Final Report
Clear Lake Watershed TMDL Monitoring Program
Proposition 13 Watershed Protection Grant Program
Lake County Watershed Protection District
April 14, 2009

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This Project funded by Proposition 13 Watershed Protection Grant Program, Grant Agreement between the State Water Resources Control Board and the Lake County Watershed Protection District, Agreement No. 03-237-555-0, as amended

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Background

Clear Lake is the largest, natural freshwater lake in California with 68 square miles of surface area and an average depth of 26 feet. Clear Lake is located within the Coast Ranges, approximately 100 miles north of San Francisco Bay at an elevation of 1326 feet NGVD.

Lakes have existed at the site of Clear Lake for 2,500,000 years, possibly making it the oldest lake in North America. The lake has changed shape over time, with a continuous lake for at least the last 450,000 years in the Upper Arm (between Lakeport and Lucerne), while the Oaks Arm and Lower Arm are less than 17,000 years old (Sims et. al., 1988).

Clear Lake lies in a broad basin in the Coast Ranges of Northern California. With a vast watershed, relatively shallow depth, and Mediterranean climate, the lake is paradise for fish and wildlife. This combination of circumstances makes Clear Lake's water warm and very productive, or eutrophic. A eutrophic lake is productive in the same way a rain forest is more productive than a desert. Studies indicate that Clear Lake is eutrophic now and has been eutrophic since the last ice age, or more than 10,000 years. Clear Lake's high productivity provides abundant food for fish and wildlife.

A steady increase in population, a process not unique to Clear Lake, has lead to increased development in the watershed, or the land that drains into the lake. Increased erosion resulting from development has increased the nutrients entering Clear Lake, changing the natural character of Clear Lake. Nutrients act like fertilizer and increase the lake's productivity. While the fish and wildlife have thrived, waters have become less clear with the growth of algae.

Depending on the water temperature and available nutrients, the amount of algae in the lake can vary greatly. Over-abundant algae populations, primarily blue-green algae, can create a situation that can be perceived as a problem to humans. Historical records indicate there was always a high algae population in Clear Lake. Development in the watershed caused algae populations to increase significantly in the 1930's, reducing the clarity of Clear Lake (Richerson et. al., 1994).

Since 1992, reduced algae growth has resulted in increased clarity in Clear Lake. With the clearer water, there has been a substantial increase in submerged aquatic plants. As with algae, most of these aquatic plants are part of Clear Lake's natural ecosystem. Aquatic plants are a valuable element of a healthy

ecosystem providing habitat for fish and other wildlife. In addition, they consume nutrients that would otherwise support algae growth. However, heavy plant growth can be a nuisance to navigation and recreation. The heavy vegetation reduces the ability of property owners and lake users to access some portions of the shoreline.

Since the mid-1800's, mercury has been mined in California. Mercury was used for gold mining, medicine, thermometers, explosives, and other uses. Mercury occurs naturally in the entire Coast Range of California, and was mined extensively in Lake County. This mining resulted in elevated mercury levels in fish and wildlife around Clear Lake. Due to elevated mercury levels in some of Clear Lake's fish, an advisory limiting the number of fish consumed Clear Lake has been issued.

Clear Lake was added to the Clean Water Act Section 303(d) List of Impaired Waterbodies for both nutrients in 1986 and mercury in 1988. As Clear Lake is listed as an impaired water body, the Central Valley Regional Water Quality Control Board (CVRWQCB) adopted the Mercury Total Maximum Daily Load (TMDL) in 2002 (CVRWQCB, 2002b) and the Nutrient TMDL in 2006 (CVRWQCB, 2006b). Both TMDL's identify the County of Lake as a responsible party and require the County to participate in monitoring programs to assess loadings and reduce pollutant loading to Clear Lake. The applicable TMDL requirements are:

- Mercury TMDL: Mercury loads from the tributaries and direct surface water runoff into the lake should be reduced to 80% of existing inputs. These inputs vary with water flow. In an average water year, the estimated load and load allocation are 18 kg/year and 14.4 kg/year, respectively. The load allocation is applied to the tributary inputs as a whole. Efforts to meet the allocation should focus on identifying and remediating hot spots of mercury loading within the tributary watersheds. On average, sediments coming from the tributaries contain lower concentrations of mercury than lakebed sediments.
- Nutrient TMDL: An average annual phosphorus load of 87,100 kg/yr is established as a target for Clear Lake. This is a 40 percent reduction in the average annual load. The Nutrient TMDL also includes an implementation plan to achieve the load reductions. The implementation plan is designed to achieve the required load reductions and eliminate the impairment to the beneficial uses in Clear Lake. The implementation plan directs Responsible Parties to estimate their loading to the lake and implement additional actions, such as best management practices to control phosphorus, if needed. Conditions in Clear Lake will be monitored to determine if the lake is in compliance with its beneficial uses. The Responsible Parties will be required to update the Central Valley Water Board on their progress towards meeting the phosphorus load reduction requirements.

Additional information on the TMDL's can be found at:
http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/clear_lake_hg/index.shtml
http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/clear_lake_nutrients/index.shtml

The Lake County Watershed Protection District (District), on behalf of the County of Lake, obtained grant funding from the State Water Resources Control Board[1] to conduct a monitoring program to comply with the anticipated TMDL's (the TMDL's had not been adopted at the time of the grant application).

The Clear Lake Watershed TMDL Monitoring Program was developed to monitor gaged streams to develop a scientifically defensible estimate of mercury (total and methyl) and nutrient loading to Clear Lake and to identify mercury "hot spots" in the surrounding watershed. Loading estimates derived from the monitoring project are intended to be utilized in the TMDL implementation plan. Hot spots identified in the watershed will be used to develop mitigation measures to reduce the annual loading of mercury to Clear Lake. A 20% reduction in loading from surficial sediments has been proposed as loading estimates are developed from the monitoring program.

Proposed Program

Mr. Thomas Smythe, Water Resources Engineer, Lake County Watershed Protection District, will manage the grant and supervise the Program. All collection of water and sediment sampling for laboratory analyses will be performed by District staff.

The Program will be in accordance with the Clear Lake Mercury and Nutrients Total Maximum Daily Load Monitoring Project Quality Assurance Project Plan, August 12, 2005 (QAPP) (Lake County Watershed Protection District, 2005). In order to meet the goal of the Program, the monitoring program was developed with the following objectives.

Objective #1: Estimates of mercury entering Clear Lake

Watershed mercury loadings to Clear Lake are seasonally variable, occurring during the fall, winter, and spring when runoff occurs. Mercury has limited solubility and is primarily bound to stream sediments, therefore, it will move primarily with larger flows which carry significant amounts of sediment. Mercury, as it exists in the watershed, is generally not biologically available nor is it harmful to humans or wildlife.

[1] Proposition 13 Watershed Protection Grant Program, Grant Agreement between the State Water Resources Control Board and the Lake County Watershed Protection District, Agreement No. 03-237-555-0, as amended

Methyl mercury is the form of mercury that is biologically available and which poses risk to human and wildlife health, however, concentrations of methyl mercury are frequently two to three orders of magnitude smaller than total mercury. Anoxic and anaerobic decomposition of organic material in aquatic environments, such as exists in the bottom of Clear Lake, transforms the particulate mercury to the biologically available methyl mercury form. Therefore, both total mercury and methyl mercury loadings will be estimated as part of this monitoring program.

To better characterize the sources of mercury, seasonal water samples will be collected from the three gaged streams (Middle Creek at Rancheria Road, Scotts Creek at Eickhoff Road, and Kelsey Creek near Soda Bay Road), see Figure 1. These gages have been operated historically by the California Department of Water Resources (DWR), however, they ceased operation in September 2005. The gages were reactivated in October 2006 by DWR. Several water samples will be taken during a single storm event to capture the characteristics of the hydrograph at the beginning of the storm event, described as first flush, during the rising leg of the hydrograph, during peak flow, and during the falling leg of the hydrograph. Water samples will be collected using ultra-clean techniques to minimize the chance of sample contamination. Sample containers were provided by the laboratory. A minimum of two personnel are required in the field to collect samples, one being “clean hands” and the second being “dirty hands”. Field conditions will be recorded utilizing the Surface Water Ambient Monitoring Program (SWAMP) field data sheet and photographs taken during each sampling event.

Mercury water samples will be shipped to Battelle Marine Sciences Laboratory, Sequim, WA (Battelle), for analysis. Samples will be shipped to the laboratory for stabilization within 48 hours, or will be stabilized in the field using pre-measured vials of acid provided by Battelle. Field stabilized samples can be held for 90 days prior to analysis. Water samples will be analyzed for total mercury utilizing EPA Method 1631 and 1631e, with detection limits of 0.2 ng/l. Methyl mercury will be measured utilizing EPA Method 1630, with a detection limit of 0.02 ng/l.

Mercury and methyl mercury flow relationships will be developed at the three gaged locations to estimate average annual mercury and methyl mercury loads. The data will be extrapolated across the entire Clear Lake watershed using accepted methodologies.

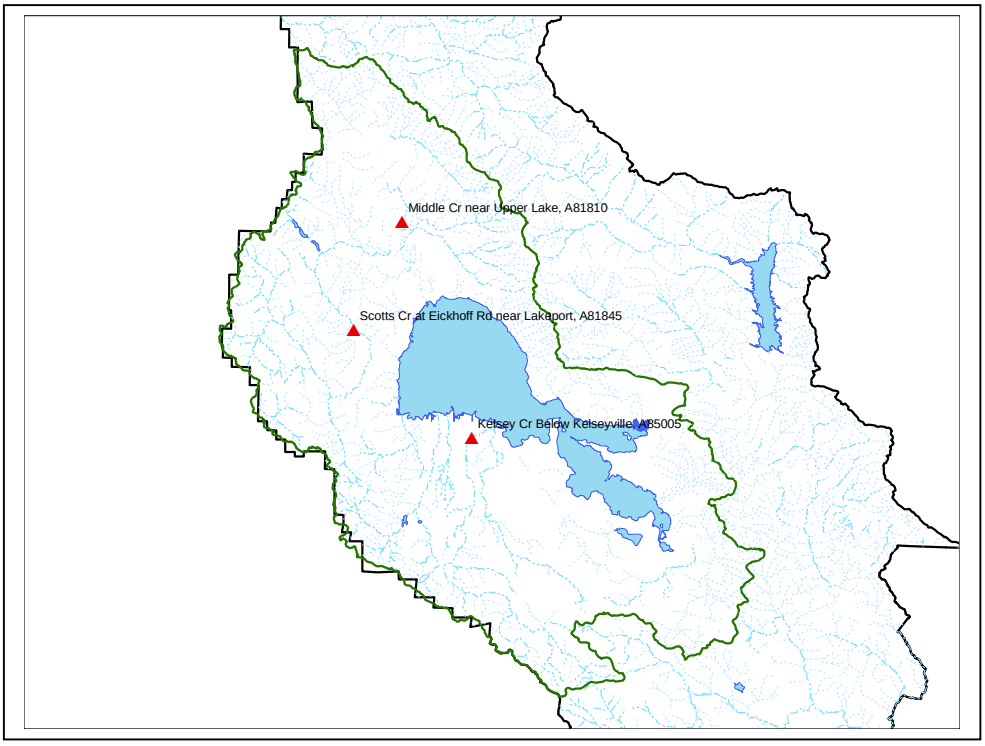

Figure 1: DWR Stream gages Used for Mercury and Nutrient Monitoring

Objective #2: Determine where the mercury sources are located (Hot spot Monitoring)

The Mercury TMDL for Clear Lake requires a reduction in total mercury watershed loading of 20 percent. The Mercury TMDL states that efforts "…should be focused on identifying and controlling inputs from hot spots." This program will focus on identifying hot spots that are elevating mercury concentrations in streams or in Clear Lake. Background concentrations of total mercury for soils in the North Coast Ranges, including the Clear Lake watershed, were established as being less than 0.2 µg/g (Cooke, 2005). "Enriched" soils are defined levels as being 0.2 µg/g to 0.4 µg/g total mercury. Hot spots are defined as soils having a total mercury concentration greater than 0.4 µg/g. Hot spots may be naturally occurring mercury and/or from anthropogenic (human caused) activities.

The Coast Ranges of California are naturally high in mercury, with most of the mercury mines occurring in the Coast Ranges (Division of Mines, 1939). Soils in the region have a natural background concentration of mercury, while other areas are geologically enriched in naturally occurring mercury deposits, primarily in the form of the sulphide ore, cinnabar (HgS). Mercury deposits and serpentinite zones are intrinsically connected through geologic processes of hydrothermal alteration. Mercury, therefore, will likely be found in distinct zones or belts throughout the Coast Range Province where fluid inclusions, typically

hydrothermally influenced, are found. In Lake County these hydrothermal areas are often fault related and driven by relatively shallow magma bodies supplying the heat and the mineral laden fluids intruded through the host country rock. Sulphide ore deposits, such as cinnabar, commonly form around magma bodies because there is a ready supply of heat, which convectively moves and circulates ore-bearing fluids. The metals, originally scattered in trace amounts in magma or surrounding solid rocks, become concentrated by circulating hot fluids and can be re-deposited, under favorable temperature and pressure conditions, to form rich mercury deposits.

Erosion of soils that contain mercury is a natural process, however, prior studies have estimated erosion has more than doubled due to anthropogenic causes (Goldstein & Tolsdorf, 1994, Richerson et. al., 2008). This increased erosion increases the mercury load to Clear Lake. Sediment cores in all three arms of Clear Lake collected by UC Davis researchers have shown sediment deposition rates increased substantially circa 1927 and have decreased substantially since 1954, however, they are still elevated above the pre-European sedimentation rates (Richerson et. al., 2008). Further reductions of anthropogenic erosion and sediment delivery to Clear Lake will reduce the mercury inputs to Clear Lake. Erosion of areas with elevated mercury concentrations (hot spots) may be a significant source of mercury to Clear Lake, therefore identifying areas with increased mercury concentrations (hot spots) will permit targeted erosion control to reduce the mercury input to Clear Lake.

Other anthropogenic mercury sources could include atmospheric deposition, landfills, point discharges of treated or untreated wastewater, urban runoff, agricultural runoff, and old mercury mines. Atmospheric deposition of 0.99 to 2.76 Kg/yr is primarily from global and regional sources located outside of Lake County, with some minor input from evasion at the Sulphur Bank Mercury Mine (Suchanek et. al., 2008) (2 kg/yr in the Mercury TMDL). Landfills, inactive and active, may also be a source of mercury, however, these sites are already regulated by the State. There are no point source discharges permitted by either the State or the County in the Clear Lake watershed. Treated wastewater is either exported from the watershed or land applied under existing State permits. Lake County and the Cities of Lakeport and Clearlake are implementing municipal stormwater management programs to comply with the National Pollutant Discharge Elimination System (NPDES) pursuant to State regulations. Agricultural runoff is regulated by the State under a discharge waiver. None of the above sources is believed to be a significant contributor to the elevated mercury levels in Clear Lake. As control of these potential sources is beyond the control of the County and/or regulated by other programs, this Program will not address atmospheric mercury deposition, landfills, point source discharges, urban runoff, or agricultural runoff. Runoff from old mercury mines has not been quantified and may be a significant contributer to the elevated mercury levels in Clear Lake.

There are eight identified abandoned mercury mines in the Clear Lake watershed (Churchill, 2002). These mines are listed in Table 1 below, and on a map in Figure 2. The precise location of only two of the mines was known prior to starting this Program, the Utopia Mine near Lucerne and the Sulphur Bank Mercury Mine (SBMM).

Table 1: Identified Mercury Mines in Clear Lake Watershed (Churchill, 2002)

MINE NAME	LAT	LONG	QUAD	MINE TYPE
ANDERSON MINE	38.861	-122.830	THE GEYSERS 7.5	UNDERGROUND
BAXTER PROSPECT	38.929	-122.774	KELSEYVILLE 7.5	UNDERGROUND
GORDON SPRINGS MINE	38.837	-122.711	WHISPERING PINES 7.5	SURFACE
KONOCTI MINE	38.997	-122.706	CLEARLAKE 7.5	SURFACE
LUCITTA MINE	38.962	-122.767	KELSEYVILLE 7.5	UNDERGROUND
SULFUR BANK MINE	38.998	-122.656	CLEARLAKE 7.5	OPEN PIT
UNNAMED MERCURY PROSPECT	38.903	-122.883	HIGHLAND SPRINGS 7.5	UNDERGROUND
UNNAMED MERCURY PROSPECT	38.873	-122.695	WHISPERING PINES 7.5	MINERAL LOC
UTOPIA MINE[2]	39.1033	-122.8078	LUCERNE 7.5	SURFACE

As the SBMM has been declared a Superfund site and has been extensively monitored by the United States Environmental Protection Agency (USEPA) and others, additional monitoring is not proposed in this Program. Numerous studies have indicated the SBMM is the primary source of the elevated mercury levels in Clear Lake. In recognition of this, the Mercury TMDL requires that mercury input from the SBMM be reduced by 95 percent. Recent estimates have attributed 85 to 99 percent of the mercury inputs to Clear Lake to be attributable to the SBMM (Suchanek et. al., 2008).

The Utopia Mine, reportedly extended below the level of Clear Lake, and had limited production in the early 20th century. Sampling will be conducted in its vicinity to determine if the mine is contributing significant mercury to runoff.

To better understand if any of these mines are hot spots, mercury concentration found in stream channel sediments will be measured at the downstream end of the various watersheds. After the initial screening of the tributaries, the sampling plan will be adaptively managed. By evaluating the data, if enriched levels

[2] Locations are approximate. When received in 2002, the Utopia Mine was located approximately 4 miles north of its actual location and was corrected based on local knowledge.

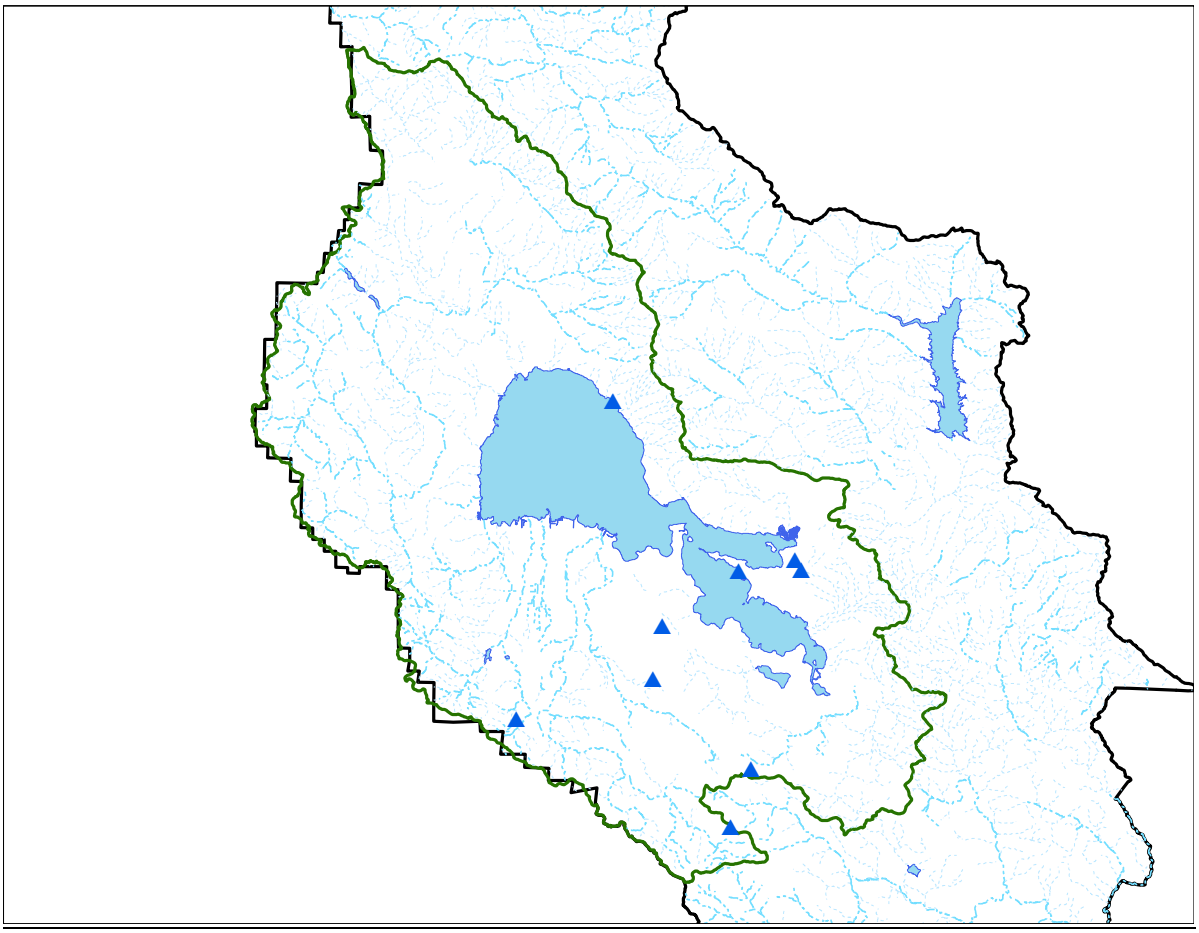

Figure 2: Identified Mercury Mines in Clear Lake Watershed (Churchill, 2002)

of mercury are detected, monitoring will continue progressively upstream until a hot spot or enriched area can be located.

