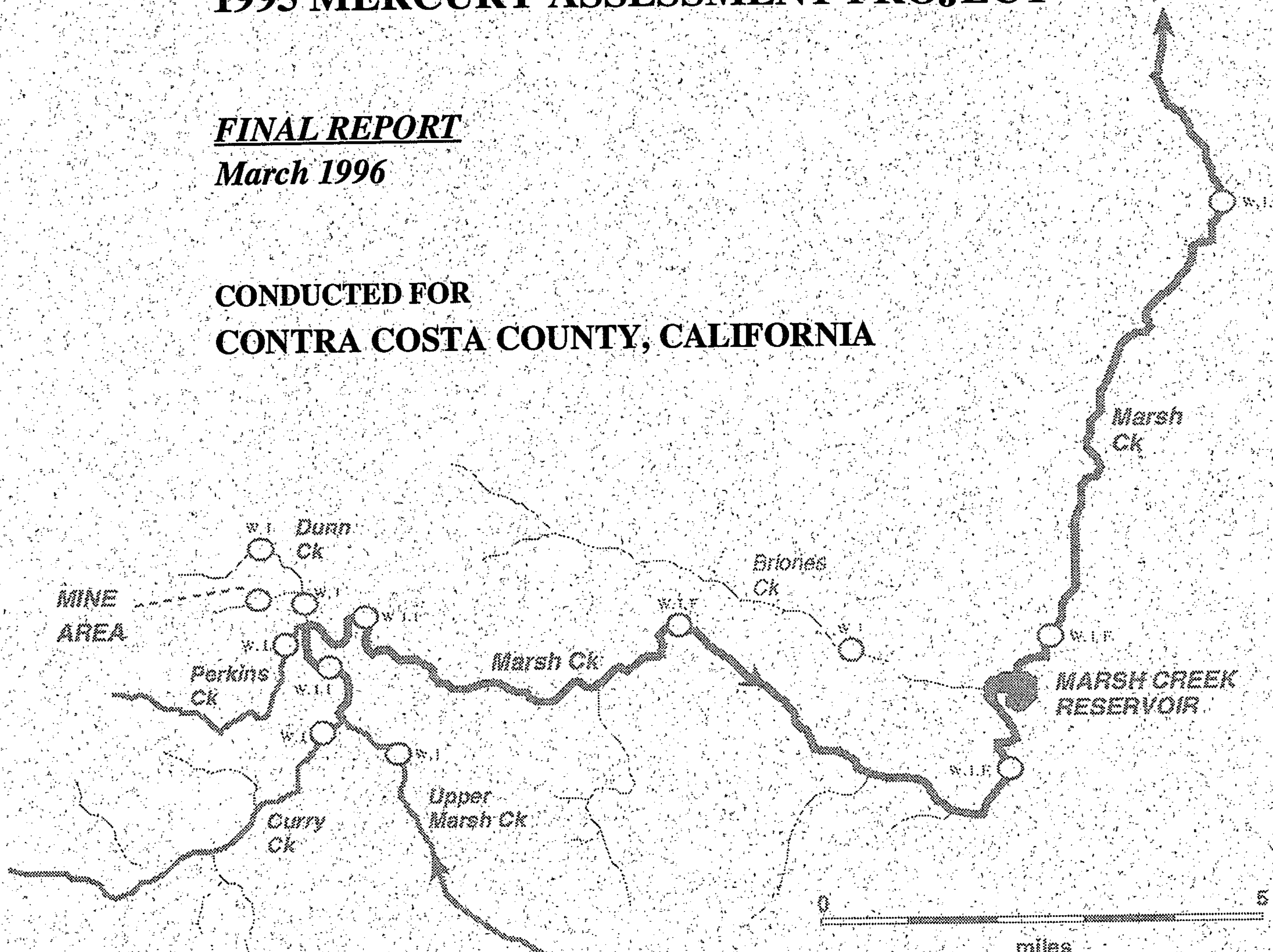
MARSH CREEK WATERSHED
1995 MERCURY ASSESSMENT PROJECT

FINAL REPORT
March 1996

CONDUCTED FOR
CONTRA COSTA COUNTY, CALIFORNIA



STUDY AND REPORT BY

Darell G. Slotton, Ph.D.
Shaun M. Ayers
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1624 Pacific Drive, Davis, California 95616
(916) 756-1001 dgslotton@ucdavis.edu

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ACKNOWLEDGEMENTS

I would like to thank Phil Harrington of the Contra Costa County Department of Public Works and Sue Loyd of the County Health Services Department for their help and support throughout this project. The Wessmans graciously provided access to the mine area on their property, provided helpful background information, and consistently exhibited a willingness and desire to help find a solution to the mercury problem on Mt. Diablo. Thanks also to the public and agency participants in the Marsh Creek Watershed Mercury Task Force for helping to move this process along.

DGS

EXECUTIVE SUMMARY

- Before this comprehensive 1995 study, the Mt. Diablo Mercury Mine was generally assumed to be the main source of mercury to the Marsh Creek watershed in Contra Costa County. However, data was not available to quantify this input, rank the mine against other potential mercury sources, or rule out the possibility of a generalized source of mercury in this mercury-enriched watershed.

- In the project reported here, water, suspended sediments, and flow were analyzed at 18 key sites throughout the Marsh Creek watershed during a high flow period. State-of-the-art collection and analytical procedures were utilized for the 48 individual water mercury analyses, producing above-detection concentration information for each of the major tributaries and potential source regions. Combining concentrations with the flow data, relative mass balances were calculated, ranking each of the tributaries as to mercury contribution to the watershed. This aqueous watershed information was supplemented by mercury analytical collections from multiple groups of aquatic invertebrate indicator species at the 12 stream sites where they were present (41 samples), and stream fish at the 6 sites where they were present (28 samples).

- The 1995 watershed-wide mercury information assembled here establishes that the mine site does indeed represent the overwhelming, ongoing source of mercury to the watershed. Mercury data from water collections and invertebrate bioindicator organisms strongly implicate the mine region as the dominant source of mercury. Mass balance calculations indicate that approximately 95% of the total input of mercury to the upper watershed derives from Dunn Creek, with an estimated 88% traceable specifically to the current exposed tailings piles of the Mt. Diablo Mercury Mine. This is a remarkably high percentage, particularly in light of the geologically mercury-rich nature of the watershed in general, and indicates that the mercury in exposed, processed, cinnabar tailings material is exceptionally available for downstream transport in water.

- The data indicates that the great majority of the mercury load emanating from the tailings is initially mobilized in the dissolved state. This dissolved mercury rapidly partitions onto particles as it moves downstream. The bulk of downstream mercury transport is thus particle-associated.

- Though Dunn Creek carried the bulk of the watershed's source mercury, this small tributary delivered less than 7% of the total water volume and less than 4% of the suspended solids load. With 95% of the mercury originating from the Mt. Diablo Mine area, but 95% of the watershed's suspended sediment load deriving from non-mine, low mercury source regions, any significant decrease in the export of mercury from the immediate mine site should result in a corresponding decline in depositional sediment mercury concentrations downstream and in Marsh Creek Reservoir. This would almost certainly help to drive down the mercury concentrations in water and the flux of mercury into aquatic organisms. With an estimated 88% of the currently exported mercury linked directly to the mine site tailings piles, mercury source mitigation work within the watershed would clearly be best directed toward this localized source.

- Though mitigation recommendations were not a part of our scope of work, we provide input on the subject at the end of this report, based on the data collected in this study, that may help to both clarify the task and direct the planning process.

- Fishes in Marsh Creek Reservoir were found to consist in 1995 of populations of small mosquito fish, native planktivorous hitch, stunted bluegill, and largemouth black bass.

The reservoir was uniformly shallow at this time, with depths averaging 5 feet. The water was organic-stained and very turbid, with heavy growths of aquatic weeds. Lack of oxygen was indicated to be a limiting factor for fish in the bottom waters during the warm season. Adult largemouth bass and possibly bluegill represent the only potential angling opportunities in the reservoir at this time.

- Marsh Creek Reservoir mercury levels were characterized in 1995 with 26 individual sediment mercury samples from surface sediment as well as deep core sections, 25 muscle mercury samples from individual adult fish, 21 muscle and 8 whole composite samples of juvenile fish, and 4 composites of reservoir invertebrates.

- Approximately 5 feet of depositional sediment had accumulated on the reservoir bottom. Reservoir sediment mercury concentrations were found to be quite uniform across the bottom and throughout the reservoir's 30+ year depositional sediment record, with the great majority of samples falling within the range of 0.36-0.80 parts per million mercury, and all sediment samples having less than 1.50 ppm mercury.

- Mercury in Marsh Creek Reservoir edible fish flesh was above the health standard concentration of 0.5 ppm in all samples of "keeper" sized bass and bluegill, with the larger bass ranging up to and slightly over 1.0 ppm muscle mercury. These levels are of concern but are not exceptional for this region of California. They are near enough to the health guidelines that a decline to levels below the guidelines may be realistically attainable, through potential mercury mitigation work in the watershed. Mercury concentrations in adult fish will likely take a number of years to change significantly, even in conjunction with a major reduction in transported watershed mercury. This is because their mercury levels are a composite of accumulations across their multi-year lives. However, mercury levels in a number of the short-lived, alternate indicator organisms utilized in this project should respond to changes in source mercury very quickly.

- With this 1995 watershed mercury assessment, a comprehensive, accurate data base has been initiated for the County, describing mercury conditions throughout the major components of the Marsh Creek watershed. This includes mercury concentration, loading, and relative mass balance data for water and suspended sediment from all major tributaries, mercury levels from aquatic biota throughout the watershed; and depositional sediment and biota mercury concentrations from Marsh Creek Reservoir. The utility of these data for use as a general baseline could be substantially increased with the sampling of selected parameters in the current water year (1996), prior to any mitigation work, to help account for natural inter-annual variability. We note that 1995 was an extremely wet, high-runoff year, while 1996 is more of an average water year. It is our strong recommendation that the County obtain as extensive and varied a baseline data record as possible prior to mitigation, and maintain selective monitoring of key sites and parameters throughout and following mitigation work. Ongoing monitoring of carefully chosen indicator samples will play an integral role in guiding and assessing the effectiveness of any mitigation efforts.

1. INTRODUCTION

The Marsh Creek watershed, in eastern Contra Costa County, is fed primarily by seasonal tributaries from the eastern slope of Mt. Diablo. Flows in the watershed range from zero in many upstream tributaries during the dry season to hundreds of cubic feet per second in downstream Marsh Creek during winter storm runoff. Marsh Creek flows through the towns of Brentwood and Oakley, ultimately emptying into the San Joaquin Delta east of Antioch.

A flood control dam was built on Marsh Creek in 1963, approximately five miles upstream of Brentwood. The resulting Marsh Creek Reservoir is now a shallow water body with extensive riparian, marsh, and aquatic weed growth, providing habitat for a variety of wildlife including resident populations of fish. The surrounding land is currently used for cattle grazing. The primary function of the reservoir is flood control. Operated by the Contra Costa Department of Public Works, it has been closed to the public throughout recent years.

An extensive residential development is planned for the area surrounding Marsh Creek Reservoir. As the existing reservoir may be incorporated into these development plans, information regarding its water quality and that of the watershed in general is of particular current interest. One potential area of concern involves mercury. The California Department of Fish and Game analyzed fish from the reservoir in 1980. These fish were found to be above existing health standards for mercury (Contra Costa County 1994).

A large, abandoned mercury mine site is present on the northeast slope of Mt. Diablo. The Mt. Diablo Mercury Mine is located within the Marsh Creek watershed, adjacent to Dunn Creek, which is a small tributary to Marsh Creek. A substantial area of exposed tailings is present at the site and, while this region contributes only a small fraction of the total flow in the watershed, it has been assumed for many years to be a major contributor to the downstream mercury accumulations. A series of sediment settling ponds were constructed in ~1980 to intercept suspended sediment from the tailings and related springs. Water collections made in the vicinity of the mine by the Central Valley Regional Water Quality Control Board demonstrated significantly elevated mercury concentrations (CVRWQCB 1994). However, these tests did not include the entire watershed and did not have a low enough level of analytical detection to obtain useful data from any but the most extremely contaminated samples. Consequently, this earlier work could not determine the relative loading of mercury to the watershed from the mine on a mass balance basis.

In early 1995, our mercury biogeochemistry research group was contracted by the Contra Costa County Department of Public Works to undertake a comprehensive assessment of mercury throughout the Marsh Creek watershed. It was our strong recommendation that a relatively thorough and up-to-date understanding of mercury dynamics throughout the watershed as a whole be obtained before mitigation plans were made. We felt that it was critical to determine the relative importance of the exposed mine site to the watershed's total mercury loading.

Mercury is naturally enriched throughout extensive areas of the Mt. Diablo region, which is why mercury was historically mined here (Ross 1940). Mercury is similarly enriched throughout much of the California Coast Range. As the majority of the water flow and associated transported material in the Marsh Creek watershed appeared to derive from tributaries other than the one containing the Mt. Diablo mine, it was quite conceivable that a significant proportion of the total mercury budget might come from more generalized watershed sources. Despite the locally contaminated nature of the mine vicinity itself, if the majority of total mercury loading came from elsewhere in the watershed, mitigation work at the mine could be relatively ineffectual.

In the first phase of our mercury assessment, we developed a sampling plan that accounted for all important watershed tributaries, major source flows at the mine site, and included stations along downstream Marsh Creek to the reservoir and well beyond. We waited for a period of high but relatively steady flows following a major storm series, when suspended material was being transported in abundance and the sites could be inter-calibrated. These conditions occurred in late March 1995 and we were able to successfully collect samples throughout the watershed within a short period of consistent flow. At each of the 18 sites, water samples were taken for analysis of mercury in both raw and filtered fractions, as well as for suspended solids concentration. The mercury samples were taken using ultra-clean techniques and were analyzed by the foremost aqueous mercury analytical laboratory in the world, providing above-detection mercury concentration data for all samples. At each site, the water flow was determined as well. With concentration and flow data for each site, it was then possible for us to calculate the total loads of mercury moving through each stretch and to compare the tributaries on a relative basis.

To supplement these water-based mercury measurements, we looked at bioindicator organisms within the watershed. At 12 collection sites, we sampled localized benthic invertebrates of several types. These invertebrates integrate the bioavailable fraction of mercury that they are exposed to over their lifetimes. In-stream fish were collected at the 6 stations where they were present. All of these samples were analyzed for mercury, to provide time-integrated information on the relative mercury trends among the different tributaries.

A second piece of essential information was the determination of current mercury conditions in Marsh Creek Reservoir, particularly within the fish populations. As the only data to have been collected there had been taken 15 years earlier, in 1980, and the actual data themselves were apparently unavailable (Contra Costa County 1994), a new survey of the reservoir was warranted.

Therefore, in a second phase of our assessment, we conducted a study of mercury in Marsh Creek Reservoir sediments and biota in September 1995. We collected surficial sediments from throughout the reservoir and obtained a record of historical sediment mercury deposition over the 30+ year history of the reservoir through sediment core samples. The reservoir's current fish populations were assessed, with tissue mercury analyses conducted on extensive samples from all types with significant representation at this time.

Table 1 summarizes the mercury analytical samples collected for both phases of this project. A total of 48 aqueous mercury analyses were made, half in raw water and half in corresponding filtered water. Total mercury was analyzed in 170 individual biotic and sediment samples, including 46 individual fish analyzed for muscle mercury from Marsh Creek Reservoir. Additional analytical samples for the project included suspended solids samples from all stream sites (22, including duplicate samples), and moisture and organic percentage analyses in 30 reservoir bottom sediment samples.

Throughout this report, the data for each major watershed parameter is generally presented both in tabular and graphic form. Map figures of each of the major data parameters are included for the watershed as a whole, as well as for the immediate mine vicinity where appropriate.

With the data collected in the two phases of the study, this report provides the County with information on current mercury levels throughout the Marsh Creek watershed and Marsh Creek Reservoir. Further, the relative importance of the various upstream source regions to the overall mercury loading in the system can be estimated. Finally, in the event that new mercury mitigation work is initiated within the watershed, a comprehensive, accurate data base has been initiated, describing mercury conditions throughout the major components of the system, including water, suspended sediment, and aquatic biota from the entire watershed and depositional sediment and biota from Marsh Creek Reservoir. Baseline data, taking into account natural inter-annual variability, can be compared to mercury levels in future collections to guide and assess the effectiveness of mitigation efforts.

Table 1. Summary of all Samples Analyzed for Mercury in This Project

	Raw Water	Filtered
Aqueous Total Mercury:	22	22
Aqueous Methyl Mercury:	2	2
TOTAL AQUEOUS SAMPLES (48 total):	24	24

	Stream	Reservoir
Invertebrate Composites:	41	4
Small Fish Whole Fish Composites:	18	8
Individual Fish Muscle Samples:	20	46
Adult Largemouth Bass:		*10*
Juvenile Largemouth Bass:		*10*
Adult Bluegill:		*1*
Juvenile Bluegill:	*4*	*11*
Hitch:	*8*	*14*
Juvenile Salmon:	*5*	
Crayfish Tail Muscle:	*3*	
Individual Fish Liver Samples:		7
Sediment:	—	26
TOTAL SOLID SAMPLES (170 total):	79	91

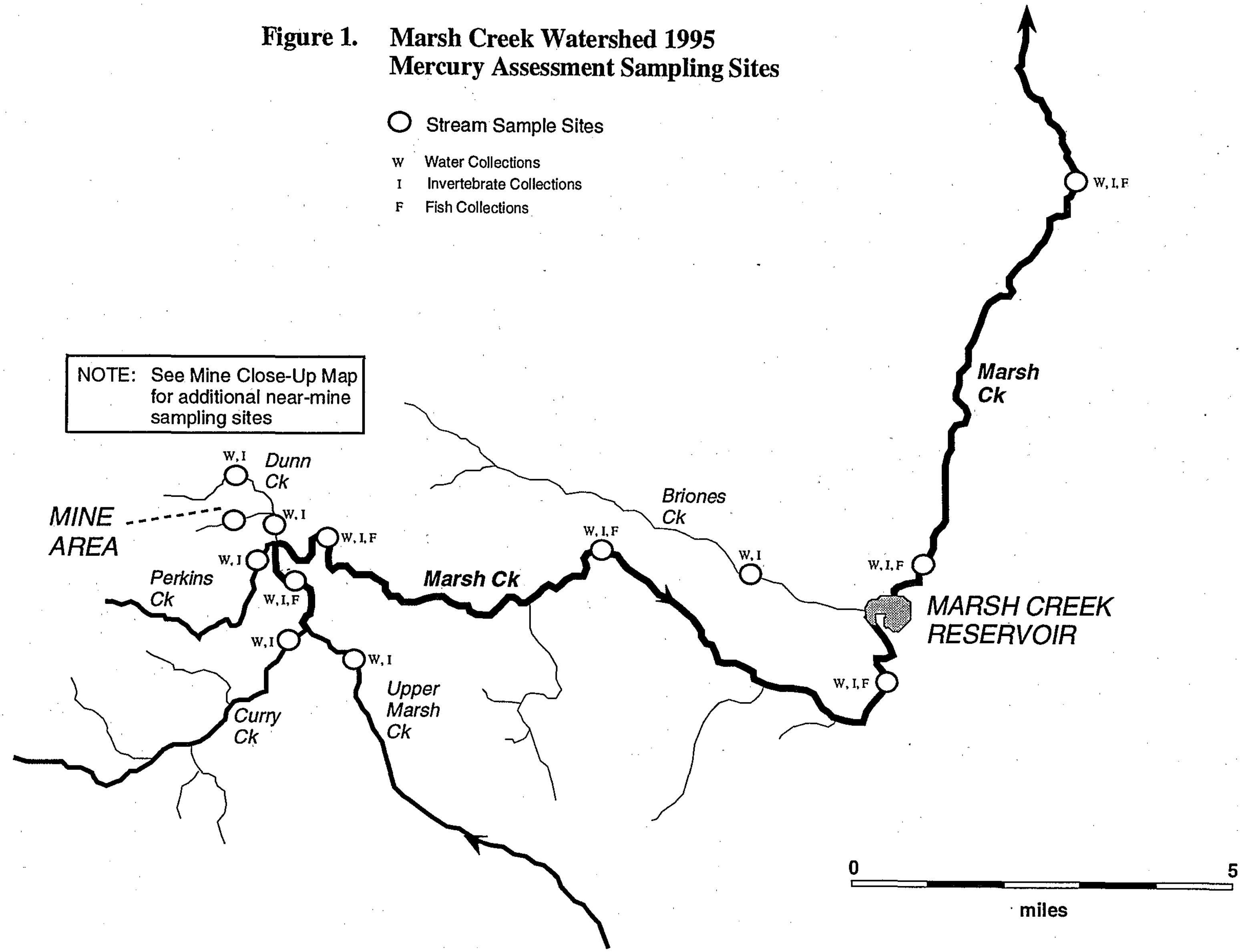
2. METHODS

2.1 Site Selection

The sampling sites utilized for the watershed portion of this project are shown in Figures 1 and 2. Sampling sites within Marsh Creek Reservoir are displayed in section 3.2 (Fig. 18).

In the watershed component of this work, our plan was to sample all significant tributaries of the Marsh Creek watershed, immediately following heavy rains. We sampled water and invertebrates from the upper section of Marsh Creek (above Curry Creek), from Curry Creek, Perkins Creek, Dunn Creek both above and below the Mt. Diablo Mercury Mine area, "My" Creek (a tributary to Dunn Creek that runs along the northern edge of the mine area), and Briones Creek. We were unable to sample two streams which enter Marsh Creek from the south along the mid section of the creek. This was because the landowners repeatedly refused us permission to make collections. However, these were relatively small creeks and their contributions to the downstream mercury load could be estimated by

Figure 1. Marsh Creek Watershed 1995 Mercury Assessment Sampling Sites



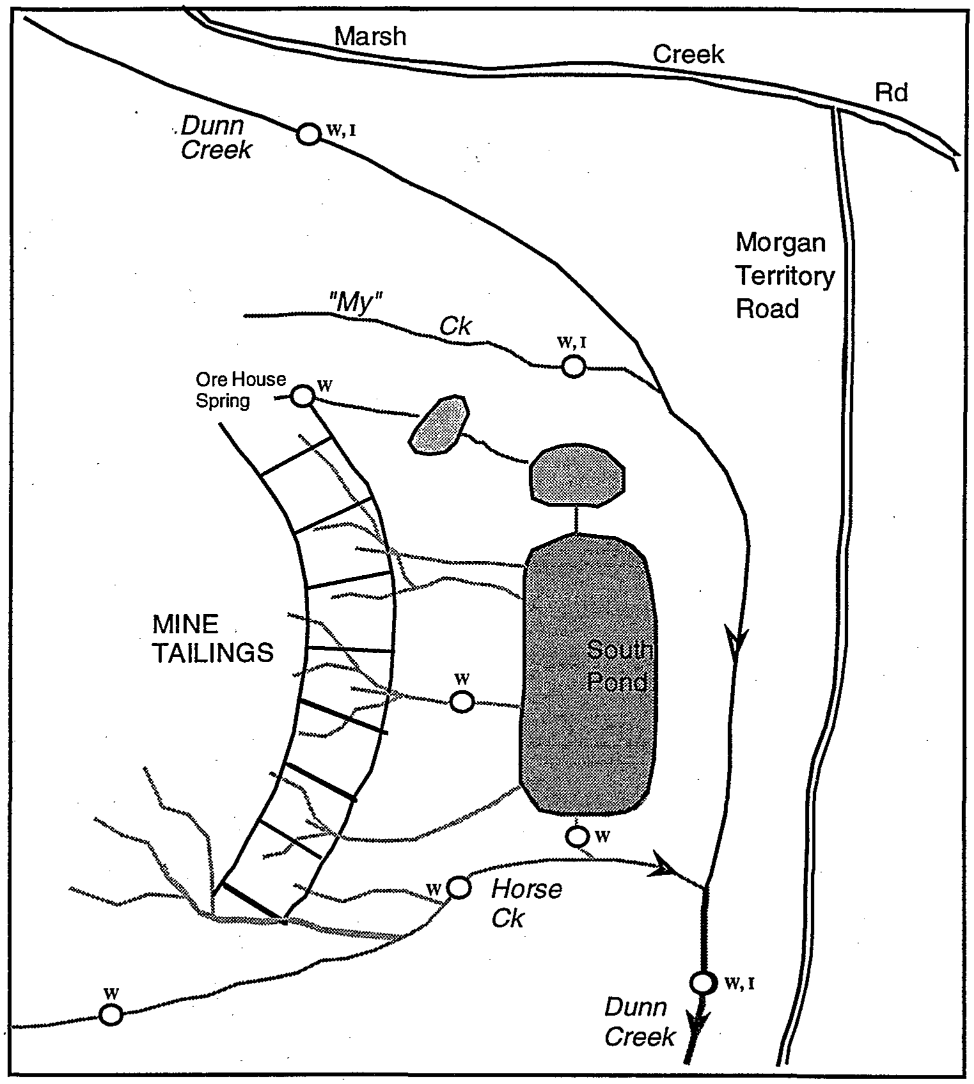


Figure 2. **1995 Mercury Assessment Sampling Sites in the Vicinity of the Mt. Diablo Mine**

O Sample Sites

W Water Collections
I Invertebrate Collections

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noting the changes or lack thereof in the various parameters at sites on Marsh Creek both above and below their inflows. As it turned out, they were insignificant to the regional mercury picture.

