5.0 CONCEPTUAL MODEL OF MERCURY BEHAVIOR IN THE GUADALUPE RIVER WATERSHED

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

5.1 OVERVIEW OF MERCURY TRANSPORT PROCESSES

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

5.1.1 TRANSPORT TO RESERVOIRS

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

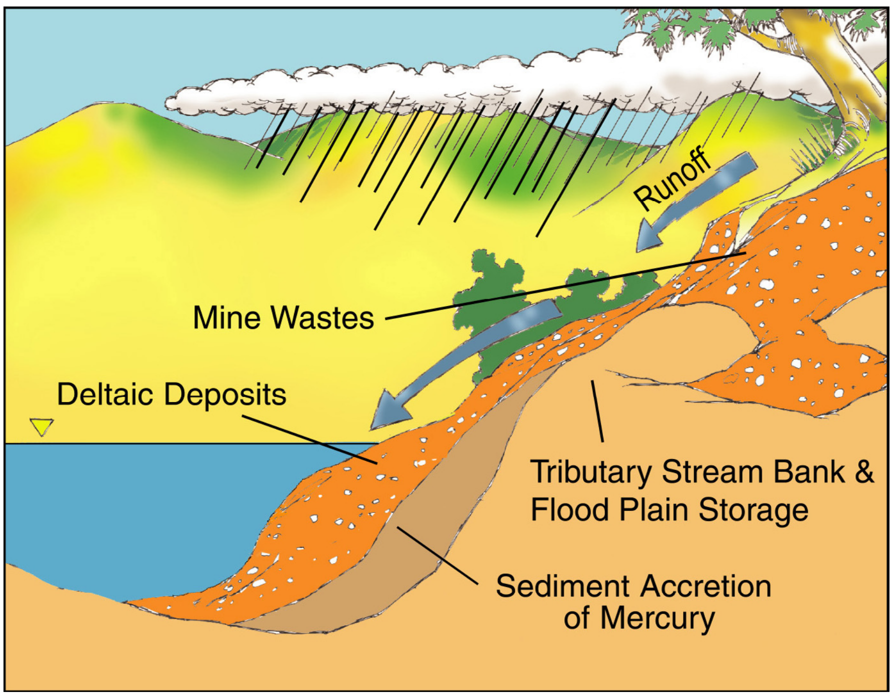


Figure 5-1. Transport to reservoirs.