Stream sediment samples will be collected in accordance with the QAPP. At the monitoring site, fine grained deposits that appear to be recently deposited will be selected for sampling. A composite sediment sample (4 to 6 separate sediment samples from the immediate vicinity will be composited for analysis) will be collected using a clean Nyglass gardening trowel. Sediment samples will be placed in sample containers (either glass or polyethylene) provided by Battelle. Sediment samples will be shipped to Battelle for analysis for total mercury. Sediment sample locations will be marked with a Garmin 60CSx Global Positioning System (GPS) and a minimum of two photographs (upstream and downstream) will be taken at each sampling location. Field data will be recorded on the SWAMP field data sheet.

Objective #3: Develop preliminary measures to reduce mercury loading

As hot spots are identified, the sites should be characterized and potential remediation measures should be evaluated to reduce mercury loading from the watershed. If mercury levels above background levels are identified in the watershed, the characteristics of the site will be further analyzed and appropriate site specific mitigation measures can be preliminarily evaluated and reviewed for remediation methods. Future projects may include design and implementation.

Objective # 4: Estimates of nutrients entering Clear Lake

External nutrient loading to Clear Lake are seasonally variable as nutrients enter the system during runoff events. These “loading” events occur in fall, winter, and spring and relate directly to storm activity. To better characterize the nutrient sources, seasonal water samples will be collected from the three gaged streams (Middle Creek at Rancheria Road, Scotts Creek at Eickhoff Road, and Kelsey Creek near Soda Bay Road), see Figure 1. These water samples will be collected concurrently with the mercury water samples discussed in Objective #1. Several water samples will be taken during a single storm event to capture the characteristics of the hydrograph at the beginning of the storm event, described as first flush, during the rising leg of the hydrograph, during peak flow, and during the falling leg of the hydrograph. Nutrient flow relationships will be developed at the three gaged locations to estimate average annual nutrient loads, and the data will be extrapolated across the entire Clear Lake watershed using accepted methodologies.

Water samples collected from gaged creeks will be tested for a suite of analytes thought to be related to nutrient loading in Clear Lake. The nutrient parameters to be monitored include the following:

- total dissolved solids;
- total suspended solids;
- sulfate;
- total iron;
- total phosphorous;
- nitrate and nitrite;
- ammonia;
- ortho-phosphate;
- total Kjeldahl nitrogen.

Samples will be grab samples. Depending on the flow, samples make be collected directly into the sample bottle, or collected with a long handled sampler and transferred directly to the sample bottle. The

nitrogen samples will have a preservative in the bottle for field stabilization of the sample. The iron sample will be collected utilizing the ultra-clean techniques described above for mercury. Field data will be recorded on the SWAMP field data sheet. Laboratory analysis will be conducted by Alpha Analytical Laboratories, Ukiah, California (Alpha), with the exception of dissolved iron, which will be analyzed by Battelle. Water samples will typically be picked up at the District's offices the day after sampling and delivered to the laboratory for preparation and analysis. On several occasions, water samples may be delivered by District personnel directly to Alpha to ensure timely sample stabilization.

Objective #5: Estimate average annual nutrient load at the gaged locations

Data collected will be used to develop nutrient and sediment flow relationships at gaged locations. The three gaged locations represent almost half of the inflows to Clear Lake. When flow calibration is completed for the gaged locations, the data will be used for this purpose. When completed, the data will be extrapolated to determine an estimated average annual loading throughout the Clear Lake Watershed.

Program Implementation

To implement the objectives described above, the District performed the following actions. The Project Team consisted of:

Thomas Smythe	Water Resources Engineer
Stanley Schubert	Assistant Water Resources Engineer
Carolyn Ruttan	Water Resources Coordinator
Charly Brown	Technician

Objective #1: Estimates of mercury entering Clear Lake

Water sampling was performed at the sites of stream gaging stations located on Middle Creek at the Rancheria Road Bridge; Scotts Creek, upstream of Eickhoff Road Bridge; at Kelsey Creek, upstream of Soda Bay Road. Sampling was conducted in accordance with the QAPP. Prior to the start of sampling, field training was conducted by two scientists from the Central Valley Regional Water Quality Control Board (CVRWQCB) on July 13, 2006, to ensure mercury samples were collected in a scientifically sound

manner to provide the best quality information. Water samples were collected during storm events over the span of two winter seasons, Water Year[3] (WY) 2007 and WY 2008.

Water samples were collected on:

- February 9, 2007: 8 samples,
- February 12, 2007: 3 samples
- February 21, 2007: 3 samples
- February 22, 2007: 9 samples
- December 19, 2007: 2 samples
- December 20, 2007: 7 samples
- January 4, 2008: 6 samples
- January 5, 2008: 4 samples
- January 25, 2008: 3 samples
- January 26, 2008: 6 samples
- January 31, 2008: 4 samples
- February 1, 2008: 4 samples
- February 2, 2008: 3 samples
- February 3, 2008: 7 samples

Both winters were short and relatively mild, especially WY 2007, and had limited periods of significant runoff, limiting the number of samples that could be obtained. Mercury water samples were shipped to Battelle Marine Sciences Laboratory, Sequim, WA (Battelle), for analysis. Chloride and sulfate analyses were analyzed by Alpha Analytical Laboratory, Ukiah, CA. (Alpha). Results were provided to the District. DWR reactivated the historic stream gages in October 2006, and has provided the District with 15 minute and average daily stream flow information. Because the gages had to be recalibrated, flow data was not available until late 2008. Stream flow information for the time of the water sample was related to the results. Water quality data at the gages is included in Appendix A. This data was analyzed with Microsoft Excel and flow-concentration regressions were developed. As most mercury delivered is sediment bound, regressions of total mercury and total suspended solids were also developed. All regressions were analyzed with a t-test at n-2 (n - number of samples) degrees of freedom to determine if the regression is significant. The probability (p) that the regression is not significant was calculated. Table 2 shows the results of these analyses. Charts showing these relationships are included in Appendix B.

[3] Surface water data is reported for Water Years. A Water Year extends from October 1 through September 30. For instance, Water Year 2007 starts on October 1, 2006 and ends on September 30, 2007.

Table 2: Regression Analyses for Mercury and Related Analytes

Analyte	Regression	R^2	n	p
Kelsey Creek Below Kelseyville				
Methyl Mercury, ng/l - Flow, cfs	MeHg = 0.00001347 * Flow + 0.06674	0.2221	26	< 0.0072
Total Mercury, ng/l - Flow, cfs	THg = 0.009749 * Flow + 8.970	0.6836	24	< 0.00001
Total Mercury, ng/l - Total Suspended Solids, mg/l	THg = 0.1104 * TSS +7.083	0.7852	26	< 0.00001
Chloride, mg/l - Flow, cfs	Cl = 11.12 * $Flow^{-0.2406}$	0.2331	24	< 0.0084
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -0.7554 * Ln(Flow) + 8.101	0.2657	24	< 0.005
Middle Creek near Upper Lake				
Methyl Mercury, ng/l - Flow, cfs	MeHg = 0.00006431 * Flow + 0.05740	0.7480	26	< 0.00001
Total Mercury, ng/l - Flow, cfs	THg = 0.04871 * Flow + 1.073	0.7938	23	< 0.00001
Total Mercury, ng/l - Total Suspended Solids, mg/l	THg = 0.1468 * TSS + 6.890	0.8995	24	< 0.00001
Chloride, mg/l - Flow, cfs	Cl = 5.614 * $Flow^{-0.1649}$	0.5594	23	< 0.00003
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -1.662 * Ln(Flow) + 16.58	0.7404	23	< 0.00001
Scotts Creek at Eickhoff Road				
Methyl Mercury, ng/l - Flow, cfs	MeHg = 0.00001520 * Flow + 0.07446	0.1563	23	< 0.0311
Total Mercury, ng/l - Flow, cfs	THg = 0.01455 * Flow + 10.78	0.6318	21	< 0.00001
Total Mercury, ng/l - Total Suspended Solids, mg/l	THg = 0.09211 * TSS + 7.591	0.8819	24	< 0.00001
Chloride, mg/l - Flow, cfs	Cl = 4.252 * $Flow^{-0.1018}$	0.2253	21	< 0.0149
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -1.218 * Ln(Flow) + 11.36	0.7460	21	< 0.00001

The average concentrations of all analytes are shown in Table 3.

Table 3: Averages of Mercury and Related Analytes

Analyte	Kelsey Creek near Kelseyville	Middle Creek near Upper Lake	Scotts Creek at Eickhoff Road
Methyl Mercury, ng/l	0.0764	0.101	0.0888
Total Mercury, ng/l	16	34.8	26.1
Chloride, mg/l	3.1	2.2	2.3
Sulfate as SO4, mg/l	3.6	7.1	3.7

Chloride was measured as an indicator of hydrothermal waters, a potential mercury source. The National Water Quality Assessment (NAWQA) for the Sacramento River watershed (USGS, 2008b) analyzed 45 separate locations within the watershed and had a chloride range of 0.138 – 160 mg/l, with an average of 10.6 mg/l. Kelsey, Middle and Scotts Creek's chloride concentrations are relatively low and within expected values. Chloride concentrations are significantly less than measured at Cache Creek at Rumsey (range of 4.4 – 160 mg/l, average of 24.7 mg/l), a location known to have significant acid mine drainage and hydrothermal spring contributions. Concentrations are well within the range of the

Sacramento River (9 locations, range of 1.1 to 9.3, average of 4.1 mg/l). Based on this chloride data, it does not appear that the three streams monitored have significant hydrothermal spring or acid mine drainage inputs.

Sulfate plays a significant role in mercury methylation and may indicate the presence of hydrothermal springs. A new paper by UC Davis researchers (Richerson et. al., 2008) suggest that increased mercury methylation may be due to increased sulfates within Clear Lake, potentially due to activities at the Sulphur Bank Mercury Mine. Data was not available for the watershed sulfate loading, therefore, sulfate was collected as part of this project. Log normal regressions were utilized as sulfate concentrations are reduced as flow increased. Utilizing the t-test with n - 2 degrees of freedom, all three decreasing relationships were significant to $p < 0.005$. Sulfate inputs for the watershed will be estimated utilizing the regressions developed.

Sulfate levels were compared to the NAWQA data for the Sacramento River Watershed (USGS, 2008b) analyzed 45 separate locations within the watershed and had a sulfate range 0.1 – 1092 mg/l, with an average of 12.9 mg/l. Kelsey, Middle and Scotts Creek's sulfate concentrations are relatively low and within expected values. Similar to the chloride results, levels were significantly less than sulfate concentrations measured in Cache Creek at Rumsey (range 6.5 - 45.1, average of 15.9 mg/l). Sulfate concentrations were within the range of the Sacramento River (9 locations, range 1.7 – 20.9 mg/l, average of 5.7 mg/l). Based on the sulfate data, concentrations are within the expected range and do not indicate significant hydrothermal spring contributions or acid mine drainage.

The regressions between flow and methyl mercury concentrations in Kelsey or Scotts Creeks are weak, however, there was a good relationship in Middle Creek. Utilizing a t-test, with n - 2 degrees of freedom, these relationships are significant at $p < 0.05$. Annual loading will be estimated utilizing the regression equations, however, as the slope of the regression is nearly flat, there is little change in methyl mercury concentrations in the range of measured flow.

Good regressions were developed for flow and total mercury for all three streams ($p < 0.00001$). There are also a good regressions between total suspended solids and total mercury for all three streams ($p < 0.00001$), confirming that most of the mercury within these streams is bound to particulate matter. The regressions equations will be used to estimate the annual mercury loadings.

These relationships were used to estimate the loads at the three stream gages. The load estimates were developed utilizing the following procedure (see Appendix C):

- Total mercury and sulfate concentrations were estimated for each day of the period of record for the gage based on the average daily flow. This introduces some error into the calculation, as flow varies during the day, however, it does provide a reasonable estimate of the anticipated concentrations.
- Due to the low regression coefficients for Kelsey and Scotts Creek, methyl mercury was calculated based on the average concentration (see Table 3).
- The daily loads were calculated based on the average daily flow and the concentration from the previous step.
- The annual loads were calculated for each gage location based on the daily loads, see Appendix D. These results are shown in Table 4.

Table 4: Average Annual Mercury Loading at Gages, without Flow Weighting[4]

Location	Annual Flow, ac-ft	Methyl Mercury, kg/yr	Total Mercury, kg/yr	Sulfate as SO4, T/yr[5]
Kelsey Creek below Kelseyville[6]	54,070	0.00510	1.28	234
Middle Creek near Upper Lake[7]	53,080	0.00662	2.33	439
Scotts Creek at Eickhoff Road[8]	56,620	0.00621	1.87	260

Due to the number of years with incomplete records, these numbers may inaccurately estimate the flows and loads of Kelsey Creek and Middle Creek. The Scotts Creek gage has a complete record from WY 1961 through 2008, with the exception of 1995[9] and 2006. We have compared average annual flows for the Scotts Creek gage for the entire period of record and the common record years for the other two gages. A weighting factor is calculated by dividing the Scotts Creek average annual flow for the complete record by the Scotts Creek average annual flow for the common record years. This weighting factor is then multiplied by the calculated loads for the respective gage. The adjusted loading estimates are shown in Table 5.

[4] All calculated loadings have been rounded off to three significant figures.
[5] Loads are expressed as metric tons
[6] Kelsey Creek estimate based on the following years of record: 1981-1990, 1992-1995, 1997-2001, 2003-2005, & 2007-2008
[7] Middle Creek estimate based on the following years of record: 1967-1976, 1978-1982, 1985, 1987-1992, 1994, 1998-2001, 2003-2005 & 2007-2008. Note numerous years have incomplete records due to data recorder failures.
[8] Scotts Creek estimated based on the following years of record: 1961-1994, 1996-2005 & 2007-2008
[9] Data from 1995 is not used as a levee failure upstream of the Scotts Creek at Eickhoff Road gage resulted in underestimation of flows in excess of 3,000 cfs after January 9, 1995. The levee was repaired before flows resumed in Fall 1995.

Table 5: Average Annual Mercury Loading at Gages, with Flow Weighting

Location	Weighting Factor	Annual Flow, ac-ft	Methyl Mercury, kg/yr	Total Mercury, kg/yr	Sulfate as SO4, T/yr
Kelsey Creek below Kelseyville	0.9478	51,250	0.00484	1.21	221
Middle Creek near Upper Lake	1.008	53,500	0.00668	2.35	442
Scotts Creek at Eickhoff Road	1	56,620	0.00621	1.87	260

Between 1998 and 2001, University of California – Davis (UC Davis) researchers collected water samples to estimate the mercury watershed load for Clear Lake TMDL for Mercury (CVRWQCB, 2002a). A similar technique was used to estimate average annual loading, however, their estimate was based on a 10-year average, 1990 - 1999. The District performed a similar analysis using the newly calculated loading rates for the same period of 1990 - 1999. We also calculated the estimated watershed loading using the same ratios utilized in the TMDL. Table 6 below compares the District's estimates to those in the TMDL.

Table 6: Comparison of District and TMDL Mercury Loading Estimates

	District Estimates		TMDL Estimates	
Gage Location	**Number of Samples**	**Average Annual Load, kg/yr**	**Number of Samples**	**Average Annual Load, kg/yr**
Total Mercury				
Kelsey Creek below Kelseyville	24	1.51	5	1.78
Middle Creek near Upper Lake	23	3.20	6	4.85
Scotts Creek at Eickhoff Road	21	2.58	5	1.24
Estimated THg Watershed Load		16.8		18.2
Methyl Mercury				
Kelsey Creek below Kelseyville	26	0.00558	5	0.0107
Middle Creek near Upper Lake	26	0.00812	6	0.0221
Scotts Creek at Eickhoff Road	23	0.00966	5	0.120
Estimated MeHg Watershed Load		0.054		0.352

The District's total mercury loading estimates are lower than the TMDL estimates, with the exception of total mercury in Scotts Creek, which is significantly higher. The District's methyl mercury loading estimates are all lower than the TMDL estimates. Based on the data available to the District, we offer the following input on why there may be differences in the two estimates:

- The TMDL estimates were based on regressions of analyte versus average daily flow, not instantaneous flow (Suchanek et. al., 2008). This will incorporate errors, especially when flow is fluctuating greatly during the day, as is frequently the case during high flows in Clear Lake tributaries. Without the actual sample times to obtain the instantaneous flows, it is not clear how this affected the estimate. This also precludes combining both data sets for calculating common regression formulas.

- The District utilized significantly more data points than the TMDL in developing its estimates. The District does not have the regressions used to develop the TMDL estimates, however, we have the data utilized for their analysis and the description in the TMDL (CVRWQCB, 2002a). We developed natural log regressions for the mercury and methyl mercury for the TMDL data and corresponding probabilities of non-significance, see Table 7. With the limited number of data points, the regression coefficients and the significance of each regression have decreased, with three of the regressions determined to be less than significant ($p > 0.05$)[10]. This will limit the accuracy of any projection of annual loading from the limited data.