In addition to the tributaries, we sampled water, invertebrates, and fish from six additional sites along the length of Marsh Creek, including a site between Curry and Perkins Creeks, a site ~1 mile downstream of the Dunn Creek inflow, another ~5 miles downstream, one ~10 miles downstream just above the reservoir, one just below the reservoir, and a final Marsh Creek site well downstream at Delta Rd, between Brentwood and Oakley. In addition to these main stream sites, we collected water from five additional sites in the vicinity of the mine itself. These included samples from Horse Creek, which flows along the south edge of the tailings, both above the tailings influence and below, just before entering Dunn Creek. Other mine area water samples included outflow from the lower settling pond, representative inflow to that pond through the tailings, and the Orehouse spring which flows into the north settling pond.

In summary: at a total of 18 sites, flows were determined and we sampled for suspended solids and for total mercury in raw and filtered water immediately after a major storm cycle. Methyl mercury was additionally analyzed from duplicate samples taken from Marsh Creek directly above the reservoir. Benthic invertebrate bioindicators were sampled at all sites containing sufficient concentrations of organisms for analysis (12 sites) and fish were taken at those stream sites where they were present (6 sites).

In Marsh Creek Reservoir, surficial sediment was collected from 8 different locations in the reservoir (Fig. 16). These were spaced so as to sample all major depositional areas. Sediment cores were taken at the centers of each of the two main basins. Fish were taken from throughout the reservoir.

2.2 Collection Techniques

2.2.1 <u>Water</u>

Water collections for mercury analysis were made in conjunction with Frontier Geosciences Laboratory, which is the most highly esteemed aqueous mercury laboratory in the world. Ultra-clean 250 ml teflon collection bottles were shipped to us, individually packaged in double zip-lock bags. Two person clean collecting protocol was used, in which the actual sample bottle was touched only by one researcher who handled nothing else and wore sterile gloves. Samples were taken in flowing water by standing mid-stream and, facing upstream, submerging the bottle in the middle of the flow. The cap was

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removed underwater, allowing the bottle to fill without coming into contact with potential surface film material, and then resealed before bringing to the surface. The bottle was then placed into the waiting isolation bags, held by the co-worker. Bagged ice packs kept the bottles cool and samples were shipped by overnight mail to Frontier Geosciences. Water samples were filtered and preserved in a trace metal clean room within 24 hours of collection, and later analyzed within standard holding times.

In conjunction with each set of aqueous mercury samples, we collected identical water into 1 liter bottles for analysis of suspended solids. These bottles were held in a separate ice chest, on ice, and were returned to our laboratory in Davis for processing within 48 hours of collection.

Flow at each of the stream sites was determined by measuring the cross sectional area of the channel along a relatively uniform stretch. A known number of meters was marked off alongside. A current float of near-neutral buoyancy was then passed through this course three to ten times. Time to the nearest 0.01 seconds was recorded for each pass.

2.2.2 Invertebrates

Stream invertebrates were taken from riffle habitat at each of the sites where they were present, i.e. from rapids or cobble bottomed stretches with maximal flow, where aquatic insects tend to be most concentrated among the rock interstices. Stream invertebrates were collected primarily with the use of a research kick screen. At each site, one researcher spread and positioned the screen perpendicular to the flow, bracing the side dowels against the bottom, while the other researcher overturned boulders and cobble directly upstream of the screen. These rocks were hand scrubbed into the flow, dislodging any clinging biota. Following the removal of the larger rocks to the side of the stretch, the underlying cobble/pebble/gravel substrate was disrupted by shuffling the boots repeatedly. Invertebrates were washed into the screen by the current. The screen was then lifted out of the current and taken to the shore, where forceps were used to pick macro-invertebrates from the screen into collection jars. This process was repeated at each site until a sufficient sample size of each taxon of interest was accumulated to permit analysis for mercury. At Marsh Creek Reservoir, samples of adult dragonflies and damselflies were taken with insect nets.

Samples were maintained in their collection jars on ice, and then cleaned in fresh water within 24 hours of collection. Cleaning was accomplished by suspending sample organisms in fresh water and, as necessary, shaking individuals in the water with teflon-coated forceps to remove any significant clinging surficial material. Cleaned organisms were stored in pre-cleaned jars with teflon-lined caps, which were frozen and then dried at 50-60 °C. The dried sample was homogenized to a fine powder with teflon-coated instruments and a glass laboratory mortar and pestle. All of these techniques have been well established and tested in extensive prior mercury research work throughout California (Slotton et al. 1995a).

2.2.3 Fish

Fish were taken from selected stream sites, where present, with baited minnow traps which were left overnight. Stream fish were also taken with seines which were pulled through certain stretches to trap fish. In Marsh Creek Reservoir, fish were collected using a boat with a variety of experimental gillnets, as well as by set line, angling, and with dip nets. Small individuals to be analyzed for mercury from both stream and reservoir were held on ice in sealed bags. They were later weighed and measured in the laboratory and homogenized into appropriate composite samples with a laboratory homogenizer. Larger fish to be analyzed were weighed and measured on site. Tissue samples for mercury analysis were excised directly in the field, using clean technique, with stainless steel scalpels. Muscle samples were taken from the dorso-lateral ("shoulder") region, as done by the California Department of Fish and Game. Tissue samples were placed directly into pre-weighed laboratory digestion tubes, which were capped with teflon liners and maintained in sealed bags. The precise weight of each tissue sample was determined by weighing the tubes containing samples (together with pre-weighed blanks) and subtracting the initial empty weights. We have utilized these techniques with great success in similar work over the past 11 years (Reuter et al. 1989, Slotton 1991, Slotton et al. 1995a, Slotton et al. 1995b)

2.2.4 Sediment

Sediment samples were taken in Marsh Creek Reservoir both from the surficial sediment at the sediment/water interface and in extended cores which penetrated deep into the sediment. Surficial sediment samples were collected with an Ekman dredge and were spooned into pre-cleaned glass jars with teflon-lined caps. Sediment cores were taken by hand with a custom-made non-metallic coring device which was driven into the bottom from the boat and then carefully pulled out and transported to shore. There, the core was extruded and sectioned, with samples retained in pre-cleaned glass jars with teflon-lined

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caps. Sediment samples were maintained refrigerated but unfrozen (so as to not alter mineral structure) until they were analyzed for mercury within 18 days of collection.

2.3 Analytical Methodology

2.3.1 Water

Total mercury in water was analyzed by dual amalgamation/cold vapor atomic fluorescence spectrometry, as developed by Bloom and Crecelius (1983). Methyl mercury was analyzed utilizing aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection, as developed by Bloom (1989). The detection levels for these extremely sensitive analyses are approximately 0.01 ng L^{-1} (parts per trillion), well below any environmental aqueous mercury levels present throughout Northern California.

Current speed was estimated by taking the average time of the near-neutral buoyancy current float to traverse the uniform test stretch of stream and dividing by the length of the stretch. The speed of the flow was then multiplied by the cross sectional area to obtain the flow volume per second.

The bulk load of total mercury moving through each stream site per day was determined by multiplying the measured aqueous mercury concentration by the corresponding measured flow (volume per second) and finally by the number of seconds in a day.

The relative mass balance contributions of bulk mercury from individual upstream source areas to downstream receiving waters were determined by assessing the proportional contributions of bulk mercury among the source flows immediately upstream at each major fork in the sampled streams. This was done by working upstream from the Marsh Creek site 1 mile below the Dunn Creek inflow. Based on the data, all significant mercury inputs occurred above this point. The calculated bulk flows of mercury of the streams contributing to this portion of Marsh Creek (Marsh Creek above Perkins Creek, Perkins Creek, and Dunn Creek) were assessed relative percentage contributions by dividing each mercury load value by the sum of the three. The total mercury input at this point was considered to be 100%. The relative contributions of tributaries upstream of these 3 stem flows were determined by successively following this procedure and multiplying the percentage bulk mercury load proportions of contributing flows by the previously calculated percent contribution of the stem flow immediately downstream (Table 6).

2.3.2 Suspended Solids

Suspended solids concentration at each site was determined by filtering a given volume of well mixed sample water through a pre-weighed glass fiber filter. The solids were retained on the filter, which was then dried at 105 °C for 24 hours. After cooling the filter in a dessicator, it was re-weighed to the nearest 0.0001 g. The weight of solids was obtained by subtracting the initial, clean weight of the filter from the weight with solids. This amount was divided by the volume of water filtered to derive the solids concentration on a milligram per liter basis. To obtain bulk loading quantities of suspended solids, the concentration data were weighted by the accompanying flows, as described for aqueous mercury.

Dry weight mercury concentration of the particulates themselves was estimated by first determining the aqueous mercury concentration attributable to the suspended solids. This was done by subtracting the aqueous mercury concentration in filtered water from the corresponding mercury concentration in raw water. This aqueous concentration, attributable to the entrained particulates, was then divided by the concentration of suspended solids in the water.

2.3.3 Fish, Invertebrate, and Sediment Total Mercury

Solid samples for mercury were analyzed using homogeneous portions. Sediment was subsampled from homogenized, wet (liquefied) samples. Identical subsamples were used to determine moisture content for dry weight conversions. Fish tissue was also analyzed on wet (fresh) samples, as is the standard procedure for governmental agencies. Mercury analyses of invertebrate samples were conducted with dried and powdered samples for uniformity, as described in Slotton et al. (1995a).

Solid samples of all types were processed by first digesting in concentrated sulfuric and nitric acids and potassium permanganate, under pressure, at 80-100 °C for three hours. They were subsequently analyzed for total mercury using a well-established modified cold vapor atomic absorption (CVAA) micro-technique, described in Slotton et al. (1995b). The level of detection for this technique is approximately 0.01 mg kg^{-1} (ppm), sufficient to provide above-detection results for nearly all aquatic sediment and biota samples in this region.

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2.3.4 Sediment Water and Organic Content

Moisture content of sediment samples was determined by weight difference between fresh, homogenized sample (10-2560 g) and the sample after drying at 105 °C to constant weight (generally 24 hours), subtracting out the weight of the weighing container. Weights were accurate to ± 0.001 g. To obtain the Loss On Ignition (LOI) estimate of organic content, the dried sample was subsequently placed in a 475 °C muffle furnace for 2 hours in order to burn off any organic matter. After cooling, the mineral moisture of hydration was returned by re-wetting the sample. The sample was again dried at 105 °C to constant weight, cooled in a dessicator, and weighed again to ± 0.001 g. The loss in weight between the initial dry sample and the sample after the muffle furnace treatment is attributed to organic matter.

2.4 Quality Assurance/Quality Control (QA/QC)

2.4.1 Water

The water samples for mercury were analyzed at Frontier Geosciences Laboratory in a single, large analytical run, accompanied by a good number of QA/QC samples. QA/QC was excellent, as summarized below in Table 2.

Table 2. Frontier Geosciences Laboratory Aqueous Mercury QA/QC (from 1 analytical run)

	Spike Recoveries (%)	Duplicate RPD (%)	Reagent Blanks (ng/L)	Filter Blanks (ng/L)	NRCC Dogfish (ppm)
Certified Level					4.57
Ideal Recovery	(100%)	(0%)	(0.00)	(0.00)	(100%)
Control Range (%)	75-125%	≤25%			75-125%
Control Range (concentration)			≤0.20 ng/L	≤0.20 ng/L	3.43 - 5.71
Recoveries (%)	100-113%	1-20%			97-107%
Recoveries (concentration)			0.10	0.12	4.42 - 4.89
(n)	n=3	n=11	n=1	n=1	n=7
Mean Recoveries (%)	105%	8%			101%
Mean Recoveries (concentration)			0.10	0.12	4.63

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2.4.2 Fish, Invertebrates, and Sediment

Extensive QA/QC accompanied all of our total mercury analyses of aquatic biota and sediment samples. For each sample batch of approximately 24 samples, a large number of QA/QC samples were included through all phases of the digestion and analysis procedures (16 total). These included 1 blank and 7 aqueous mercury standards, 2 pairs of samples of standard reference materials (4 total) with known mercury concentrations, 2 duplicates of analytical samples, and 2 spiked analytical samples. These 16 additional samples per analytical run were used, as always, to ensure the reliability of the data generated. The QA/QC results for this portion of the work are summarized in Table 3.

Table 3. D.G. Slotton Laboratory Total Mercury QA/QC Summary (from 8 analytical runs)

	Std Curve R^2	Spike Recoveries	Duplicate RPD	NBS Tuna	IAEA Tuna	NBS Sediment	BCR Sediment
Certified Level (ppm)				0.95	4.70	1.47	0.67
Ideal Recovery	1.000	(100%)	(0%)	(100%)	(100%)	(100%)	(100%)
Control Range (%)	≥0.975	75-125%	≤25%	75-125%	75-125%	75-125%	75-125%
Control Range (ppm)				0.71-1.19	3.60-6.00	1.10-1.84	0.50-0.84
Recoveries (%)	0.998-1.000	87-108%	0.2-18.8%	88-120%	93-104%	97%	90-100%
Recoveries (ppm)				0.84-1.14	4.37-4.87	1.42-1.43	0.60-0.67
(n)	n=8	n=18	n=21	n=16	n=15	n=2	n=6
Mean Recoveries (%)	0.999	98%	5%	106%	98%	97%	96%
Mean Recoveries (ppm)				1.01	4.61	1.43	0.64

The extensive set of aqueous standards was used to construct an accurate curve of mercury concentration vs atomic absorbence for each analytical run. The standard curve R^2 values for the mercury runs utilized in this project all fell between 0.998 and 1.000, well above the control range of ≥ 0.975. The standard reference material samples included two fish standards and two sediment standards. All recoveries were within the 75% - 125% control levels, at 88-120%. Sample duplication was excellent, with relative % difference (RPD) having a mean value of 5% among 21 total paired samples. Spike recoveries were also consistently good, with recoveries of 87% - 108%, as compared to the 75% - 125% control levels.

3. RESULTS

3.1 Watershed

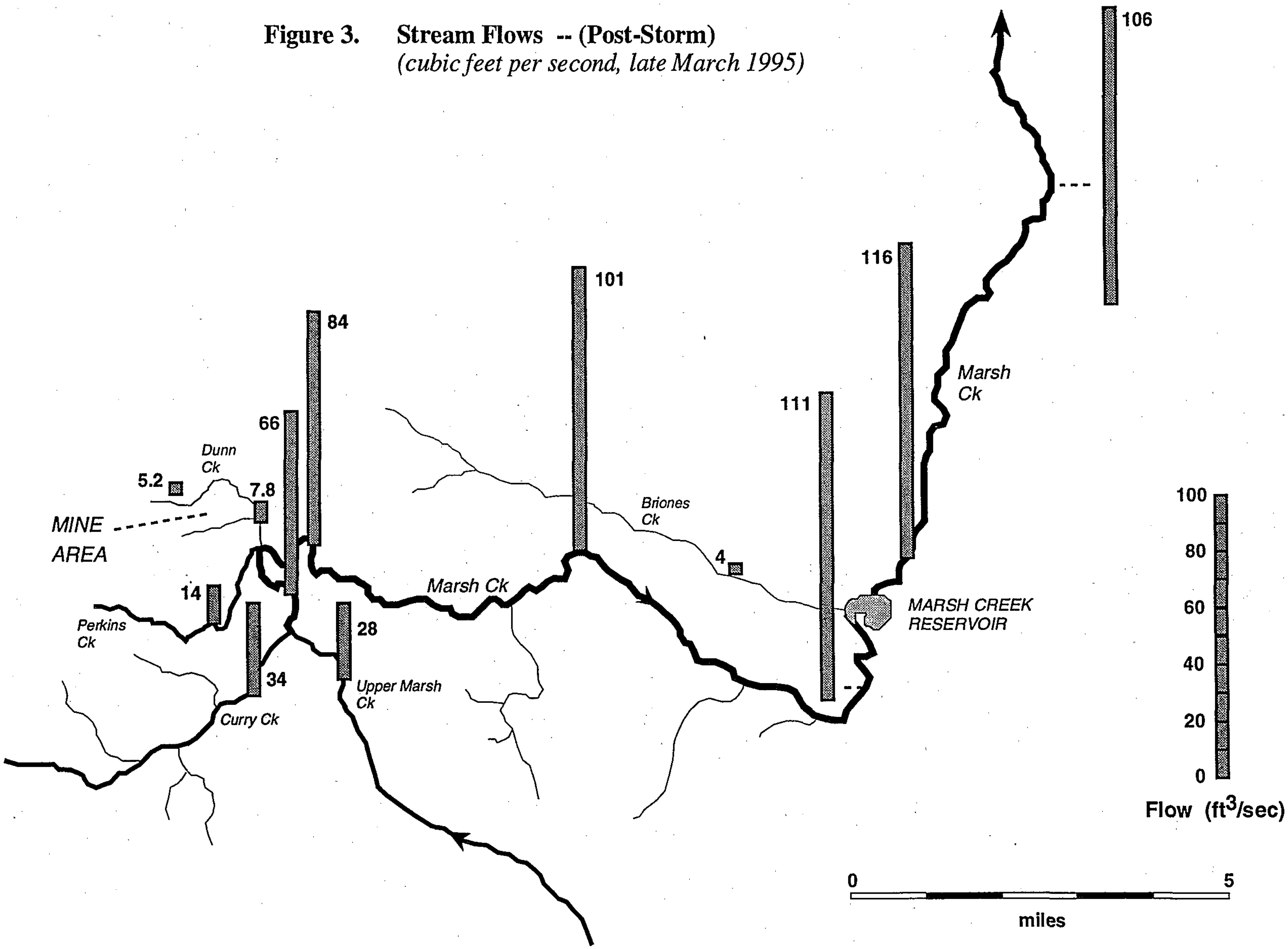
3.1.1 Water

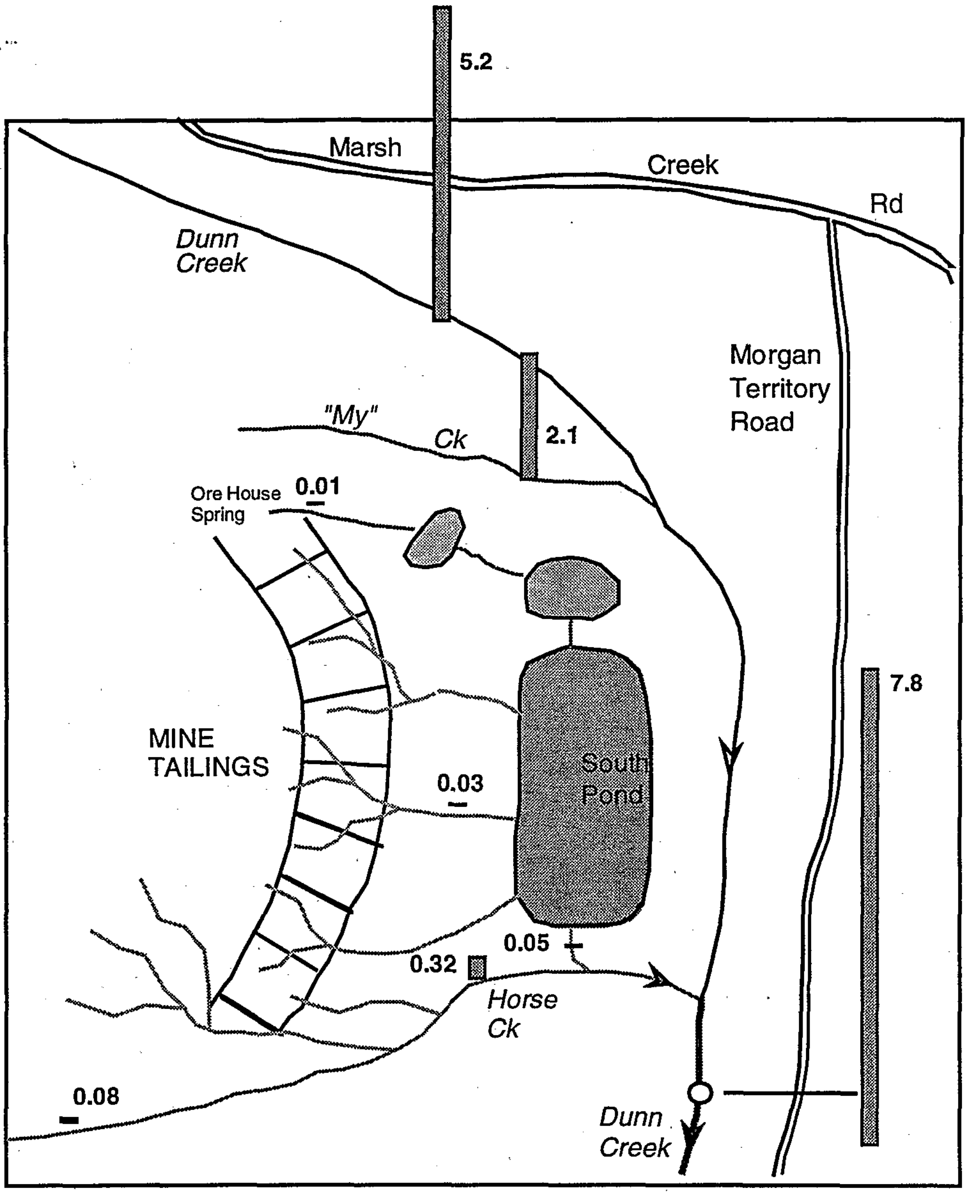
We determined flows and collected water samples for mercury and suspended solids at 18 individual sampling sites distributed throughout the Marsh Creek watershed. These collections were made within a 48 hour period during high runoff flow conditions in late March 1995, following an extensive series of storms. A considerable effort was made to obtain these samples within as close a time period as possible, during high but relatively stabilized flow conditions. Flow values are presented in Table 4 and Figures 3 and 4. Concentration data for suspended solids and aqueous mercury are presented in Table 4 and Figures 5 and 6. Calculated bulk mercury loads, on a grams per day basis for each site, can be found in Table 5 and Figures 7 and 8. Mass balance data quantifying the overall proportional mercury contributions of the various source tributaries to downstream receiving waters are presented in Table 6 and Figures 9 and 10.

