This focus enables the proposed TMDL to concentrate on the endpoint of the mercury TMDL, i. e., the fish. Fish integrate all the processes that supply mercury to the ecosystem, transform mercury to methylmercury, and ultimately represent the accumulation of methylmercury through the food web into the fish, which then act as the source and the risk to humans and wildlife. It is the goal of this TMDL to protect the health of humans and wildlife. Some of the means to protect the health of humans and wildlife might include reducing sources of mercury, reduce environments conducive to the methylation process, or to reduce bioaccumulation of the methylmercury. Identifying these means is part of the TMDL process. It is clear from the data presented that the limnology of the reservoirs are markedly different. The role of the differences in the potential for methylation and bioaccumulation might help elucidate the best way to assess the possible ways to reduce risk. Furthermore, atmospheric sources (largely from global background) play a large role in the risk. Understanding the relative importance of different sources and how they interact with unique environmental conditions will provide a challenge to this TMDL.

Specific Comments

Based on the presentations and the conceptual model itself, along with the discussion that took place in the meeting, I offer the following suggestions that are meant to enhance the work undertaken to answer the specific hypotheses listed in Chapter 4:

1. To better understand processes, Tetra Tech should consider the use of small fish as bioindicators. Young of the year of predator species will provide ‘quick-turnaround’ measures of processes and possible ameliorations that could take place. It will still be necessary to monitor the older fish as health indicators.

Response: *The Task 5 fish sampling program will target collection of age 1 California roach (*Hesperoleucus symmetricus*), which is an abundant, small prey fish that feeds primarily on insects and crustaceans. Thus, this type of fish is expected to respond quicker to changes in mercury concentrations in the water and/or sediment. EPA is also planning to collect fish from the reservoirs. Their sampling will also focus on age-1 or young-of-the-year fish.*

2. To accurately perform event sampling, large volume samples (LVS = 5 liters) are likely to represent the best estimates of loading of mercury. Thus, these apply to the wet season. Smaller samples may be representative enough for dry season events.

Response: *We are collecting samples using the same procedure as used for the dry weather sampling to have comparable samples. SFEI is collecting samples from the Guadalupe River at the Highway 101 gauging station intended for detailed loading calculations.*

3. Such LVS should be taken to describe some of the downstream transport, and could logically be collected – for at least some samples – as close-event samples, to characterize the shape of the relationships between, for example, suspended load of sediments and mercury with the hydrograph.

Response: *This type of sampling is being conducted by SFEI at a downstream flow gauging station (Guadalupe River at Highway 101).*

4. One comment that seemed important is that the wet season is the loading to the bay for mercury and is dominated by transport processes, and the dry season is the period when transformation processes dominate mercury risks. It is the latter that is the most important for determining risks within the watershed, while transport processes may or may not have much effect on mercury risks in the bay. If the mercury transported into the bay is deposited into the sediments, then it is likely that the impact of this mercury on risk will be less important than direct mercury inputs from the atmosphere that dominate water column mercury. A key issue about the bay is that the focus there is not on methylmercury. It will be important to use the same focus for both Guadalupe and the bay if we are really to do a useful TMDL.

Response: *The Guadalupe River TMDL needs to provide information for the Bay and the other waterbodies that are on the TMDL list, which include creeks and reservoirs. Thus, both transport of total mercury and methylation needs to be addressed.*

5. Some other sources may need assessment to quantify the sources of mercury risk. These are listed on p. 2-34 of the CM, and several are repeated here to emphasize their potential role in the Guadalupe River watershed:
 - a. Litter fall may introduce mercury to the river/reservoir system by trapping atmospheric mercury whether obtained from global background sources or from mercury that evades from the mine wastes.
 - b. It might be worthwhile to consider estimating evasion of mercury from different landscapes in the watershed.
 - c. Groundwater may be a quantitatively important source, though this is unlikely based on previous experience.
 - d. Within reservoirs, particulate transfer ('detrital rain') during the summer months of stratification may be an important removal process from surface layers, but this removal may enhance methylation in the anoxic hypolimnion.
 - e. Bedload transfer of mercury may be quantitatively important, especially during the wet season. The bioavailability of this mercury will require assessment to determine if it merely is transferred into the bay sediments where it will largely be sequestered.