5.1.2 Creek/River Processes at High Flow

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

5.1.3 Creek/River Processes at Low Flow

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

5.2 Overview of Mercury Transformation and Biological Uptake

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

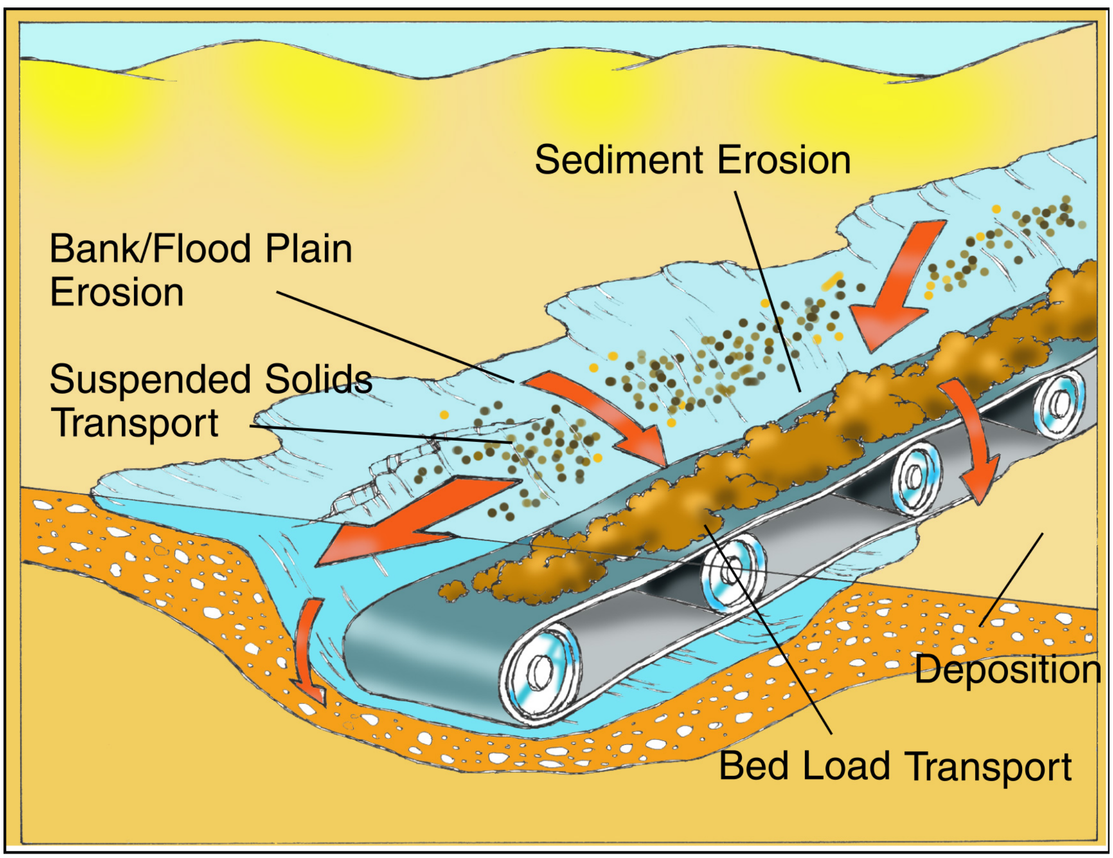


Figure 5-2. Creek/river processes at high flow.

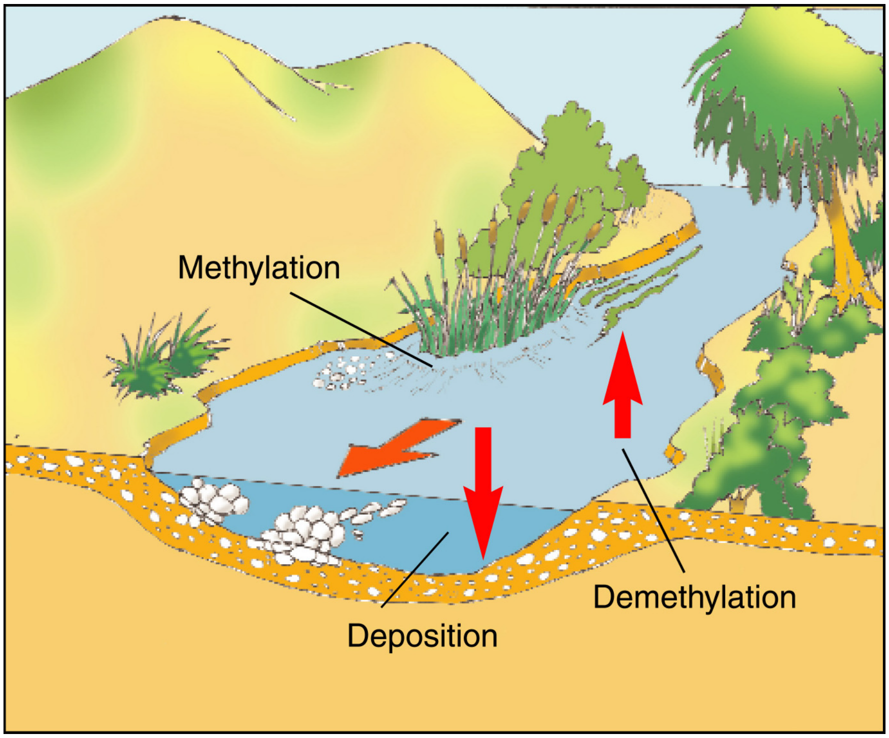


Figure 5-3. Creek/river processes at low flow.