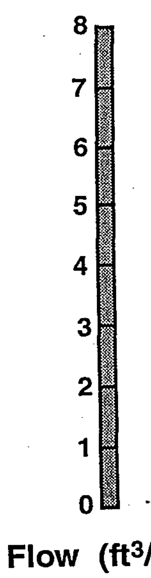
Table 4. Watershed Flow; Aqueous Mercury and Suspended Solids Concentration Data

Site	Flow (cfs)	Aqueous Total Mercury Raw (ng/L)	Aqueous Total Mercury Filtered (ng/L)	Suspended Solids All (TSS) (mg/L)	Suspended Solids Solids Hg (dry ppm)
Upper Marsh Creek	28.30	3.24	1.29	16.10	0.10
Curry Creek	33.70	5.18	1.49	32.00	0.12
Marsh Ck above Perkins Ck	65.60	4.69	1.34	32.10	0.10
Perkins Creek	13.90	8.89	4.11	3.00	1.59
Upper Dunn Creek	5.20	3.60	2.73	1.50	0.60
Upper Horse Creek	0.08	25.50	16.00	1.10	8.64
"My" Creek	2.10	381.00	28.40	10.90	32.41
OreHouse Spring	0.01	1,940.00	71.00	11.40	164.00
Trickle coming from tailings	0.03	58,400.00	54,100.00	77.20	56.37
South Pond outlet	0.05	59,100.00	59,100.00	26.10	0.00
Horse Creek @ tailings	0.32	25,000.00	21,900.00	104.00	29.8
Dunn Ck below mine confluence	7.80	949.00	226.00	13.50	53.60
Marsh Ck below Dunn Ck conf.	83.60	79.30	21.40	19.40	2.99
Mid Marsh Ck @ rd. crossing	101.00	52.80	10.10	24.60	1.74
Marsh Ck above Reservoir	111.00	37.67	8.80	23.10	1.25
Briones Ck @ Deer Valley Rd.	4.10	5.84	2.03	61.20	0.06
Marsh Ck below Reservoir	116.00	43.70	7.47	34.60	1.05
Marsh Ck @ Delta Rd.	107.00	37.80	6.44	53.80	0.58
		Aqueous Methyl Mercury Raw (ng/L)	*Aqueous Methyl Mercury* Filtered (ng/L)		
Marsh Ck above Reservoir		0.204	0.112		

Figure 3. Stream Flows -- (Post-Storm)
(cubic feet per second, late March 1995)







Note scale (vs 100 ft³/sec scale used in whole watershed map)

Figure 4. **<u>Stream Flows</u> in the Vicinity of the Mt. Diablo Mine**
(Late March 1995)

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3.1.1.1 *Relative Flows*

Flow values, in units of cubic feet per second (cfs), are presented in Table 4 and Figures 3 and 4. Flow data were collected as a key parameter for bulk load and mass balance calculations. At the time of these samplings, major tributary streams in the Marsh Creek watershed each contributed flows of between 4 and 34 cubic feet per second to Marsh Creek. The flows measured in Marsh Creek itself demonstrated a characteristic, steady increase moving downstream, incorporating the inputs of the various tributaries as well as groundwater inflows. Flow was estimated at approximately 100 cfs at a site halfway between the Dunn Creek confluence with Marsh Creek and the downstream reservoir. Flows at and below the reservoir were an additional 5-15% higher.

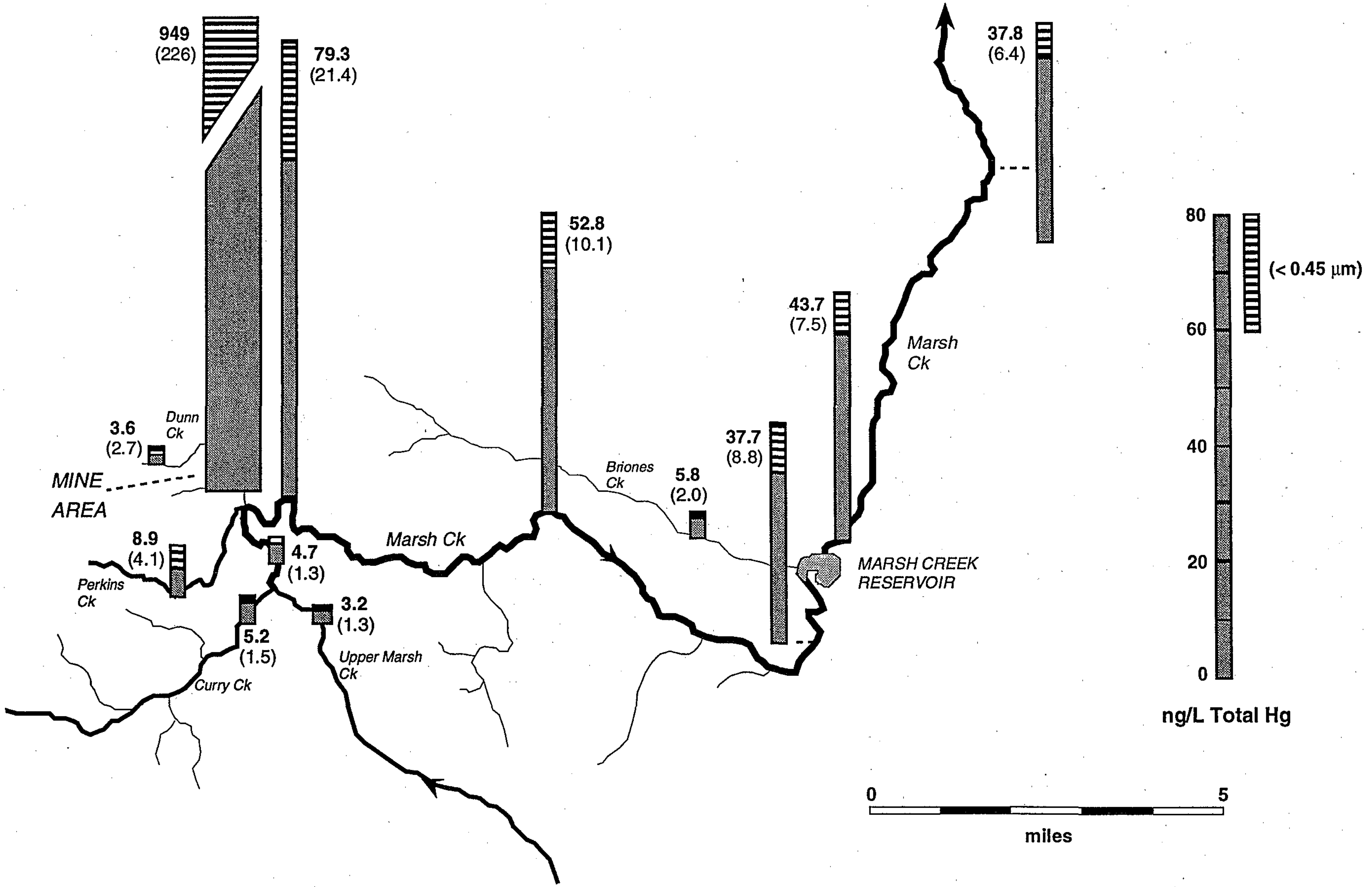
Of the ~115 cfs flow noted immediately above and below the reservoir in this sampling, three major upstream tributaries together accounted for 69% (~80 cfs) of the total. These were upper Marsh Creek, Curry Creek, and Perkins Creek. The water volume measured in Dunn Creek (7.8 cfs), which includes all flows derived from the Mt. Diablo mine area, amounted to less than 7% of the downstream flow. Further, the great majority of this water was derived from regions away from the mine, including the upper portions of Dunn Creek (5.2 cfs) and Horse Creek (0.08 cfs). "My" Creek, which is north of and relatively peripheral to the main tailings region, accounted for a further 2.1 cfs. Flows emanating specifically from the area of exposed tailings were estimated at only 0.28 cfs at the time of this sampling (lower Horse Creek minus upper Horse Creek, South Pond outflow minus Orehouse spring flow). This tailings-specific flow, at 0.24%, was less than one quarter of 1% of the total downstream water flow noted at the reservoir.

3.1.1.2 *Aqueous Mercury Concentrations*

Mercury was analyzed in homogenized, representative water samples taken from each of the 18 sites throughout the Marsh Creek watershed. Each sample was further divided into a filtered (≤ 0.45 μm) and raw water sample, each of which was analyzed for total mercury. Duplicate samples taken at the inflow to Marsh Creek Reservoir were also analyzed for methyl mercury. Aqueous mercury concentrations, in units of nanograms per liter (ng L^{-1}, = parts per trillion), are presented in Table 4 and Figures 5 and 6 Mercury measured in the filtered fraction is displayed superimposed on the total mercury data bars in the figures, and in parentheses in the figure data.

It is apparent in Figure 5 that; <u>on a concentration basis</u>, aqueous mercury levels in Dunn Creek downstream of the Mt. Diablo mine were significantly higher than the concentrations seen in all other tributaries to Marsh Creek, as well as upstream of the mine.

Figure 5. Marsh Creek Watershed Aqueous Mercury Concentrations *(ng/L, late March 1995)*



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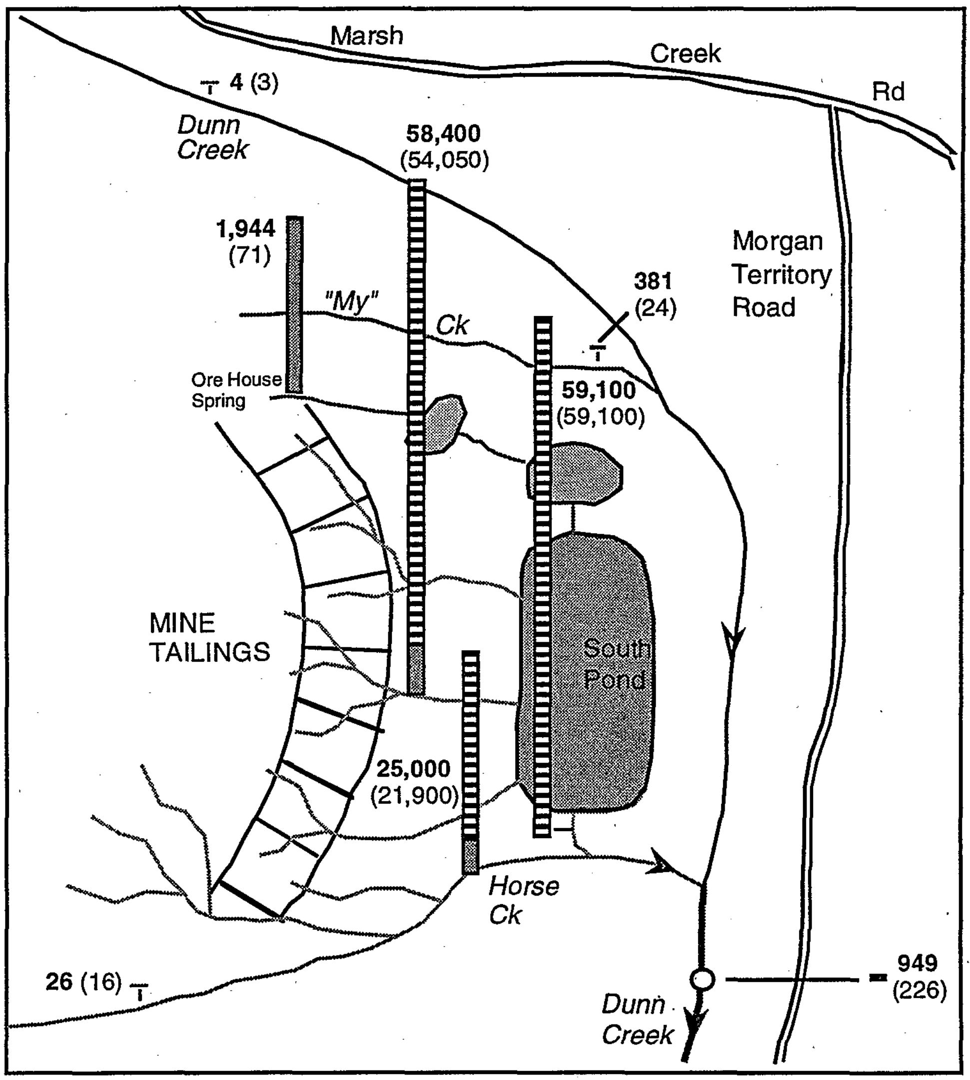


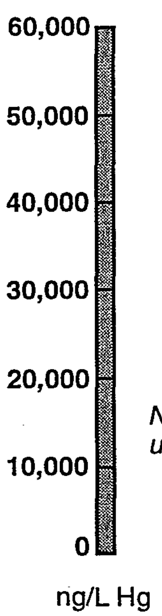
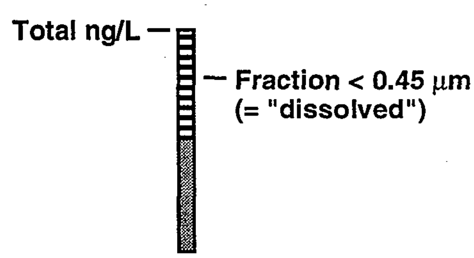


Figure 6. **Aqueous Mercury Concentrations in the Vicinity of the Mt. Diablo Mine**
(Late March 1995)

Note scale (vs 0-80 ng/L scale used in whole watershed map)



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The mercury concentrations found in the other main tributaries, at 3.2-8.9 ng L^{-1}, were two orders of magnitude lower than the 949 ng L^{-1} concentration found in Dunn Creek below the mine. The great impact of the mine-region Dunn Creek flows to Marsh Creek is apparent in the large increase in Marsh Creek aqueous mercury concentrations below the Dunn Creek confluence. Upstream levels of 3.2-8.9 ng L^{-1} increased to 79.3 ng L^{-1}, measured one mile below the confluence. Aqueous mercury concentrations remained elevated below this point in the watershed, at > 37 ng L^{-1} as far downstream as the town of Oakley.

The close-up map of aqueous mercury concentrations in the immediate vicinity of the Mt. Diablo mine (Fig. 6) demonstrates that the very high mercury levels seen in Dunn Creek are clearly derived from the mine itself. The stream "My" Creek, which borders the north extent of the tailings region, was quite high in mercury at 381 ng L^{-1}, while flows emanating from the tailings themselves were massively contaminated, with levels ranging from 25,000 - 60,000 ng L^{-1}. The Orehouse spring was also quite high, though far lower in mercury than the downslope tailings flows, at 1,944 ng L^{-1}. This small spring, however, contributed very little to the overall water volume from the site, with its flow at this time measured at just 0.01 cubic feet per second (Fig. 4).

Previous water sampling in the region by the Central Valley Regional Water Quality Control Board utilized less sensitive analytical techniques that placed most watershed samples below the 0.00002 mg L^{-1} (20 ng L^{-1}) level of detection (CVRWQCB 1994). However, above detection results were obtained from 4 of the earlier samples, including a Dunn Creek sample directly below the mine inflows (600 ng L^{-1}) and 3 sites in the direct vicinity of the tailings and settling pond (16,000 - 70,000 ng L^{-1}). These December 1994 levels were quite similar to the corresponding concentrations we found in our 1995 work.

In addition to the maximally contaminated flows from the mine tailings themselves, it is notable that all of the Marsh Creek watershed tributaries which showed any significant elevation in mercury concentration, relative to the entire data base, derived from the same slope of Mt. Diablo; i.e. the region between Perkins Creek and "My" Creek.

It is a very important observation that nearly all of the mercury detected in the heavily contaminated, near-tailings flows was found to be in the *filtered* fraction; i.e. the "dissolved" state. The sample of representative tailings seepage moving into the settling pond was found to contain 58,400 ng L^{-1} total mercury, with 54,050 ng L^{-1} (93%) measured in the filtered fraction. Water leaving the settling pond had 59,100 ng L^{-1} total mercury, with an identical concentration (a full 100%) measured in the filtered fraction. The somewhat diluted but higher volume flow in Horse Creek had a total mercury concentration of 25,000 ng L^{-1}, with 21,900 ng L^{-1} (88%) accounted for by the filtered fraction. These collections were in marked contrast to samples from all other sites throughout the watershed, where the majority of the total aqueous mercury was in the particulate fraction. In downstream Dunn Creek and Marsh Creek, the filtered fraction accounted for only 17-27% of the total aqueous mercury. Further, it is likely that much of the downstream "filtered" mercury fraction was not truly "dissolved", but was associated with particulates and colloids that were simply smaller than the 0.45 μm standard pore size used in filtration. In contrast, the filtered mercury fraction that constituted virtually the entire mercury load in flows sampled at the tailings themselves likely originated from truly dissolved mercury, as suggested by the acidity (low pH) in the immediate vicinity of the ore body and settling pond.

This data indicates that the extremely high mercury concentrations in the tailings flows are derived specifically from the dissolution of mercury from the tailings. The tailings of this historic mercury mine are by definition rich in mercury. Once in the dissolved state, this mercury can become highly mobile. Mercury presumably dissolves readily into water in the immediate vicinity of the tailings due to the characteristic presence of sulfides in the ore. This sulfur, when exposed to rainwater, promotes the formation of sulfuric acid. The acid dissolves ore constituents that would otherwise remain in solid form, including the metals iron and mercury. The iron creates the orange stain characteristic of much acid mine drainage. This happens as the low pH is subsequently neutralized by dilution with other water and the dissolved metal begins to precipitate out of solution. Mercury likely precipitates fairly rapidly as well, as evidenced by the decline in the proportion of filtered mercury seen downstream of the immediate mine area. However, we note that the freshly formed, tiny, flocculent particles that result from the precipitation of formerly dissolved metals are themselves extremely susceptible to downstream transport, if exposed to significant flow energy. Therefore, it is our interpretation that this process of the tailings mercury dissolving into runoff seepage water is, either directly or indirectly, supplying much of the greatly elevated mercury concentrations seen in the downstream watershed.

The downstream shift in aqueous mercury partitioning, from dissolved mercury in the immediate vicinity of the tailings to particulate mercury dominating the remainder of the downstream watershed, indicates that the tailings-based dissolved mercury rapidly adsorbs to particulate material upon leaving the mine site.

An additional finding brought out by this data involves the main settling pond at the mine site, which captures much of the overland and through-flow from the tailings. The mercury measured in the outflow from this pond was entirely in the dissolved state. It was also essentially identical to representative tailings seepage that was flowing *into* the pond, both in character and mercury concentration. We conclude that, <u>in its current configuration</u>

and pH, the settling basin may not be effectively "settling out" a significant proportion, if any, of the aqueous mercury flowing into it. This is particularly the case under storm-related, elevated flow conditions, when the great majority of overall transport in the watershed occurs.

3.1.1.3 *Bulk Loads*

The mercury concentration data describe the local water quality conditions present at each of the sampling sites at the time of these collections. Aqueous mercury concentration is also a critical parameter with regard to localized biological uptake in the stream ecosystem. However, for considerations of overall mercury loading from the watershed to the downstream reservoir and beyond, we needed to determine the actual quantities of mercury that move through each of the stretches. This was accomplished by weighting the concentration information at each of the sites by the corresponding flow values that we determined at the time of sampling. In this way, we have been able to estimate the mercury *loads* deriving from the various tributaries, on a grams mercury per day basis. This data is presented in Table 5 and in Figures 7 and 8.

Clearly, Dunn Creek below the mine region is contributing the vast majority of mercury to the downstream reaches of Marsh Creek. All of the other tributaries, combined, accounted for approximately 1 gram of daily high flow mercury load at the time of this assessment, as compared to over 18 grams per day calculated to be moving concurrently through lower Dunn Creek toward Marsh Creek. Loads in Marsh Creek below the Dunn Creek confluence, at 10-16 grams per day as far downstream as Oakley, were dramatically greater than levels seen upstream of this confluence and in other tributaries away from mine influence. The mine inset map (Fig. 8) demonstrates that the great majority of the Dunn Creek mercury load derives specifically from the tailings piles. The greater proportion of this tailings-derived load enters lower Horse Creek without moving through the settling pond. A load of 19.6 grams of mercury per day was calculated for lower Horse Creek above the settling pond outlet, while the corresponding mercury load moving out of that pond was calculated at 7.2 grams per day.

At the time of this sampling, the data indicates that a portion of the upstream mercury load was actively sedimenting out of the water column in the course of moving downstream. Total aqueous mercury loads generally declined, moving downstream from the mine area. This occurred near the mine (Fig. 8) as well as along the length of Marsh Creek below the Dunn Creek confluence (Fig. 7). The combined mercury loads from Horse Creek (19.6 g/day), the settling pond (7.2 g/day), "My" Creek (2.0 g/day), and

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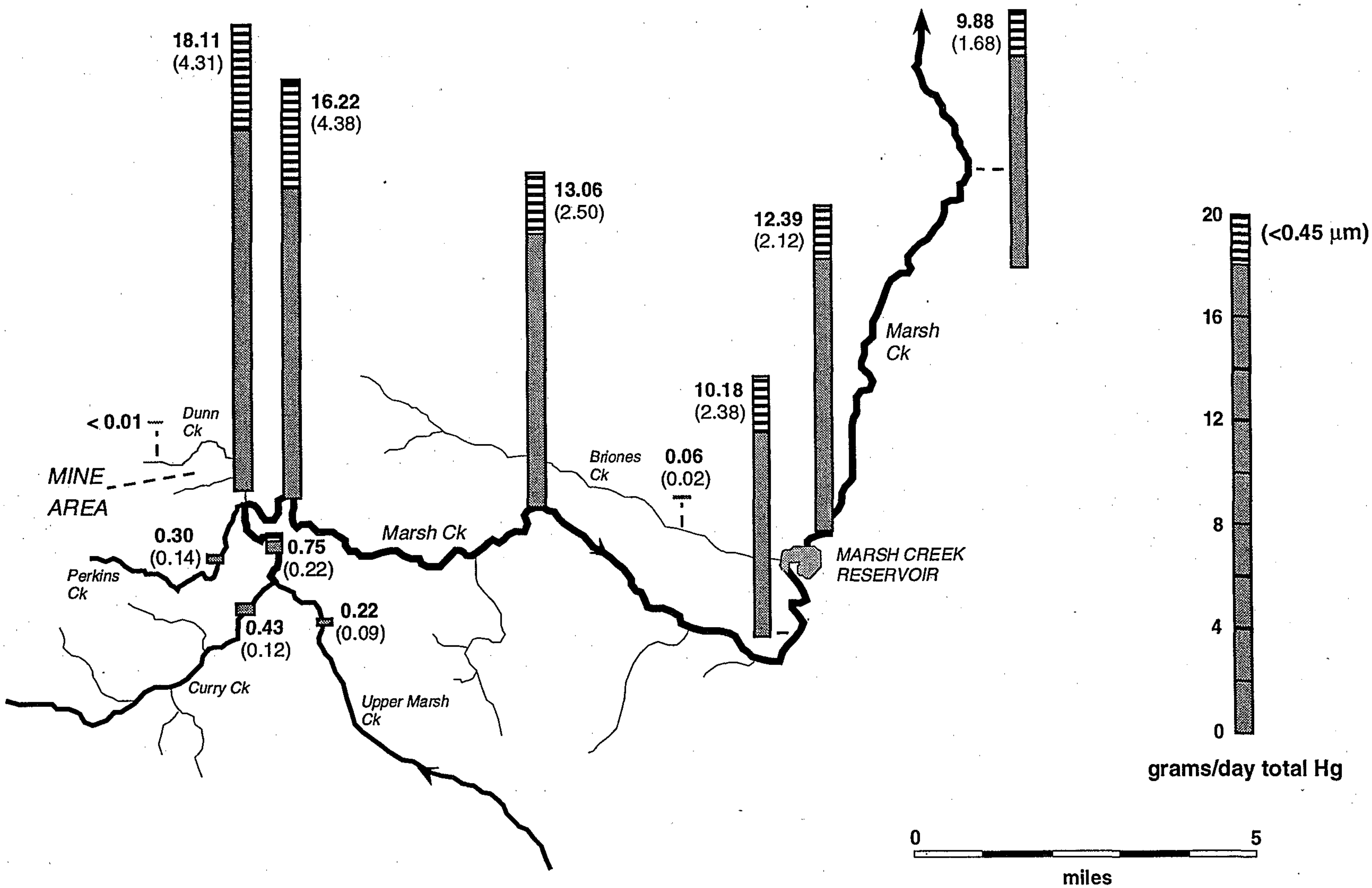
Figure 7. **Marsh Creek Watershed**
Aqueous Mercury <u>Bulk Loads</u>
(grams mercury per day, late March 1995)



