

REDISTRIBUTION OF MERCURY FROM CONTAMINATED LAKE SEDIMENTS OF CLEAR LAKE, CALIFORNIA

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Abstract. Mining operations conducted at the Sulphur Bank Mercury Mine at Clear Lake, California, from 1872–1957, together with acid mine drainage since abandonment, deposited ca. 100 metric tons of mercury (Hg) in the sediments of Clear Lake. In 1992 Hg in surficial sediments (up to 183 mg kg⁻¹ total Hg and 15.9 µg kg⁻¹ methyl Hg) exhibited a classic point source distribution with maximum concentrations adjacent to the mine. However, the ratio of methyl:total Hg in sediments increased with distance from the mine, suggesting either differential transport of methyl Hg or a non-linear relationship between sediment inorganic Hg concentrations and methylation. Water exhibited an even more gradual decline in total Hg concentrations with distance from the mine, in both unfiltered bottom water (max. ca. 70 ng L⁻¹) and filtered surface water (max. ca. 7 ng L⁻¹). In comparison with other studies, Clear Lake exhibits high total Hg in sediment and water, yet relatively low methyl Hg concentrations. Our findings indicate a non-linearity between total and methyl Hg concentrations in sediments. The ratio of methyl:inorganic Hg is approximately 2 orders of magnitude higher in the water column than in the sediments, making the methyl fraction much more available for down-gradient transport away from the mine. Particulate Hg comprises ca. 33–94% of the total Hg and ca. 25–78% of the methyl Hg in the water column. Geothermal springs do not appear to represent a significant source of Hg to Clear Lake. The present pattern of Hg distribution in Clear Lake shows that water column transport plays some role in the lake-wide contamination of methyl Hg, but high methylation at relatively low inorganic Hg concentrations cannot be ruled out. No quantitative estimate of the area of sediments requiring remediation is possible from these descriptive data alone.

Key words: aquatic, Clear Lake, mercury, mining, pollution, sediments, water

1. Introduction

1.1. OBJECTIVE OF STUDY

The central objective of our study was to characterize the distribution of total mercury (Hg) and methyl Hg (both inorganic and organic) in all major abiotic (sediments, particles, water) and biotic (plankton, benthic invertebrates, fishes) pools in the Clear Lake ecosystem, and suggest mechanisms for the redistribution of Hg from a point source, an abandoned Hg mine. The data reported here

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represent the abiotic portion of a baseline study conducted as a part of an Ecological Assessment (for the U.S. EPA, Region IX) at the Sulphur Bank Mercury Mine Superfund site at Clear Lake, California (Suchanek *et al.*, 1993). These data provide preliminary evidence of how a relatively extensive aquatic ecosystem has been contaminated with methyl Hg from a point source of inorganic Hg over several decades.

Previous data (see Chamberlin *et al.*, 1990; Suchanek *et al.*, 1993, 1995) indicate that inorganic mercury (Hg) declines steeply and exponentially away from the mine site, implicating the mine as a point source for contamination of sediments. As we show in this paper, methyl Hg also declines away from the mine site, but much less steeply. This difference in the distribution of the two species is consistent with either (1) differential down-gradient transport of methyl Hg or (2) a non-linear relationship (e.g. Michaelis-Menton) between sediment inorganic Hg and sediment methylation rates at sites distant from the mine. Inorganic Hg in the biotic portion of this aquatic ecosystem (Suchanek *et al.*, 1993, and unpublished data in preparation) declines monotonically away from the mine for benthic organisms, plankton and fish, but methyl mercury shows no obvious decline in biota away from the mine. The distribution data presented here thus show a complex relationship between inorganic Hg loading and the resulting 'downstream' contamination of the ecosystem with methyl Hg. In this respect our data are similar to those published from other systems in showing little to no correspondence between inorganic Hg and methyl Hg concentrations.

Detailed investigations of transport and methylation processes will be required to understand Hg ecotoxicology in this and other systems. Presently, ecosystems like Clear Lake contaminated with large amounts of inorganic mercury pose a hazard which is difficult to evaluate.