5.2.1 SUPPLY OF HG TO THE WATER COLUMN IN IMPOUNDMENTS AND STREAMS

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

5.2.2 DEVELOPMENT OF ANOXIC CONDITIONS IN DEEP WATERS IN IMPOUNDMENTS

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

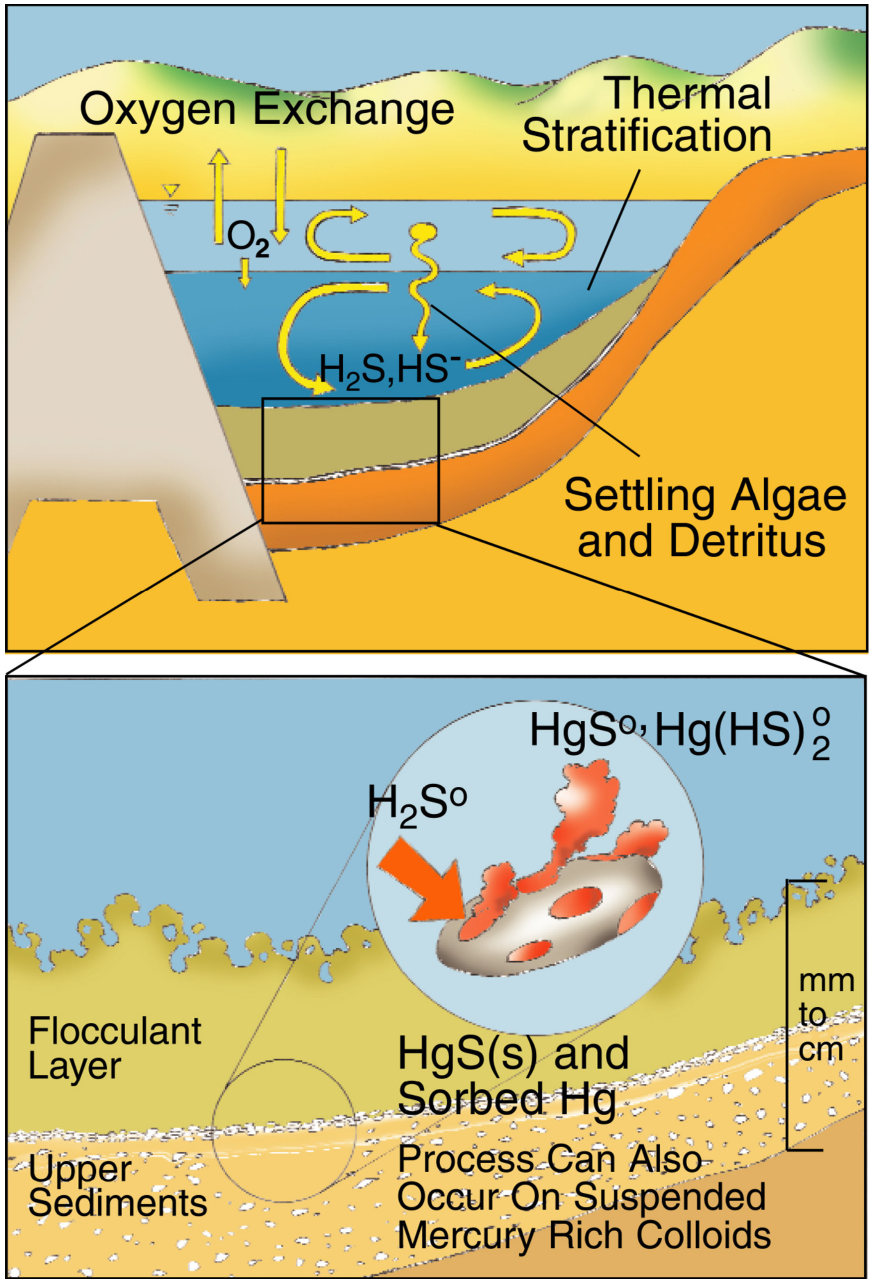


Figure 5-4. A possible pathway for accelerated weathering of mercury solids.

5.2.3 Mercury Methylation

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

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

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

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

5.2.4 Uptake of Methylmercury

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

5.2.5 Bioconcentration of Mercury

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

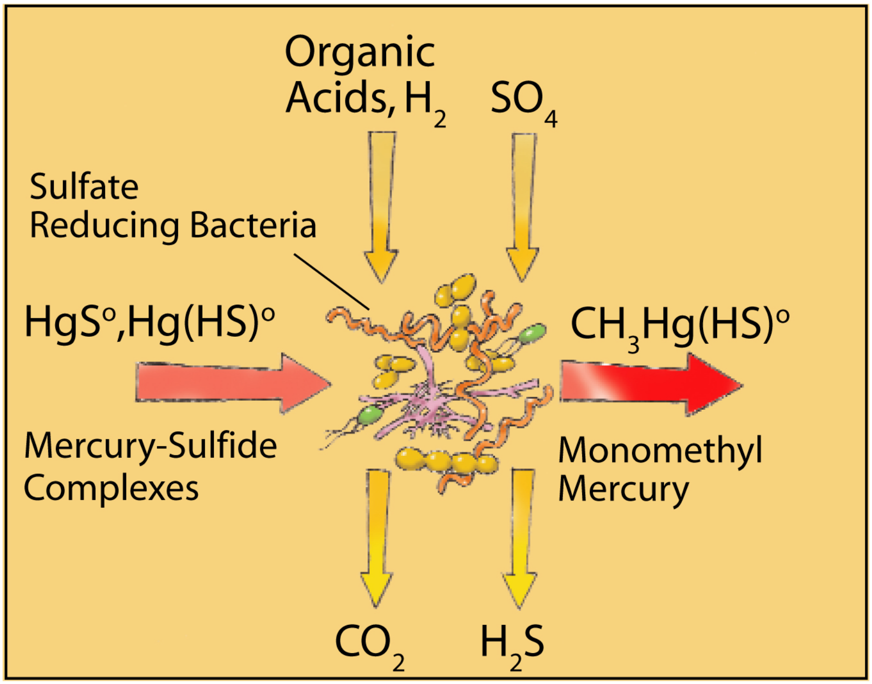


Figure 5-5. Mercury methylation reducing bacteria.