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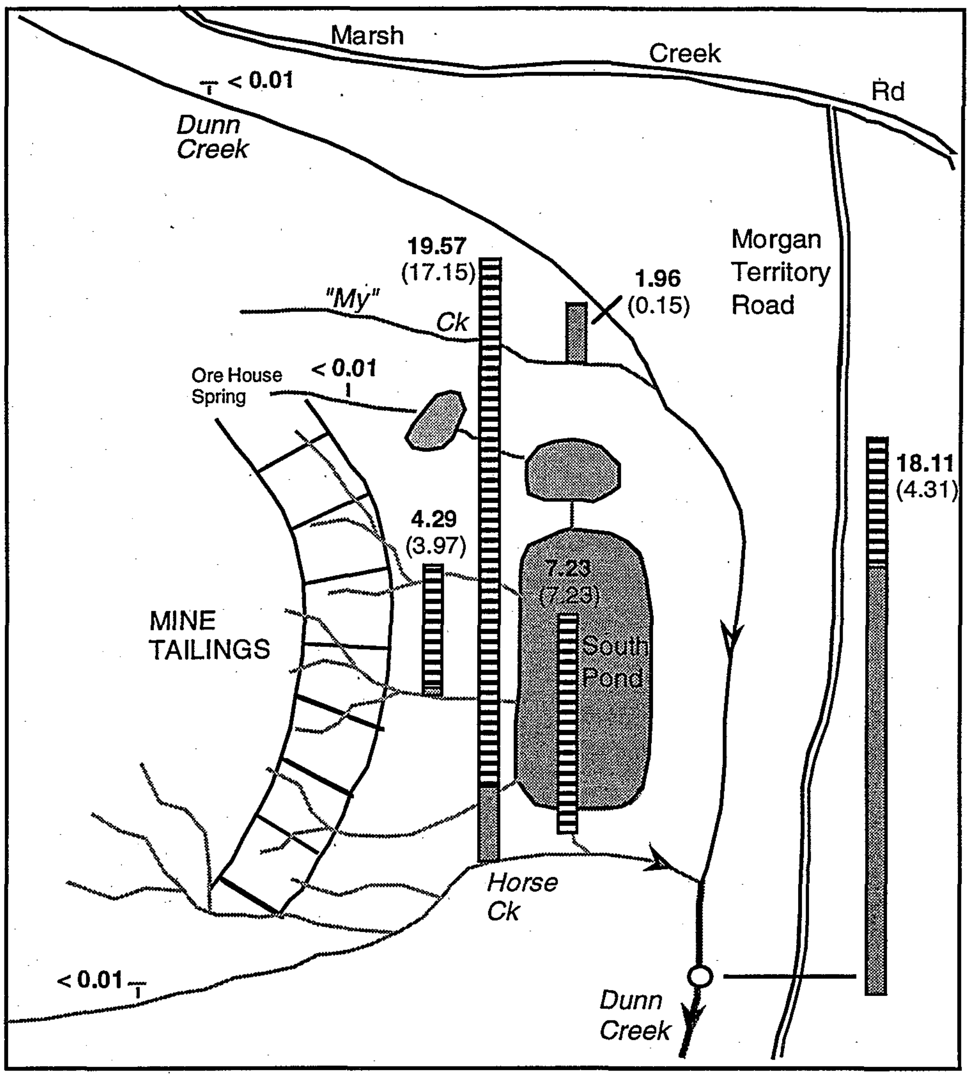

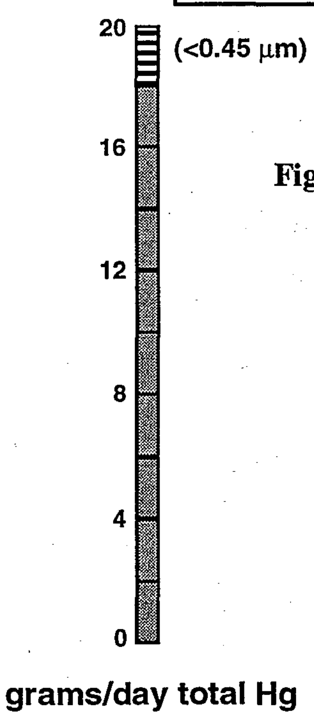

Figure 8. **Aqueous Mercury <u>Bulk Loads</u> in the Vicinity of the Mt. Diablo Mine**
(Measured Concentrations x Measured Flows)
(Late March 1995)

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Table 5. Watershed Aqueous Mercury and Suspended Solids Bulk Loading Data

Site	*Aqueous Total Hg* Raw (*grams/day*)	*Aqueous Total Hg* Filtered (*grams/day*)	*Suspended Solids* (TSS) (*kilograms/day*)
Upper Marsh Creek	0.224	0.089	1,110.0
Curry Creek	0.427	0.123	2,640.0
Marsh Ck above Perkins Ck	0.753	0.215	5,160.0
Perkins Creek	0.302	0.140	102.0
Upper Dunn Creek	0.046	0.035	18.4
Upper Horse Creek	0.005	0.003	0.2
"My" Creek	1.960	0.146	55.9
OreHouse Spring	0.048	0.002	0.3
Trickle coming from tailings	4.290	3.970	5.7
South Pond outlet	7.230	7.230	3.2
Horse Creek @ tailings	19.600	17.100	81.2
Dunn Ck below mine confluence	18.100	4.310	257.0
Marsh Ck below Dunn Ck conf.	16.200	4.380	3,960.0
Mid Marsh Ck @ rd. crossing	13.100	2.500	6,070.0
Marsh Ck above Reservoir	10.200	2.380	6,250.0
Briones Ck @ Deer Valley Rd.	0.059	0.020	614.0
Marsh Ck below Reservoir	12.390	2.120	9,800.0
Marsh Ck @ Delta Rd.	9.880	1.680	14,100.0
	Aqueous Methyl Hg Raw (*grams/day*)	*Aqueous Methyl Hg* Filtered (*grams/day*)	
Marsh Ck above Reservoir	0.055	0.030	

upper Dunn Creek (0.05 g/day) totaled 28.8 grams per day, while the load measured in Dunn Creek just below the mine site was considerably lower at 18.1 grams per day. The load in downstream Marsh Creek one mile below the Dunn Creek confluence was still lower at 16.2 grams per day. The decline in the mercury load suspended in the water column continued, moving downstream, with 13.1 g/day measured at the site halfway down to the reservoir and 10.2 g/day measured just above the reservoir. This consistent pattern indicates that a portion of the mercury load was falling out of the current along with sedimenting particulates. However, we note that much or all of the previously suspended sediment that settles out within the channel itself during post-storm and lower flow conditions may ultimately be transported downstream to the reservoir and beyond under higher flow conditions, particularly with the spike increases in flow typical during large storm events.

The bulk load data additionally indicates that all significant mercury loading to the Marsh Creek watershed is accounted for by the upper watershed tributaries. The steady drop in aqueous mercury loads measured in Marsh Creek, from the Dunn Creek confluence down to the reservoir, precludes the possibility of any important additional inputs of mercury from other sources along that stretch.

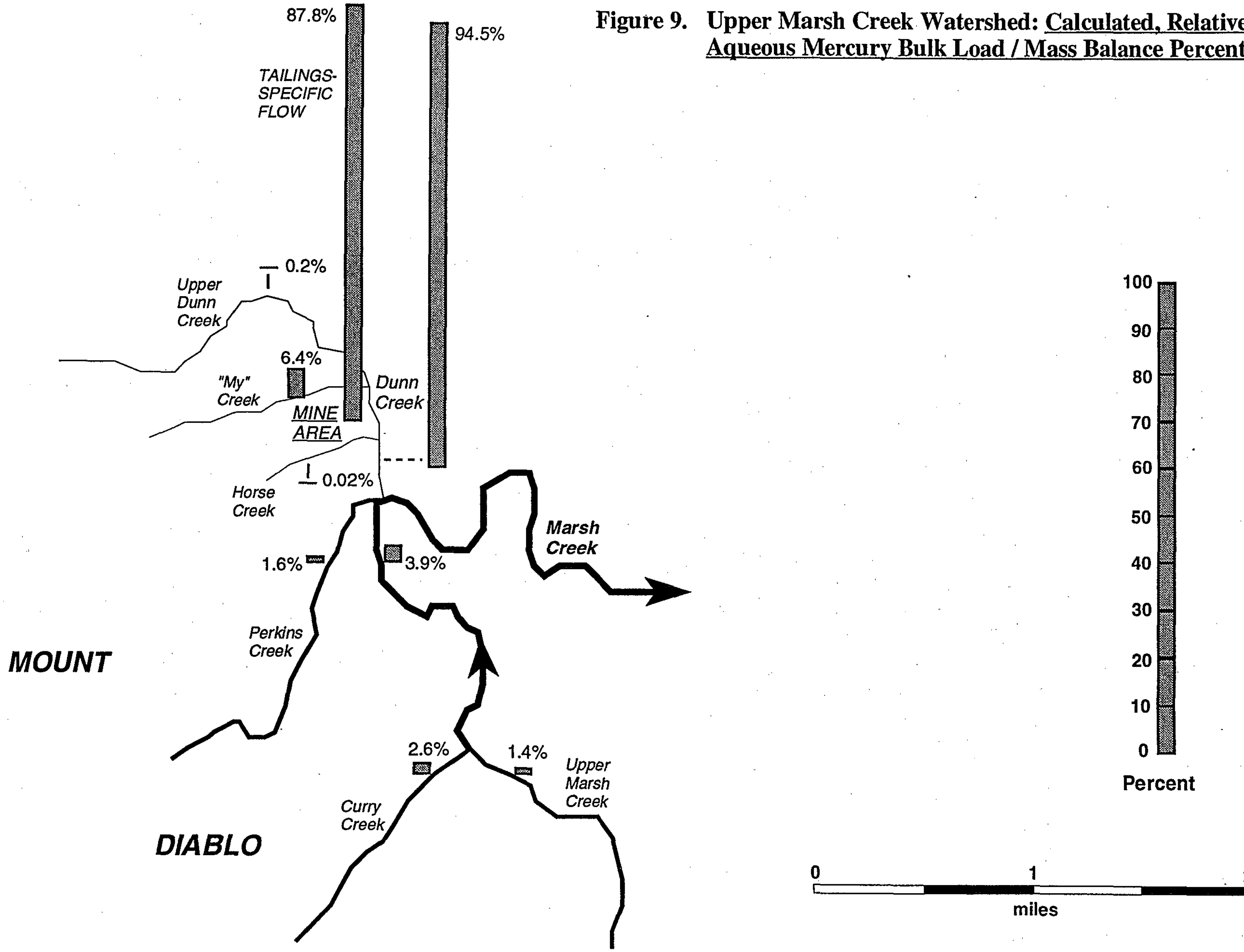
3.1.1.4 *Mercury Mass Balance*

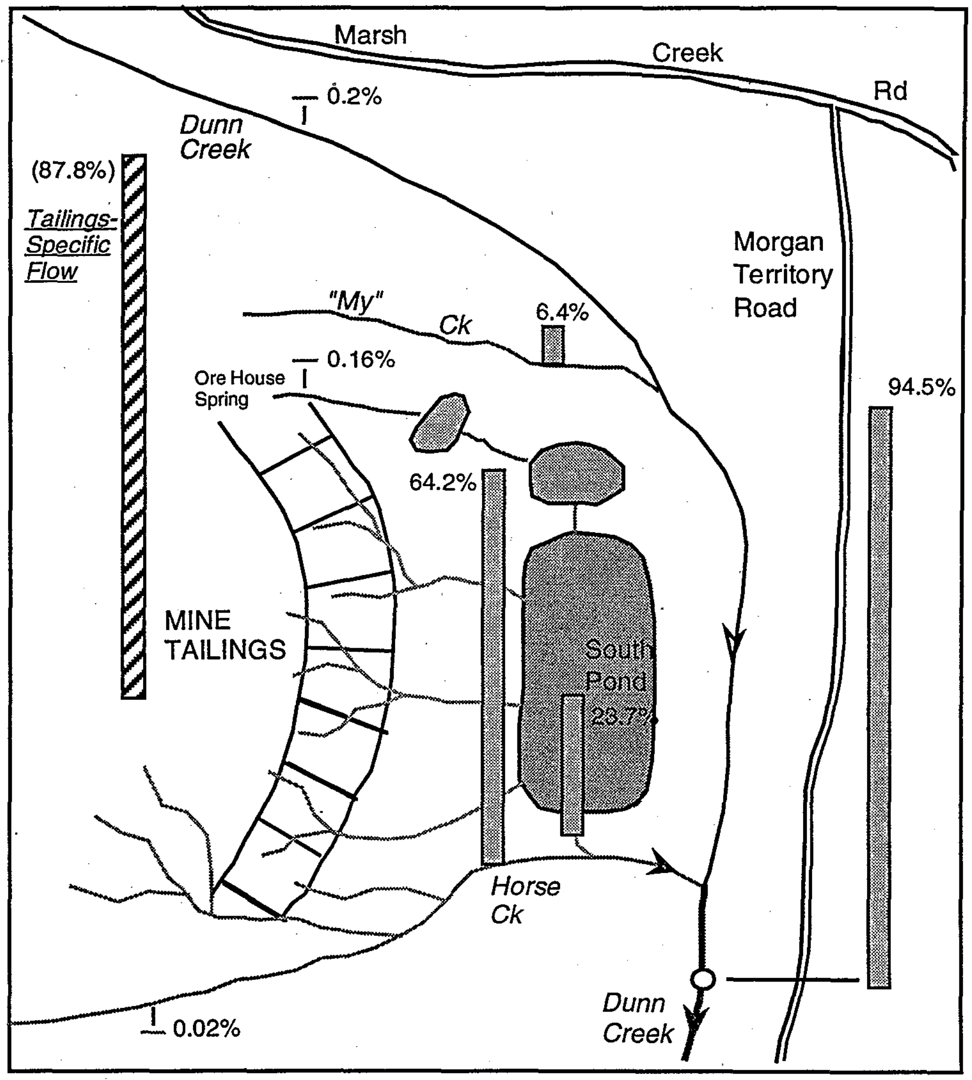
Table 6. Calculated Relative Mercury Mass Balance Contributions of Upper Watershed Sources

Site	Raw Total Hg (grams/day)	%	Filtered Total Hg (grams/day)	%
Perkins Creek	0.30	1.6%	0.14	3.0%
Marsh Creek above Perkins Creek	0.75	3.9%	0.22	4.6%
Dunn Creek below mine confluence	18.11	94.5%	4.31	92.4%
	(19.17)	(100.0%)	(4.67)	(100.0%)
Marsh Creek above Perkins Creek	0.75	(3.9%)	0.22	(4.6%)
Upper Marsh Creek	0.22	1.4%	0.09	1.9%
Curry Creek	0.43	2.6%	0.12	2.7%
	(0.65)	(3.9%)	(0.21)	(4.6%)
Dunn Creek below mine confluence	18.11	(94.5%)	4.31	(92.4%)
Upper Dunn Creek	0.05	0.2%	0.03	0.1%
"My" Creek	1.96	6.4%	0.15	0.5%
South Pond Outlet	7.23	23.7%	7.23	27.2%
Horse Creek at Tailings	19.57	64.2%	17.15	64.5%
	(28.81)	(94.5%)	(24.56)	(92.4%)
TAILINGS ALONE				
Horse Creek at Tailings	19.573	64.21%	17.146	64.51%
(- Upper Horse Creek)	- 0.005	- 0.02%	- 0.003	- 0.01%
	19.568	64.19%	17.143	64.50%
	(+)		(+)	
South Pond Outlet	7.230	23.72%	7.230	27.20%
(- OreHouse Spring)	- 0.048	- 0.16%	- 0.002	- 0.01%
	7.182	23.56%	7.228	27.20%
TAILINGS ALONE	26.75	**87.8%**	24.37	**91.7%**

Based on the data collected during this representative post-storm, elevated flow sampling, we have constructed a mass balance of the relative contributions of mercury to the watershed from the various upstream tributaries. These tributaries have been

Figure 9. Upper Marsh Creek Watershed: Calculated, Relative Aqueous Mercury Bulk Load / Mass Balance Percentages





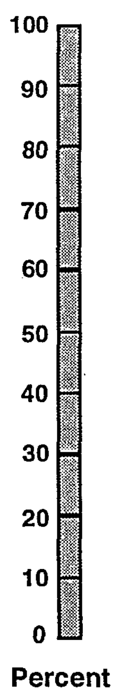


Figure 10. **<u>Calculated, Relative Aqueous Mercury Bulk Load / Mass Balance Percentages</u>**
In the Vicinity of the Mt. Diablo Mine
(Relative to total mercury loads throughout the entire upper watershed of Marsh Creek; late March 1995)

demonstrated to provide essentially all of the watershed's mercury loading. The data are presented in Table 6 and in Figures 9 and 10. The technique used to arrive at these values is described in section 2.3.1. These are our best estimates of the true proportional inputs of mercury from the different source regions to the Marsh Creek watershed.

In this analysis, the Dunn Creek inflow to Marsh Creek represents 94.5% of the total mercury loading to the upper watershed. Though the bulk of the water and transported sediment derive from upper Marsh Creek, Curry Creek, and Perkins Creek, these major tributaries accounted for only 5.5% of the watershed's mercury.

Of the 94.5% of the watershed mercury estimated to derive from Dunn Creek, it is apparent that the overwhelming majority comes from the Mt. Diablo mine. The upper stretches of Dunn Creek and Horse Creek, above the influence of the mine, together with the Orehouse spring flow, accounted for less than 0.4% of the total mercury (Fig. 10). "My" Creek contributed a moderate load of 6.4%. We are not clear at this time whether this particular stream is amenable to straightforward mitigation options.

Our major interest is in the flows emanating from the tailings themselves, as they are a very localized source that represent the County's best and most cost-effective mitigation focus for watershed mercury cleanup, if they in fact constitute the majority of the source. The data indicate that this is indeed the case. Subtracting out the small mercury loads of the Orehouse spring and upper Horse Creek, the relative mercury loading to the entire watershed derived specifically from this comparatively small region of mine tailings is estimated to be approximately 88%. The majority of this tailings-based load (64.2% in this analysis) enters lower Horse Creek without passing through the settling basin.

This information suggests that mitigation work directed specifically at the mine tailings, in order to lessen the export of mercury, may be a very sensible and cost-effective approach.

3.1.1.5 *Suspended Solids*

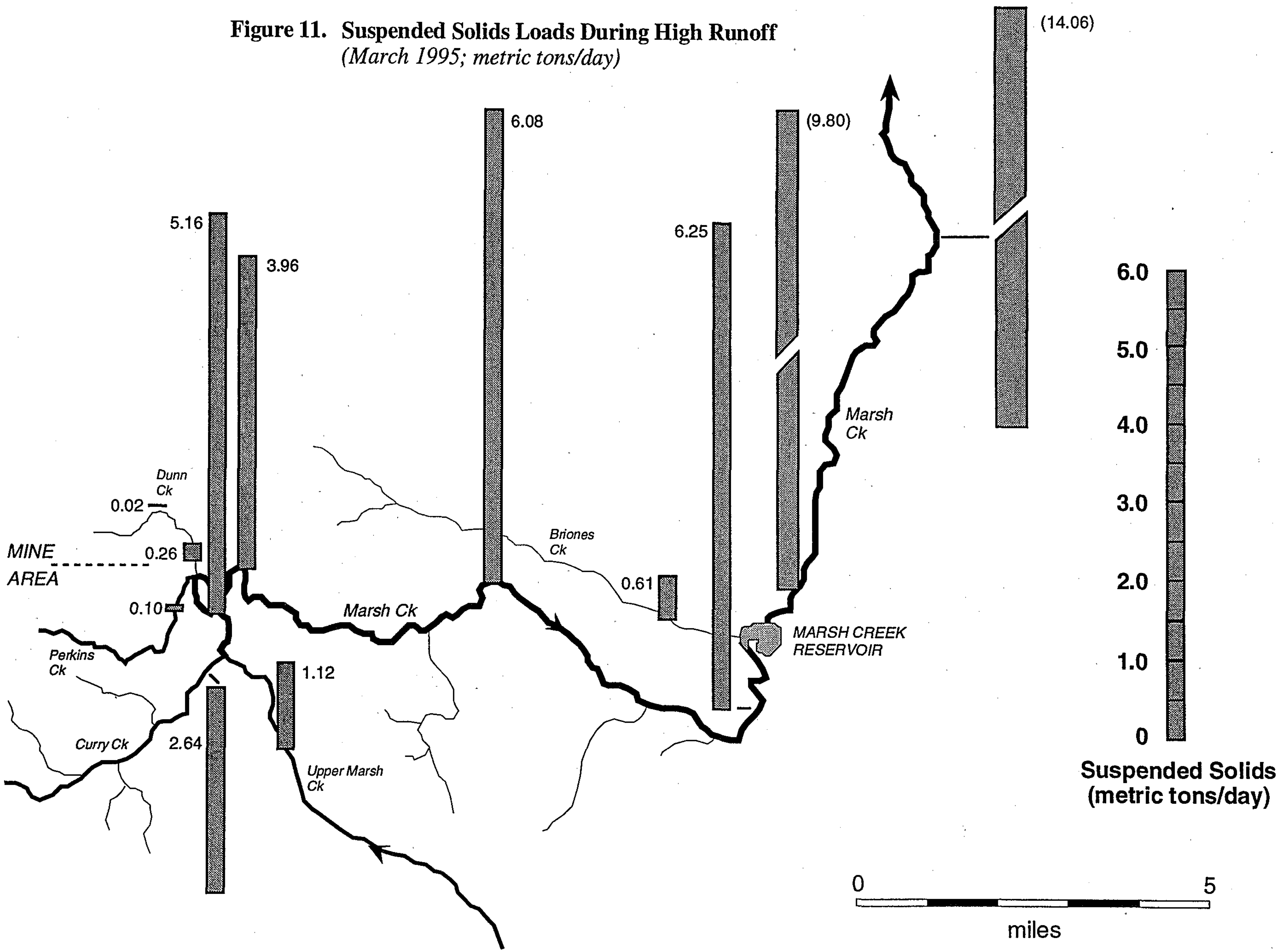
Suspended solids (TSS) data for the 18 stream sites are presented on a concentration basis (mg L^{-1}, = parts per million) in Table 4. This is a measure of particulate matter, primarily sediment, in the water. Suspended solids are of importance to mercury dynamics as they generally constitute the major vector of downstream mercury transport in running water. Mercury can be incorporated into the mineral matrix of particles as well as surface-adsorbed. Upon loosing velocity in the downstream reservoir and delta, these particulates deposit at the bottom as sediments and constitute the bulk of the total mercury in those systems.

Highest concentrations of TSS were seen in the flows on and around the tailings (to 104 mg L^{-1}), where iron and other metals were actively precipitating. The small Briones Creek, which drains farmland, was relatively very turbid as well (61 mg L^{-1}). Upper Marsh Creek and Curry Creek (~32 mg L^{-1}), the dominant sources of flow to the watershed, were quite turbid with suspended solids during this post-storm sampling period, while Perkins Creek (3 mg L^{-1}), "My" Creek (11 mg L^{-1}), upper Horse Creek (1 mg L^{-1}), and upper Dunn Creek (1.5 mg L^{-1}) were flowing quite clear. Below the Dunn Creek confluence, suspended solids concentrations in Marsh Creek generally increased steadily, moving downstream toward the reservoir and below (19 mg L^{-1} below the Dunn Creek confluence, increasing to 54 mg L^{-1} near Oakley).

As described above for mercury, the actual bulk loads of suspended solids moving through the different stream sections at the time of this sampling can be calculated by weighting the measured concentrations of TSS by the corresponding flows. These data are presented in Table 5 in units of kilograms per day and, Figure 11, as metric tons (1,000 kilograms, = 2,200 pounds) per day. The pattern is in sharp contrast to the mercury findings. Whereas the Dunn Creek mercury load overwhelmingly dominated that of the entire watershed, the suspended solids entering Marsh Creek from Dunn Creek represented only a very small fraction of the overall suspended solids load measured in downstream Marsh Creek. The Dunn Creek suspended solids load was calculated to be 0.26 metric tons/day, as compared to a combined 6.86 metric tons/day measured at the reservoir inflows. The Dunn Creek contribution of suspended solids therefore represented less than 4% of the total load measured entering the reservoir. While approximately 88% of the watershed's mercury was calculated to derive from the tailings piles at the Mt. Diablo mine, these suspended solids data indicate that an estimated 95% of the drainage's suspended solids load comes from tributaries which were found to be relatively very low in mercury--i.e. those tributaries other than Dunn Creek (including "My" Creek) and Perkins Creek.