Response: *a) We have sent leaf litter samples to Dr. Milena Horvat at the Jozef Stefan Institute in Slovenia for analysis. The results will be reported in the Data Collection Report. Estimates of litterfall and its contribution to mercury in the creeks and reservoirs will be made in that Data Collection Report.*

b) Evasion of mercury will be estimated for different land cover types in the watershed and its significance evaluated. The results will be presented in the Data Collection Report.

c) Based on the information available, groundwater is not considered to be a quantitatively important source. Many of the creeks draining the former mining area do not flow in the dry season.

d) Comment noted. The Task 5 sampling is designed to provide additional information on mercury concentrations in the epilimnion and hypolimnion throughout the summer as stratification develops.

e) Mercury bioavailability is being evaluated in sediments by analyzing mercury in different size fractions. Sequential Extractions will be conducted on sediment samples where the samples are leached with water and different strength acidic solutions and the mercury concentrations determined separately in each fraction. The results will be presented in the Data Collection Report.

6. Some pilot studies using limnocorrals might answer some specific questions. Some suggested experiments include sediment mercury removal or capping, the use of FeII and/or nitrate additions to determine the effects of the additions on mercury transport and transformations.

Response: *Experiments such as these may be considered as part of the implementation phase of the TMDL.*

7. Similar experiments might help determine the relative role of water versus sediments as methylmercury sources.

Response: *The Task 5 sampling includes collection of water and sediment samples from key locations, which may provide some information. Experiments may be considered as part of the implementation phase of the TMDL.*

8. Consider the possible use of Lexington Reservoir as a control for the reservoirs most affected by the Almaden mine wastes.

Response: *Sampling of the tributaries entering Lexington Reservoir is being conducted to determine if elevated mercury is present due to either the natural geologic formations, atmospheric deposition from the furnaces in the mining district, or unknown small mine operations. Data from Lexington Reservoir and watershed will be compared to that for the other reservoir watershed.*

Comments of Conceptual Model for the Guadalupe TMDL Project

By

James Rytuba
U. S. Geological Survey, Milpitas, California

November 13, 2003

Overall Comments

The conceptual model for the Guadalupe River Watershed TMDL is comprehensive and well written. The figures for displaying Hg loadings for various parts of the watershed are particularly useful.

To make the conceptual model complete a section on mercury atmospheric emissions from various mine wastes and altered areas in the watershed should be added. For other comparable watersheds containing mercury mineralized areas and mine sites, about 15-20 Kg/year of Hg are released by this process. Gustin and others (2003) provide a methodology for estimating mercury evasion from mine sites and mineralized areas.

Response: *Estimates of mercury atmospheric emissions will be made. These estimates will be reported in the Data Collection Report.*

The relatively high methylmercury in surface waters of the reservoirs and the exceptionally high value in Lake Almaden suggest that some process or factors in the surface water are contributing to these high values. Hg atmospheric emissions from contaminated soils and mine wastes can become sequestered in plants through uptake of Hg through their leaves. Some small portion of Hg in plants becomes methylated. It is possible that litter washed into the reservoirs is relatively high in Hg and possibly MeHg. Analysis of litter and organic debris in reservoirs may be useful in resolving the source for MeHg.

Response: *Plant samples along Guadalupe Creek were analyzed previously. Estimates of litterfall and its significance will be made.*

The concentration of mercury in mine wastes increases as grain size decreases such that the fine grain size fraction can be considerably higher than the bulk mercury concentration of the tailings (see Kim and others 2003). The mine wastes and tailings in the upper part of the watershed still retain a grain size distribution that includes a fine grained fraction that can release Hg-enriched colloids during the wet season. In the lower part of the watershed, tailings present in the relatively coarse-grained bed

load and bank deposits have likely had the Hg enriched fine fraction removed. Further characterization of Hg in the bed load and bank deposits in the lower part of the watershed should assess the relative endowment of mercury in these two sediment compartments. This work should help to explain the processes that lead to the relatively sharp increases in loading in the lower part of the watershed.