Table 7: Regression Analysis for UC Davis Mercury Data

Analyte	Regression	R^2	n	p
Kelsey Creek Below Kelseyville				
Methyl Mercury, ng/l - Flow, cfs	MeHg = 0.04752 * ln(Flow) - 0.1226	0.7124	5	< 0.0121
Total Mercury, ng/l - Flow, cfs	THg = 9.585 * ln(Flow) - 29.64	0.695	5	< 0.019
Middle Creek near Upper Lake				
Methyl Mercury, ng/l - Flow, cfs	MeHg = 0.09477 * ln(Flow) - 0.2601	0.5967	6	< 0.0836
Total Mercury, ng/l - Flow, cfs	THg = 26.71* ln(Flow) - 92.47	0.83	6	< 0.0114
Scotts Creek at Eickhoff Road				
Methyl Mercury, ng/l - Flow, cfs	MeHg = -0.06773 * ln(Flow) + 0.533	0.3631	5	< 0.449
Total Mercury, ng/l - Flow, cfs	THg = 1.958 * ln(Flow) + 2.600	0.4355	5	< 0.206

- The TMDL utilized natural log regressions, while the District used linear regressions. This will introduce some differences in the loading calculations. Natural log regressions can incorrectly estimate mercury and methyl mercury concentrations at lower, and more frequent, flows than a linear regression. For instance, the regression equations for Kelsey and Middle Creeks can estimate a negative mercury concentration and load at low flows (< 35 +/- cfs).
- The TMDL data for the Scotts Creek gage has a wide “scatter” at low flows. We note that the mercury and methyl mercury concentrations at the lowest flow are greater than the next highest flows by factors of 12 and 20, respectively. In fact, the methyl mercury concentration at the lowest flow is 4.5 times as large as the next greatest concentration. This actually resulted in a negative correlation (methyl mercury decreases as flow increases), the only negative correlation we calculated for methyl mercury. We also note that the TMDL calculated methyl mercury load is more than three times as great as the combined calculated methyl mercury load of Kelsey and Middle Creeks, although all three watersheds are approximately the same size.

[10] The t-test is used primarily for linear regressions, and is less seldom used for non-linear regressions.

The District feels that that the number of samples collected over a greater range of flows in WY's 2007 and 2008 leads to better fit in the regression equations, improved statistical significance of the relationships and an improved estimate of annual loading, therefore, the District believes its estimates of mercury and methyl mercury loading at the three gages more accurately represent the actual loadings.

We used the loadings at the three gages streams to estimate the total watershed loading as they represent 33 percent of the lake's watershed and 29 percent of the estimated inflow to the lake. Extrapolation of loading from these three subwatersheds to the entire Clear Lake watershed is based on the assumption that these subwatersheds are representative of the entire watershed, The hot spot monitoring (see Objective #2) indicates most of the Clear Lake watershed has similar mercury/stream sediment ratios, with the exception of several small watersheds at the east end of Clear Lake (Schindler and Burns Valley Creek watersheds) and the vicinity of the Utopia Mine, which have elevated mercury concentrations. Based on this, approximately 95 percent of the Clear Lake watershed can be expected to have similar mercury loadings, therefore, extrapolation of loadings from the three gaged locations is a reasonable assumption. Annual loading to Clear Lake is estimated using the following procedures:

- Extrapolation based on mercury loading being proportional to drainage area (see Table 8):
    - The flow weighted average annual flows and loads (Table 5) are utilized.
    - The gaged watershed areas were calculated based on District produced GIS mapping.
    - The entire Clear Lake watershed area was calculated based on District produced GIS mapping.
    - The flow weighted average annual flows and loads were multiplied by the ratio of the area of the Clear Lake watershed to the gaged watersheds.

- Extrapolation based on mercury loading being proportional to flows (see Table 9):
    - The flow weighted average annual flows and loads (Table 5) are utilized.
    - Annual Clear Lake inflow from the watershed is estimated as the sum of the average annual discharge at the USGS Cache Creek at Lower Lake gage and the water lost by average annual evaporation. The inflow is the sum of watershed inflows and direct precipitation. Groundwater inflow is assumed to be insignificant (Richerson et. al., 1994). Direct precipitation on the lake is subtracted from the total inflow (equals total outflow) to obtain the amount of inflow from the watershed.
    - The flow weighted average annual flows and loads were multiplied by the ratio of the average annual flows of the Clear Lake watershed to the flows in the gaged watersheds.

Table 8: Watershed Mercury Loading, Estimate Based on Drainage Areas

Gaged watersheds	Kelsey Creek	27,900	ac	
	Middle Creek	31,900	ac	
	Scotts Creek	35,700	ac	
	Total	95,600	ac	
Clear Lake Watershed		289,000	ac	
Multiplier		3.020		
Location	**Discharge (ac-ft/yr)**	**Methyl Mercury, kg/yr**	**Total Mercury, kg/yr**	**Sulfate as SO4, T/yr**
Kelsey Creek below Kelseyville	51,250	0.00484	1.21	221
Middle Creek near Upper Lake	53,500	0.00668	2.35	442
Scotts Creek at Eickhoff Road	56,620	0.00621	1.87	260
Subtotal	161,000	0.0177	5.43	924
Clear Lake Watershed	488,000	0.0536	16.4	2,790

Table 7: Watershed Mercury Loading, Estimate Based on Flows

Gaged Watersheds	161,400	AF	Average Lake Level = 3.85 ft R	
Cache Creek near Lower Lake	298,000	AF	Surface Area @ 3.85 ft R = 41,592	
Evaporation Loss	146,000	AF	Average Annual Evaporation = 42 in.	
Outflow = Inflow	444,000	AF		
Direct Precipitation	-91,800	AF	Average Annual Precipitation = 26.5 in.	
Watershed Inflow	352,000	AF		
Multiplier	2.180			
Location	**Discharge (ac-ft/yr)**	**Methyl Mercury, kg/yr**	**Total Mercury, kg/yr**	**Sulfate as SO4, T/yr**
Kelsey Creek below Kelseyville	51,250	0.00484	1.21	221
Middle Creek near Upper Lake	53,500	0.00668	2.35	442
Scotts Creek at Eickhoff Road	56,600	0.00621	1.87	260
Subtotal	161,400	0.0177	5.43	924
Clear Lake Watershed	352,000	0.0386	11.8	2,010

Total mercury loading is estimated to be 65 to 90 percent of the estimates in the Mercury TMDL, and methyl mercury loading is estimated to be 11 to 15 percent of the estimates in the Mercury TMDL. These are refinements to the loadings based on improved data, and do not appear to be an actual reduction in loading, therefore, we recommend the State revise the loading estimates in the Mercury TMDL during its next update. As the Mercury TMDL is based on total mercury loading, the small reduction in watershed total mercury loading and significant change in methyl mercury watershed loading are not anticipated to have a significant impact on the implementation measures included in the Mercury TMDL.

The total mercury loading estimate or 11.8 to 16.4 kg/yr is within the 0.9 to 48.4 kg/yr estimates in the recently developed mercury budget for Clear Lake (Suchanek et. al., 2008).

The sulfate loadings estimates of 2,010 to 2,790 metric tons (T) appear to be consistent with the sulfate budget estimates of Richerson et. al. (in publication) which include a standing mass of sulfate in Clear Lake of approximately 17,000 T. As the flow – sulfate regression is an inverse relationship (sulfate concentration decreases as flow increases), the limited high flow data should not adversely impact the sulfate budget estimate.

Objective #2: Determine where the mercury sources are located

The Mercury TMDL for Clear Lake requires a reduction in total mercury watershed loading of 20 percent. The Mercury TMDL states that efforts "…should be focused on identifying and controlling inputs from hot spots." This program will focus on identifying hot spots that are elevating mercury concentrations in streams or in Clear Lake. It is likely these hot spots will be non-point sources of mercury. Mercury sources, such as erosion of legacy deposits from abandoned mines and naturally occurring mercury deposits, will be targeted by the program. The program will not emphasize potential mercury sources that are currently regulated under other programs, such as landfills. Mercury hot spot monitoring data is included in Appendix D.

Locations of historic mercury mines/prospects were obtained from the California Geological Survey (CGS) (Churchill, 2002). Nine abandoned mercury mines/prospects were identified in the Clear Lake watershed.

- Based on the coordinates of the Anderson Mine provided by the CGS, the mine is located in the Russian River watershed, not the Clear Lake watershed. Review of the February 2006 aerial photographs obtained by the county did not indicate any mines in this vicinity. There are also some indications it may the same as the Anderson Springs Mine (Sparks, 2008), which is located in the Putah Creek watershed to the south. The CGS lists both the Anderson Mine and the Anderson Springs Mine as separate mercury mines in distinctly different locations. A 1939 Quicksilver Properties map (Division of Mines, 1939)[11] lists an Anderson Mine in the vicinity of Anderson Springs (the same location the CGS identifies as the Anderson Springs Mine) and shows numerous mines within the Sulphur Creek watershed, see Figure 3. The 1939 Quicksilver Properties map shows an unnamed mine/claim approximately 1.5 miles to the southeast within the High Valley Creek

[11] This map was received in December 2008, therefore, new information from the map could not be pursued in great detail.

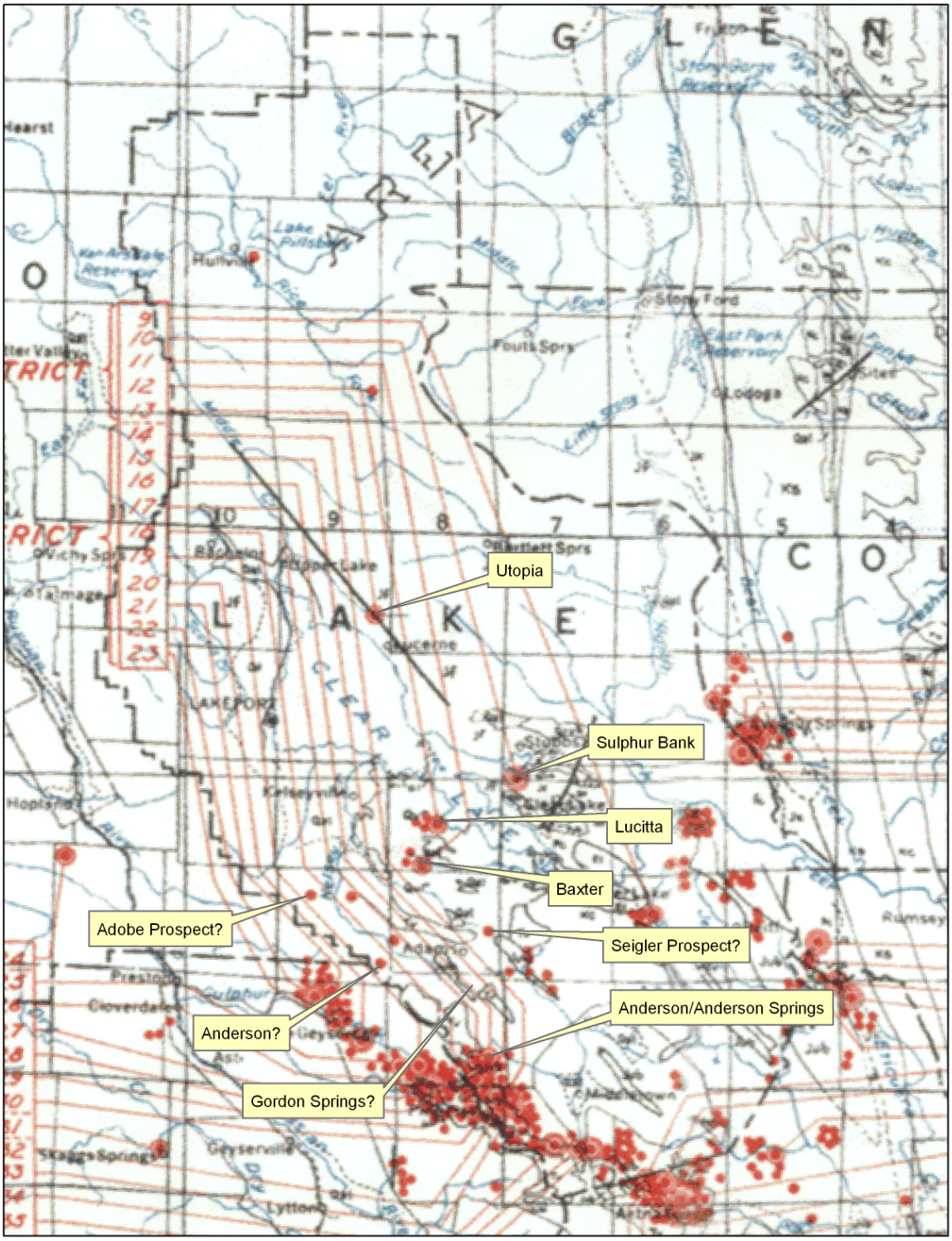

Figure 3: Excerpt of Quicksilver Properties Map, 1939 (Division of Mines. 1939

subwatershed (tributary to Kelsey Creek and Clear Lake). Due to the late receipt of the Quicksilver Properties map, this site was not investigated. Sediment hot spot monitoring in Kelsey Creek several miles downstream showed a total mercury concentration of 0.0286 µg/g, indicating that there is not a significant mercury contribution to Kelsey Creek above background levels. Additional research is necessary to verify the location of the Anderson Mine.

- The Baxter Prospect could not be located. CGS coordinates placed it within the McIntire Creek subwatershed (tributary of Cole Creek and Clear Lake), and near the S-Bar-S white rock mine within the Thurston Creek watershed, a terminal watershed (non-tributary to Clear Lake). Most of the hydrothermally modified andesite (white rock) is within the Thurston Creek watershed. This portion of the Thurston Creek watershed is believed to be a caldera with active hydrogen sulfide vents in numerous locations around its perimeter (Lehrman, 1990). Geothermal wells were also located in this area. As this mine is likely within the same hydrothermal complex as the S-Bar-S quarry and the Konocti Mine, it is potentially a mercury source. An alternate location may be the G. L. Hildebrand prospect, with a reported location approximately 1,300 feet north-northeast of the CGS location (Sparks, 2008). This is also in the McIntire Creek watershed. The 1939 Quicksilver Properties map (Division of Mines, 1939) shows the mine in the vicinity of the upper McIntire Creek watershed, however, the resolution is inadequate to accurately locate the mine. Review of the 2006 aerial photographs indicate a suspicious clearing approximately 2,600 feet north-northeast of the CGS reported mine site (38°56’9”N 122°46’18”W), which is in the Thurston Creek watershed. Due to the late identification of this potential mine site, no site visits or sampling was conducted. Stream sediment hot spot monitoring in McIntire Creek at Highway 175 showed total mercury concentrations of 0.102 µg/g, which is elevated above the measured Clear Lake watershed background levels, however, it is still significantly less than the hot spot concentration provided by the CVRWQCB. As the sediment sample was taken in an area of very slow moving water with abundant wetland vegetation, it does not indicate that there is a significant mercury contribution to McIntire Creek from the Prospect.
- The Gordon Springs Mine could not be located. The coordinates provided place the mine in Boggs Mountain Demonstration State Forest (BMDSF). The BMDSF manager did not have records of any old mines on the property, with the exception of a shale pit in the Big Canyon Creek watershed (Putah Creek). The 1939 Quicksilver Properties Map did not show a mine near this location. A Gordon Springs Road is located approximately one mile to the west-southwest, however, there is no evidence of mines in the vicinity. Family stories indicate William Gordon kept the mine secret from his family (Sparks, 2008), and the precise location of the mine is unknown. Sediment hot spot monitoring in Kelsey Creek at Bottle Rock Road showed a total mercury concentration of 0.0260 µg/g,

indicating that there is not a significant mercury contribution to Kelsey Creek above background levels.

- The Lucitta Mine and the Konocti Mine were determined to be in the same vicinity on the southeast flank of Mount Konocti. The CGS mine coordinates erroneously located the Konocti Mine between the Oaks and Lower Arms of Clear Lake, approximately 4 miles northeast of the mined areas on the southeast side of Mount Konocti, across the Lower Arm of Clear Lake. Review of the 2006 aerial photographs show extensive surface workings and older roads on the southeast flank of Mount Konocti. The 1939 Quicksilver Properties map (Division of Mines, 1939) shows the Lucitta Mine in this location and three other unnamed mines, and does not show a mine across the Lower Arm of Clear Lake. A "white rock" mine is located in this area and is known locally as the Bell Mine. All mining stopped at the Bell Mine around 1980. The approximate mine location is near 38°57'23"N, 122°45'33"W. The site is located entirely within the Thurston Creek watershed, a terminal watershed not tributary to Clear Lake. This mine site was not sampled as it does not contribute sediments to Clear Lake.
- The SBMM was declared an USEPA Superfund site in 1990 and has been extensively monitored. No additional monitoring will be conducted at the SBMM with this project.
- Two unnamed mercury prospects were identified. Based on the locations provided by CGS, they are located in the Adobe Creek and Seigler Creek watersheds. Discussions for each site follow:
  - The Adobe Creek Prospect could not be located. Discussions with numerous long time residents did not reveal any knowledge of mercury mining in this area of the County. Review of the 1939 Quicksilver Map (Division of Mine, 1939) show an unnamed mine in the same vicinity as the CGS coordinates, however, the resolution is inadequate to accurately locate the mine. No specific sampling will be conducted to locate this mine. Sediment hot spot monitoring in Adobe Creek at Bell Hill Road showed a total mercury concentration of 0.0302 µg/g, indicating that there is not a significant mercury contribution to the Adobe Creek watershed above background levels.
  - The Seigler Creek Prospect could not be located. The location is in the vicinity of numerous hydrothermal springs and outcrops of hydrothermally altered andesite. The old Seigler Springs Resort is also in this vicinity and has numerous hot and cold springs. Review of the 1939 Quicksilver Map (Division of Mine, 1939) show an unnamed mine in the same vicinity as the CGS coordinates, however, the resolution is inadequate to accurately locate the mine. Seigler Creek will be monitored downstream to determine if mercury is elevated downstream. Sediment hot spot monitoring in Seigler Creek at Seigler Canyon Road showed a total mercury concentration of 0.0714 µg/g, indicating that there is not a significant mercury contribution to Seigler Creek above background levels.
- The Utopia Mine is located along the current right-of-way for State Highway 20, on the north side of Lucerne. The CGS coordinates for the mine were located in the Clover Creek watershed,

approximately four miles to the north of the actual location (this is also near the location shown in the 1939 Quicksilver Properties map). The mine property was located on maps of the Clear Lake shoreline prepared by the State Lands Commission (State Lands Commission, 1970), which indicated a property owned by the Utopia Quicksilver Company. Discussions with long time residents revealed knowledge of the mine adjacent to the road, including childhood memories of playing in the mine entrances. It was not clear whether these were adits and/or shaft entrances. The actual location of the mine workings were not pinpointed prior to sampling. Initial sampling locations were selected based on the estimated location of the mine and taken within the lake to determine if the abandoned mine was contributing mercury to Clear Lake. Sampling proceeded as follows:

October 2006: Nine lakebed sediment samples (1 field duplicate) were collected in a four by two grid opposite of the estimated location of the Utopia Mine, see Figure 4. In addition, one lakebed sample

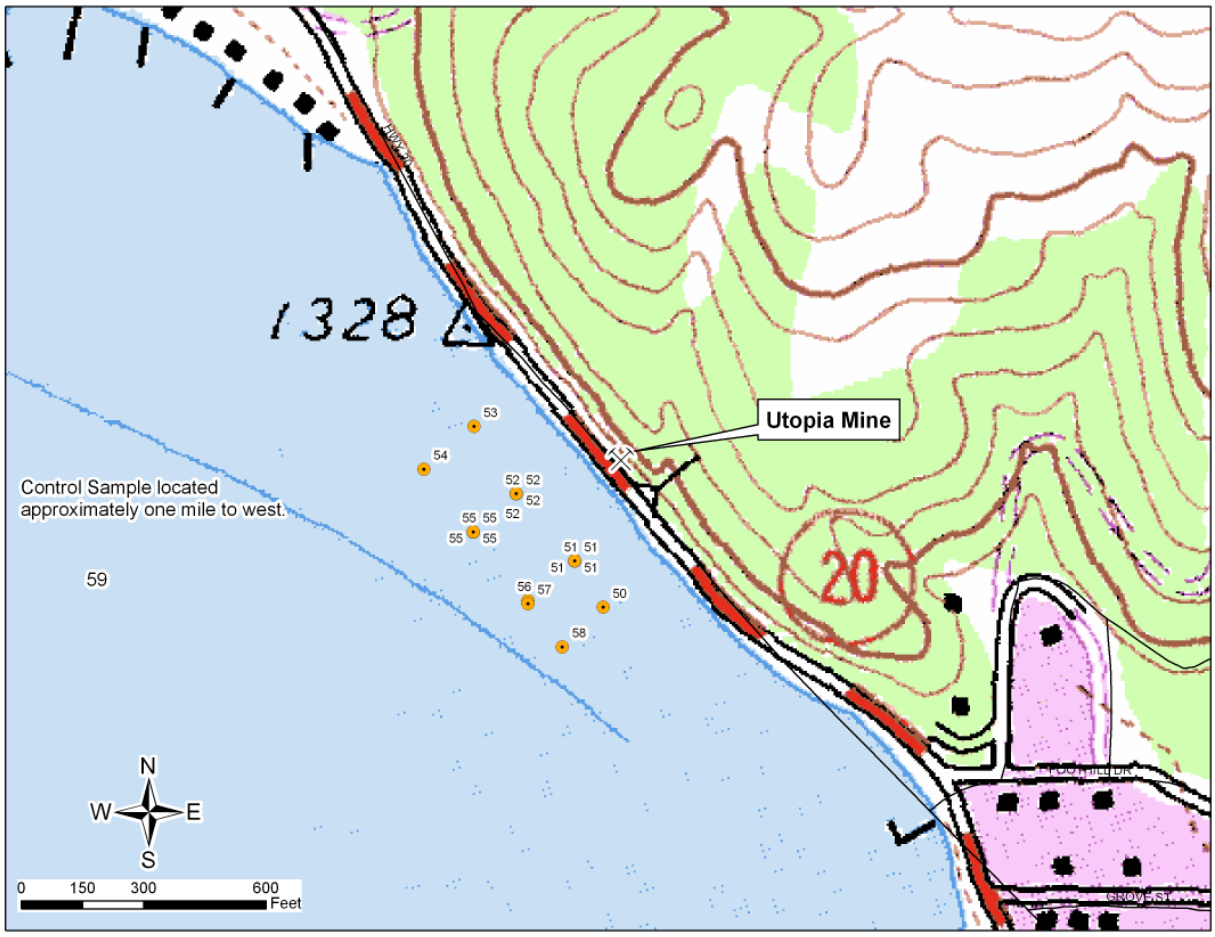

Figure 4: Mercury Sampling Sites near Utopia Mine, October 2006

was collected approximately one mile off shore to act as a control. Lakebed sediment samples collected from Clear Lake were collected using an Ekman Dredge lowered from the District's 18 foot aluminum boat.