1.2. CLEAR LAKE CONTAMINATION HISTORY AND MERCURY DATA

Mining operations (first for sulfur, then for Hg) from 1872 to 1957 removed between 4400 and 7000 metric tons of Hg from the Sulphur Bank Mercury Mine (Chamberlin *et al.*, 1990), located at the eastern end of Clear Lake, CA (Figure 1). During this period, waste rock piles were built up at the site along 380 m of the lake's shoreline. Chamberlin *et al.*, 1990 estimated that erosion of these piles and direct dumping into the lake resulted in ca. 100 metric tons of Hg being stored in Clear Lake sediments. Seepage of Hg contaminated outflow waters from the waste piles and from the flooded mine pit were previously estimated to be very small. However, the wet 1994–95 winter initiated large acid mine drainage outflows rich in mercury from the Sulphur Bank site, and core data are consistent with a chronic inorganic mercury load of approximately 400 kg yr^{-1} (Suchanek *et al.*, 1997). Aeolian deposition from the on-site ore retort stack plume is also a potential historic source of Hg in lake sediments. The prevailing wind is onshore (relative to the mine), but winter winds would sometimes have blown the plume westward

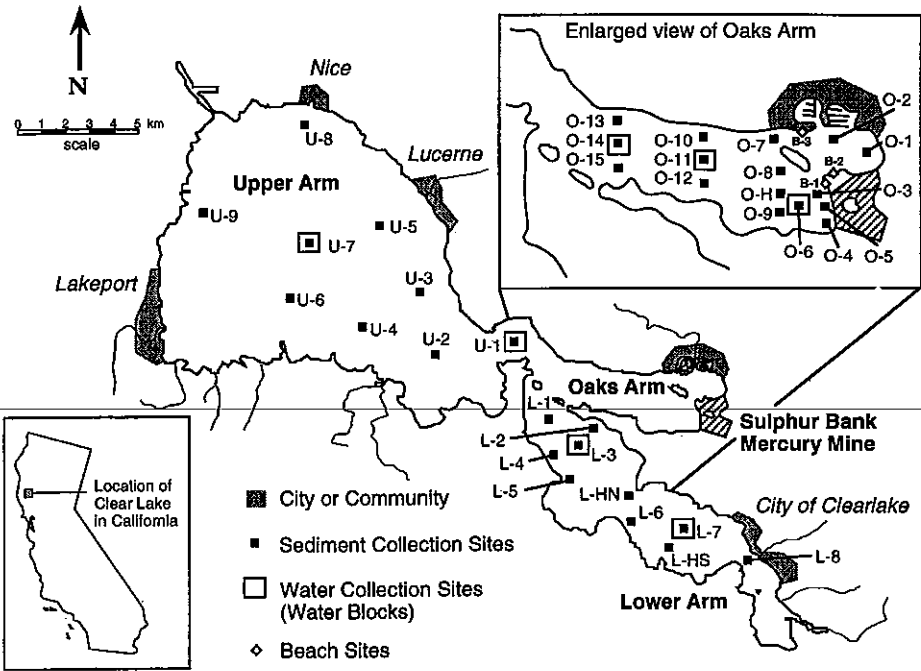


Figure 1. Map of Clear Lake and sampling sites.

over the lake. Elevated levels of Hg in Clear Lake were first detected in 1970 by the California Department of Health Services (summarized in CVRWQCB, 1987). Since that time, hundreds of sediment, water, and fish tissue samples have been collected near the mine site and elsewhere in Clear Lake and analyzed for total Hg (summarized in Suchanek *et al.*, 1993; 1995; 1997; 1998).

The bulk of Hg in aquatic systems typically is associated with sediments, due to a high affinity for solid phases. Several previous studies of Hg in Clear Lake surficial sediments (CVRQCB, 1987; Chamberlin *et al.*, 1990; Suchanek *et al.*, 1993) demonstrate an exponential decline in total (i.e. primarily inorganic) Hg concentrations away from the mine, ranging from as high as 250 mg kg^{-1} to non-detectable levels (Figure 2). In addition to inorganic Hg, aquatic sediments also generally contain trace to low fractions of organic Hg species, primarily methyl Hg (CH_3Hg^-). Methyl Hg usually constitutes from 0.01 to 1% of the total mercury present in sediments (Jackson *et al.*, 1982; Robertson *et al.*, 1987), though reports of levels from 0.0001 to 9.8% exist (Berman and Bartha, 1986; Wilkin and Hintelman, 1991). No previous study has measured methyl Hg in Clear Lake sediments.