Response: *Samples of bank and bottom sediment are being collected under the Task 5 sampling at five locations in the lower watershed and four locations in other parts of the watershed. These samples will be analyzed for mercury, MeHg, and particle size distribution. Mercury will also be analyzed in separate size fractions from the various locations. Because the mine wastes from this area are coarse (often up to 3" size), the particle size relationship to mercury may differ from other areas with finer wastes. The mine wastes here are calcines and not fine-grained tailings.*

Ground water may contribute some small portion of Hg to the watershed. This is particularly possible in the Guadalupe Reservoir where mine workings are present under the reservoir. Water in the extensive underground mine workings at New Almaden are a potential source of Hg and sulfate. The numerous seeps along the creek opposite the New Almaden park entrance indicate that some mine waters are being released to the watershed.

Response: *Comment noted. Sampling of the creek at different locations in the wet and dry season will help determine the significance of seeps as a source. Mercury and sulfate were measured in two creeks fed by mine seeps.*

M. Sexauer Gustin¹, M. Coolbaugh², M. Engle², B. Fitzgerald¹, R. Keislar³, S.E. Lindberg⁴, D. Nacht¹, J. Quashnick¹, J. Rytuba⁵, C. Sladek², H. Zhang⁴, R., 2003, Zehner¹ Atmospheric mercury emissions from mine wastes and surrounding geologically enriched terrains Environmental Geology, Mercury special issue, v.43, p. 339-351 <http://link.springer-ny.com/link/service/journals/00254/contents/02/00629/paper/s00254-002-0629-5ch110.html>
Kim, C.S., Brown Jr., G.E., and Rytuba, J.J., 2003, Geological and anthropogenic factors influencing mercury speciation in mine wastes: an EXAFS spectroscopy study: Applied Geochemistry, v. (see attached PDF)

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Comments of Conceptual Model for the Guadalupe TMDL Project

By

James G. Wiener (Technical Review Panelist)
University of Wisconsin-La Crosse

November 13, 2003

Overall Comments

The draft Conceptual Model – An Excellent Framework

The draft Conceptual Model prepared for the Guadalupe River Watershed Mercury TMDL Project is generally sound and provides an excellent foundation for focusing future efforts on the Project. The emphasis on the abundance, bioaccumulation, and transport of *methylmercury* is appropriate, given that the aquatic mercury problem stems from the production of methylmercury, its subsequent bioaccumulation and biomagnification in food webs, and the associated methylmercury exposure of organisms (including humans) atop aquatic food webs. In addition, the concentration of methylmercury in fish (reliably estimated via determination of total mercury) is an important and appropriate endpoint, given that consumption of fish is the primary pathway for exposure of humans and wildlife to methylmercury.

High Methylmercury Concentrations in Water and Fish

This reviewer emphasizes the following points regarding the mercury data synthesized in the draft Conceptual Model report. First, the concentrations of methylmercury measured in oxic surface waters in parts of this aquatic system are exceptionally high relative to published values for other surface waters. Second, methylmercury comprises an unusually large fraction of the total mercury present in the reservoirs, relative to recently published values for other surface waters. Third, the concentrations of total mercury measured in fish (noting that total mercury is a reliable estimate of methylmercury concentration in fish tissue) residing in parts of this aquatic system are also unusually high, with values falling within the range of concentrations reported for fish sampled during the early to mid 1970s from grossly polluted waters receiving mercury in discharges from industrial sources.

Key Questions for Developing Effective Remedial Strategies

In my view, the following questions are key to the development of effective remedial strategies for mercury in the Guadalupe River watershed. First, what are the dominant sources of inorganic mercury that is being converted to methylmercury? Second, where is most of the methylmercury being produced? It is tempting to assume that the reservoir sediments are a primary source of inorganic Hg(II) and a primary zone of methylation. However, a “detrital rain” of algae – containing both Hg(II) and high-quality organic matter – onto anoxic, methylating layers of the water column could also be an important source of Hg(II) for methylation in the reservoirs. In Calero Reservoir, for example, the concentration of methylmercury in deep water is comparatively high relative to other reservoirs. Calero Reservoir is not directly influenced by mining but does receive water transferred from mining-affected sources (Figure 2-13a in Conceptual Model Report). Does this suggest that the overlying water column is an important source of Hg(II) for methylation?