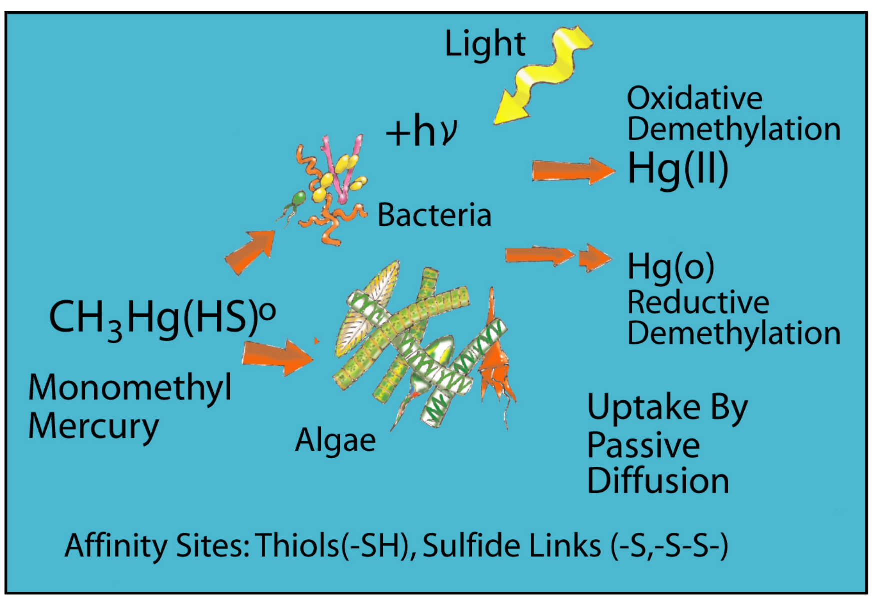


Figure 5-6. Uptake of sulfate-methylmercury

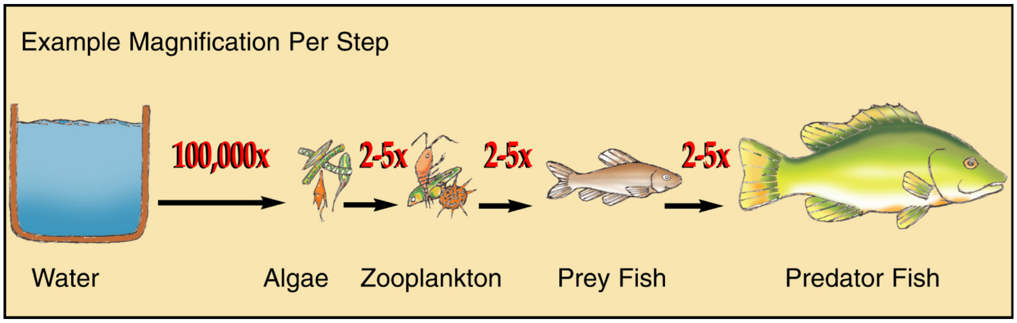


Figure 5-7. Food chain biomagnification of methylmercury.