The boat was anchored and a dredge sample was taken from one side of the boat. Four small samples of mud from inside the dredge were taken using a clean plastic spoon, making sure not to collect a sample from the surface of the sample or next to the edge of the dredge. A second dredge sample was collected from the opposite side of the boat, and the samples composited in the same manner. All samples were composited and placed in sample containers (either glass or polyethylene) provided by Battelle. Samples were stored in dry ice and express shipped to Battelle for analysis for

Table 8: Lakebed Sediment Sample Results, Mercury Monitoring near Utopia Mine, October 2006

			Total Mercury, µg/g		Methyl Mercury, ng/g	
Position	Number	Solids	MSLLabID	Value	MSLLabID	Value
N39.10039 W122.80719	50	50.3	2635-44	12.76	2635-44	0.514
N39.10070 W122.80744	51	67.6	2635-45 r1	17.07	2635-45 r1	0.349
N39.10070 W122.80744	51	67.6	2635-45 r2	2.68	2635-45 r2	0.357
N39.10070 W122.80744	51	67.6	2635-45 r1 rd	2.81		
N39.10070 W122.80744	51	67.6	2635-45 r1 rd-ad	2.78		
N39.10070 W122.80744	51	67.6	2635-45 r2 rd	5.16		
N39.10070 W122.80744	51	67.6	2635-45 r2 rd-ad	5.05		
N39.10115 W122.80795	52	66.3	2635-46 r1	5.70	2635-46	0.234
N39.10115 W122.80795	52	66.3	2635-46 r1 rd	3.07		
N39.10115 W122.80795	52	66.3	2635-46 r1 rd ad	3.02		
N39.10115 W122.80795	52	66.3	2635-46 r2 rd	1.49		
N39.10115 W122.80795	52	66.3	2635-46 r2 rd ad	1.42		
N39.10160 W122.80832	53	70.7	2635-47	1.83	2635-47	0.345
N39.10131 W122.80875	54	33.5	2635-48	0.92	2635-48	1.45
N39.10089 W122.80832	55	30.0	2635-49 r1	1.55	2635-49	1.42
N39.10089 W122.80832	55	30.0	2635-49 r1 rd	1.93		
N39.10089 W122.80832	55	30.0	2635-49 r1 rd-ad	1.94		
N39.10089 W122.80832	55	30.0	2635-49 r2 rd	6.07		
N39.10089 W122.80832	55	30.0	2635-49 r2 rd-ad	5.97		
N39.10043 W122.80784	56	31.0	2635-50	1.08	2635-50	1.39
N39.10041 W122.80784	57	30.6	2635-51	1.22	2635-51	1.43
N39.10012 W122.80754	58	29.0	2635-52	0.79	2635-52	1.43
N39.09165 W122.82207	59	19.1	2635-53	1.63	2635-53	1.66

total mercury and methyl mercury. Sample locations were marked with the GPS, however, photographs of each sample site were not taken.

In addition, one lakebed sample was collected approximately one mile off shore to act as a control. Lakebed sediment mercury concentrations in the Upper Arm of Clear Lake had been established by monitoring conducted for USEPA as part of the SBMM evaluation and will be used to compare with the control sample (Suchanek, 1997). The results for the total mercury are shown in Table 10.

The results were problematic for Battelle, as several of the laboratory duplicates for total mercury (part of Battelle's QA/QC) had significantly different results. Repeated duplicate samples also provided significantly different results. Microscopic analysis by Battelle scientists showed small reddish particles, possibly cinnabar, within the lake sediment samples. The non-homogeneity of the sediment samples could be problematic in identifying hot spots, therefore, the District revised its protocol for all future sediment sampling to require duplicate laboratory analyses.

Lakebed sediment samples 50, 51, 52 and 55 all have total mercury concentrations significantly greater than the concentration in Sample 59, the control sample. The total mercury concentration is Sample 59 of 1.63 µg/g is consistent with previous monitoring in the lake conducted by UC Davis for USEPA (Suchanek et. al., 1997). Total mercury concentrations in Samples 50 and 51 were 12.76 µg/g and as high as 17.07 µg/g, respectively.

Methyl mercury levels were significantly lower at all sample sites near the mine site than in the deep water sediment sample (Sample 59). The lower methyl mercury concentrations were probably due to the shallow depth and more oxygenated sediments. This also indicates the lakebed sediments are not subject to the high methylation rates similar to near the SBMM (Shipp & Zierenberg, 2008). The high mercury methylation rates at the SBMM have been linked to active acidic mine drainage. Based on the limited data, significant subsurface acid mine drainage from the Utopia Mine does not appear to exist.

These results identified a hot spot in Clear Lake at, or in the vicinity of, the Utopia Mine. Additional sampling was determined to be necessary to identify the mine and determine the extent of the hot spot and elevated mercury levels.

In February 2007, fifteen sediment samples were collected on the east side of Highway 20 to determine the extent of elevated mercury concentrations at the surface. These sediment samples were collected from fine sediments in drainages which appeared to be recent (last winter) deposits.

The GPS data and results from Battelle were merged into a data set based on the month of sampling, and this data was imported into the Arc View Geographic Information System (GIS). The photograph locations were also linked to the database within the GIS. The Utopia Mine had not yet been precisely located and it was judged necessary to determine if geologic trends (faults and hydrothermal activity) in the area influenced the elevated readings. All samples had duplicate analyses performed, due to the previously experienced non-homogeneity. The results are shown in Figure 5.

Elevated total mercury concentrations were observed at numerous locations along the Highway 20 frontage, with the highest concentrations (9.26 µg/g) near the estimated location of the Utopia Mine. At the estimated mine site, a drainage flows over the highway cut slope, then flows to the south in a

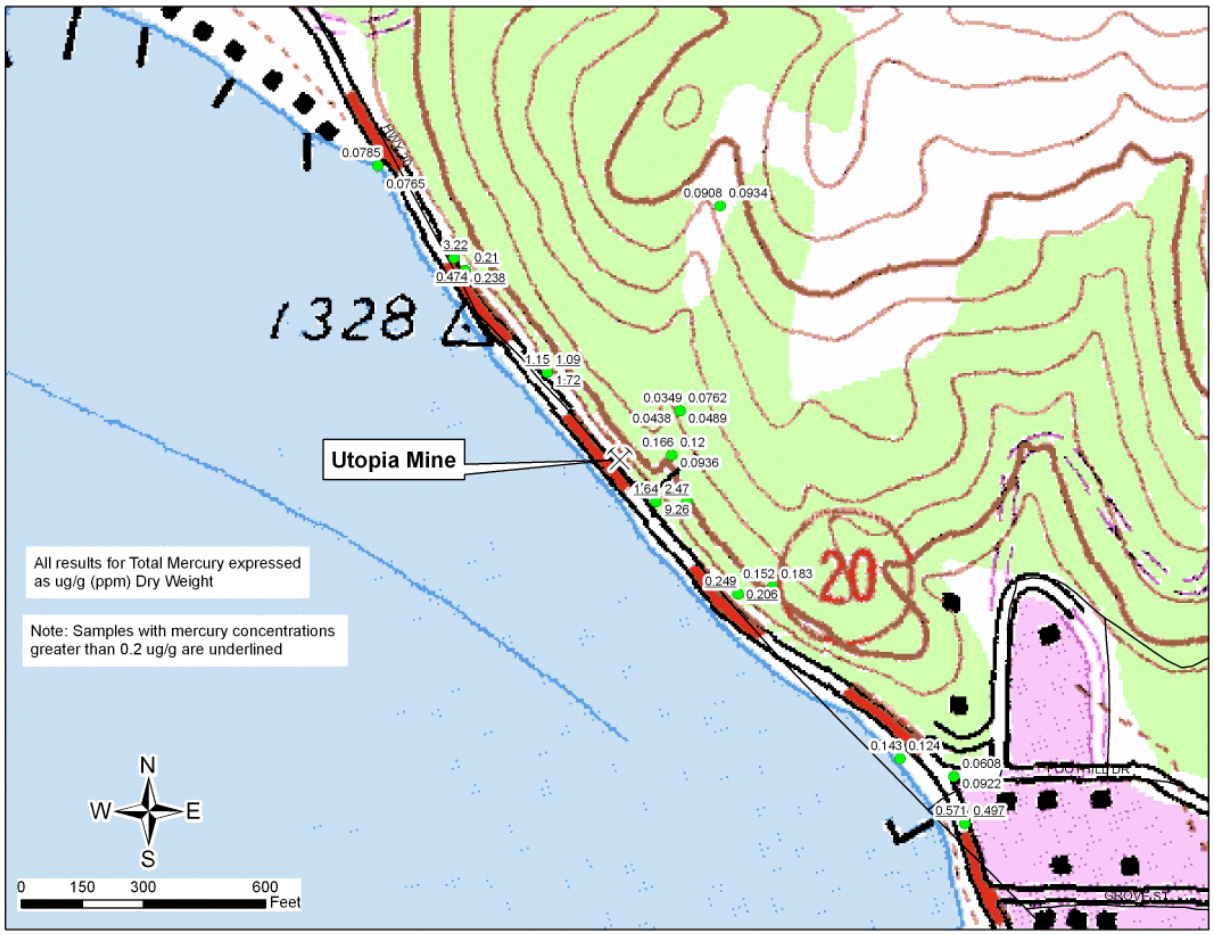

Figure 5: Mercury Sampling Sites near Utopia Mine, February 2007

roadside ditch to the culvert under Highway 20 immediately north of Foothill Drive. With this drainage pattern, the high total mercury concentrations in the roadside ditch north of the presumed mine site

and the high concentrations in the roadside ditch south of Foothill Road could not be explained. Possible explanations are that the mercury hot spot is larger than the original mine location and/or contaminated sediments from other sources could contribute to the elevated total mercury concentrations. Additional sampling was determined to be necessary to better identify the mine and other potential hot spots and elevated mercury levels.

During meetings of the Clear Lake TMDL Stakeholder Committee[12], Caltrans personnel were informed of our initial findings. Alex Arevalo, Caltrans Transportation Engineer, researched the files for information regarding the Utopia Mine. Mr. Arevalo provided the District with copies of highway improvement plans from circa 1962 that identify two adits for the Utopia Mine approximately 160 feet apart and six feet above the highway pavement, see Figure 6. He also located some references to the mine in a right-of-way appraisal (Caltrans purchased the right-of-way for the 1962 highway widening that included the two mine adits) and a subsequent letter. After visiting the mine site, Mr. Arevalo was able to identify the northwest adit and photographed a concrete “cap” that sealed the adit. He was unable to locate documentation of who sealed the adit, or when. Mr. Arevalo was unable to locate the southeast adit, approximately 160 feet to the southeast of the northwest adit, although he did identify an outcropping of reddish soil near the approximate adit location.

In August 2007, fourteen lakebed sediment samples were collected from the lake, thirteen from near the shoreline near the mine and one control sample approximately one mile off shore, see Figure 7. All samples were analyzed in duplicate. Elevated total mercury concentrations were measured directly opposite the northwest mine adit and to the southeast. Concentrations were not as high as measured in October 2006, however, due to the non-homogeneity of the sediment in this area, repeatability of mercury sediment analyses has proven difficult. The results of the methyl mercury analyses are shown in Figure 8. Several samples had methyl mercury concentrations greater than the control concentration of 0.867 ng/g. These locations were not near the actual mine site and do not indicate a pattern of acid mine drainage coming from the Utopia Mine.

In September 2007, thirty four sediment samples were collected near the Utopia mine, see Figure 9. The sample locations in the drainages surrounding the Utopia Mine were selected by the drainages leading away from the location of the mine and by interpretation of geologic maps. Fault locations were selected for resampling on the premise that interaction with fault contacts and hydrothermal solutions were instrumental in the formation of the mercury deposits, as is the case for a majority of the mines in Lake County. During this site visit the location of the northwest adit of the Utopia Mine

[12] The Committee was formed to cooperatively comply with the requirements of the Mercury and Nutrient TMDL’s

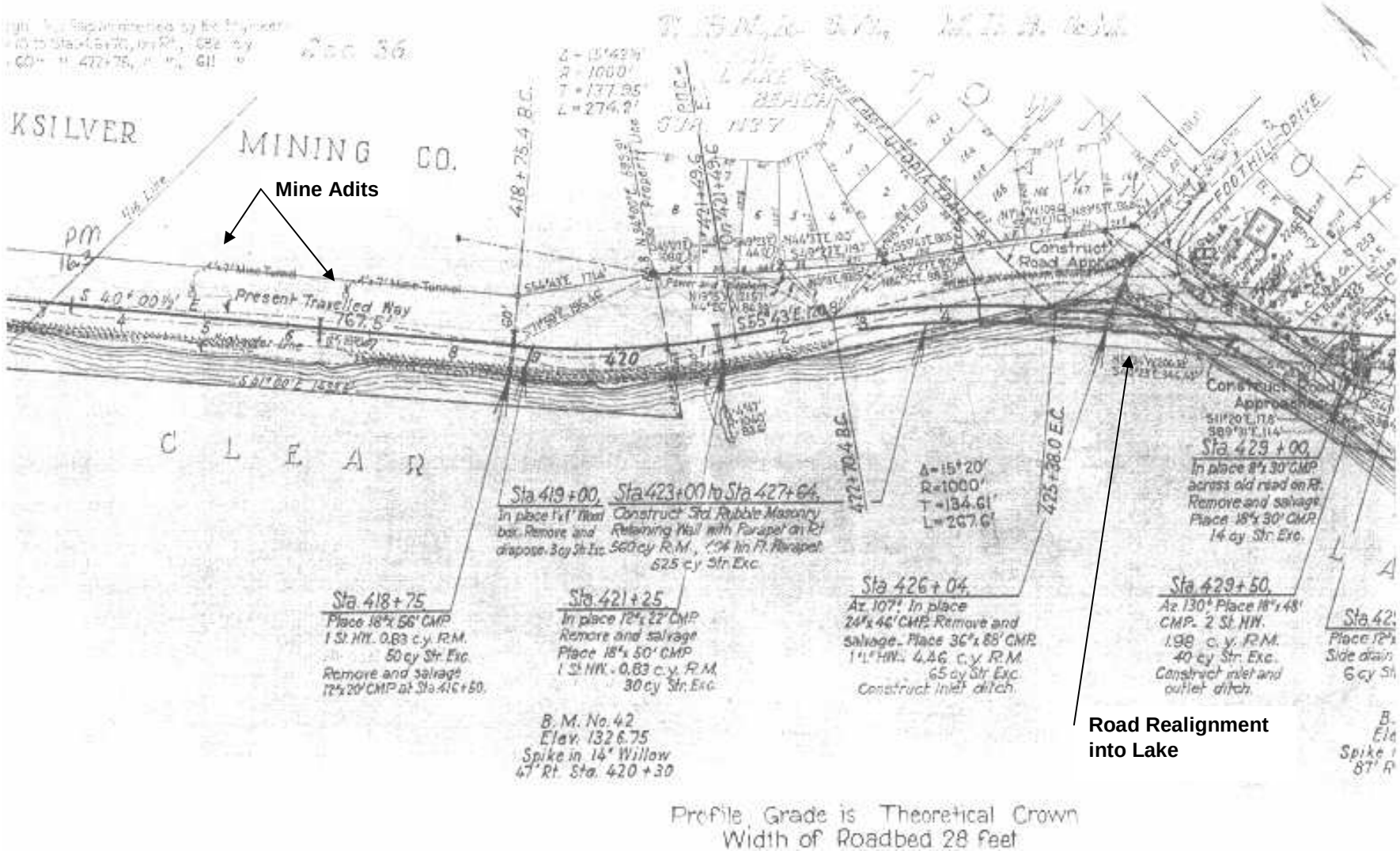

Figure 6: Excerpt of State Highway 20 Improvement Plans showing two adits of Utopia Mine and roadway realignment at Foothill Drive

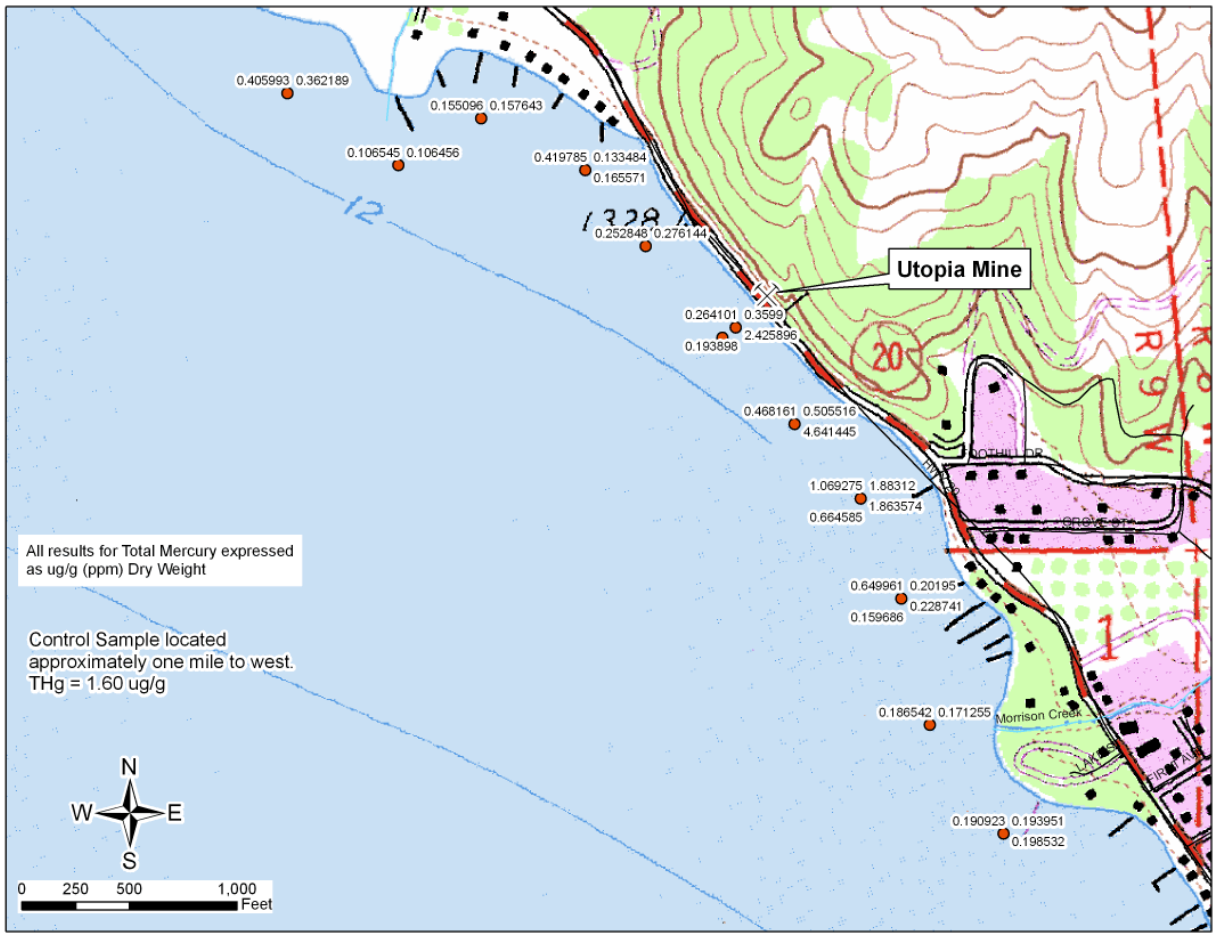

Figure 7: Mercury Sampling Sites near Utopia Mine, August 2007

was located and GPS coordinates obtained. The northwest adit coordinates are 39°6'5"N 122°48'24"W, WGS 1984. While no mapped faults exist in the immediate area of the Utopia Mine adits, field evidence suggested the presence of a minor, discontinuous, fault contact near the approximate location of the southeast adit.