In Table 4 and Figure 12 we have estimated the mercury concentration of the suspended particulates at the different sites, in consistent units of dry weight milligrams of mercury per kilogram suspended sediment (mg kg^{-1}, = parts per million). We note that the dominant sources of suspended sediment to the watershed--upper Marsh Creek, Curry Creek, and the small tributaries entering Marsh Creek along its lower length--were measured or demonstrated to be very low in suspended sediment mercury concentration, on the order of 0.1 ppm. This is in comparison with Marsh Creek TSS mercury levels between the Dunn Creek confluence and the reservoir of 1.3-3.0 ppm. Clearly, if the load of mercury emanating from the Mt. Diablo mine site can be significantly lessened, the natural suspended sediment loads transported through the Marsh Creek watershed in future

Figure 11. Suspended Solids Loads During High Runoff
(March 1995; metric tons/day)



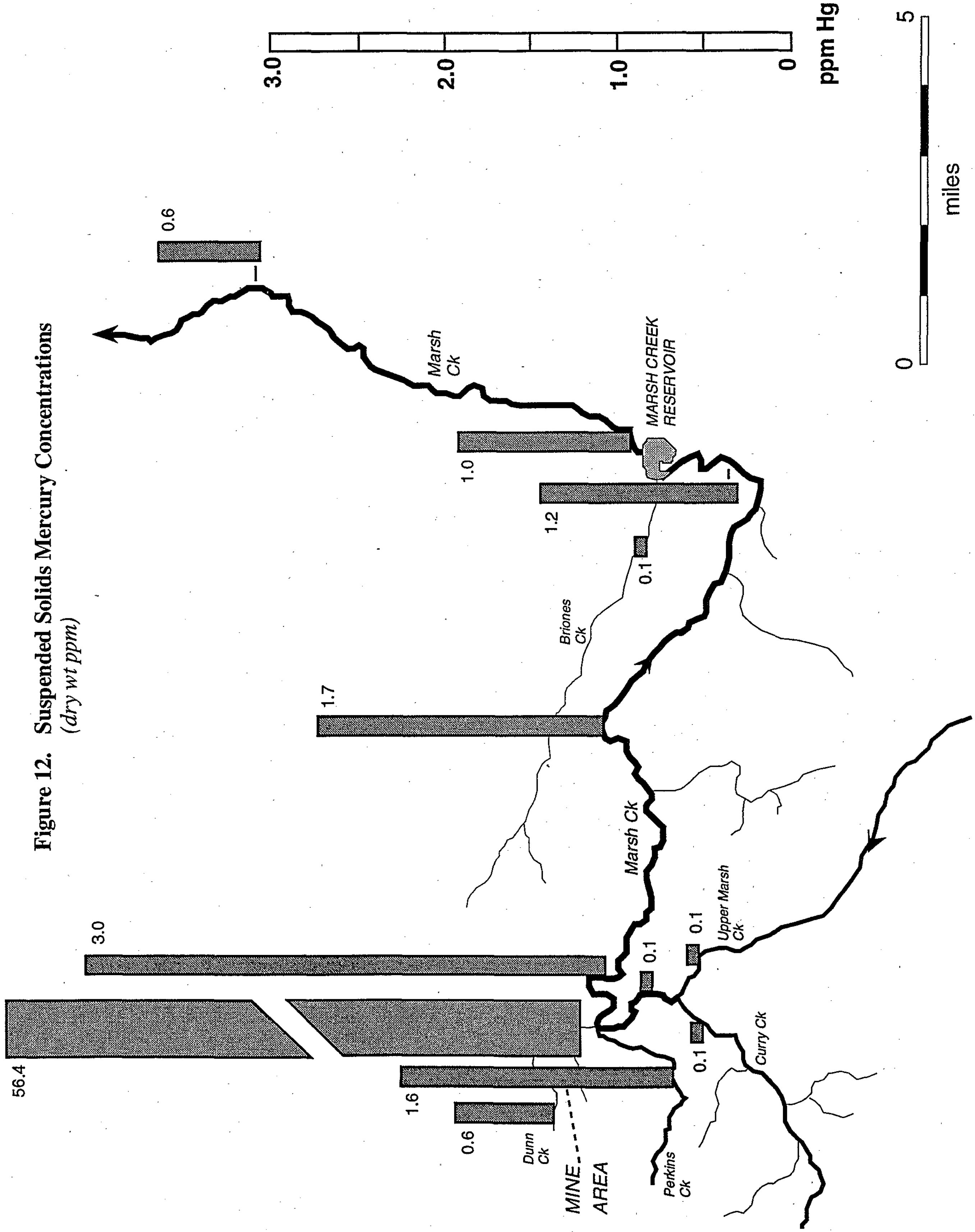


Figure 12. Suspended Solids Mercury Concentrations
(dry wt ppm)

storm seasons should plummet in average mercury concentration, as the great majority of sediment transported in this drainage has been shown to be quite low in mercury content. This material can then form a natural, lower mercury "treatment" for the Marsh Creek Reservoir bottom sediments in future years.

3.1.2 Stream Invertebrates

Stream invertebrates that were analyzed for this project are illustrated in Figure 13. The mercury data for the watershed invertebrate samples are presented in Table 7 and in Figures 14 and 15. Native in-stream invertebrate species have proven to be excellent monitors of mercury bioavailability in California streams and rivers (Slotton et al. 1995a). Because they incorporate mercury into their bodies throughout their lives, they can provide a time-integrated measure of stream conditions, as compared to standard "point-in-time" grab sampling for water. The mercury incorporated into local aquatic biota is, by definition, specifically the bioavailable fraction, which can be of paramount importance for management considerations. Additionally, many of these species are ideal indicators of highly localized conditions, as compared to fish which can and often do migrate extensively. The benthic invertebrate species we focused on in this work typically remain within a very limited area throughout their lives. They thus function as relatively static biological probes of the fraction of mercury in the water that is bioavailable.

At the majority of sampling stations, we were able to collect specimens from three distinct trophic feeding levels of invertebrates in sufficient quantity for mercury analysis. Macro-invertebrates were not present in the smaller, more ephemeral flows in the immediate mine region. Near the base of the aquatic food chain were mayfly nymphs (Ephemeroptera) from several herbivorous genera. Perlodid stoneflies were also taken at most of the sites. These are medium-sized invertebrate predators which feed on small to medium invertebrates. At the top of the invertebrate food chain in the upper watershed are the large-jawed hellgrammites (Corydalidae), which can reach several inches in length and are voracious predators of all other co-occurring species. We additionally took samples of aquatic "hair worms" of the order Nematomorpha. These organisms have a complex life cycle, deriving from the terrestrial ecosystem, and do not feed while in the stream. They thus provide limited information, presumably linked to direct uptake of mercury from the water. The majority of biotic mercury is typically accumulated through the food chain in the diet, particularly in the higher trophic levels (Lindberg et al. 1987, Gill and Bruland 1990).

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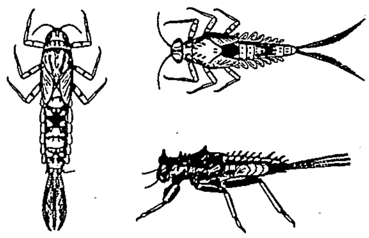
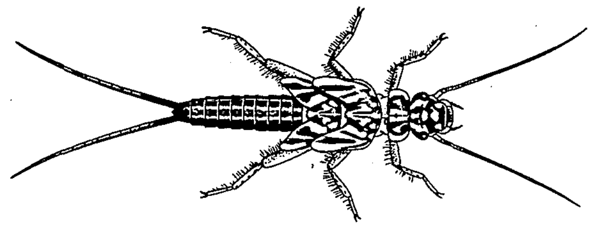
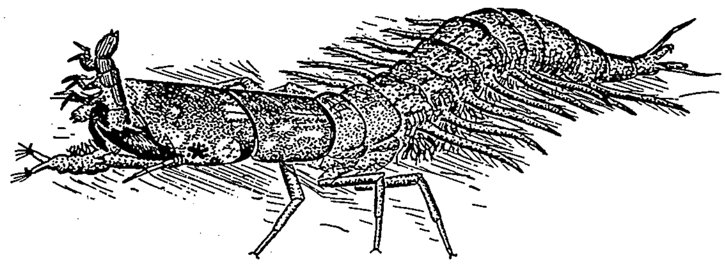
Figure 13. Stream Invertebrates Analyzed in This Project
(illustrations taken from McCafferty 1981, Goldman 1981)



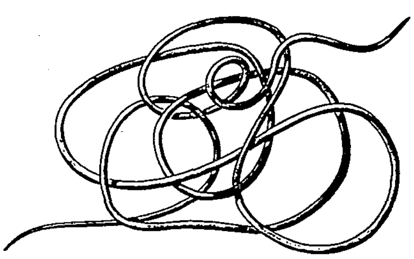
Mayflies (Ephemeroptera)
(~1/2 inch)
Siphloneuridae
Baetidae
Ephemerellidae



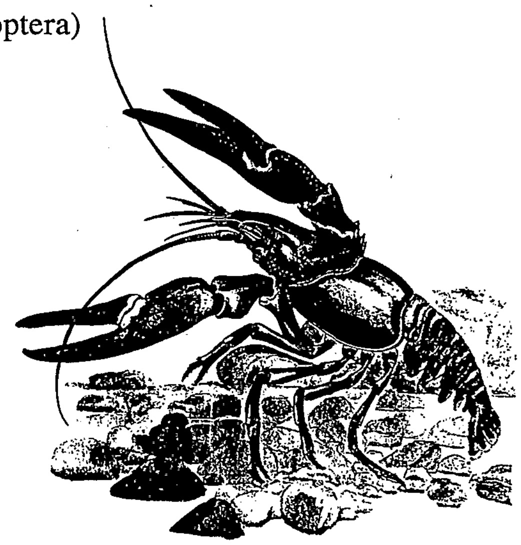
Stoneflies (Plecoptera)
Perlodidae (~1 inch)



Hellgrammites (Megaloptera)
Corydalidae (2-4 inches)



Horsehair Worms
(Nematomorpha)



Crayfish (Decapoda)
Pacifasticus

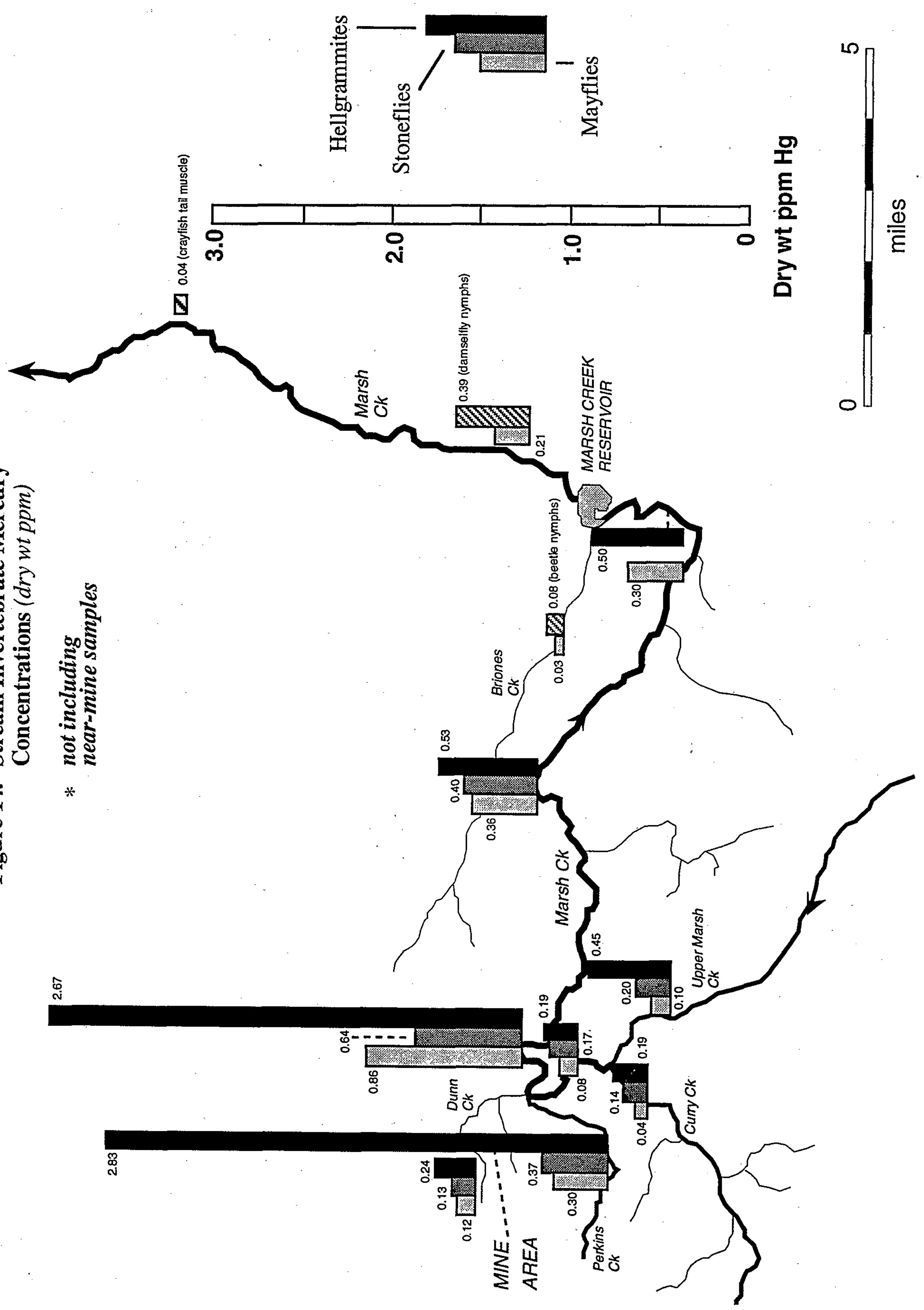


Figure 14. Stream Invertebrate Mercury Concentrations *(dry wt ppm)*

* ***not including near-mine samples***

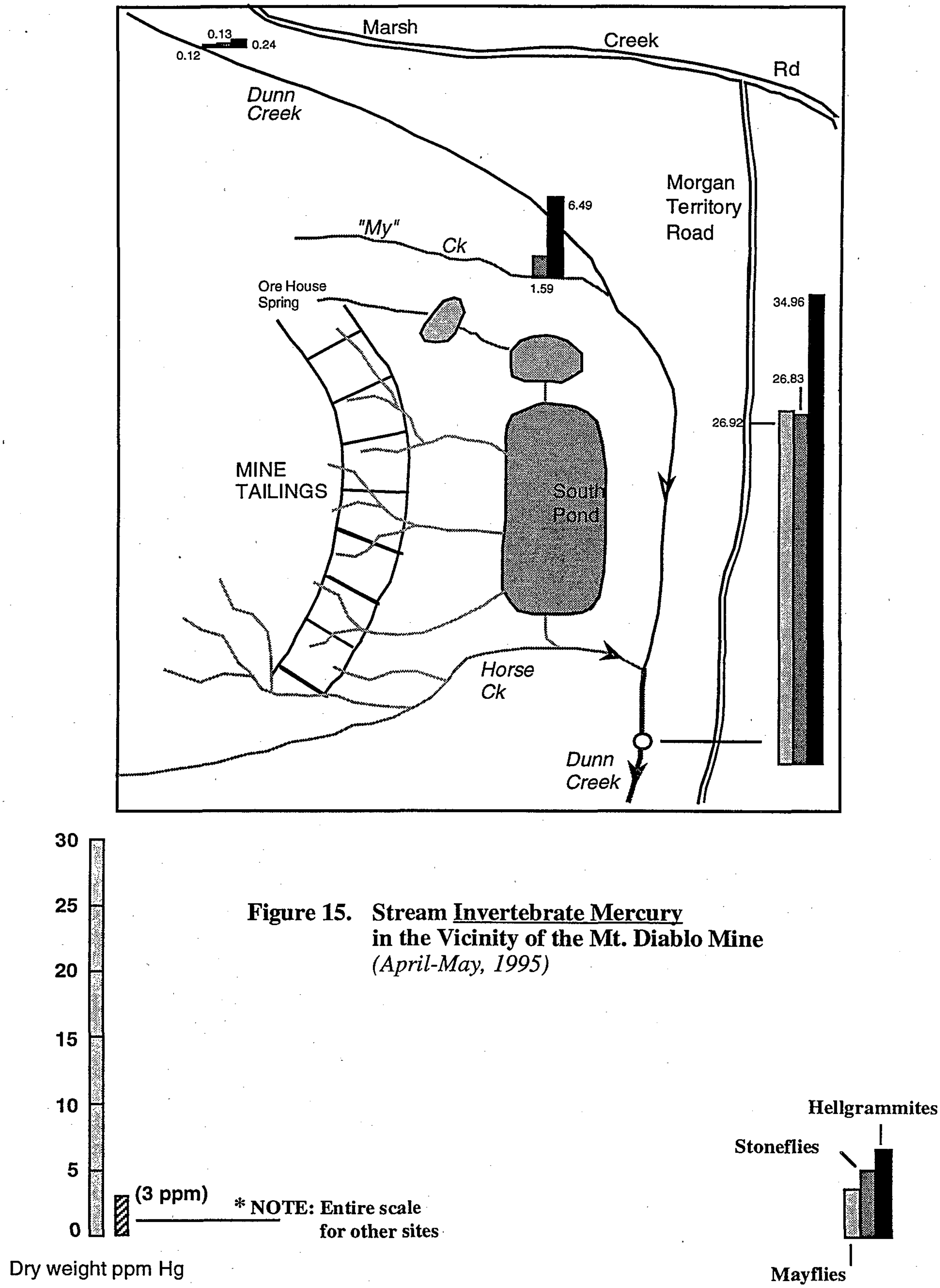


Figure 15. **Stream Invertebrate Mercury in the Vicinity of the Mt. Diablo Mine**
(April-May, 1995)

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Table 7. Stream Invertebrate Mercury Concentrations *(dry weight ppm)*

SITE	Nematomorpha Horsehair Worms *Water Uptake Only*	Ephemeroptera Mixed Mayflies *Herbivores*	Plecoptera Perlodid Stoneflies *First Order Predators*	Megaloptera Medium Hellgrammites *Second Order Predators*
Upper Marsh Creek	0.06	0.10	0.20	0.45
Curry Creek	0.10	0.04	0.14	0.19
Marsh Ck above Dunn Ck	0.06	0.08	0.17	0.19
Perkins Creek	0.38	0.30	0.37	2.83
Upper (clean) Dunn Creek	0.06	0.12	0.13	0.24
"My" Creek	0.32		1.59 §	6.49
Dunn Creek below Mine		13.80	16.00	23.80
Marsh Ck below Dunn Ck	0.29	0.52	0.64	2.67
Middle Marsh Creek	0.09	0.36	0.40	0.53
Briones Creek		0.05	0.08 ¥	
Marsh Ck above Reservoir		0.30		0.50
Marsh Ck below Reservoir		0.21	0.39 †	

Alternate 1° predators: § Rhyacophyllid caddis larvae
¥ Predaceous beetle nymphs
† Damselfly nymphs

The invertebrate mercury data indicate that the trend within the watershed for bioavailable mercury generally parallels that seen for aqueous mercury concentrations (section 3.1.1). Massive spike concentrations were apparent in Dunn Creek invertebrates immediately below the inflows from the mine site (27-35 ppm, dry weight). Biota from "My" Creek and Perkins Creek were also relatively elevated, though to a lesser degree, as were aqueous mercury concentrations in these streams. In particular, the hellgrammite samples from Perkins Creek (2.83 ppm) and "My" Creek (6.49 ppm) were significantly elevated. Concentrations were low throughout the invertebrate food chain at most sites upstream and away from the mine influence. Samples from upper Dunn Creek, above the mine, were two orders of magnitude lower in accumulated mercury than near-mine samples, at 0.06-0.24 ppm. Levels from upper Marsh Creek, Curry Creek, and Briones Creek were in a similar low range.

Along Marsh Creek, invertebrate mercury concentrations were dramatically higher downstream of the Dunn Creek confluence as compared to the relative "control" levels seen upstream of this point. Concentrations generally declined with increasing distance downstream from the mine. Comparable samples were not available at the downstream site near Oakley, though we were able to take several crayfish, which we analyzed for tail muscle mercury (Table 9, Fig. 14). These were quite low at ~0.04 ppm wet wt, ~0.18 ppm dry wt.

Within each site, mercury concentrations in the various trophic groups generally increased with feeding level, with predatory stoneflies typically containing higher levels than herbivorous mayflies, and the large predatory hellgrammites generally having the greatest concentrations.

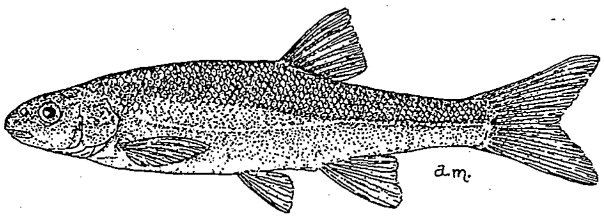
We again point out that both the aqueous concentration data and these data from bioindicator stream organisms provide information on relative localized water quality in the various tributaries. For questions of absolute, bulk contributions of mercury from each of the streams to the entire watershed, the bulk loading/mass balance types of information are more relevant (section 3.1.1.4 - 3.1.1.5). Both approaches provide important, though potentially very different, information.

3.1.3 Stream Fish

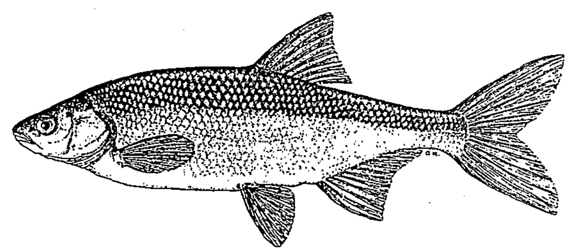
Illustrations of the stream fishes collected in this project can be found in Figure 16. Data collected from the in-stream fish samples are presented in Tables 8 and 9 and Figure 17. Fish were present at a subset of the sampling sites, primarily in the main channel of Marsh Creek downstream of Dunn Creek. Fish were not present in smaller upstream tributaries, presumably due to annual dry-season losses of water. While larger fish were found in Marsh Creek within a mile above the reservoir, upstream fish were limited to "minnows". These small species consisted of California roach (*Hesperoleucus symmetricus*), mixed with juvenile hitch (*Lavinia exilicauda*) closer to the reservoir. Below the reservoir, the character of the creek changes such that roach and hitch are no longer present. Fish taken downstream of the reservoir consisted of small bluegill (*Lepomis macrochirus*), together with a collection of juvenile (parr) Chinook salmon (*Oncorhynchus tshawytscha*) taken near Oakley.