5.3 Mercury Behavior in Reservoirs: Knowns and Unknowns

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

5.3.1 Reservoir Conditions

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

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

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

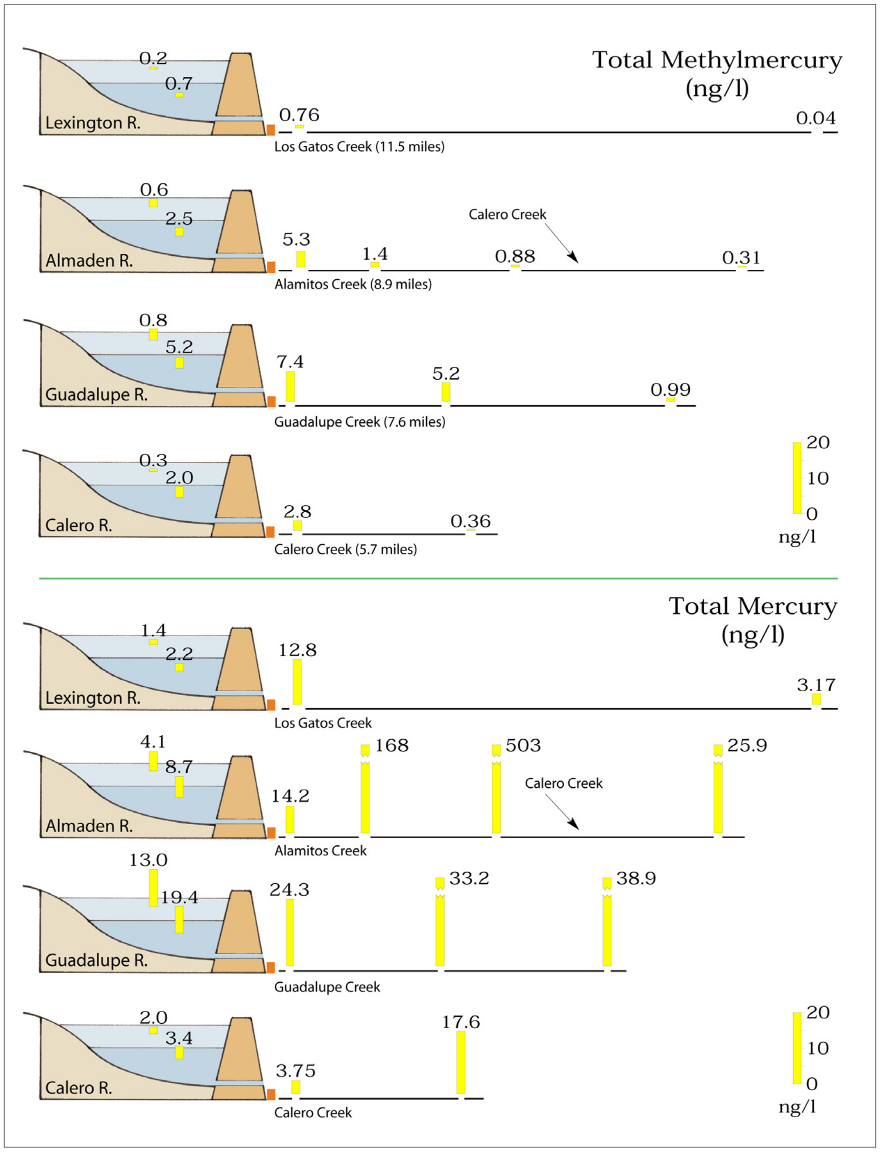


Figure 5-8. Average concentrations of total mercury and methylmercury in the central part of the four reservoir systems in the dry season (Data for the downstream creeks are from July 2003.)

5.3.2 Results of Hypothesis Testing: (Reservoirs)

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

Reservoir Hypothesis 1

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

Discussion – Reservoir Hypothesis 1

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

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

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

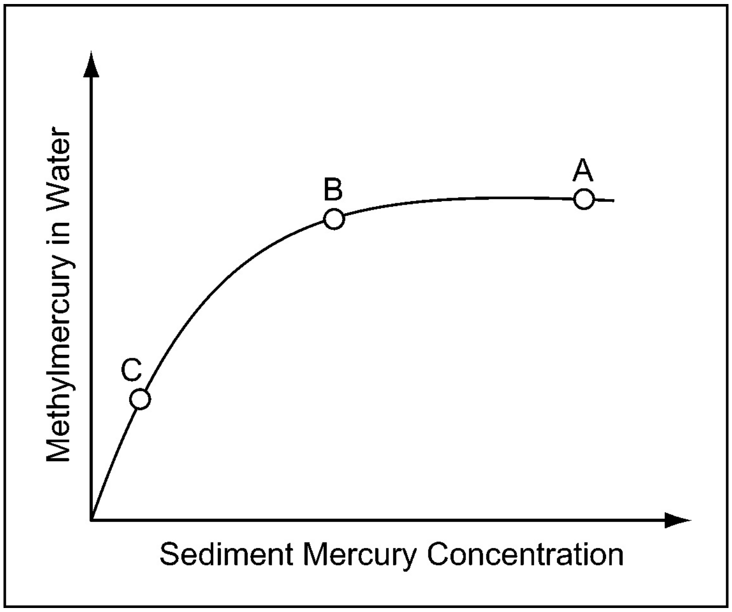


Figure 5-9. Hypothesized relationship between sediment mercury and methylmercury concentrations in water