- Elliot Creek and its tributaries (located approximately one quarter mile to the northwest) did not exhibit total mercury levels much higher than noted during the hot spot monitoring for the Clear Lake watershed. One of the analyses of the sample collected from Elliot Creek near Highway 20 had a concentration of 0.171 µg/g, while the other two samples had concentrations of 0.0914 and 0.0806 µg/g. Elevated mercury concentrations are not exhibited upstream, nor are there any significant tributaries that could contribute mercury to the stream. Total mercury in Clear Lake near the mouth, as sampled in August 2007, did not exhibit elevated mercury levels. It does not appear that Elliot Creek and its tributaries contain any significant hot spots.
- The small tributary northwest of the mine (southeast of Elliot Creek), was sampled. Total mercury levels were near background levels until the drainage reached the road ditch, where total mercury levels essentially doubled. One sediment sample in a minor tributary (16 acre) had total mercury

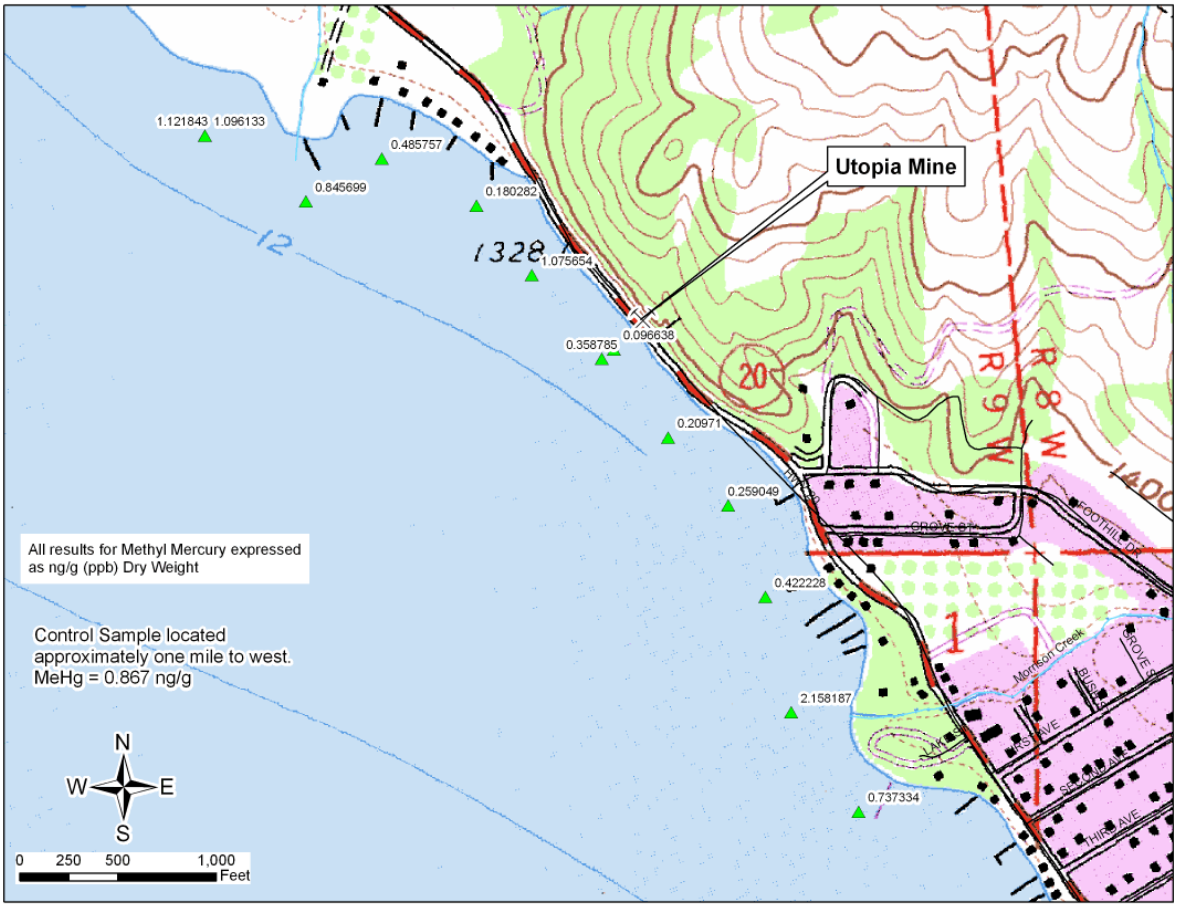

Figure 8: Methyl Mercury Sampling Sites near Utopia Mine, August 2007

concentrations of 0.198 – 0.216 µg/g. This tributary represents less than 20 percent of the watershed upstream of Highway 20 and may intersect the minor fault contact that intersects the approximate southeast adit of the Utopia Mine and may the source of the increased mercury concentrations. It does not appear to represent a significant source of mercury to Clear Lake.

Elevated sediment total mercury concentrations were noted all along the highway ditch. These concentrations did not follow a distinct pattern. The highest total mercury concentrations were south of Foothill Drive. While reviewing the 1962 highway improvement plans, Figure 6, it is evident that the highway was constructed on fill placed within the margins of Clear Lake in the vicinity of Foothill Drive. This is reinforced with the lakebed maps (State Lands Commission, 1970), which shows the location of Zero Rumsey (normal low water for Clear Lake) in October 1958, as surveyed by the Division of Highways, is within fifteen feet of the centerline of Highway

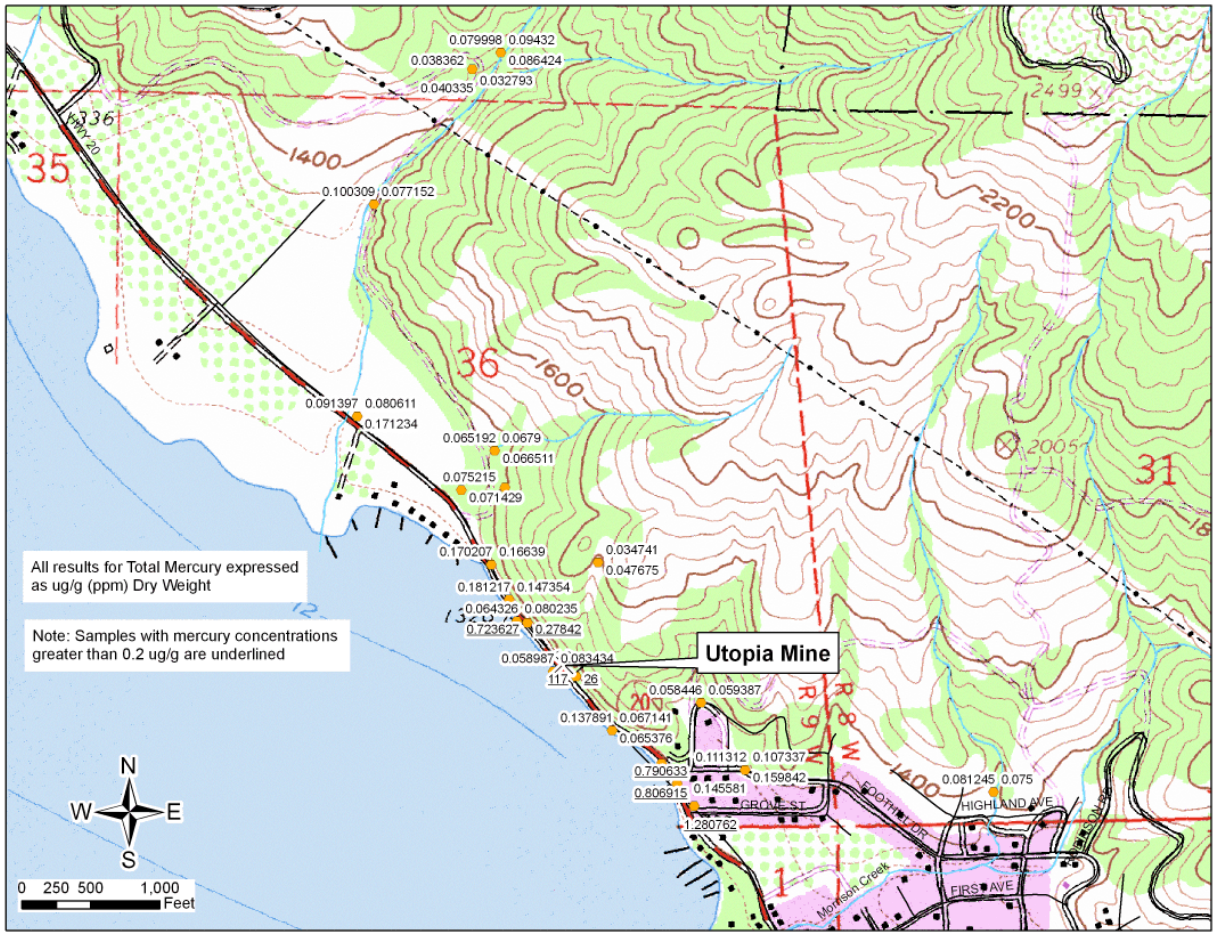

Figure 9: Mercury Sampling Sites near Utopia Mine, September 2007

20. A note on the sheet also indicates this area was filled for highway construction. The 1962 project included widening of the highway through the entire road cut adjacent to the Utopia Mine. If soil with elevated mercury levels from the vicinity of the Utopia Mine was utilized for fill in the project, it could explain the elevated total mercury levels observed that are not downstream of the mine. There is no evidence of erosion in this highway ditch, primarily due to low flows and a very flat gradient resulting in very low flow velocities. Therefore, it is unlikely this hot spot contributes significant mercury to Clear Lake.

- In the small drainage that comes over the cut slope near the inferred position of the southeast mine adit, a small outcropping of weathered, reddish soil was observed, see Figure 10. This is probably the same reddish soil outcropping identified by Mr. Arevalo, see page 29. Two samples were collected at this location. The samples were shipped to Battelle in a separate container and analyzed for total mercury by Battelle. The samples were pulverized prior to analysis to improve the reliability of sample analyses. The results are presented in Table 11. This location is

Figure 10: Outcropping of reddish soil near inferred location of southeast adit of Utopia Mine. The camera bag in this photograph is 1 ½" x 2 ½" x 4 ¼".

Table 9: Total Mercury Concentrations in Outcropping of Reddish Soil near Utopia Mine

Sample No.	MSL Sample ID	THg (µg/g)
S-513-000204	2809-33r1	77.8
S-513-000204	2809-33r2	145
S-513-000204	2809-33r3	117
S-513-000243	2809-34r1	52.5
S-513-000243	2809-34r2	32.5
S-513-000243	2809-34r3	26
S-513-000243	2809-34r4	39.5
Average		70.0

obviously a hot spot that is eroded from flow over the cut slope, however, due to its size, is not likely to contribute significant mercury input to Clear Lake. Mercury concentrations in the highway ditch directly below the hot spot range from 1.64 to 9.26 µg/g (Sample S-513-000062), however, concentrations of total mercury in the sediments in the highway ditch downstream (southeast)

range from 0.124 to 0.249 (Samples S-513-000070 and S-513-000068). It does not appear that significant mercury is continuing to move off site from this hot spot.

- Four sediment samples were collected along the beach adjacent to Highway 20 in the mine. The results of these analyses are shown in Table 12. Two samples showed slightly elevated total mercury levels, however, they do not qualify as hot spots. The road embankment next to the beach is essentially fully protected from wave erosion from Clear Lake, therefore it probably is not a significant source of mercury to Clear Lake.

Table 10: Total Mercury Concentrations in Beach Samples near the Utopia Mine

Sample No.	MSL Sample ID	THg (µg/g)
S-513-000074	2809-37r1	0.0765
S-513-000074	2809-37r2	0.0785
S-513-000241	2809-14r1	0.0643
S-513-000241	2809-14r2	0.0802
S-513-000242	2809-15r1	0.261
S-513-000242	2809-15r2	0.0590
S-513-000242	2809-15r3	0.0834
S-513-000244	2809-16r1	0.0654
S-513-000244	2809-16r2	0.138
S-513-000244	2809-16r3	0.0671
Average		0.0973

Based on all the samples collected near the Utopia Mine, we do not believe the Mine is continuing to contribute significant amounts of mercury to Clear Lake. The elevated levels of total mercury in Clear Lake (greater than background of 1.6 µg/g in Upper Arm lake sediments) near the mine are opposite the mine. There are no longer culverts under the highway at this location (the 1962 plans show several 12” and 18” culverts in this area that are not longer visible/present). This mercury in the

lake sediments appears to be due to the original working at the Utopia Mine and/or construction/reconstruction of Highway 20.

Based on the data available, the Utopia Mine does not appear to be a hot spot that is contributing significantly to elevated levels of mercury and methyl mercury in Clear Lake for the following reasons:

- The area of elevated mercury concentrations in lake sediments near the mine is limited,
- Low methyl mercury concentrations in the lake sediments near the mine do not indicate significant subsurface acid mine drainage into the lake from the mine,
- There has not been evidence in past monitoring programs of mercury contamination from the vicinity of the Utopia Mine, and
- There does not appear to be significant ongoing input of mercury from the Utopia Mine site.

Of the nine mercury mines/prospects identified by the CGS as being within the Clear Lake watershed, two were accurately located (Sulphur Bank and Utopia), Two were located in the Thurston Creek watershed (non-tributary to Clear Lake), and the remaining five (Anderson, Baxter, Gordon Springs and two unnamed prospects) could not be accurately located. With the exception of the Sulphur Bank Mercury Mine, the mines do not appear to be contributing significantly to the elevated mercury levels in Clear Lake. When mercury mines/prospects are identified and located in the Clear Lake watershed, monitoring should be conducted to determine if significant sources of mercury are leaving the mine site.

Watershed Hot Spot Monitoring

In October 2006, forty-two sediment samples were collected throughout the watershed. Data from the hot spot monitoring is included in Appendix D. Sampling sites were selected on major streams at publicly accessible locations. The goal was to obtain an initial “snap shot” of where the greatest mercury concentrations, and presumably hot spots, were located. These sediment samples were collected from fine stream sediments which appeared to be recent (last winter) deposits. The GPS data and results from Batelle were merged into a data set based on the month of sampling, and this data was imported into the ArcView Geographic Information System (GIS). The photograph locations were also linked to the database within the GIS. The results of the initial watershed sampling are shown in Figure 11. Large format maps are included of the hot spot monitoring at the end of this report. From the initial sampling, it did not appear that any “hot spots” (THg > 0.4 µg/g) were identified within the watershed. Only one sediment sample collected on Cole Creek at Wildcat Road had
total mercury levels above 0.2 µg/g (the assumed background level). In addition, we have included the results of the United States Geological Survey (USGS) Geochemical Survey (USGS, 2008) in Figure 11. The USGS samples are grab samples of soil that were analyzed with Cold Vapor Atomic Absorption Spectrometry. One of the USGS Geochemical Survey sites near Eight Mile Valley in the upper Scotts Creek watershed, tested with total mercury levels of 0.19 and 0.35 µg/g (all USGS sediment samples had duplicate analyses). From the initial sampling, it appears that most of the watershed is below the background level and there are not any hot spots. Background levels in the Clear Lake watershed appear to be less than 0.1 µg/g (average of 0.047 µg/g, standard deviation of 0.036 µg/g based on initial sampling).