The California roach and juvenile hitch were prepared for mercury analysis in the form of whole fish, multiple individual composites (Table 8). This is the technique typically used for roach in other metals biomonitoring work in California (Hellawell 1986, Reuter et al. 1989,1995, Bodega Research Associates 1995). Composites were made of similar sized individuals, with up to five different size classes composited separately for each site, depending on the range of sizes taken. The much larger hitch individuals taken just upstream of the reservoir were analyzed for muscle mercury rather than whole body composite concentrations. A subset of the fish taken downstream of the reservoir were also analyzed for muscle mercury, in addition to whole fish composite mercury. Muscle

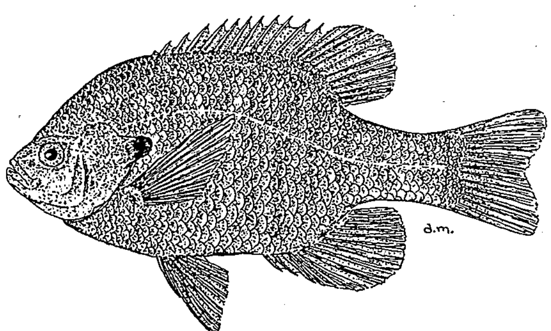
Figure 16. Stream Fish Species Sampled in This Project
(illustrations taken from Moyle 1976)



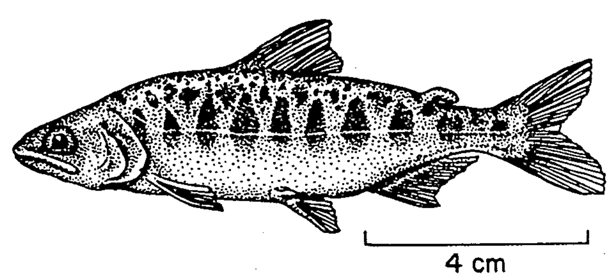
California Roach
Hesperoleucus symmetricus
(2-5 inches)



Hitch
Lavinia exilicauda
(juveniles 2-5 inches + 7-8")

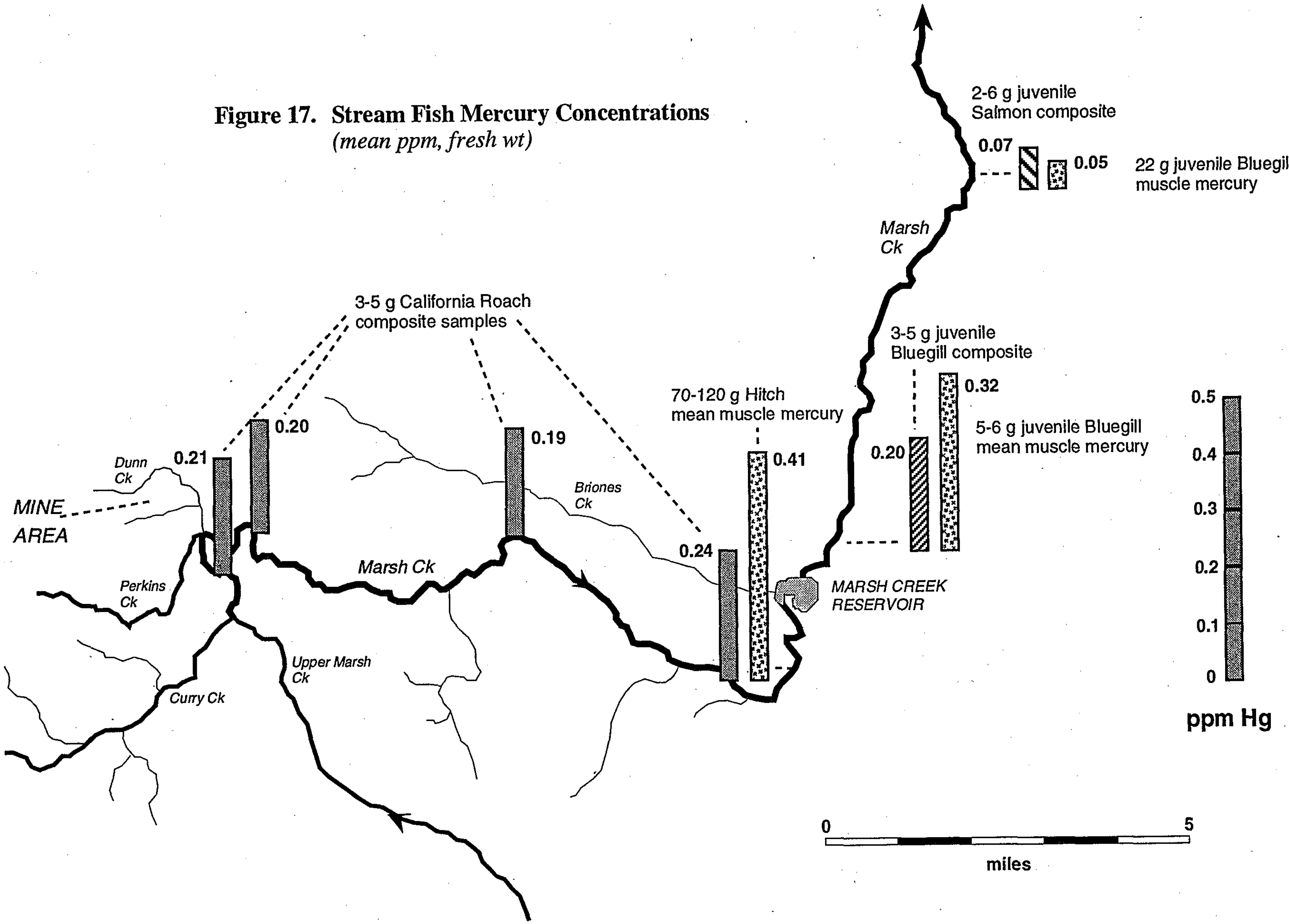


Bluegill
Lepomis macrochirus
(2-5 inches)



juvenile (parr) Chinook Salmon
Oncorhynchus tshawytscha
(juveniles 2-4 inches)

Figure 17. Stream Fish Mercury Concentrations
(mean ppm, fresh wt)



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mercury analyses (Table 9) were conducted on those fish for which the majority of comparative information exists in the form of muscle mercury concentrations.

Because fish were basically absent in the watershed upstream of the Dunn Creek confluence, it was not possible to use them as indicators of water quality differences between mine-impacted and control waters. Also, because fish are free to migrate up and down the creeks on each side of the reservoir, their accumulated mercury cannot be definitively linked with the location of capture. Additionally, the presence of different fish species above as compared to below the reservoir introduces a level of uncertainty to comparisons of fish mercury levels between these two areas. Consequently, the information provided by the stream fish data is somewhat limited. Because of these considerations, we supplemented fish collections with the invertebrate mercury work, described in section 3.1.2. However, some useful conclusions may be drawn from the stream fish data.

Mercury concentrations in the composite fish samples from spring 1995 (Table 8) were quite similar among the Marsh Creek sites between upper Marsh Creek and just below the reservoir. Among similar sized fish (2-5 g) including California roach, juvenile hitch, and juvenile bluegill, mercury concentrations were within the comparatively narrow range of 0.13-0.25 ppm. Except for a single, anomalously higher mercury individual roach from upper Marsh Creek, composites of all sizes (2-19 g) from these sites had mercury concentrations that fell within this range. There is no indication of a size vs mercury trend in this small-fish composite data.

Only a single individual roach was collected upstream of the Dunn Creek confluence, approximately one half mile upstream of Perkins Creek in Marsh Creek, despite repeated sampling efforts over several days. The similar mercury level in this fish (0.21 ppm) as compared to the range of levels seen downstream (0.13-0.25 ppm) suggests that this fish may have been a migrant from downstream. The lack of additional fish here indicates that the site was above the normal range of fish in the creek, a function of the annual disappearance of surface water each dry season. Therefore, it is likely that the individual roach taken here may have been a relatively recent migrant--and its mercury content may not reflect local conditions. Based on the aqueous mercury concentration data and the stream invertebrate findings, fish residing throughout the year in Marsh Creek above the Dunn Creek confluence would be expected to have significantly lower mercury than downstream fish.

Of the minnow composite samples, only a single individual roach exhibited a mercury concentration greater than 0.25 ppm. This 9 g individual had anomalously higher mercury concentration, at 0.71 ppm, nearly three-fold greater than the next highest values. As this fish was collected from the site 1 mile below the Dunn Creek confluence, we hypothesize that it may have lived much of its life within the immediate influence of the Dunn Creek mine-impacted flows.

Table 8. Marsh Creek Fish Composite Samples (Whole Fish) Mercury Concentrations *(fresh/wet weight ppm Hg)*

Species	Weight *(g)*	Length *(mm)*	Individuals in Comp.	Hg *(wet wt ppm)*
1 mile above Dunn Ck Confluence				
California Roach	4.2	72	n=1	0.21
1 mile below Dunn Ck Confluence				
California Roach	4.1	72	n=2	0.20
" "	9.0	93	n=1	0.71
~5 miles below Dunn Ck confluence				
California Roach	1.5	52	n=11	0.25
and	2.2	63	n=16	0.23
juvenile Hitch	4.0	72	n=19	0.19
" "	7.5	85	n=5	0.18
" "	19.2	115	n=1	0.24
1 mile above Marsh Ck Reservoir				
California Roach	2.8	65	n=5	0.13
" "	4.0	76	n=3	0.24
" "	6.9	84	n=2	0.15
0.5 mile below Marsh Ck Reservoir				
juvenile Bluegill	1.7	50	n=9	0.24
" "	3.4	61	n=3	0.19
" "	5.4	70	n=3	0.21
Downstream near Oakley				
juvenile Salmon	3.6	70	n=5	0.07

A collection of larger hitch individuals (72-117 g, 1-3 yrs) was made one mile above the reservoir. We also noted several large goldfish in the creek at this location, which were likely the grown results of earlier releases by the public. Large fish were not found in the creek upstream of this region. Muscle mercury concentrations in the 8 larger hitch taken upstream of Marsh Creek Reservoir, at 0.29-0.51 ppm (Table 9), were very similar to levels measured in adult hitch within the reservoir (section 3.2.3, Table 11).

The juvenile bluegill samples taken immediately below the reservoir were similar in both size and mercury concentration to upstream roach and juvenile hitch, on a whole body

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Table 9. Marsh Creek Fish Muscle (Fillet) Mercury Concentrations *(fresh/wet weight ppm Hg)*

Identification	Weight *(g)*	Length *(mm)*	Muscle Hg *(wet wt ppm)*
1 mile above Marsh Ck Reservoir			
Hitch	72	177	0.44
"	73	181	0.30
"	88	194	0.40
"	90	196	0.35
"	97	197	0.51
"	106	208	0.51
"	114	205	0.46
"	117	205	0.29
0.5 mile below Marsh Ck Reservoir			
juvenile Bluegill	5.2	68	0.22
" "	5.3	71	0.35
" "	5.8	71	0.40
Downstream near Oakley			
juvenile Salmon	2.2	60	0.01
" "	2.5	63	0.01
" "	3.9	72	0.06
" "	4.0	72	0.06
" "	5.6	80	0.02
1 yr Bluegill	22	113	0.05
Crayfish (tail meat)	8.5	39¥	0.04
" "	12.2	39¥	0.03
" "	16.8	41¥	0.04

¥ Lengths for crayfish are standard carapace lengths, not total lengths.

composite basis (1.7-5.4 g, 0.19-0.24 ppm Hg). While these are quite different fish species, at this small size their feeding habits are relatively similar, with food items dominated by small in-stream invertebrates. The similar mercury concentrations measured at this time indicate that bioavailable mercury had been moving out of and/or through the reservoir in previous months. The aqueous mercury data (section 3.1.1.2) indicates that this was clearly the case under post-storm, high flow conditions. In addition to whole body composites, we analyzed muscle mercury in several 5-6 g juvenile bluegill taken downstream of the reservoir (Table 9). Muscle concentrations were somewhat higher than the whole body levels (0.22-0.40 ppm muscle vs 0.19-0.24 whole body). This is often the case. In ongoing research at the University of California, we repeatedly find muscle tissue to be the major repository for mercury in fish (Reuter et al. 1989, Slotton 1991, Suchanek et al. 1993, Slotton et al. 1996).

The samples taken from downstream Marsh Creek near Oakley provide some interesting comparative information. Here, we collected five small parr salmon (2-6 g), a one year old bluegill (22 g), and several adult crayfish. Muscle mercury in all of these samples, as well as composite mercury in the parr salmon, was significantly lower than that seen in fish from upstream Marsh Creek and the reservoir. Concentrations were all ≤ 0.07 ppm Hg. Once again, while the upstream roach and juvenile hitch are very different fish than the juvenile salmon, at this small size they are quite similar in body form and in the diet imposed by their size. Salmon parr such as these were almost certainly born in the only gravel spawning areas available on Marsh Creek downstream of the reservoir; i.e. just below the reservoir. As they only migrate downstream at this life stage (Moyle 1976), they could not have originated from outside of the watershed. Therefore, the mercury in these samples provides a reasonable measure of mercury bioavailability in downstream Marsh Creek, as compared to upper watershed roach and juvenile hitch of the same size. The levels were approximately one third of concentrations seen upstream.

While the direct comparison between parr salmon and roach of the same size may be complicated by the fact that roach of the same size can be considerably older, we found the same trend in the other samples. The bluegill taken near Oakley was also very low in mercury (0.05 ppm), despite being considerably larger than the comparative samples from just below the reservoir. Similarly, the crayfish tail meat samples were all very low, at 0.03-0.04 ppm Hg. These organisms are relatively sedentary as compared to fish, and can thus provide a good measure of localized conditions, integrated over their lifespans. In our work with crayfish throughout the Sierra Nevada, we have consistently found them to contain mercury at levels greater even than co-occurring hellgrammites, with concentrations generally similar to those of local fish (Slotton et al. 1995a). This results from their consumption of dead fish, the preferred food of these scavengers. On a comparable dry weight basis, the crayfish tail meat concentrations near Oakley were 0.15-0.20 ppm Hg. This is considerably lower than invertebrate samples of any trophic level taken between the Mt. Diablo mine area and the reservoir, and much lower than the hellgrammite mercury concentrations, which ranged from 0.50 ppm to far greater levels.

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3.2 Marsh Creek Reservoir

3.2.1 Reservoir Sediment

Table 10. Marsh Creek Reservoir Sediment Laboratory Data

Identification	Sediment Depth (cm)	(inches)	Hg (dry wt ppm)	% Water	% Organic (dry wt)
Surficial Sediment-- Large (East) Basin					
SW Quadrant	(surficial sediment)		0.49	75.1%	5.8%
SE Quadrant	(surficial sediment)		0.35	69.5%	4.7%
NE Quadrant	(surficial sediment)		0.46	70.6%	4.3%
NW Quadrant	(surficial sediment)		0.44	67.0%	5.6%
Center	(surficial sediment)		0.47	70.6%	4.3%
Surficial Sediment-- Small (West) Basin					
N Side	(surficial sediment)		0.39	50.9%	4.2%
S Side	(surficial sediment)		0.46	53.1%	4.5%
Center	(surficial sediment)		0.49	48.4%	3.9%
Core 1: Large (East) Basin--Center					
section 1	5	2	0.53	53.4%	5.7%
section 2	24	9	0.54	46.5%	4.3%
section 3	42	17	0.71	54.8%	5.9%
section 4	60	24	0.64	53.7%	4.4%
section 5	78	31	0.80	40.7%	3.8%
section 6	97	38	1.48	51.4%	6.4%
section 7	115	45	0.58	49.2%	4.0%
section 8	129	51	0.68	40.0%	3.4%
section 9	139	55	0.36	35.3%	3.4%
section 10	148	58	0.24	21.8%	1.2%
Core 2: Small (West) Basin--Center					
section 1	5	2	0.58	49.7%	5.5%
section 2	23	9	0.52	46.4%	6.0%
section 3	41	16	0.51	40.6%	5.4%
section 4	57	22	0.41	34.7%	5.5%
section 5	77	30	0.36	33.7%	5.3%
section 6	100	39	0.71	49.8%	6.4%
section 7	122	48	0.52	38.5%	4.4%
section 8	145	57	1.03	39.7%	5.3%

We characterized the current mercury concentrations in Marsh Creek Reservoir bottom sediments by sampling surficial bottom sediment at 8 locations distributed throughout the reservoir. The record of historic mercury deposition in the reservoir was determined by taking extended sediment cores into the bottom at the centers of each of the two main

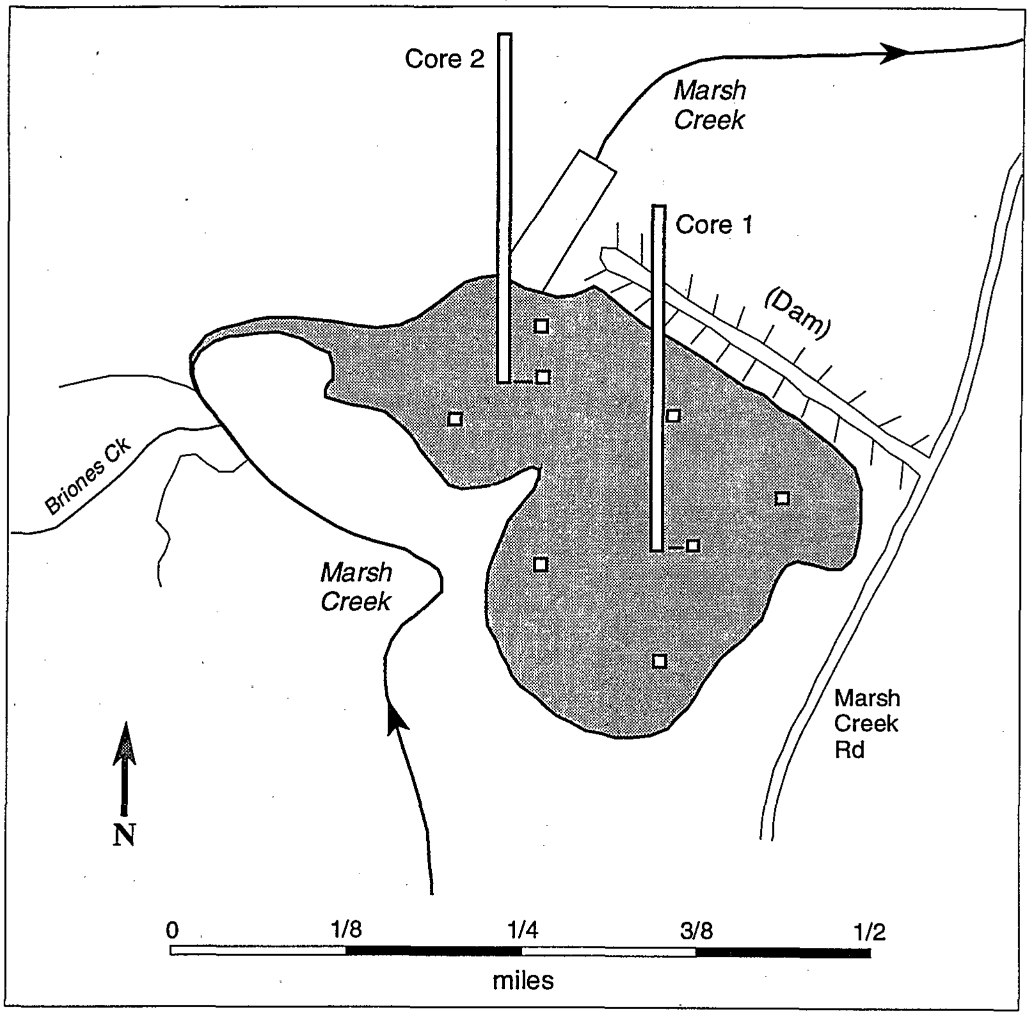


Figure 18. Marsh Creek Reservoir Sediment Sampling Sites
(September 1995)

□ -- Surficial sediment sampling sites

basins. These cores were sectioned and analyzed throughout their lengths for mercury and general sediment parameters. The reservoir sediment data is presented in Table 10. Sampling locations are displayed in Figure 18. Graphic representations of the core data are shown in Figures 19 and 20.

Surficial sediment mercury concentrations, which correspond to the most recent deposition from the watershed, were very similar throughout the reservoir at 0.35-0.49 ppm (mean = 0.44 ppm). This is very comparable to the 0.40 ppm result obtained by Levine-Fricke (1993a) for a sediment sample taken within the water line of the reservoir in July 1993. While mercury levels were relatively uniform, the sediment character was somewhat different between the two basins. The surficial sediment in the larger, eastern basin was higher in moisture content and somewhat higher in the percentage of organic matter. This is consistent with the smaller, western basin being the location of the direct inflows from Marsh Creek. The associated inputs of new sediment from the watershed will initially be of larger grain size and lower moisture percentage near the inflow, as that is where the heavier material will drop out of the water as the current slows. New deposition in other areas of the lake, further away from the inflow, will be dominated by the fine particulates which remain suspended in the water long enough to reach those areas. Subsequent increases in organic percentage and moisture content are particularly likely where there is extensive weed growth, as has been the case in this shallow reservoir.

The core taken in the center of the large, eastern basin (Core 1) reached all the way to the original terrestrial bottom material, which was nearly five feet beneath the current sediment/water interface. As the reservoir was built in 1963, this profile includes the entire 32 year history of sediment deposition from 1963 to 1995. The underlying terrestrial material was distinctive in its orange/tan coloration, crumbly texture, and dryness, as compared to the gray to black, fine sediments that constituted the subsequent aquatic sediment deposition.

Core sub-samples for laboratory analysis were taken within homogeneous sections of the core, rather than at specific intervals. Different periods of deposition were apparent in the core record as distinct color and textural shifts, with uniform bands of gray, black, and intermediate shades. The underlying terrestrial soil was quite different visually from any of the overlying material. The profiles of laboratory analytical parameters show this as well (Fig. 19). The values for mercury concentration, moisture content, and organic percentage were notably lower in the terrestrial material, as compared to the overlying aquatic sections of the core. Within the aquatic sediment layers, values of all three parameters varied within relatively narrow ranges. In the top 4.5 feet of the Core 1 sediment, mercury ranged between 0.5 and 1.5 ppm, moisture content was 40-55%, and organic percentage ranged

Figure 19. Marsh Creek Reservoir 1995 Sediment Core 1: Larger, Eastern Basin Profiles

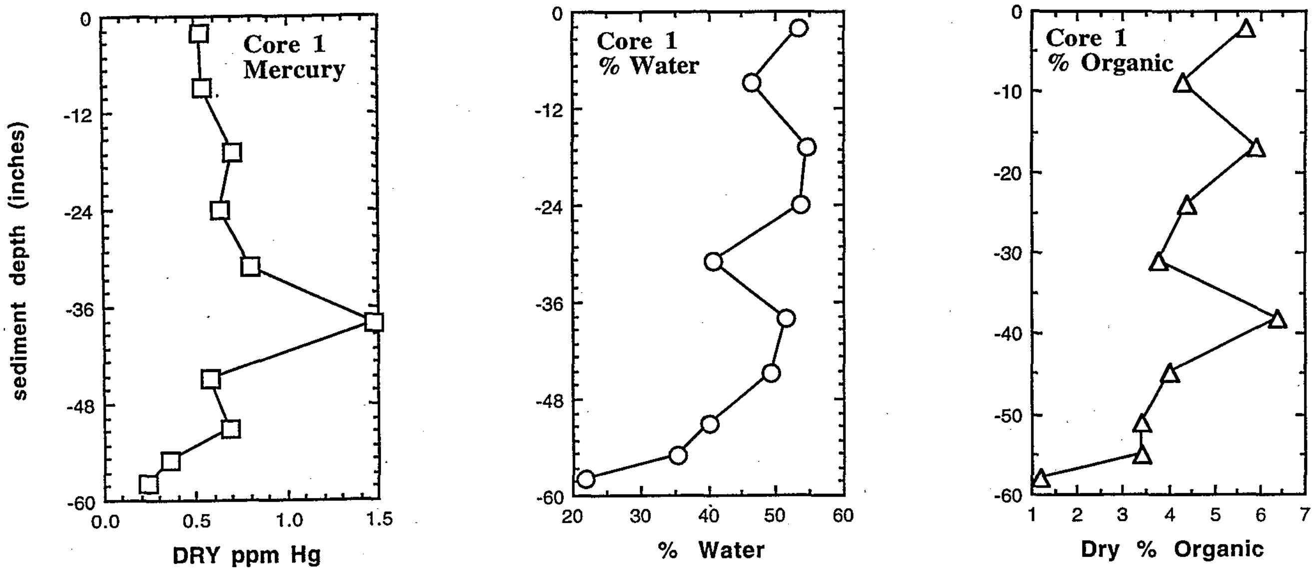
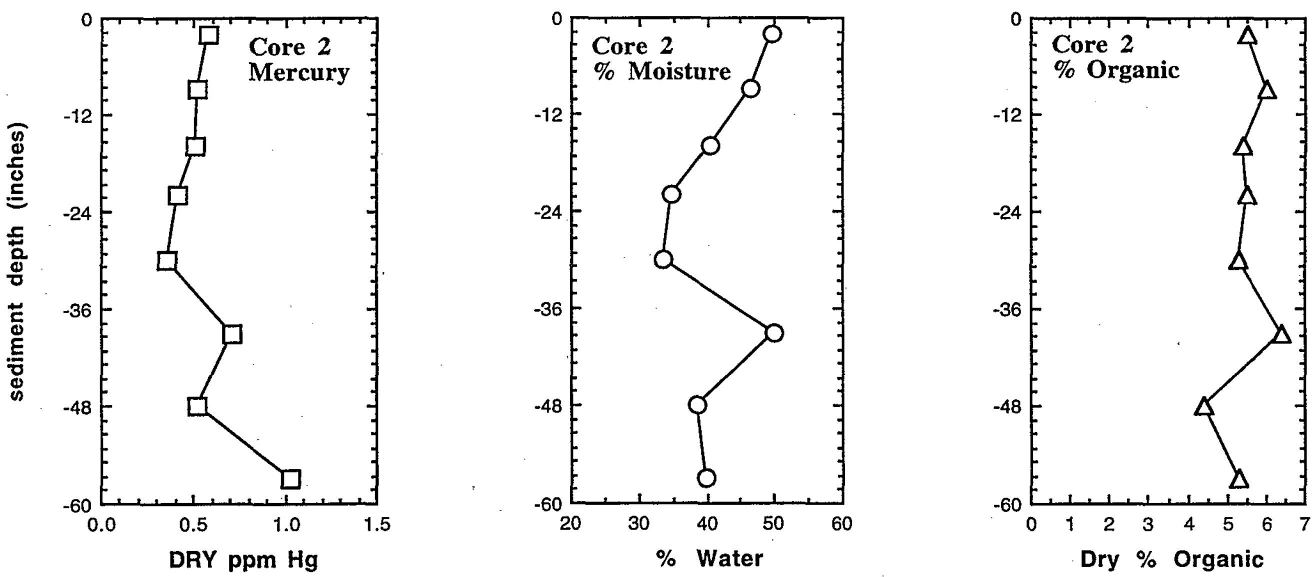


Figure 20. Marsh Creek Reservoir 1995 Sediment Core 2: Western (Inflow) Basin Profiles



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between 3.5% and 6.5%. This record indicates that, over the 30+ year history of Marsh Creek Reservoir, depositional sediments from the upper watershed remained fairly consistent in their character. In fact, with the exception of the 1.5 ppm mercury value at approximately 3 foot depth in the core, the mercury levels in this sediment were remarkably uniform, at 0.53-0.80 ppm. It is interesting to note that the underlying soil was significantly lower in mercury, at 0.24 ppm.