Response: *The Task 5 sampling of Guadalupe and Almaden Reservoirs in both the epilimnion and hypolimnion throughout the summer as stratification develops will provide helpful information to confirm the previous relative mercury concentrations and to evaluate the water column as a potential source of inorganic Hg due to algae and other organic carbon. Outlet samples from the two reservoirs will also be collected and analyzed for mercury to evaluate the effect on downstream creeks.*

Suggestions for Future Studies

1. Other measurements – pertaining to hydrology, ecology, and limnology – will be needed to interpret the mercury data collected, to understand mercury cycling and transport in the watershed, and to identify potentially effective remedial measures.

Response: *The Task 5 sampling of Guadalupe and Almaden Reservoirs in both the epilimnion and hypolimnion throughout the summer as stratification develops and sampling of the tributaries in the wet season will provide additional helpful information.*

2. The sampling and analysis of resident prey fish (preferably of a nearly uniform age, such as age-1 or 1 year), may provide a much more sensitive indicator of the abundance of methylmercury in aquatic food webs in this watershed than would analysis of long-lived predatory fishes. Analysis of total mercury in predatory fish could be expected to indicate gradual (multi-year) trends in the abundance of methylmercury, whereas annual sampling and analysis of small prey fish would probably reveal annual changes in the supply of methylmercury.

Response: *The Task 5 fish sampling program will target collection of age 1 California roach (*Hesperoleucus symmetricus*), which is an abundant, small prey fish that feeds primarily on insects and crustaceans. Thus, this type of fish is expected to respond quicker to changes in mercury concentrations in the water and/or sediment*

than large predator fish. EPA is also planning to collect fish from the reservoirs. Their sampling will also focus on age-1 or young-of-the-year fish.

3. The progressive removal of methylmercury from stream water in reaches downstream from the reservoirs could be caused by (i) demethylation (photodemethylation was inferred in the draft Conceptual Model report), (ii) biological uptake by periphyton and/or other organisms, or (iii) both of these processes. It is important to be able to discriminate between demethylation and biological uptake, given that the first process leads to destruction of methylmercury whereas the second can lead to food-web transfer of methylmercury to upper trophic levels. Periphyton, which readily accumulate methylmercury, appeared to be abundant on stream substrates in photos shown at the technical review meeting.

Response: *Estimates of photodemethylation along the streams will be made to see if that explains the observed loss of mercury downstream of the reservoirs. These estimates will be presented in the Data Collection Report.*

Periphyton is less abundant in the reaches below, but near the Almaden Reservoir, compared to reaches below McKean Road, which have a more open canopy.

4. As the project progresses, mesocosm-scale manipulative experiments could be done to evaluate potential remedial approaches within the watershed. Such work could then be expanded to the pilot-scale level in an adaptive management framework, an approach that could be very effective for linking and advancing science and management in this watershed project.

Response: *Experiments such as these may be considered as part of the implementation phase of the TMDL.*

Minor Questions, Suggestions, and Comments

1. The mercury associated with organic matter is associated largely with sulfur (not carbon) on the DOM. Statements in reference to complexation of mercury with dissolved organic carbon (e.g., pages 3-1 and 4-6 in the draft Conceptual Model report) should instead refer to dissolved organic matter (not DOC).

Response: *There are many references that discuss the relationships between mercury and organic carbon. Also, DOC is the measured parameter not DOM. In soil profiles, mercury sometimes follows the carbon and not sulfur. In any event, this is a minor difference, because in most systems, DOC and DOM are closely correlated.*

2. Concentrations of chlorophyll *a* in the reservoirs were low, despite the abundance of total phosphorus and seemingly productive fish populations (page 3-3 in the draft

Conceptual Model report). Are phytoplankton being intensively grazed in these waters?

Response: *Based on the limited fish sampling, the fish biomass at the reservoirs appears to be large. The low chlorophyll a concentrations could be attributable to intense grazing. However, additional measurements are needed to quantify chlorophyll a concentrations and phytoplankton biomass in the reservoirs.*

3. Morphometric maps of the reservoirs would be useful. For example, what proportion of the reservoir bottom area in each reservoir is above the thermocline during summer stratification.

Response: *Bathymetric maps of the reservoirs have been requested, but only partial information has been received to date. The volumes of cold water below the thermocline are available for Guadalupe Reservoir.*