Additional sampling was determined to be necessary in the Schindler Creek, Burns Valley Creek and Cole Creek watersheds because of total mercury levels in excess of 0.1 µg/g. Additional sampling was not conducted in the upper Scotts Creek watershed, as the land is nearly entirely managed by the Bureau of Land Management (BLM), and total mercury concentrations were well below the background level at the confluence of the North and South Forks of Scotts Creeks (where the creek leaves federally managed

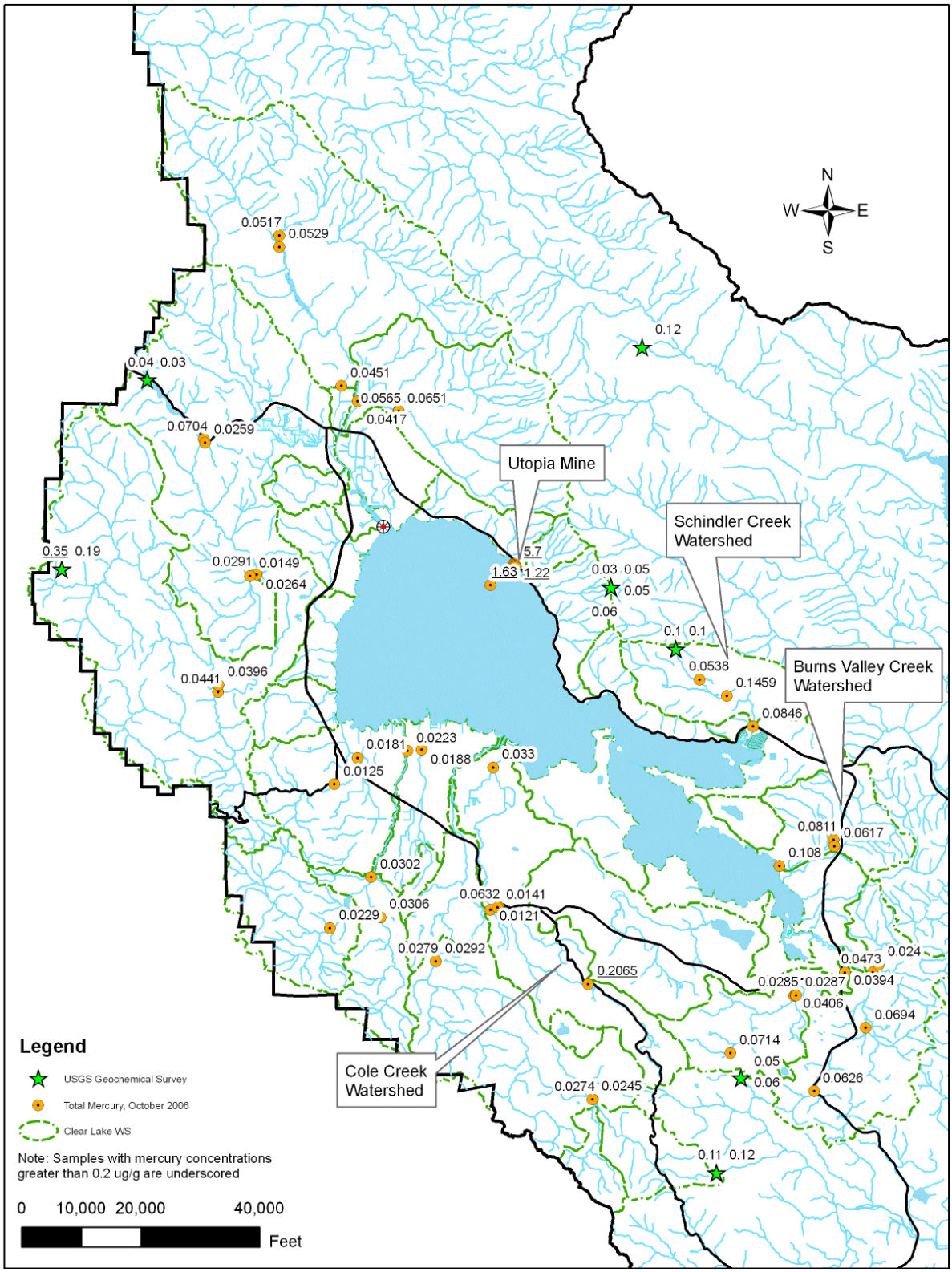

Figure 11: Initial Mercury Hot spot Monitoring, October 2006

lands) and remained well below background levels downstream, indicating there are not significant elevated mercury contributions from upstream hot spots. We encouraged BLM staff to collect sediment samples on BLM managed land in accordance with our approved QAPP and the District would have the sediment samples analyzed. BLM did not collect additional sediment samples.

In October 2007, follow up sediment sampling was conducted. Seven sediment samples were collected in the Schindler Creek watershed, five sediment samples were collected in the Burns Valley Creek watershed and five sediment samples were collected in Cole Creek watershed.

Sediment sampling in the Schindler Creek watershed is shown in Figure 12.

- The October 2006 sediment samples had concentrations measured as high as 0.146 µg/g, significantly higher than the watershed background level of 0.1 µg/g. All other sediment samples were within the watershed background level of 0.1 µg/g, including the westernmost sediment sample, which is near the reported location of an “old miners” cabin (Shauger, 2007). As the one sediment sample was significantly higher than the Clear Lake background concentrations, additional sampling was determined to be necessary.
- In October 2007, seven sediment samples were collected. All samples were analyzed as duplicates, in case of sample non-homogeneity. Four sediment samples had total mercury concentrations greater than 0.2 µg/g. Total mercury concentrations near the State Highway 20 – Schindler Creek bridge were approximately twice that measured in October 2006 (2006: 0.0846, 2007 average: 0.1665).
- Two additional sediment samples were collected in February 2008 to verify the highest concentration measured in October 2007, however, the results had significantly lower mercury concentrations. Field observations and review of the geology of the Schindler Creek watershed did not reveal any geological reason for elevated mercury to be in the area.

It appears that the Schindler Creek watershed has a slightly higher background total mercury concentration than the majority of the Clear Lake watershed. This confirms limited stream sampling results by others (CVRWQCB, 2002a) (CH2MHill, 2006), which have indicated higher mercury concentrations in Schindler Creek suspended sediments than other monitoring locations to the west. As the mercury concentrations are only slightly above the background level for the Clear Lake watershed, and Schindler Creek comprises approximately 2.5 percent of the Clear Lake watershed, it does not appear to be a significant source of the elevated mercury levels in Clear Lake.

Sediment sampling in the Burns Valley Creek watershed is shown in Figure 13.

- Three sediment samples were collected in the Burns Valley Creek watershed in October 2006. Total mercury levels appeared to be higher than the Clear Lake watershed levels (average of 0.084 µg/g), with a maximum concentration of 0.108 µg/g near the mouth. While this total mercury level did not

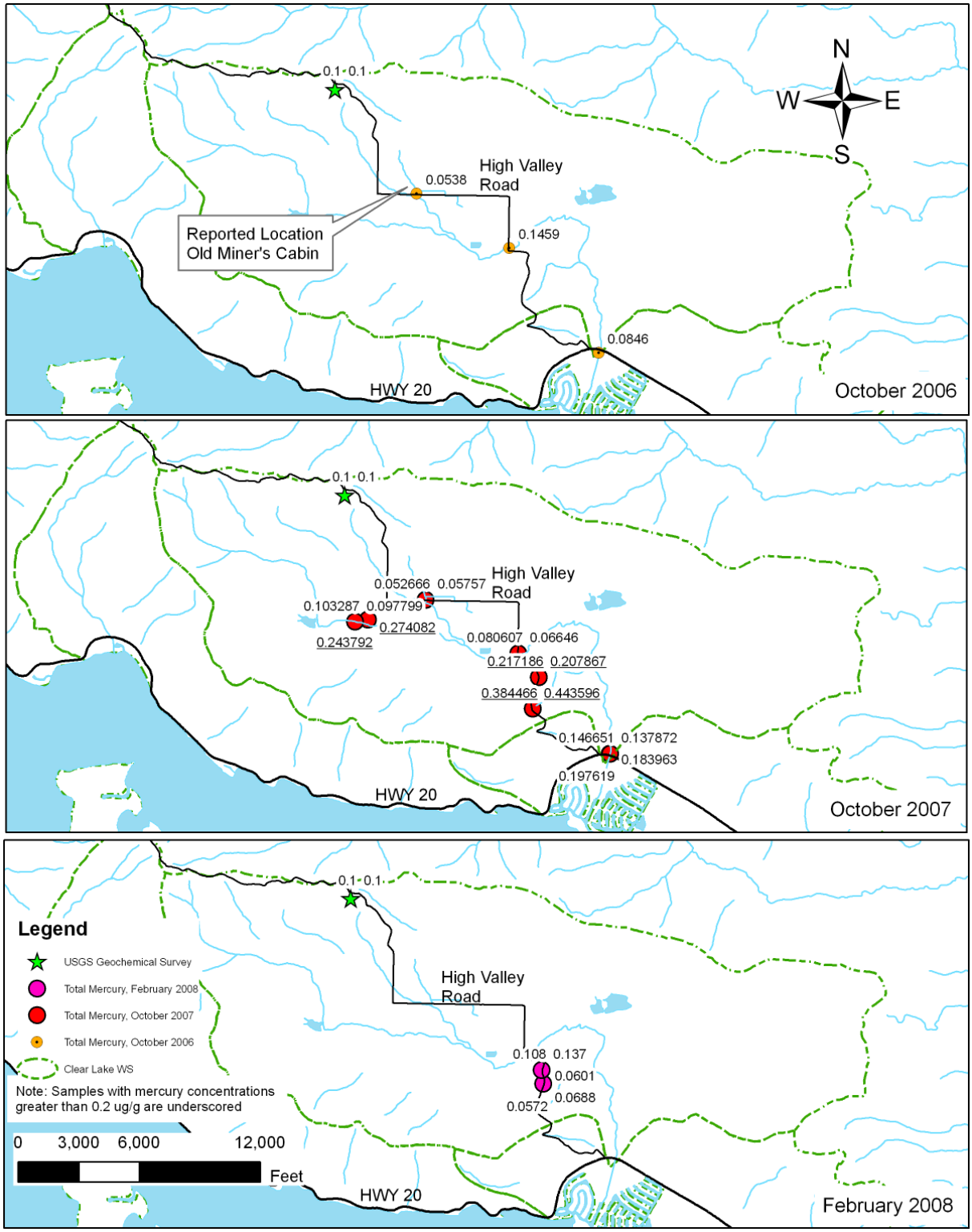

Figure 12: Mercury Hot Spot Monitoring, Schindler Creek Watershed

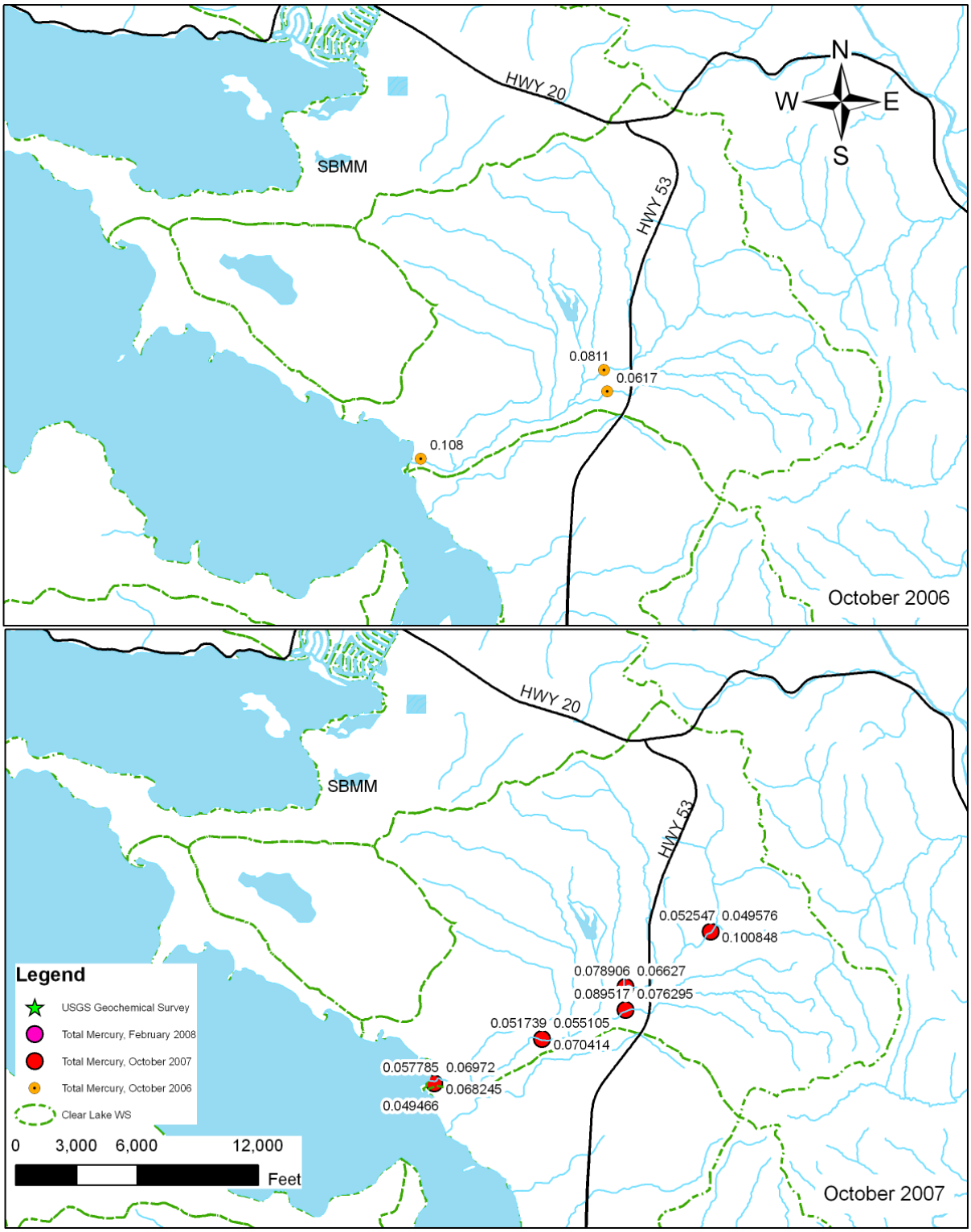

Figure 13: Mercury Hot Spot Monitoring, Burns Valley Creek Watershed

qualify as “elevated”, due to the watershed’s proximity to the Sulphur Bank Mercury Mine, it was determined that additional sampling was necessary.

- In October 2007, an additional five sediment samples were collected and analyzed as duplicates. Total mercury concentrations were slightly lower (average of 0.063 µg/g), with a maximum concentration of 0.101 µg/g.

It appears that the watershed has a slightly higher background total mercury concentration than the majority of the Clear Lake watershed, however, as Burns Valley Creek comprises approximately 2.5 percent of the Clear Lake watershed, it does not appear to be a significant source of the elevated mercury levels in Clear Lake.

Sediment sampling in the Cole Creek watershed is shown in Figure 14.

- Four sediment samples were collected in October 2006, three near Bottle Rock Road and one at Wildcat Road off of Highway 175. While the sediment samples near Bottle Rock Road had low total mercury concentrations (average of 0.0298 µg/g), the sample collected from Cole Creek at Wildcat Road had an elevated total mercury concentration of 0.2065 µg/g. Additional sampling was determined to be necessary.
- In October 2007, five additional sediment samples were collected. Total mercury concentrations at Bottle Rock Road were confirmed at 0.0292 µg/g. A sample collected from McIntire Creek had total mercury concentrations of 0.102 µg/g, slightly higher than watershed background concentration. A sample collected from Cole Creek at Wildcat Road had an average total mercury concentration of 0.872 µg/g, indicative of a hot spot, over four times as high as the previous sample. A sample collected from Cole Creek at Highway 175, approximately 1.8 miles upstream had average total mercury concentration of 0.0977 µg/g. The furthest upstream sample was collected between Salminas Meadow and Loch Lomond had had an average total mercury concentration of 0.156 µg/g. The replicate analyses of this upstream sample had concentrations varying by a factor of 3, indicating the sample was non-homogenous. It was unclear why the total mercury concentrations were so high in Cole Creek at Wildcat Road, and similar high concentrations are not noted upstream or downstream. This portion of the Cole Creek watershed is adjacent to Mount Hanna and is almost entirely made up of andesite deposits, with small areas of basalt and dacite. There are also numerous springs in the area, especially in the area to the south of the Wildcat Road Bridge over Cole Creek. While most of these springs are fresh water, there is a possibility of mercury being present in some spring water, which could contribute to the high total mercury levels at the Wildcat Road Bridge. Additional sampling in the tributaries south of the bridge was required to determine if this is a source of mercury.

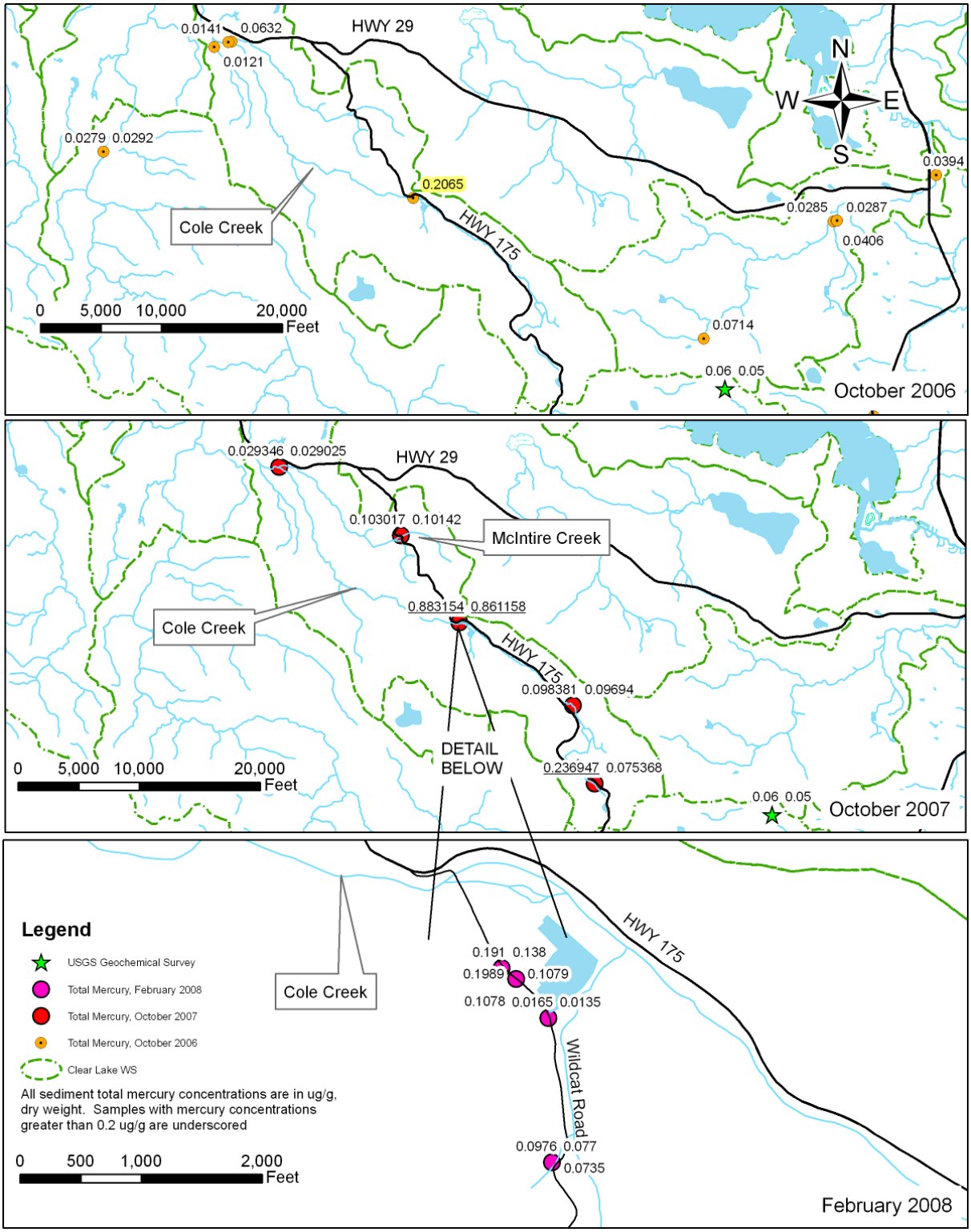

Figure 14: Mercury Hot Spot Monitoring, Cole Creek Watershed

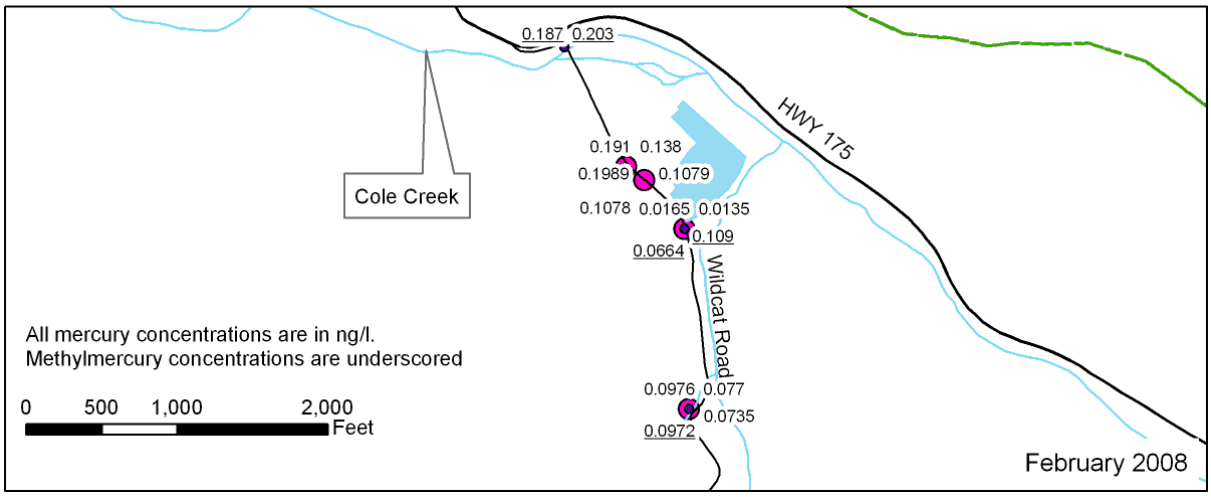

Figure 15: Aquatic Mercury Sampling, Cole Creek Watershed

- In February 2008, six stream sediment samples were collected. Total mercury concentrations ranged from 0.0135 to 0.199 µg/g, with a mean concentration of 0.0944 µg/g, in the samples. Total mercury concentrations increased to the north, closer to the Wildcat Road Bridge. Four water samples were also collected, see Figure 15. Flows were low, and representative of base flow conditions. Aqueous total mercury concentrations ranged from 9.19 to 20.2 ng/l, also with concentrations increasing to the north. Methyl mercury concentrations ranged from 0.0664 to 0.203 ng/l, also with concentrations increasing to the north. Based on the other stream sampling conducted with this project, the total and methyl mercury concentrations at Cole Creek are high, with the 0.203 ng/l value being the fifth highest concentration measured. Cole Creek is slow moving at this location and had moderate turbidity, which could contribute to the high methyl mercury concentrations.