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

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

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

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

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

Conclusion – Reservoir Hypothesis 1

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

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

Reservoir Hypothesis 2

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

Results – Reservoir Hypothesis 2

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

Conclusion - Reservoir Hypothesis 2

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

Reservoir Hypothesis 3

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

Results - Reservoir Hypothesis 3

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

Conclusion - Reservoir Hypothesis 3

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

5.4 MERCURY BEHAVIOR IN CREEKS: KNOWNS AND UNKNOWNS

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

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

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

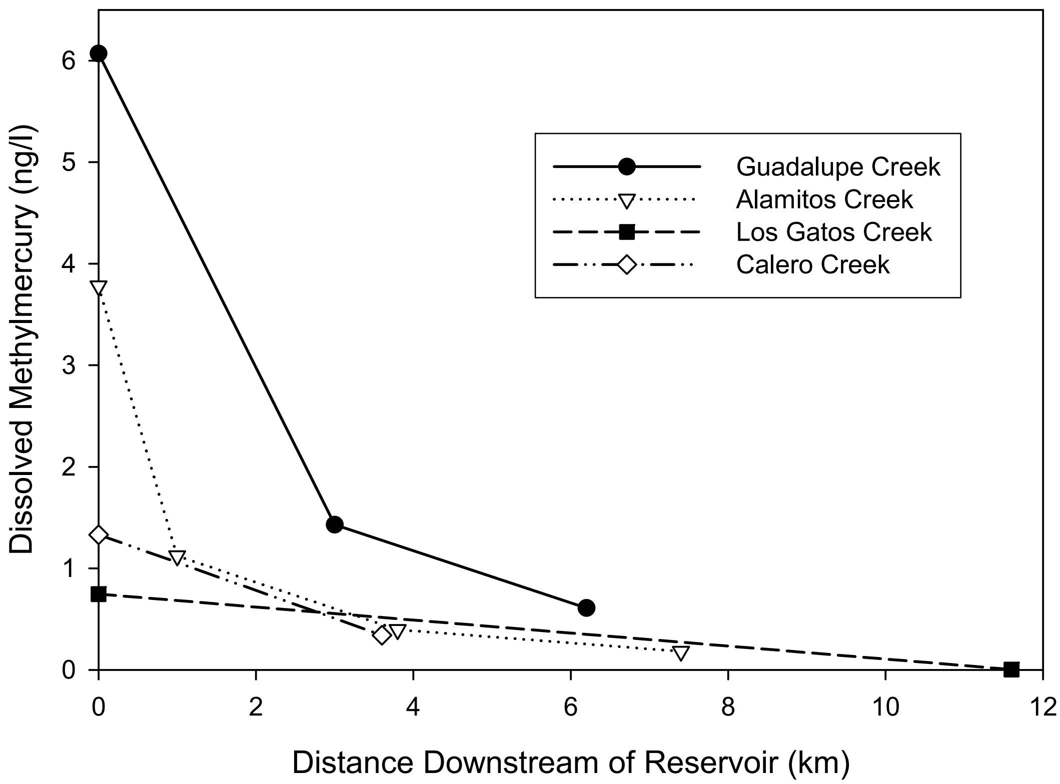


Figure 5-10. Dissolved methylmercury in creeks downstream of the reservoirs, July 2003

5.4.1 Results of Hypothesis Testing: Creeks

Creek Hypothesis 1

Most of the mercury is transported in the wet season.