Core 2, from the western basin of the reservoir, was taken to a similar depth of approximately 5 feet (Fig. 20). However, in this core we were not able to reach an underlying terrestrial layer. This was apparent both visually and in the laboratory parameters. Color varied between light gray through black zones throughout the core, including the bottom layers. Texture varied between clays, silts, and sands throughout, all of which are depositional materials. Moisture and organic contents did not show a notable change at the bottom. Moisture varied between 33% and 50% throughout the core, while organic percentage ranged between 4.4% and 6.4%.

Similar to Core 1, mercury concentrations in Core 2 were very steady at 0.36-0.71 ppm, with a higher excursion to 1.03 ppm near the 5 foot depth. These levels are similar to concentrations found in earlier sampling from this basin of the reservoir. Levine-Fricke conducted limited sediment core work near the inflowing delta in October 1993, taking 10 replicate samples of surficial delta sediment and 10 replicate samples from approximately 3 foot depth in the sediment (Levine-Fricke 1993b). Mercury concentrations from that sampling ranged between 0.12 and 0.40 ppm (mean = 0.23 ppm) in the surficial sediment and between 0.24 and 0.48 ppm (mean = 0.35 ppm) in the samples from 3 foot depth. Our Core 2, taken at the center of the western basin from a boat, was presumably composed of smaller grain-sized deposition as compared to delta deposits. The somewhat lower mercury results in the delta samples may be partly a function of grain size. We have found that, similar to other metals, mercury concentrations in particulate depositional material typically rises exponentially with decreasing grain size (Slotton and Reuter 1995).

The slight historic increase at 5 foot depth in Core 2 may correspond to the 1.5 ppm mercury spike seen in Core 1 at 3 feet. As Core 2 was taken near the inflow from Marsh Creek, it would be expected to receive greater vertical accumulations of depositional material than the (offset) eastern basin. This is where the bulk of the heavier particles will fall out of the current, upon reaching the still waters of the reservoir, in the natural process of delta formation. Significant layers of fine to medium sand were indeed present in Core 2. This, in fact, is what limited the depth to which we could drive the core. Because the depositional rate at this site was greater than in the east basin clays/silts, the mercury increase at 5 feet could easily correspond to the peak seen at 3 foot depth in Core 1. In any case, mercury levels in both of the core profiles fell within a quite narrow range of concentrations.

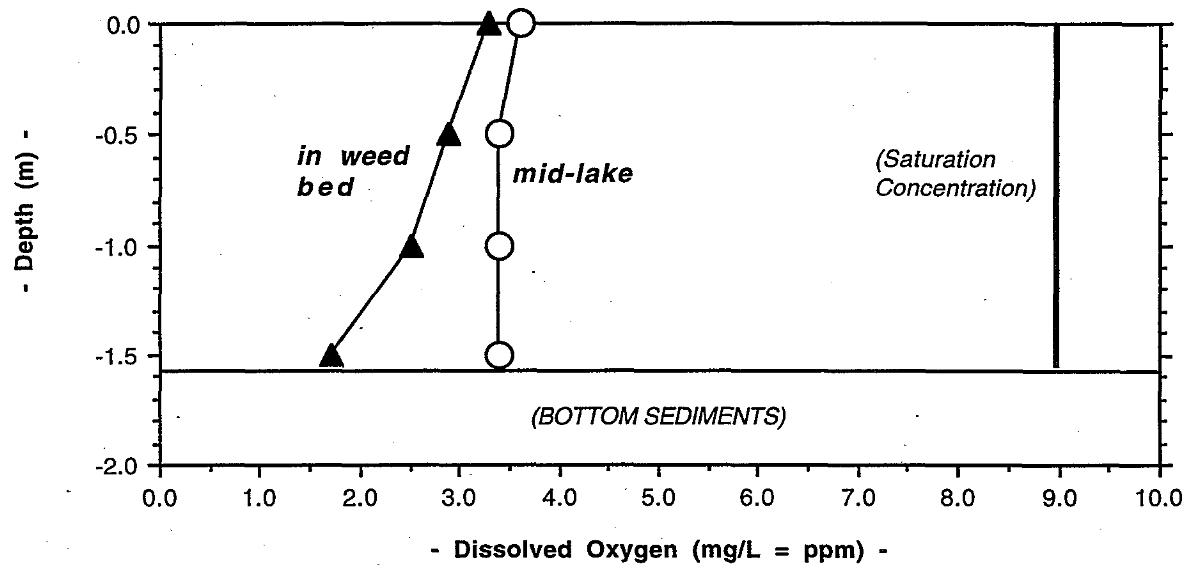
The similar mercury levels found across the 32 year reservoir depositional sediment record are consistent with the upstream mine having remained in a similar state of mercury loading to the watershed throughout this period. Another conclusion to be drawn from the uniform depositional mercury levels is that the construction of the settling basin beneath the mine tailings in ~1980 has apparently not resulted in a significant decrease in depositional mercury in the downstream reservoir.

3.2.2 Reservoir General Limnology

In the course of sampling the reservoir with a variety of techniques, we were able to characterize the fish populations present, as well as the general limnology of the system. In the sediment core studies (section 3.2.1) we found that the reservoir has already filled in with depositional sediment to a depth of approximately 5 feet. At the time of our reservoir work (September 1995), the resulting water column was found to be quite shallow throughout, with depths of 6 feet or less. Consequently, aquatic macrophytes (large aquatic plants) have been able to establish dense weed beds over large areas of the reservoir. The genus *Potamogeton* dominated at this time, with a dense fringe of cattail (*Typha*) and bullrush (*Scirpus*) around the margins. The water was quite turbid, with a Secchi visibility consistently under 0.5 m (< 20 inches). The turbidity was apparently largely due to brown, organic staining of the water.

While the dense weed growth will produce oxygen during the day it, together with general organic metabolism, will consume oxygen during dark hours when photosynthesis ceases. We took early morning oxygen and temperature profiles through the water column on a mid-September date to investigate the potential for significant oxygen depletion in the reservoir water (Fig. 21). Temperature at this time was very uniform at 20.9-21.5 °C (69.6-70.7 °F), indicating no appreciable thermal stratification. Indeed, during the previous night, strong breezes had stirred the waters of the reservoir. Despite being well mixed and uniform at the midlake, open water location, morning oxygen levels were quite low from surface to bottom, at approximately 3.5 ppm. This was only 39% of the normal solubility (saturation) level for oxygen at this elevation and water temperature (8.9 ppm). Within a representative aquatic weed bed, oxygen was at a similar level near the surface (3.2 ppm), while concentrations dropped steadily toward the bottom, to a level of 1.7 ppm, or 19% of normal solubility. Most fish cannot live under extended periods with oxygen below approximately 1-2 ppm (Moyle 1976). It is very likely that during mid-summer, with greater temperatures, increased biological respiration rates, and calmer weather, extensive anoxia may be a routine condition, particularly in the bottom waters of the reservoir.

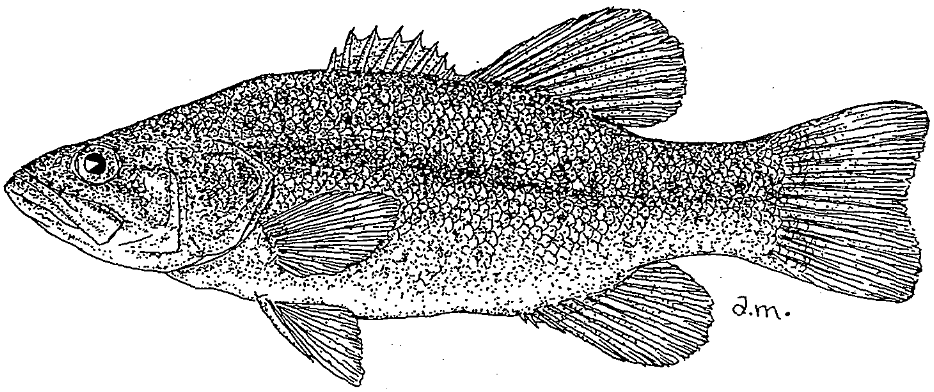
Figure 21. Marsh Creek Reservoir Dissolved Oxygen Profiles
(September 17, 1995; early morning profiles)



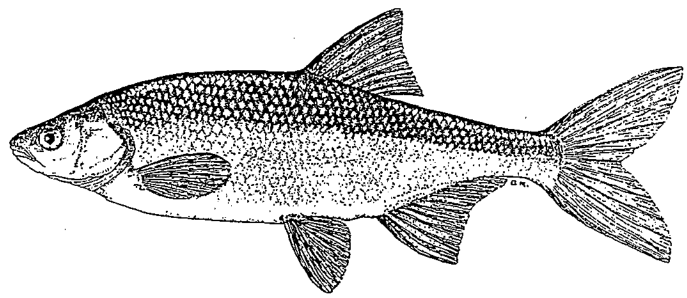
This finding of potentially prohibitively low oxygen occurrences is consistent with the variety of fish species found to inhabit the reservoir at this time. No bottom dwelling fish were taken, despite repeated sampling efforts with a variety of gill nets and set lines that have proven quite effective in other systems. Common bottom fish that would otherwise be likely to occur include catfish and bullhead, native suckers, and carp. The absence of these fish in our sampling indicates either that they were never introduced or that they may be unable to maintain significant numbers within the bottom waters of the reservoir under current conditions.

Of the four fish populations that were found, all were midwater and surface species (Fig. 22). Fish of any significant size, in terms of angling, included hitch (*Lavinia exilicauda*), a native planktivore that reaches approximately 1.5 pounds and 14 inches, and largemouth black bass (*Micropterus salmoides*), a prized gamefish that can reach over 5 pounds. Hitch inhabited the open areas of the reservoir in fairly abundant numbers, while the bass mainly stayed in open channels among the weed beds. Juvenile bass were prevalent, in addition to moderate numbers of adult bass in a range of sizes and ages. The

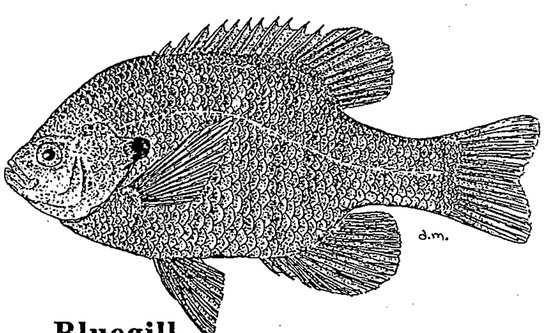
Figure 22. Marsh Creek Reservoir Fish Species Sampled in 1995
(illustrations taken from Moyle 1976)



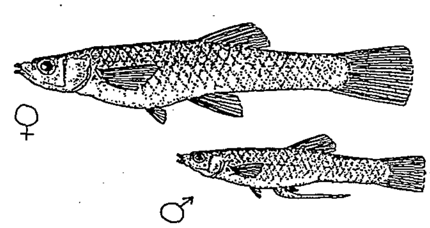
Largemouth Black Bass
Micropterus salmoides
(11-16 inches)



Hitch
Lavinia exilicauda
(10-13 inches)



Bluegill
Lepomis macrochirus
(to 8 inches)



Mosquito Fish
Gambusia affinis
1-2 inches)

other two fish species included mosquito fish (*Gambusia affinis*) and bluegill sunfish (*Lepomis macrochirus*). The surface-feeding mosquito fish were numerous at the shoreline and within the weed beds. These are very small fish, generally under 2 inches in length. The bluegill population was fairly dense and was characterized by stunted growth; i.e. a large number of very small fish. This is a frequent competitive outcome for bluegill in small, shallow water bodies (Moyle 1976). We only sampled a single bluegill of a size likely to be kept by anglers (8 inches, 1/2 pound). The great majority of bluegill were under 5 inches in length. We conclude that, under current reservoir conditions, adult largemouth bass are likely to be the only fish potentially sought for and taken by anglers.

The results of this 1995 fish assessment, as compared to that by the California Department of Fish and Game in 1980, differ in that redear sunfish and catfish were noted in 1980 but not in 1995 (Contra Costa County 1994). Additionally, the bass in the reservoir were reported to be smallmouth black bass in 1980, whereas they were clearly largemouths in 1995. This may reflect either a change in populations due to stocking or, more likely, an earlier misprint.

3.2.3 Reservoir Biota Mercury

A key component of this project was to assess the current levels of mercury contamination in Marsh Creek Reservoir biota, with the primary focus being fish within the range of sizes and types likely to be taken by anglers. For our assessment, we kept 10 "keeper" largemouth bass in a variety of sizes and ages for analysis. We also took 14 adult hitch, 1 large bluegill, and a range of additional biota samples that provide data comparable to other mercury work conducted throughout the state by our research group at the University of California and by state agencies.

In Table 11, the muscle mercury concentrations from sampled adult reservoir fish are presented, together with weight and length data. Liver mercury was also analyzed from a subset of the fish. The muscle mercury results are plotted graphically against fish size in Fig. 23. For both of the larger species, hitch and largemouth bass, muscle mercury levels demonstrated typical patterns of increasing mercury concentrations with increasing size/age of fish. Hitch, within the range of adult sizes common in the reservoir, varied in muscle mercury concentration from approximately 0.3 ppm at 0.6 pounds to approximately 0.5 ppm at 1.0 pounds. Adult largemouth bass muscle mercury ranged from just over 0.6 ppm at 1 pound to approximately 1.0 ppm at 3 pounds. These relationships were quite consistent across the 14 adult hitch and 10 adult largemouth bass sampled in this work. The single sampled bluegill individual that was potentially of angling size had muscle mercury at 0.63 ppm, intermediate between the adult hitch and adult largemouth bass levels. As hitch consume low trophic level foods (primarily algae and zooplankton), they will generally accumulate less mercury than the piscivorous (fish eating) largemouth bass. The bluegill diet consists mainly of small invertebrates, which are trophically intermediate relative to the diets of the other two species.

Table 11. Marsh Creek Reservoir Adult Fish Tissue Mercury Concentrations *(fresh/wet weight ppm Hg)*

	Weight *(g)*	Length *(mm)*	Muscle Hg *(wet wt ppm)*	Liver Hg *(wet wt ppm)*
Hitch				
	285	266	0.26	0.33
	298	280	0.37	
	310	270	0.31	
	313	283	0.33	
	346	292	0.50	
	350	290	0.46	
	350	301	0.41	
	370	295	0.48	
	380	303	0.41	
	402	309	0.48	
	406	316	0.47	
	420	310	0.55	
	437	301	0.43	0.45
	480	322	0.48	
Bluegill				
	215	196	0.63	0.77
Largemouth Bass				
	412	283	0.64	0.55
	480	295	0.66	
	560	302	0.59	
	815	348	0.86	
	870	344	0.71	0.36
	930	343	0.72	
	1,030	372	0.84	
	1,040	362	0.90	0.58
	1,160	387	0.92	
	1,155	403	1.04	1.21

The U.S. FDA health standard for mercury in fish flesh is 1.0 ppm. However, the criterion recommended by the U.S. Academy of Sciences, the California Department of Health Services, and the great majority of other nations internationally is 0.5 ppm (TSMP 1990). In Fig. 20, the reservoir fish muscle mercury concentrations are compared to the 0.5 ppm criterion. The levels clearly straddle the line, with the "keeper" sized bluegill and largemouth bass all being well above the 0.5 ppm level. The bass ranged up to and even

Figure 23. Mercury Concentrations in Adult Fish From Marsh Creek Reservoir *(fish collected September 1995)*

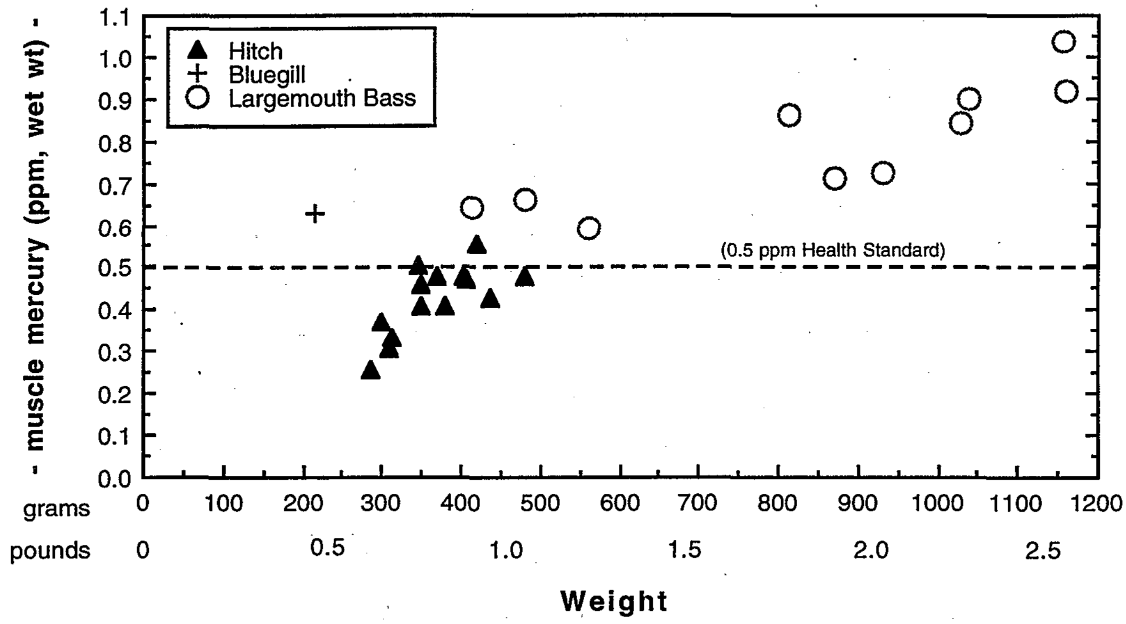
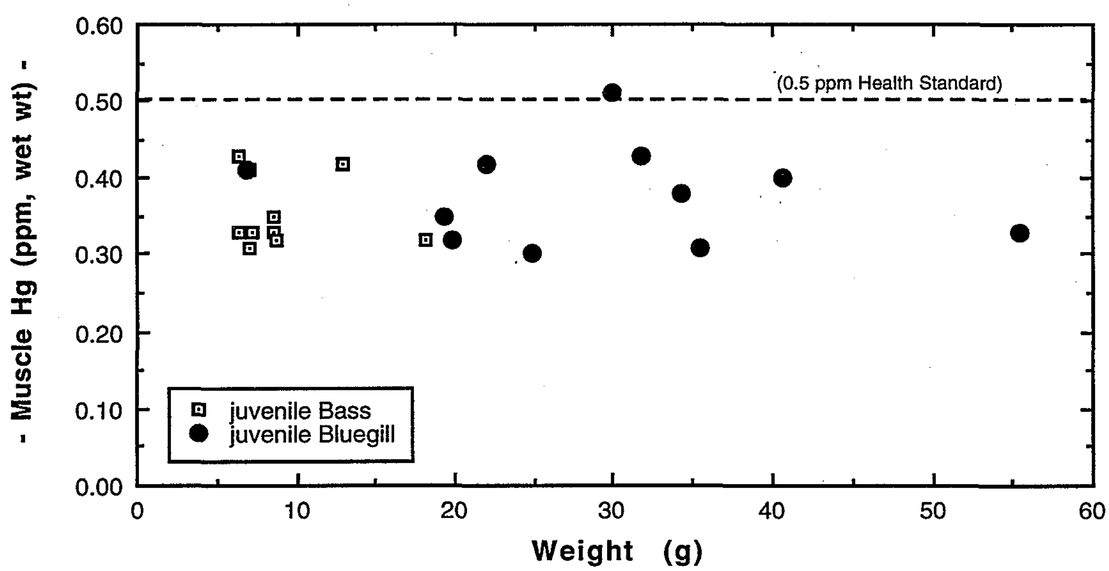


Figure 24. Mercury Concentrations in Juvenile Fish From Marsh Creek Reservoir *(fish collected September 1995)*



above the FDA 1.0 ppm standard in the larger individuals. These concentrations are clearly high. However, while of concern, they are not exceptionally high for this region of California, where mercury contamination is widespread. In our own research and that of other institutions and government agencies, similar levels have been reported from other water bodies directly impacted by mercury mines, including Lake Nacimiento and Lake Herman (TSMP 1990). Depending on the characteristics of the lake, some mine impacted sites have lower fish mercury levels, such as Clear Lake (Suchanek et al. 1993, Slotton et al. 1996), while others have higher levels, such as Davis Creek Reservoir north of Lake Berryessa (Reuter et al. 1989, Slotton et al. 1995b) and the small reservoirs near the New Almaden mine (TSMP 1990). Fish mercury levels nearly as high as those in Marsh Creek Reservoir can also be found in a number of the Sierra Nevada foothill reservoirs which have trapped mercury dating from the gold mining era of the 19th century (TSMP 1990, Slotton et al. unpublished data).

The muscle mercury concentrations in Marsh Creek Reservoir fish in 1995 can thus be considered to be too high for regular consumption, but not exceptionally high for northern California. An important consideration is that the levels were close enough to the health criteria that, if bioavailable mercury in the reservoir could be lowered by a significant fraction, future reservoir fish might be brought well under the guideline levels.