Based on the sediment and water sampling conducted in this upper section of Cole Creek, there are elevated total and methyl mercury levels. With the limited data, the source of the elevated mercury levels is unknown. As the sediment total mercury concentrations downstream at Bottle Rock Road are low (3 samples with average total mercury concentration of 0.0242 µg/g), the area of elevated mercury levels appears to be a small portion of the watershed and does not appear to be a significant source of the elevated mercury levels in Clear Lake.

The ratio of total mercury to total suspended solids (THg/TSS) determined by the stream monitoring program (see Objective #1) is an indicator of the background concentration of mercury within the watershed. The measured THg/TSS ratio ranged from 0.09211 to 0.1468 µg/g, well below the background level of 0.2 µg/g. When we compare these concentrations to the concentrations in the sediment cores taken by UC Davis researchers in the Upper Arm (Richerson et. al., 2008), the pre-1927

THg/TSS ratio of the two cores in the Upper Arm are 0.26 and 0.35 µg/g (Cores UA-03-1996 and UA-03-2000, respectively). With the stream suspended sediment mercury concentration approximately one-half of the historic pre-European concentration, this would indicate there are no significant mercury hot spots in Scotts, Middle and Kelsey Creeks upstream of the measurement points.

Objective #3: Develop preliminary measures to reduce mercury loading

With the exception of the Sulphur Bank Mercury Mine and the Utopia Mine, no old mercury mines have been definitively located in the Clear Lake watershed. If additional mercury mines, or other mines that have mercury enriched soils, are located in the Clear Lake watershed, they should be evaluated to determine if they are contributing mercury to the watershed. If old mines are contributing significant mercury to the Clear Lake watershed, remedial actions should be developed for the specific mine.

The only confirmed hot spot from the monitoring program is the Utopia Mine, which, based on the available data, does not appear to be contributing significant quantities of mercury to Clear Lake. Implementation of BMP's by Caltrans and the County in the vicinity of Foothill Drive to reduce or eliminate erosion at the hot spots and minimize erosion in the highway ditch would be most effective at reducing the small quantity of mercury that is being contributed by the hot spots.

Removal of the lake sediments with elevated mercury levels would be problematic and could result in spreading mercury contaminated sediments within the lake. As the area of elevated mercury levels is small, especially in comparison to the mercury contamination in the Oaks Arm near the SBMM, it does not appear to be reasonable to remove these sediments from the lake.

The other potential contribution from the area would be eroding of any fill utilized in the highway construction that had elevated mercury levels. The area is currently protected from the wave erosion from Clear Lake. In the event that maintenance and or improvements require the removal of riprap, best management practices should be utilized to ensure soil contaminated with mercury is not introduced to Clear Lake.

In the event additional sampling and/or investigations indicate the Utopia Mine is contributing significant mercury loading to Clear Lake, additional remedial actions will be warranted.

Hot spots and soil with elevated mercury concentrations could occur anywhere within the County. Implementation of Best Management Practices (BMP's) should be practiced by all land management agencies and enforced in their permits. This will minimize the introduction of mercury contaminated soils to Clear Lake and other watersheds. Continued and improved implementation of BMP's will reduce the

watershed mercury inputs to Clear Lake as required by the Mercury TMDL. In the event that a mercury hot spot is identified, remedial actions may be required to reduce any mercury contributions to insignificant levels.

Objective # 4 & #5: Estimates of nutrients entering Clear Lake and Estimate average annual nutrient load at the gaged locations

Water samples collected from gaged creeks were tested for a suite of analytes thought to be related to nutrient loading in Clear Lake. The nutrient parameters included the following as stipulated in the QAPP for water samples:

- total dissolved solids;
- total suspended solids;
- sulphate;
- total iron;
- total phosphorous;
- nitrate and nitrite;
- ammonia;
- ortho-phosphate;
- total Kjeldahl nitrogen

Water sampling was performed at the sites of the DWR stream gaging stations located on Middle Creek at the Rancheria Road Bridge; Scotts Creek, upstream of Eickhoff Road Bridge; at Kelsey Creek, upstream of Soda Bay Road, see Figure 1. Grab samples were collected either directly into the sample bottle or with a twice flushed dipper, then transferred to the sample bottle. Total iron samples were collected using ultra-clean methods (see Objective #1). Samples were collected during storm events over WY 2007 and WY 2008. The goal was to obtain data from the rising and falling limb of each storms' hydrograph and as near as practicable to the peak flow. Due to the flashy nature of Clear Lake tributaries, gathering data at the peak flow of each watercourse was problematic, as many of the peak flows did not coincide with daylight hours. As personnel safety was the primary concern during storm events, staff did not sample in the absence of daylight.

Samples were collected on:

- February 9, 2007: 8 samples,
- February 12: 3 samples
- February 21: 3 samples
- February 22: 9 samples
- December 19, 2007: 2 samples

- December 20, 2007: 7 samples
- January 4, 2008: 6 samples
- January 5, 2008: 4 samples
- January 25, 2008: 3 samples
- January 26, 2008: 6 samples
- January 31, 2008: 4 samples
- February 1, 2008: 4 samples
- February 2, 2008: 3 samples
- February 3, 2008: 7 samples

Both winters were short and relatively mild, especially WY 2007, and had limited periods of significant runoff, limiting the number of samples that could be obtained. All water samples were shipped to Alpha for analysis, except for Total Iron, which was shipped to Battelle for analysis. Results were provided to the District. DWR reactivated the stream gages in October 2006, and has provided the District with 15 minute and average daily stream flow information. Because the gages had to be recalibrated, flow data was not available until late 2008. Stream flow information for the time of the sample was related to the results provided by Alpha and Battelle. Data is included in Appendix A. This data was analyzed with Microsoft Excel and flow-concentration regressions were developed. All regressions were analyzed with a t-test at n - 2 (n – number of samples) degrees of freedom to determine if the regression is significant. The probability (p) that the regression is not significant was calculated. Table 13 shows the results of these analyses. Charts showing these regressions are included in Appendix B.

The average concentrations for all analytes are shown in Table 14.

Nitrogen – flow relationships proved problematic. All gages showed a weak or good regression ($p < 0.05$) with at least one of the species of nitrogen (ammonia, nitrate or total Kjeldahl nitrogen (TKN)), however, clear patterns did not exist. Nitrite was tested in 2007, however, none was detected in the 29 samples analyzed. Nitrite was not analyzed in 2008. We calculated total nitrogen from the sample results and have developed regressions, however, the resulting regression coefficients were low (0.277 - 0.672), although all regressions tests as significant ($p < 0.004$). The weak flow-nitrogen relationships make it difficult to accurately estimate the watershed nitrogen loading at the gages and to Clear Lake, however, we will estimate total nitrogen loading using the regression equations.

Phosphorus – flow regressions have been more successful. While there is no relationship between orthophosphate and flow ($0.192 < p < 0.434$), there are good relationships between total phosphorus and flow ($p < 0.00001$). There are strong relationships between total phosphorus and total suspended solids, confirming past studies that have determined a majority of the total phosphorus load is bound with the

Table 11: Regression Analyses for Nutrients and Related Analyses

Analyte	Regression	R^2	n	P
Kelsey Creek Below Kelseyville				
Ammonia, mg/l - Flow, cfs	NH3 = -0.0003630* Flow + 0.2754	0.5699	7	< 0.025
Nitrate as NO3, mg/l - Flow, cfs	NO3 = 0.00005532 * Flow + 0.6317	0.0738	19	< 0.131
Total Kjeldahl Nitrogen, mg/l - Flow, cfs	TKN = 0.0003164 * Flow + 0.5797	0.2148	17	< 0.0302
Total Nitrogen as N, mg/l - Flow, cfs	TN = 0.0003175 * Flow + 0.4730	0.2771	25	< 0.0034
Ortho-Phosphate as P, mg/l - Flow, cfs	oP = -0.000004062 * Flow + 0.08804	0.0023	15	< 0.4338
Total Phosphorus, mg/l - Flow, cfs	TP = .00007420 * Flow + 0.06672	0.7572	20	< 0.00001
Total Phosphorus, mg/l - Total Suspended Solids, mg/l	TP = 0.0006640 * TSS + 0.06050	0.9158	19	< 0.00001
Total Iron, ug/l - Flow, cfs	Fe = 5.804 * Flow	0.7275	26	< 0.00001
Total Iron, ug/l - Total Suspended Solids, mg/l	Fe = 56.84 * TSS + 893.2	0.9402	26	< 0.00001
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -0.7554 * Ln(Flow) + 8.101	0.2657	24	< 0.005
Total Dissolved Solids, mg/l - Flow, cfs	TDS = 243 * Flow-0.1537	0.3634	24	< 0.0009
Total Suspended Solids, mg/l - Flow, cfs	TSS = 0.09149 * Flow	0.8307	22	< 0.00001
Total Solids, mg/l - Flow, cfs	TS = 0.0759 * Flow + 129.3	0.7847	23	< 0.00001
Middle Creek near Upper Lake				
Ammonia, mg/l - Flow, cfs	NH3 = -0.0004010 * Flow + 0.2701	0.1271	4	< 0.3216
Nitrate as NO3, mg/l - Flow, cfs	NO3 = -0.0002185 * Flow + 0.5532	0.2546	17	< 0.0196
Total Kjeldahl Nitrogen, mg/l - Flow, cfs	TKN = 0.0005712 * Flow + 0.06086	0.6910	17	< 0.00002
Total Nitrogen as N, mg/l - Flow, cfs	TN = 0.0004592 * Flow + 0.1146	0.6721	24	< 0.00001
Ortho-Phosphate as P, mg/l - Flow, cfs	oP = -0.00002077 * Flow + 0.1020	0.0584	15	< 0.192
Total Phosphorus, mg/l - Flow, cfs	TP = 0.0003040 * Flow + 0.005882	0.9175	22	< 0.00001
Total Phosphorus, mg/l - Total Suspended Solids, mg/l	TP = 0.0008550 * TSS + 0.05560	0.9725	22	< 0.00001
Total Iron, ug/l - Flow, cfs	Fe = 17.82 * Flow	0.8767	25	< 0.00001
Total Iron, ug/l - Total Suspended Solids, mg/l	Fe = 52.29 * TSS + 1698	0.9490	23	< 0.00001
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -1.682 * Ln(Flow) + 16.70	0.7385	23	< 0.00001
Total Dissolved Solids, mg/l - Flow, cfs	TDS = 142.8 * Flow-0.0767	0.1930	22	< 0.0203
Total Suspended Solids, mg/l - Flow, cfs	TSS = 0.3300* Flow	0.9446	23	< 0.00001
Total Solids, mg/l - Flow, cfs	TS = 0.3455 * Flow + 45.69	0.9476	24	< 0.00001
Scotts Creek at Eickhoff Road				
Ammonia, mg/l - Flow, cfs	y = -0.0004888 * Flow - 0.4293	0.6197	5	< 0.0571
Nitrate as NO3, mg/l - Flow, cfs	NO3 = -0.00007992 * Flow + 0.7490	0.0480	16	< 0.2075
Total Kjeldahl Nitrogen, mg/l - Flow, cfs	TKN = -0.008965 * Flow + 109.6	0.1717	17	< 0.0494
Total Nitrogen as N, mg/l - Flow, cfs	TN = 0.0003764 * Flow + 0.2731	0.4693	21	< 0.0003
Ortho-Phosphate as P, mg/l - Flow, cfs	oP = 0.00002382 * Flow + 0.06436	0.0432	13	< 0.2477
Total Phosphorus, mg/l - Flow, cfs	TP = 0.0001821 * Flow + 0.06932	0.7409	19	< 0.00001
Total Phosphorus, mg/l - Total Suspended Solids, mg/l	TP = 0.0009812 * TSS + 0.04611	0.8985	20	< 0.00001
Total Iron, ug/l - Flow, cfs	Fe = 9.785 * Flow	0.6169	23	< 0.00001
Total Iron, ug/l - Total Suspended Solids, mg/l	Fe = 46.51 * TSS + 2035	0.9464	23	< 0.00001
Sulfate as SO4, mg/l - Flow, cfs	SO4 = -1.218 * Ln(Flow) + 11.36	0.7460	21	< 0.00001
Total Dissolved Solids, mg/l - Flow, cfs	TDS = 194.5 * Flow-0.1091	0.3363	21	< 0.0029
Total Suspended Solids, mg/l - Flow, cfs	TSS = 0.1860 * Flow	0.6499	19	< 0.00002
Total Solids, mg/l - Flow, cfs	TS = 0.1625 * Flow + 147.2	0.6713	21	< 0.00001

Table 12: Averages of Nutrients and Related Analytes

Analyte	Kelsey Creek near Kelseyville	Middle Creek near Upper Lake	Scotts Creek at Eickhoff Road	Comments
Ammonia as NH3, mg/l	Mostly "Not Detected", cannot get meaningful number			Multiple ND's not included
Nitrite	ND	ND	ND	
Nitrate as NO3, mg/l	0.68	0.42	0.66	Multiple ND's not included
Total Kjeldahl Nitrogen, mg/l	0.84	0.68	0.75	Multiple ND's not included
Total Nitrogen as N, mg/l	0.71	0.49	0.64	
Orthophosphate, mg/l	0.084	0.078	0.099	Multiple ND's not included
Total Phosphorus as P, mg/l	0.154	0.275	0.356	
Total Iron, ug/l	5,916	13,494	11,233	
Sulfate as SO4, mg/l	3.6	7.1	3.7	
Total Dissolved Solids, mg/l	100	95	101	
Total Suspended Solids, mg/l	125	246	207	
Total Solids, mg/l	225	327	308	

sediment. Annual orthophosphate loads will be developed by multiplying the average orthophosphate concentration by the annual flow. The regression equations will be used to estimate total phosphorus loads.

Iron is a micro-nutrient that is necessary for nitrogen fixation, a common feature with many of the nuisance blue-green algae in Clear Lake. Total iron was measured and good to strong relationships to flow were identified ($0.62 < R^2 < .88$, $p < 0.00001$). Strong relationships were also apparent between total iron and total suspended solids ($0.94 < R^2 < 0.95$, $p < 0.00001$), indicating a majority of the iron enters the lake in particulate form. Total iron loading will be estimated using the regression equations.

Sulfate has been suggested to play a significant role in sediment nutrient cycling and mercury methylation. UC Davis researchers (Richerson et. al., 2008) suggest that increased nutrient cycling may be due to increased sulfates within Clear Lake, potentially due to activities at the Sulphur Bank Mercury Mine. Data was not available for the watershed sulfate loading, therefore, sulfate was collected as part of this project. Kelsey Creek showed a weak sulfate – flow relationship ($p < 0.05$), however, good relationships were observed in Middle and Scotts Creeks ($p < 0.00001$). Sulfate concentrations are reduced as flow increased. As discussed previously in the document, estimates of sulfate concentrations and loads will be based on the regression analyses.

Good regressions were developed between flow and total suspended solids ($R^2 > 0.65$, $p < 0.00002$), with the weakest relationship being in Scotts Creek. Loading will be estimated based on these regressions.

These regressions were used to estimate the loads at the three stream gages. The estimates were developed utilizing the following procedure:

- Total nitrogen, total phosphorus, total iron, sulfate and total suspended solids concentrations were estimated for each day of the period of record for the gage based on the average daily flow. This introduces some error into the calculation, as flow varies during the day, however, it does provide a reasonable estimate of the anticipated concentrations. Concentrations of ortho-phosphate were estimated based on the average measured concentration.
- The daily loads were calculated based on the average daily flow and the concentration from the previous step.
- The annual loads were calculated for each gage location based on the daily loads, see Appendix D. These results are shown in Table 15.

Table 13: Average Annual Nutrient Loading at Gages, without Flow Weighting

Location	Discharge, ac-ft/yr	oP, kg/yr	P, kg/yr	TSS, T/yr	Fe, T/yr	SO4, T/yr	Tot N, T/yr
Kelsey Creek below Kelseyville	54,070	5,610	9,620	6,370	404	234	53.7
Middle Creek near Upper Lake	53,080	5,110	14,300	15,000	814	439	28.0
Scotts Creek at Eickhoff Road	56,620	6,920	18,800	14,300	750	260	47.9

Due to the number of years with incomplete records, these numbers may inaccurately estimate the flows and loads of Kelsey Creek and Middle Creek. The Scotts Creek gage has a complete record from WY 1961 through 2008, with the exception of 1995[13] and 2006. We have compared average annual flows for the Scotts Creek gage for the entire period of record and the common record years for the other two gages. A weighting factor is calculated by dividing the Scotts Creek average annual flow for the complete record by the Scotts Creek average annual flow for the common record years. This weighting factor is then multiplied by the calculated loads for the respective gage. The adjusted loading estimates are shown in Table 16.

Table 14: Average Annual Nutrient Loading at Gages, with Flow Weighting

Location	Weighting Factor	Discharge (ac-ft/yr)	oP, kg/yr	P, kg/yr	TSS, T/yr	Fe, T/yr	SO4, T/yr	Tot N, T/yr
Kelsey Creek below Kelseyville	0.9478	51,260	5,310	9,120	6,040	383	221	50.9
Middle Creek near Upper Lake	1.008	53,500	4,780	13,300	14,100	761	410	26.6
Scotts Creek at Eickhoff Road	1	56,620	6,920	18,800	14,300	750	260	47.9

[13] Data from 1995 is not used as a levee failure upstream of the Scotts Creek at Eickhoff Road gage resulted in underestimation of flows in excess of 3,000 cfs after January 9, 1995. The levee was repaired before flows resumed in Fall 1995.