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

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

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

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

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

Creek Hypothesis 2

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

Results - Creek Hypothesis 2

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

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

Conclusion - Creek Hypothesis 2

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

5.5 Mercury Behavior in Guadalupe River: Knowns and Unknowns

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

5.5.1 Data Specific to Guadalupe River

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

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

5.5.2 CURRENT UNDERSTANDING OF MERCURY BEHAVIOR IN GUADALUPE RIVER PERTINENT TO TMDL

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

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

5.5.3 RESULTS OF HYPOTHESIS TESTING: GUADALUPE RIVER

River Hypothesis 1

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

Results – River Hypothesis 1

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

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

Conclusion – River Hypothesis 1

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

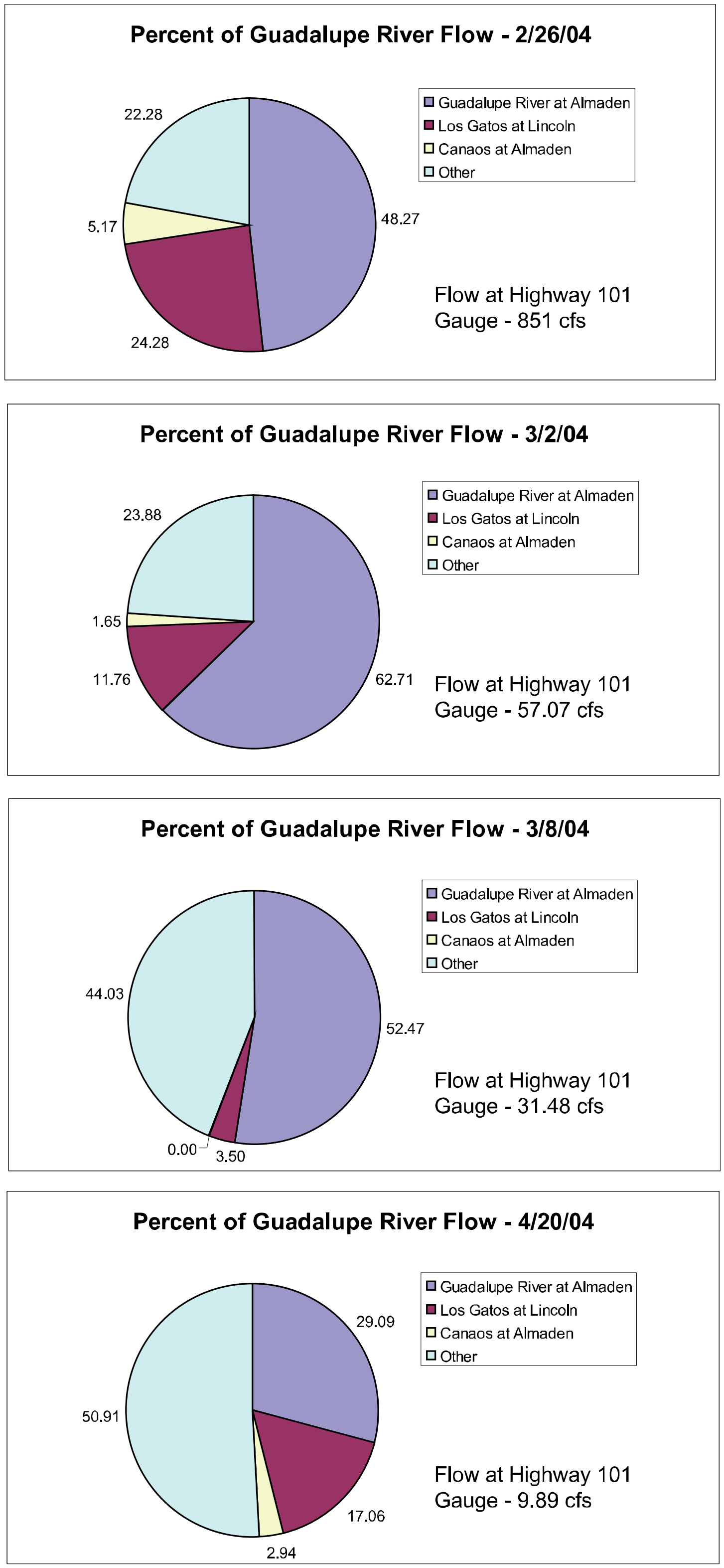
Additional data are needed to refine the sources of mercury to the river. Stormdrain sampling of total, particulate, and dissolved mercury and stormdrain sediment during high flow runoff events would be helpful for several large drains to the lower river. Both the mouths of Guadalupe and Alamitos Creeks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

River Hypothesis 2

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

Results – River Hypothesis 2

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



Flows used are average daily flows

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

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

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

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

Conclusion - River Hypothesis 2

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

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

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

River Hypothesis 3

Guadalupe River is a net sink for methylmercury.

Results – River Hypothesis 3

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

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

Conclusion – River Hypothesis 3

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

5.6 MERCURY BIOACCUMULATION IN FISH

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

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

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

5.6.1 MERCURY BIOCONCENTRATION AND BIOACCUMULATION IN FISH

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

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

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

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

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

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

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

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

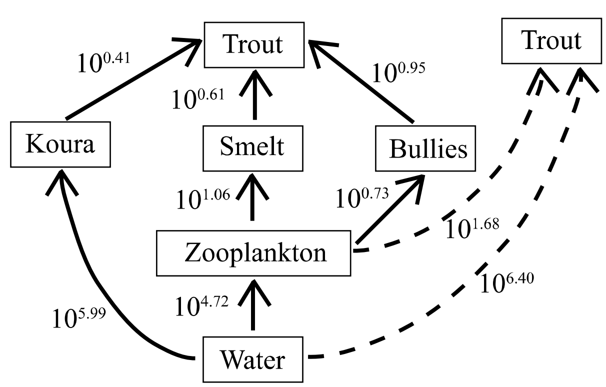


Figure 5-12. Bioaccumulation model for the trout food web in New Zealand Lakes (after Kim and Burggraaf, 1999). Dashed lines do not represent direct linkages but are included to show bioaccumulation factors between food-web elements.