In addition to the large fish, we collected extensive samples of juvenile bass, juvenile bluegill, mosquito fish, and reservoir invertebrates. These types of samples will be extremely useful as bioindicators of potential year-to-year changes in mercury bioavailability in the reservoir, in conjunction with any mitigation trials upstream at the Mt. Diablo mine and/or in the reservoir itself. While the "bottom line" test of effectiveness for mitigation work will ultimately be determined by significant declines in muscle (fillet) mercury in the larger, edible fish of the reservoir, the larger fish accumulate their mercury over several to many years time. Because of this, their mercury concentrations can change only slightly within time scales of a year or two, even with major changes in environmental mercury. They generally do not show significant corresponding changes in their tissue mercury levels until they have lived the greater proportion of their lives under the new conditions (Slotton et al. 1995b). A major research focus of the senior author over the past decade has involved working with alternate bioindicator organisms, supplemental to adult fish, to develop approaches that can determine changes in pollutant exposure at a much finer scale, in terms of both time and location. We are using some of those tools in this project, including the invertebrate work in the upper watershed and the juvenile fish and invertebrate work in Marsh Creek Reservoir.

The young-of-year bass and small bluegill will be particularly useful (Table 12, Fig. 24). Muscle mercury concentrations in these small fish were quite consistent across the range of sizes present, falling between 0.30 ppm and 0.43 ppm in all 10 of the sampled juvenile bass (mean = 0.36 ppm) and in 10 of the 11 sampled small bluegill (mean = 0.37 ppm). One bluegill was somewhat higher, at 0.51 ppm. Because the young-of-year fish can have only accumulated mercury in the year they are sampled, these consistent 1995 levels can be compared in future years to corresponding levels in new young-of-year fish, to determine relative changes in exposure.

Table 12. Marsh Creek Reservoir Juvenile Fish Muscle (Fillet) Mercury Concentrations *(fresh/wet weight ppm Hg)*

Juvenile Bluegill Muscle Mercury			Juvenile Largemouth Bass Muscle Mercury		
Weight *(g)*	Length *(mm)*	Hg *(ppm)*	Weight *(g)*	Length *(mm)*	Hg *(ppm)*
6.9	72	0.41	6.4	78	0.33
19.4	99	0.35	6.4	80	0.43
19.8	100	0.32	7.0	80	0.41
22.0	104	0.42	7.1	80	0.31
24.9	104	0.30	7.3	82	0.33
30.0	112	0.51	8.5	87	0.35
31.7	114	0.43	8.6	89	0.33
34.3	117	0.38	8.7	89	0.32
35.4	118	0.31	12.9	98	0.42
40.7	124	0.40	18.2	111	0.32
55.4	131	0.33			

In addition to the small fish muscle mercury samples, we made composite, whole body samples of young-of-year bass and mosquito fish (Table 13). These composites, grouped by size class for each species, provide additional measures of short term reservoir mercury bioavailability. They also can be compared to the composite small fish data generated in the watershed work (section 3.1.3). As seen for muscle, whole body mercury concentrations in the juvenile bass were very similar among the range of sizes present, at 0.23-0.29 ppm. The levels in whole body composites were somewhat lower than those analyzed in muscle tissue. This is frequently the case, as muscle is the major site of mercury accumulation in fish (Reuter et al. 1989, Slotton 1991, Suchanek et al. 1993, Slotton et al. 1996). The tiny mosquito fish were also consistent in their whole body composite mercury levels, at 0.15-0.20 ppm among the dominant range of sizes. A single much larger individual, potentially several years old, had anomalously higher mercury concentration, at 0.57 ppm.

Table 13. Marsh Creek Reservoir Biota Composite Samples (Whole) Mercury
(wet wt ppm Hg, fish; dry wt, invertebrates) September 1995

Identification	Weight	Length	Individuals	Hg
(g)	*(mm)*	In Comp.	*(ppm)*	
Juvenile Largemouth Bass	(6.9)	(78)	n=5	0.29
Whole Fish Composite Samples	(8.6)	(88)	n=3	0.26
" " "	12.9	98	n=1	0.24
" " "	18.2	111	n=1	0.23
Gambusia (Mosquito Fish)	(0.1)	(20)	n=62	0.20
Whole Fish Composite Samples	(0.2)	(30)	n=32	0.15
" " "	0.5	38	n=1	0.15
" " "	2.1	57	n=1	0.57
Predatory Invertebrate Composite Samples (*dry* weight ppm Hg)				
Coenagrionid Damselflies	(winged adults)		n=25	0.09
Aeschnid Dragonflies	(winged adults)		n=4	0.27
Libellulid Dragonflies	(winged adults)		n=2	0.39

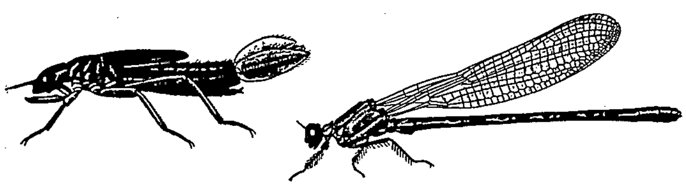
As final bioindicators of reservoir mercury, we took reservoir damselflies (Coenagrionidae) and two types of dragonfly (Aeschnidae and Libellulidae) in composite samples of winged adults (Table 13, Fig. 25). These were dried and powdered, similar to the watershed invertebrate samples. Damselflies and dragonflies are good indicators of reservoir conditions as they spend the majority of their lives in the aquatic stage, consuming other aquatic invertebrates, and continue to consume primarily reservoir-derived invertebrates even after becoming winged adults. The dragonfly composites contained 0.27 ppm mercury for one type and 0.39 ppm for the other. The smaller damselflies had a lower level of 0.09 ppm.

All of these samples provide initial baseline data of current mercury bioavailability in the reservoir. They can be compared to similar collections in future years, to determine the extent of potential changes in mercury availability.

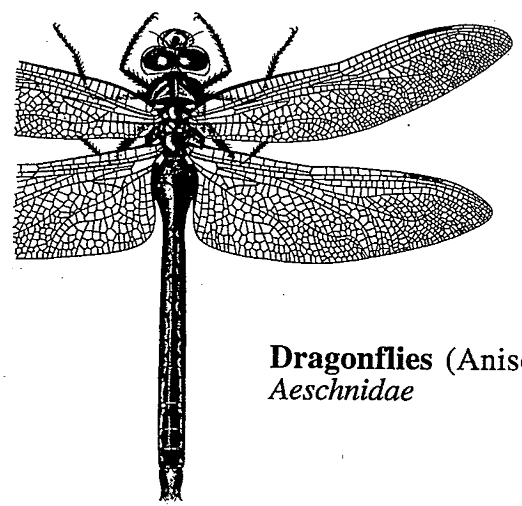
Figure 25. Marsh Creek Reservoir Invertebrates Sampled in This Project

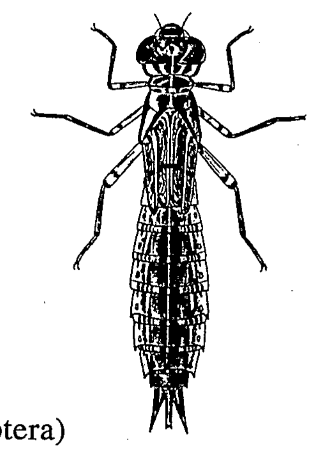
(winged adults taken, adults and aquatic stages shown)

(illustrations taken from McCafferty 1981)

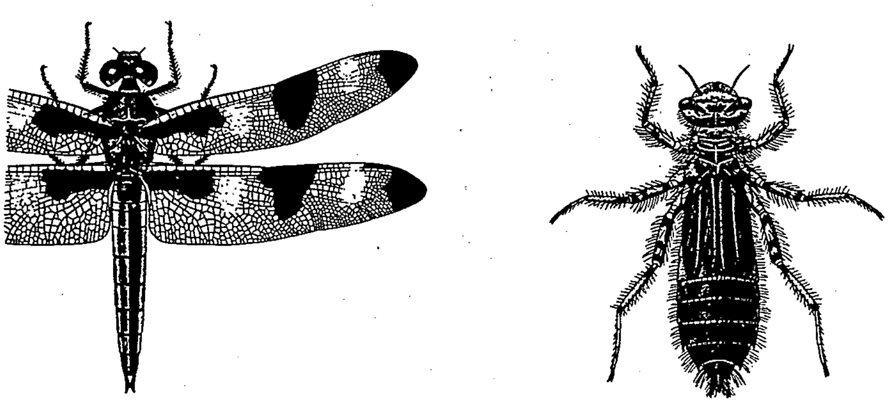


Damselflies (Zygoptera)
Coenagrionidae





Dragonflies (Anisoptera)
Aeschnidae



Dragonflies (Anisoptera)
Libellulidae

4. DISCUSSION AND CONCLUSIONS

Prior to this study, the Mt. Diablo Mercury Mine was generally assumed to be the dominant source of mercury to the Marsh Creek watershed. However, data was not available to quantify this input, rank the mine against other potential mercury sources, or rule out the possibility of a generalized source of mercury in this mercury-enriched watershed. Now, with the 1995 watershed mercury information assembled here, we can establish that the mine site does indeed represent the overwhelming source of mercury to the watershed. By collecting consistent, above detection aqueous mercury concentration data, together with accompanying flow information, from all major source areas, it has been possible to rank the various inputs on a mass balance basis. While the various loading values measured were specific to the particular flow regime during the sampling period, the relative contributions are of greater importance.

Both the aqueous mercury data and those from the invertebrate bioindicator organisms strongly implicate the mine region as being the dominant source of mercury in the Marsh Creek watershed. The aqueous mercury mass balance calculations indicate that approximately 95% of the total input of mercury to the upper watershed derives from Dunn Creek. The mine area itself was the clear source region for the mercury, with an estimated 88% of the total input of mercury to the upper watershed traceable specifically to the current exposed tailings piles. This is a remarkably high percentage, particularly in light of the geologically mercury-rich nature of the watershed in general, and indicates that the mercury in exposed, processsed, cinnabar tailings material is exceptionally available for aqueous transport downstream.

The data indicates that the great majority of the mercury load eminating from the tailings is initially mobilized in the dissolved state. This dissolved mercury rapidly partitions onto particles as it moves downstream. The bulk of downstream mercury transport is thus particle-associated.

In marked contrast to the massive mercury loads carried by lower Dunn Creek, this small tributary delivered less than 7% of the watershed's total flow and less than 4% of the suspended solids load. As downstream mercury accumulations are greatly dominated by the sediment burden, a lowering of mercury concentrations in the downstream surficial sediments would almost certainly help to drive down both the aqueous mercury concentrations and the corresponding flux of mercury into biota. With 95% of the mercury originating from the Mt. Diablo Mine area, but 95% of the watershed's suspended sediment load deriving from non-mine, low mercury source regions, any significant decrease in the export of mercury from the immediate mine site should result in a corresponding decline in surficial sediment mercury concentrations downstream and in Marsh Creek Reservoir. With an estimated 88% of the currently exported mercury linked directly to the tailings piles themselves, mercury source mitigation work within the watershed would clearly be best directed toward this localized source.

Though mitigation recommendations were not a part of our scope of work, we have several comments on the subject that may help to both clarify the task and direct the planning process:

1. In order to reduce the downstream export of mercury from the Mt. Diablo Mercury Mine, we believe that the major mitigation focus should be directed toward source reduction from the tailings piles themselves, with subsequent containment of the remaining mobile mercury fraction being a secondary consideration.

2. The data we have assembled here indicate that source reduction of mobile mercury from the tailings will best be accomplished by diminishing the flow of water through the tailings. Rather than being a problem of direct erosion of tailings material, in solid particle form, to downstream, it appears that the predominant mode of mercury mobilization from the tailings involves the acidification of runoff/seepage water by the processed, high sulfur ore material, and the subsequent dissolution of mercury from the ore into the acidic water. Very similar trends are concurrently being found at the EPA Superfund site at Clear Lake's Sulfur Bank Mercury Mine.

3. Lowering the flow of water through the tailings can be accomplished by (a) diverting any runoff that originates from outside of the tailings zone and (b) diminishing the movement of direct precipitation into and through the tailings. Diversion of upslope surface and groundwater flows away from the tailings will likely be the simplest and most cost-effective procedure to begin with. As part of this operation, upper Horse Creek should be diverted directly to Dunn Creek, bypassing the tailings (Fig. 26).

4. Direct water inputs to the tailings from precipitation are more problematical, but can be significantly lessened with a variety of revegetation schemes. Central to the most effective of these techniques is the application of a soil cover over the tailings that is sufficiently thick and porous to hold the average winter precipitation. Through the careful revegetation of the slope with appropriate, hardy plant species, much of this soil water can be annually soaked up and removed to the atmosphere through evapotranspiration. While grasses may be most efficient at initially stabilizing the slope, perennial shrubs and trees exhibit the greatest rates of evapotranspiration and

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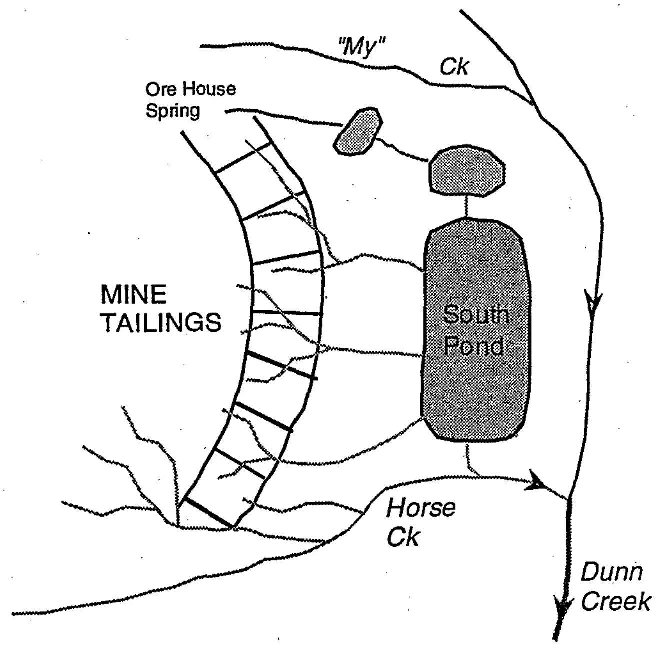
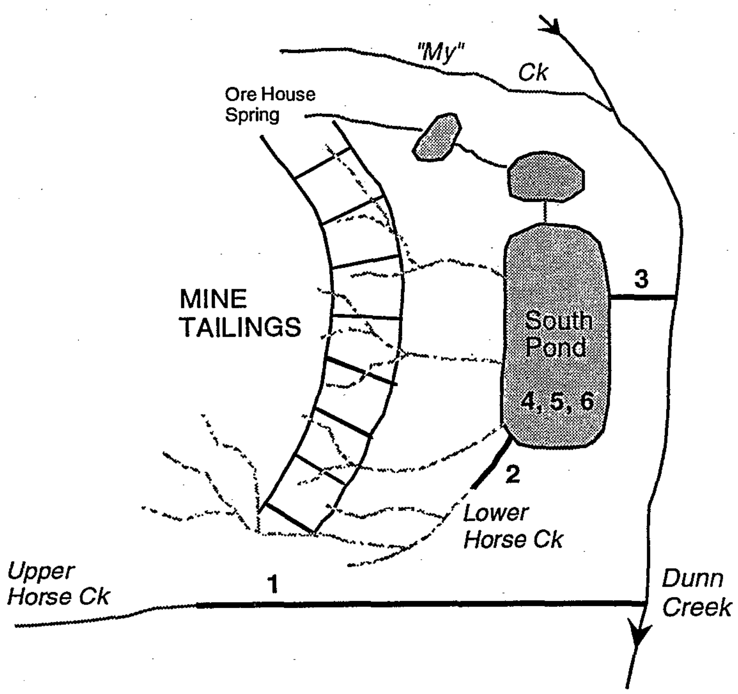
Figure 26. Current Mine Site Creek and Settling Pond Configurations vs Modification Options



a. Current configuration



b. Potential modifications

1. Pipe upper Horse Ck past tailings directly to Dunn Ck.
2. Divert lower Horse Ck into South Pond.
3. Construct new South Pond outlet on east side.
4. Deepen South Pond.
5. Periodically lime South Pond.
6. Periodically dredge South Pond.

have thus been found to be the most effective in removing accumulated soil water (Mary Ann Showers, California Department of Conservation, personal communication).

5. Any containment/treatment scheme for the remaining mobile mercury eminating from the tailings region will be enhanced by source reduction. Because the current principal sediment settling basin does not appear to be providing the desired level of effectiveness, we would suggest some modifications (also shown in Fig. 26):

   (a) As lower Horse Creek contained the majority of the mercury loads eminating from the tailings, it should be diverted into the pond.

   (b) Because much of the tailings inflow enters the pond near the southwest corner, the outflow should be relocated to a part of the pond distant from the inflow, i.e. to the east side of the pond. This will be even more essential if lower Horse Creek is diverted into the pond.

   (c) Consider deepening the pond, making more room for the deposition of precipitating solids and rendering them less susceptible to sediment resuspension.

   (d) Consider periodic liming of the pond to lower the acidity of the water and promote the rapid precipitation and deposition of dissolved metals.

   (e) Occasional dredging out of the accumulated depositional material may be necessary. This could be accomplished with minimal consequences to downstream by working in the dry season and temporarily sealing the outflow for the operation.

   Again, all aspects of secondary containment will be enhanced by source reduction of water, sediment, and associated mercury from the tailings.

Mercury in Marsh Creek Reservoir edible fish flesh was above the health standard concentration of 0.5 ppm in all samples of "keeper" sized bass and bluegill, with the larger bass ranging up to and slightly over 1.0 ppm muscle mercury. Fish accumulate mercury in their muscle (fillet) tissue almost entirely in the methyl form. Methyl mercury is naturally produced from inorganic mercury mainly as a metabolic byproduct of certain bacteria (Gill and Bruland 1990). As methyl mercury was measured to be quite low in storm runoff inflows to the reservoir (0.20 ng/L, Table 4), it is likely that a significant proportion of the methyl mercury accumulating in Marsh Creek Reservoir fish is produced within the reservoir from inorganic mercury associated with depositional sediments. Any lowering of the reservoir depositional sediment mercury concentration, through upstream mine site mitigation work, should act to reduce the rate of mercury methylation in the reservoir.

warranted, it may be possible to further reduce mercury methylation rates within the reservoir through water column manipulation to minimize anoxia. This is an area that we are currently investigating in our mercury biogeochemical research work.

With this 1995 watershed mercury assessment, a comprehensive, accurate data base has been initiated for the County, describing mercury conditions throughout the major components of the system. This includes mercury concentration, loading, and relative mass balance data for water and suspended sediment from all major tributaries, biota mercury levels from throughout the watershed, and depositional sediment and biota mercury concentrations from Marsh Creek Reservoir. The utility of these data for use as a general baseline could be substantially increased with the sampling of selected parameters in the current water year (1996), prior to any mitigation work, to help account for natural inter-annual variability. We note that 1995 was an extremely wet, high-runoff year, while 1996 is more of an average water year. It is our strong recommendation that the County obtain as extensive and varied a baseline data record as possible prior to mitigation, and maintain selective monitoring of key sites and parameters throughout and following mitigation work. Ongoing monitoring of carefully chosen indicator samples, both at the mine and in downstream receiving waters, will play an integral role in guiding and assessing the effectiveness of any mitigation efforts.

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5. LITERATURE CITED

Bloom, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Canadian Journal of Fisheries and Aquatic Sciences*, 46:1131-1140.

Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at sub nanogram per liter levels. *Marine Chemistry*, 14:49-59

Bodega Research Associates. 1995. 1994-1995 Monitoring data for Hunting Creek and Knoxville Creek drainages, McLaughlin Mine Project, Lake and Napa Counties, California, 85 pp. *Report for Homestake Mining Company.*

Contra Costa County. 1994. Cowell Ranch Project, Administrative Draft EIR, October 10, 1994.

CVRWQCB. 1994. Mt. Diablo Mercury Mine, Contra Costa County. Memo from Alexander MacDonald of the Central Valley Regional Water Quality Control Board to Jack Wessman and the Contra Costa County Health Services Department, December 27, 1994.

Gill, G.A. and K.W. Bruland. 1990. Mercury speciation in surface freshwater systems in California and other areas. *Environmental Science and Technology*, 24(9):1302-1400.

Goldman, C.R. (ed). *Freshwater Crayfish--Volume V.* Papers from the fifth international symposium on freshwater crayfish, Davis, California, USA, 1981.

Hellawell, J.M. 1986. *Biological indicators of freshwater pollution and environmental management.* Elsevier Applied Science Publishers LTD, Essex, United Kingdom.

Levine-Fricke. 1993a. Letter report and proposal, Marsh Creek sediment sampling and results of mercury analysis at the Cowell Ranch property, Brentwood, California. August 26, 1993 memo from Levine-Fricke consultants to Gary Craft of the Cowell Ranch Project.

Levine-Fricke. 1993b. Results of soil and water sampling and screening health risk calculations, Cowell Ranch property, Brentwood, California. December 30, 1993 memo from Levine-Fricke consultants to Gary Craft of the Cowell Ranch Project.

Lindberg, S., P.M. Stokes, and E. Goldberg. 1987. Group report: Mercury. Chapter 2 in *Lead, Mercury, Cadmium, and Arsenic in the Environment.* T.C. Hutchinson and K.M. Meema, eds. John Wiley and Sons Ltd, 17-33.

McCafferty, W.P. 1981. *Aquatic Entomology.* Jones and Bartlett Publishers, Boston, 448 pp.

Moyle, P.B. 1976. *Inland fishes of California.* University of California Press, Berkeley, Los Angeles, London. 405 pp.

Ross, C.P. 1940. Quicksilver deposits of the Mount Diablo District, Contra Costa County, California. *United States Department of the Interior*, Bulletin 922-B, 31-54.

Reuter, J.E., D.G. Slotton, R.P. Axler, and C.R. Goldman. 1989. Analysis of the Long-Term Environmental Monitoring Program for Davis Creek Watershed Surface Waters--January 1, 1982 - June 30, 1989. *Report for Yolo County.* 268 pp.

Reuter, J.E., D.G. Slotton and C.R. Goldman. 1995. Evaluation of McLaughlin Gold Mine Project in Yolo County as Related to Surface Waters in the Davis Creek Watershed--July 1, 1994 - June 30, 1995. *Report for Yolo County.* 212 pp. (Similar reports from 1987-1988, 1990-1994).

Slotton, D.G. 1991. Mercury bioaccumulation in a newly impounded Northern California reservoir. *Doctoral dissertation, University of California, Davis*, December 1991. 363 pp.

Slotton, D.G. and J.E. Reuter. 1995. Considerations of heavy metal bioavailability in intact and resuspended sediments of Camanche Reservoir, California, USA. *Marine and Freshwater Research*, 46:257-265.

Slotton, D.G., S.M. Ayers, J.E. Reuter, and C.R. Goldman. 1995a. Gold mining impacts on food chain mercury in northwestern Sierra Nevada streams. *Technical Completion Report for the University of California Water Resources Center, Project W-816*, August 1995, 46 pp.

Slotton, D.G., J.E. Reuter, and C.R. Goldman. 1995b. Mercury uptake patterns of biota in a seasonally anoxic northern California reservoir. *Water, Air, and Soil Pollution*, 80:841-850.

Slotton, D.G., T.H. Suchanek, L.H. Mullen, C.E. Woodmansee, and P.J. Richerson (1996: in preparation). Trends in fish muscle and organ mercury at EPA Superfund site Clear Lake, California.

Suchanek, T.H., P.J. Richerson, D.G. Slotton, L.A. Woodward, L.J. Holts, and C.E. Woodmansee. 1993. A survey and evaluation of mercury in: sediment, water, plankton, periphyton, benthic invertebrates and fishes within the aquatic ecosystem of Clear Lake, California. *Report prepared for EPA Region IX. Ecological Assessment: Sulfur Bank Mercury Mine Superfund Site, Clear Lake, California.* 113 pp., plus appendices.

TSMP 1990. Toxic Substances Monitoring Program: Ten year summary report, 1978-1987. *State of California Water Resources Control Board publication* 90-1WQ, August 1990. Prepared by Del Rasmussen and Heidi Blethrow, Division of Water Quality.