The loadings at the three gages streams were used to estimate the total watershed loading, as they represent 33 percent of the lake's watershed and 29 percent of the estimated inflow to the lake. Extrapolation of loading from these three subwatersheds to the entire Clear Lake watershed is based on the assumption that these subwatersheds are representative of the entire watershed. The majority of the Clear Lake watershed is similar to the three subwatersheds that were measured in soil types, cover types and general land use. The major difference is that no "urban areas" are upstream of the gages, with the exception of the low density developments in the Cobb Mountain area. Runoff from the more densely populated communities[14] has not been measured. These communities comprise approximately 10,300 acres, or 3.6 percent of the Clear Lake watershed. These communities comprise a small portion of the watershed and tend to be on less steep terrain and less susceptible to erosion, therefore, extrapolation of loadings from the three gaged locations is a reasonable assumption. Annual loading to Clear Lake is estimated using the following procedures:

- Extrapolation based on nutrient loading being proportional to surface area (see Table 17):
    - The flow weighted average annual flows and loads (Table 16) are utilized.
    - The gaged watershed areas were calculated based on District produced GIS mapping.
    - The entire Clear Lake watershed area was calculated based on District produced GIS mapping.
    - The flow weighted average annual flows and loads were multiplied by the ratio of the area of the Clear Lake watershed to the gaged watersheds.

Table 15: Watershed Nutrient Loading, Estimate based on Drainage Area

Utilize Flow Weighted Annual Loads							
Gaged watersheds	KCK	27,950 Ac					
	MCU	31,930 Ac					
	SCS	35,700 Ac					
	Total	95,580 Ac					
Clear Lake Watershed		289,000 Ac					
Multiplier		3.024					
Location	**Discharge (ac-ft/yr)**	**oP, kg/yr**	**P, kg/yr**	**SS, T/yr**	**Fe, T/yr**	**SO4, T/yr**	**Tot N, T/yr**
Kelsey Creek below Kelseyville	51,250	5,310	9,120	6,040	383	221	50.9
Middle Creek near Upper Lake	53,500	4,780	13,300	14,100	761	410	26.6
Scotts Creek at Eickhoff Road	56,620	6920	18,800	14,300	750	260	47.9
Subtotal	161,400	17,000	41,300	34,400	1,890	892	125
Clear Lake Watershed	488,000	51,400	125,000	104,000	5,730	2,700	379

- Extrapolation based on nutrient loading being proportional to flows (see Table 18):
    - The flow weighted average annual flows and loads (Table 16) are utilized.

[14] 2000 Census block data of at least 1 person per acre

- Annual Clear Lake inflow from the watershed is estimated as the sum of the average annual discharge at the USGS Cache Creek at Lower Lake gage and the water lost by average annual evaporation. The inflow is the sum of watershed inflows and direct precipitation. Groundwater inflow is assumed to be insignificant (Richerson et. al., 1994). Direct precipitation on the lake is subtracted from the total inflow (equals total outflow) to obtain the amount of inflow from the watershed.
- The flow weighted average annual flows and loads were multiplied by the ratio of the average annual flows of the Clear Lake watershed to the flows in the gaged watersheds.

Table 16: Watershed Nutrient Loading, Estimate based on Flows

Gaged Watersheds	161,400 AF		Average Lake Level = 3.85 ft R				
Cache Creek near Lower Lake	298,000 AF		Surface Area @ 3.85 = 41,590 ac				
Evaporation Loss	145,600 AF		Average Annual Evaporation = 42 in/yr				
Outflow = Inflow	443,600						
Direct Precipitation	-91,850		Average Annual Precipitation = 26.5 in.				
Inflow	351,700 AF						
Multiplier	2.180						
Location	**Discharge (ac-ft/yr)**	**oP, kg/yr**	**P, kg/yr**	**SS, T/yr**	**Fe, T/yr**	**SO4, T/yr**	**Tot N, T/yr**
Kelsey Creek below Kelseyville	51,250	5,310	9,120	6,040	383	221	50.9
Middle Creek near Upper Lake	53,500	4,780	13,300	14,100	761	410	26.6
Scotts Creek at Eickhoff Road	56,620	6,920	18,800	14,300	750	260	47.9
Subtotal	161,400	17,000	41,300	34,400	1,890	892	125
Clear Lake Watershed	351,700	37,100	89,900	75,000	4,130	1,940	273

Following are some comparisons of these results with prior loading studies for Clear Lake.

Clean Lakes Report, 1994: The Clean Lakes Report (Richerson 1994) estimates the Clear Lake annual phosphorus load to be 158,000 kg/yr, significantly higher than the above estimates. The Clean Lakes report utilizes phosphorus measurements collected in WY's 1992 and1993, and calculates an average over the time period of WY's 1969 through 1993. The loading regressions were based on seven data points for each of Scotts and Kelsey Creeks, and six data points for Kelsey Creek. The Clean Lakes Report also estimates 70 percent of the phosphorus is removed from the Scotts Creek flow by Tule Lake, a large floodplain/wetland located downstream of the gaging station. Without this assumption, which is not included in the current estimates, the differences between the two estimates would be greater.

The estimate for suspended solids is approximately two-thirds of the estimate of 110,000 to 158,000 metric tons (T) of total solids[15] in the Clean Lakes Report (Richerson et. al., 1994). The current

[15] Suspended solids loadings were not estimated.

monitoring measured an average dissolved solids of 100 mg/l. Using the hydraulic budget figures from the Clean Lakes Report, this accounts for 38,900 T/yr of dissolved solids (12,331 l/s x 1 kg/l x 86,400 s/d x 365 d x 100 x 10^{-6}), reducing the estimate to 71,000 to 119,000 T/yr of suspended solids, essentially equal to the current estimate of 75,000 to 104,000 T/yr.

We were unable to locate the raw data for the Clean Lakes Report, however, the changes in load estimates are likely due to the number of samples and time period utilized for estimating the average annual load. Some of the data utilized in the Clean Lakes Report was also incorporated in the Clear Lake Basin Watershed Analysis.

Clear Lake Basin Watershed Analysis, 1999: The Clear Lake Basin Watershed Analysis (Lake County Flood Control and Water Conservation District, 1999) analyzed data from 1993 through 1998. This report utilized a similar procedure for calculating loads at the three stream gages, including using a weighted flow adjustment. The results are presented with the current results in Table 19.

Table 17: Loading Estimates, Clear Lake Basin Watershed Analysis, 1999

Gage	Flow, ac-ft	Total P, kg/yr	Ortho-P, kg/yr	TSS, T/yr
Watershed Analysis, 1999				
Kelsey Creek below Kelseyville	51,900	25,500	3,360	12,400
Middle Creek near Upper Lake	62,300	24,100	3,730	18,200
Scotts Creek at Eickhoff Road	61,600	32,400	3,090	20,700
TMDL Monitoring, 2009				
Kelsey Creek below Kelseyville	51,260	9,120	5,310	6,040
Middle Creek near Upper Lake	53,500	13,300	4,780	14,100
Scotts Creek at Eickhoff Road	56,620	18,800	6,920	14,300
Ratio 2009/1999				
Kelsey Creek below Kelseyville	98.8%	35.8%	158%	48.7%
Middle Creek near Upper Lake	85.9%	55.4%	128%	77.4%
Scotts Creek at Eickhoff Road	91.9%	58.0%	224%	68.9%

There are significant differences between the results of the 1999 analysis and the 2009 (current) analysis. After reviewing the methodologies and calculations, we offer the following possible explanation for the differences in the data sets.

- Flows: We evaluated the original calculations in the 1999 analyses and did not find any significant differences[16] in the calculations, therefore, the changes in flows are probably due only to the change in record length.

[16] The 1999 calculation for Scotts Creek did not include WY 1981, a dry year. This affects the average annual flow by less than one percent.

- Total Phosphorus: The 1999 data includes total phosphorus that was analyzed at Hopland Research and Extension Center while the 2009 total phosphorus data was analyzed by Alpha Labs. Both laboratories are reliable, therefore, we do not believe there is a problem with the data analyses. The 1999 data includes many more data points at larger flows (> 1,500 cfs) which are critical in defining the slope of the regression. The regressions are similar in slope and intercept, however, the 1999 regressions result in higher calculated total phosphorus concentrations at the lower flows (< 1,500 cfs) for all three streams, which could contribute to higher annual loading as this includes a majority of the annual flow. In the case of Kelsey Creek, the 1999 Flow-Total Phosphorus has high variability and the relationship is very weak ($R^2 = 0.15$)and essentially parallels the 2009 regression ($R^2 = 0.76$) at a total phosphorus concentration approximately 0.2 mg/l higher, resulting in a much higher total phosphorus loading for Kelsey Creek (0.2 mg/l for 51,900 ac-ft/yr equals 12,800 kg/yr) . Utilizing the t-test, this relationship is significant to $p < 0.02$, while all other relationships are significant to $p < 0.0001$. We are unable to explain the reasons for the differences in these results, however, we suspect it may be due to inconsistent sample collection and/or handling prior to 2000 which may have lead to high variability in results and erroneous conclusion in phosphorus loading. The limited number of samples analyzed above 1,000 cfs during the most recent sampling may also lead to erroneous conclusions in the loading estimates.
- Ortho-Phosphorus: The 1999 ortho-phosphorus data was analyzed using a colorimeter owned by the District. The 2009 ortho-phosphorus data was analyzed by Alpha Labs using EPA Method 300.0, including a fully developed QA/QC program. Review of the records which include all the pre-2000 data does not show the colorimeter was calibrated against more precise laboratory analyses, such as EPA 300.0, on a regular basis, nor was there a developed QA/QC program. Therefore, we consider all the ortho-phosphate data prior to 2000 suspect.
- Total Suspended Solids: The 1999 total suspended solids data was analyzed by District staff in a District lab utilizing the difference between total solids and total dissolved solids as determined using Standard Methods procedures 2540. Review of the records which include all the pre-2000 data does not show the analyses calibrated against independent laboratory analyses, nor was there a developed QA/QC program. The regressions are similar in slope with Scotts Creek giving nearly the identical slope (0.182-0.186) for both sets of data and Middle Creek providing similar slopes (0.286-0.330). The similarity in these slopes appear to indicate the earlier data analyses were providing reasonable results, as they are similar to the current results. In the case of Kelsey Creek, slopes are different by a factor of two (0.0915-0.192). The current slope of the Kelsey Creek data is approximately one half of the Scotts Creek slope and one third of the Middle Creek slope, and may not be a good indicator of actual suspended solids loading. The current Kelsey Creek data has only two data points at flows greater than 1,500 cfs, which could bias the results, resulting in the significantly lower slope. Utilizing the t-test, all relationships are significant to $p < 0.00002$. Additional

sample collection and analysis at higher flows is necessary to refine the relationships for all three gages, especially Kelsey Creek.

Due to discrepancies in the sample procedures and analyses, comparison of the two data sets is problematic, especially with total phosphorus and ortho-phosphorus. Current loading estimates appear to be less than the 1999 estimates, however, limited sampling at high flows in WY's 2007 and 2008 may result in underestimation of the annual loads. Additional sampling following the procedures in the QAPP as was done is WY 2007 and 2008 during high flows would also help to refine these relationships.

To the best of our knowledge, this is the first measurement of iron, sulfate and nitrogen entering the lake from the watershed.

- Iron and sulfate play major roles in nutrient cycling from the sediments (Richerson et. al., 2008), therefore, an understanding of the watershed load is important if they are the controlling the amount of phosphorus cycling within the lake. Internal phosphorus loading is estimated to be three times the external phosphorus loading in drought years (Richerson et. al., 1994) and plays a major role in the algal productivity of Clear Lake.
- During the 1970's and 1980's, Clear Lake was dominated by blue-green algae, most of which were able to "fix" nitrogen from the atmosphere, therefore, researchers have not measured nitrogen inflows from the watershed. Alex Horne estimated that nearly 43 percent (500 T) of the nitrogen in the lake in 1970 (a wet year[17]) was from nitrogen fixation and 40 percent (461 T) of the nitrogen was from surface inflow, however, this was a period when nitrogen fixing blue-green algae played a major role in Clear Lake. With the improved clarity and reduced blue-green algal blooms since 1991, nitrogen fixation probably contributes less to the nitrogen budget than in 1970. With nitrogen from the watershed potentially exceeding one half of the nitrogen budget under current conditions, the amount of inflow could be important in Clear Lake's limnology.

As iron is primarily bound to sediment, the limited data obtained during high flows may result in underestimation of the iron loading. As sulfate is inversely proportional to flow, and the slope of the flow – total nitrogen regression is relatively flat, the estimated loadings will be minimally impacted by the limited data set. Additional monitoring is necessary to verify the regressions and estimated loadings. Additional research is necessary on Clear Lake's limnology to understand the meaning of the iron, sulfate and nitrogen inflows.

The current phosphorus and total suspended solids load estimates are significantly lower than previous estimates. It is unclear whether this is a real reduction in loading or a difference in estimates due to different monitoring and analysis protocols and sample data. Additional monitoring, especially at high flows, using improved the protocols is required to improve the current estimates. The quality of previous

[17] Annual flow in Scotts Creek was 153 percent of average in 1970

monitoring data is in question due to inconsistent monitoring practices and protocols. The Nutrient TMDL utilized this data to calibrate the watershed loading model, which affects the accuracy of the Nutrient TMDL. Information on iron, sulfate and nitrogen inflows is now available to assist in the understanding of Clear Lake limnology.

Conclusions

The Clear Lake Watershed TMDL Monitoring Program was developed to monitor gaged streams to develop a scientifically defensible estimate of mercury (total and methyl) and nutrient loading to Clear Lake and to identify mercury "hot spots" in the surrounding watershed.

Total and methyl mercury concentrations were monitored during Water Years 2007 and 2008 at three stream gage locations within the Clear Lake watershed, Kelsey Creek below Kelseyville, Middle Creek near Upper Lake and Scotts Creek at Eickhoff Road. Flow–concentration regressions were developed for the three locations. Average annual subwatershed loading rates were calculated at all three locations, which were extrapolated to the entire Clear Lake watershed. Watershed average annual total mercury loads were estimated to be 11.8 to 16.4 kg/yr, which is consistent with previous watershed loading estimates. Watershed average annual methyl mercury loads were estimates to be 0.0386 to 0.0536 kg/yr. These estimates are less than the 18 kg/yr total mercury and 0.35 kg/yr methyl mercury loading estimates included in the Mercury TMDL, however, these estimates are lower primarily due to increased data, not an actual reduction in watershed mercury loading.

Chloride and sulfate concentrations were also monitored at the three gages as indicators of contribution from hydrothermal waters and/or acid mine drainage. Average chloride concentrations ranged from 2.2 to 3.1 mg/l, which is within the expected concentrations for the Sacramento River watershed for streams that do not have significant hydrothermal or acid mine drainage contributions. Average sulfate concentrations ranged from 3.6 to 7.1 mg/l which is within the expected concentrations for the Sacramento River watershed for streams that do not have significant hydrothermal or acid mine drainage contributions. Flow–sulfate concentration regressions were developed and average annual loading rates were estimated at 2,010,000 to 2,700,000 kg/yr for the Clear Lake watershed. This estimate is consistent with recent estimates of a standing mass of sulfate in Clear Lake of 17,000,000 kg (Richerson et. al., 2008).

Nine abandoned mercury mines/prospects were identified in the Clear Lake watershed by the California Geological Survey. Each of these mine sites is a potential mercury source (hot spot). Five mine sites could not be accurately located, with two mines possibly being located outside the Clear Lake watershed. Stream sediment monitoring downstream of the reported mine sites did not exhibit elevated mercury levels. Two mine sites are located in the Thurston Creek watershed, which is not tributary to Clear Lake.

The Sulphur Bank Mercury Mine was not investigated as it is an USEPA Superfund site and has had extensive monitoring. The Utopia Mine was located on State Highway 20 on the north side of Lucerne. Lake sediment samples (22) indicated limited areas of significantly elevated mercury levels in Clear Lake. Forty-nine sediment samples were collected at and near the mine site, to characterize the extent of elevated mercury levels in the area. A small outcropping of mercury enriched soil (average of 70 µg/g) occurs in a drainage at the mine site. Additional areas with elevated mercury concentrations were identified, some of which are not downstream of the mine site. It appears that mercury enriched soil may have been used to construct the highway in this vicinity. From the limited data, it appears that much of the mercury deposited in Clear Lake near the Utopia Mine is from mining and highway construction, and that the Utopia Mine does not appear to be a significant continuing source of mercury to Clear Lake.

Stream sediment samples were collected throughout the Clear Lake watershed to locate hot spots, or locations with elevated mercury levels (> 0.4 µg/g) in the sediments. Forty-two initial sediment samples were collected and mercury concentrations averaged 0.047 µg/g with a standard deviation of 0.036 µg/g, significantly less than the background level for the North Coast of 0.2 µg/g. Additional monitoring (25 sediment samples and 4 water samples) was conducted in the Schindler, Burns Valley and Cole Creek subwatersheds, as these subwatersheds had at least one sample greater than 0.1 µg/g. No hot spots were confirmed in the Clear Lake watershed, although these subwatersheds do appear to have higher background levels of mercury than the remaining portions of the Clear Lake watershed. Mercury concentrations in the suspended sediments are nearly half of the pre-European mercury concentrations in the deep sediments in the upper arm of Clear Lake, indicating there are not significant anthropogenic mercury sources upstream of the three stream gages.

Nutrient concentrations were monitored during Water Years 2007 and 2008 at three stream gage locations within the Clear Lake watershed, Kelsey Creek below Kelseyville, Middle Creek near Upper Lake and Scotts Creek at Eickhoff Road. Analytes monitored include total dissolved solids, total suspended solids, sulfate, total iron, total phosphorus, nitrate and nitrite, ammonia, ortho-phosphate and total Kjeldahl nitrogen. Flow – concentration regressions were developed for the three locations. Average annual subwatershed loading rates were calculated at all three locations, which were extrapolated to the entire Clear Lake watershed, see Table 20.

Table 18: Watershed Nutrient Loading Estimates

Ortho-P, kg/yr	Total P, kg/yr	Suspended Solids, T/yr	Iron, T/yr	Sulfate, T/yr	Total Nitrogen, T/yr
37,100 – 51,400	89,900 – 125,000	75,000 - 104,000	4,130 – 5,730	1,940 - 2,700	273 - 379

Total phosphorus estimates are significantly lower than previous estimates, including the TMDL, which estimate the average annual phosphorus load at 158,000 kg/yr. The lower estimates may be due to lack of recent monitoring data at high flows (> 1,000 cfs), as Water Years 2007 and 2008 were dry with limited opportunities to sample large flows. Additional nutrient monitoring, especially during high flows, is necessary to verify the validity of these loading estimates. There are also issues with the quality of data collected by the District during the 1990's which formed the basis of the Clean Lakes Report (Richerson et. al., 1994) and the Nutrient TMDL. The Clear Lake watershed model utilized in the Nutrient TMDL developed average annual phosphorus loads during a drought period based on phosphorus monitoring that may not have had adequate QA/QC. This, in combination with the unverified Clear Lake model, places doubt on the accuracy of the phosphorus loading target developed for the Nutrient TMDL.

Total suspended solids estimates in the Clean Lakes Report (Richerson et. al., 1994) are essentially the same as the current estimates.

Iron, sulfate and total nitrogen budgets were developed. Additional monitoring, especially at high flows, is necessary to verify the estimated loadings. Additional research is necessary on Clear Lake's limnology to understand the meaning of the iron, sulfate and nitrogen inflows.

References:

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