5.6.2 Current Understanding of Bioaccumulation in Impoundments

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

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

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

Panel A: October – May

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

Panel B: June – September

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

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

Panel C: September – October

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

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

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

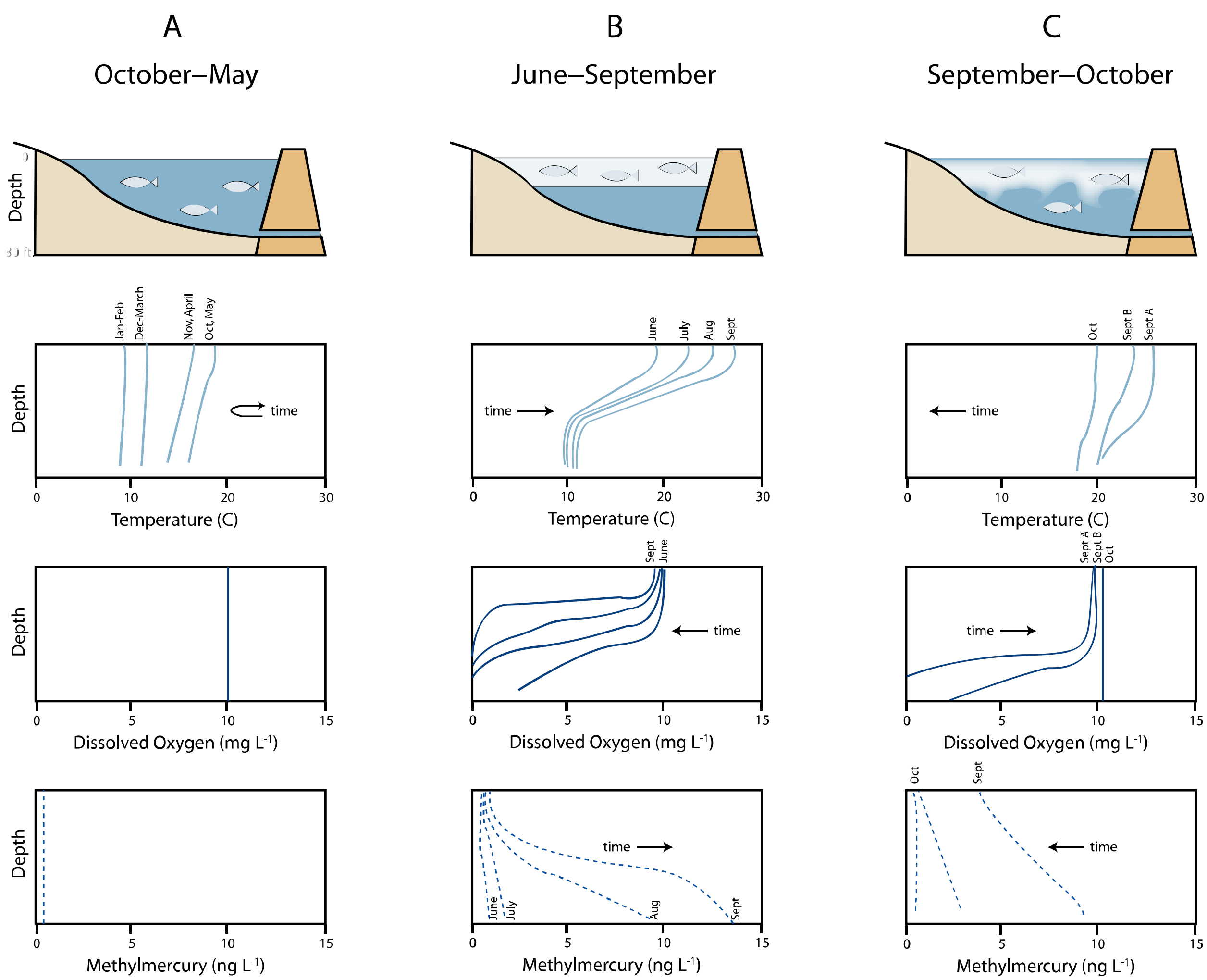


Figure 5-13. Annual hydrologic cycle in reservoirs: temperature, dissolved oxygen, and methylmercury.

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

5.6.3 Current Understanding of Bioaccumulation in Streams

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

5.6.4 Hypothesis and Data Requirements: Bioaccumulation

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

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

Results—Bioaccumulation Hypothesis 1

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

Conclusions—Bioaccumulation Hypothesis 1

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