Our understanding of Hg species in the water column of lakes was seriously limited before improved, cleaner analytical techniques for aqueous Hg eliminated contamination and lowered practical detection limits by 3 orders of magnitude (Gill and Fitzgerald, 1987; Bloom, 1989). Using these techniques, Gill and Bruland

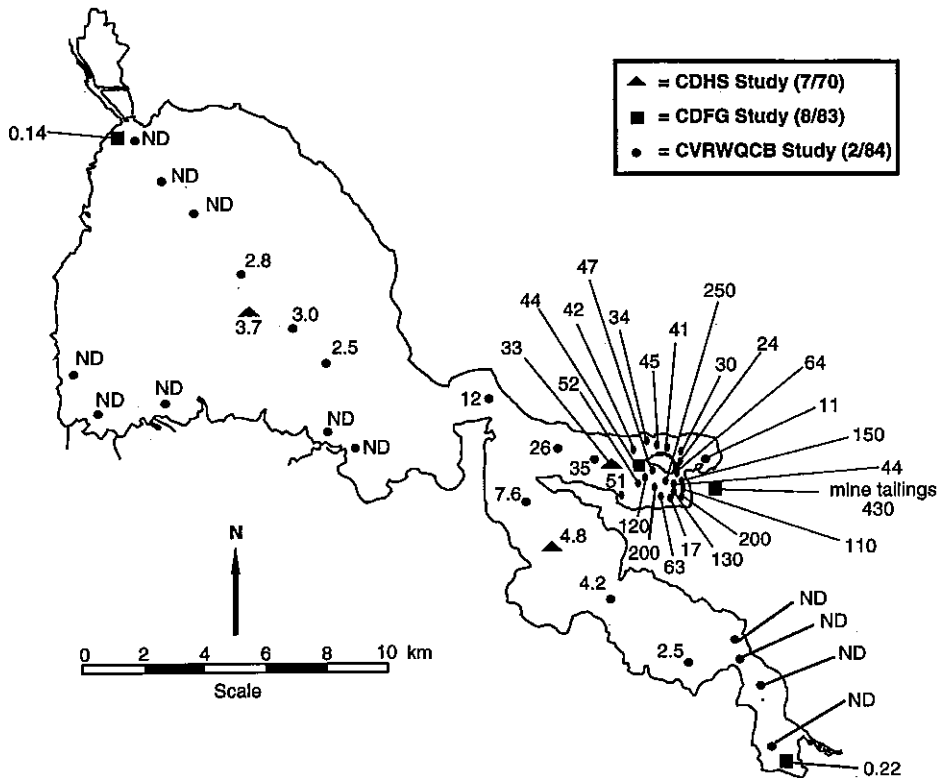


Figure 2. Total Hg (mg kg^{-1}) in historical sediment samples from three studies: California Department of Health Sciences (CDHS 1970); California Department of Fish and Game (CDFG 1983); and the Central Valley Regional Water Quality Control Board (CVRWQCB 1984). Those sites with ND had $< 0.2 \text{ mg kg}^{-1}$ of total Hg.

(1990) surveyed aqueous Hg levels for California water bodies (including Clear Lake during February and April of 1987), and found total Hg concentrations to be generally higher at Clear Lake (especially in the particulate fraction) than most other California sites. In the Gill and Bruland (1990) study, the highest value near the mine was only 104 ng L^{-1} ($= 520 \text{ pM}$), or ca. half the earlier detection limits. Previous higher estimates of aqueous Hg in Clear Lake (summarized in Chamberlin *et al.*, 1990; Benham, 1993) are thus presumably spurious (G. Gill, personal communication).

2. Materials and Methods

Clear Lake is a shallow (mean depth = 8.1 m), polymictic, highly eutrophic lake with an area of ca. 17,670 ha in the northern California Coast Range (Goldman and Horne, 1983; Richerson *et al.*, 1994). It is believed (through core analyses)

to be the oldest freshwater lake in North America (Sims and White, 1981). The lake is divided into three sub-basins connected by a narrow strait referred to as the Narrows (Figure 1). Rates of exchange between the sub-basins have not been measured. Clear Lake is also located in a geologically active region with numerous active geothermal springs emitting gas (mostly CO₂) and water from the lake bottom.

Field sampling was conducted during September 1992 at 35 sampling stations distributed among the three arms of Clear Lake (Figure 1). The most intensive series of samples were collected closest to the mine site in the Oaks Arm where, based on previous studies, it was anticipated that the steepest gradients of sediment-associated Hg concentrations would exist. Sites were selected using depth contours, distance from shore, and presence or absence of upwelling gases and/or water from geothermal springs.

Surficial sediment samples were collected from 35 lakebed benthic sampling stations using a 6 inch Ekman dredge and from 3 beach sediment sampling stations. Samples for analysis were taken from the top 5 cm of each dredge. Field replicates were obtained by collecting two independent Ekman grabs at each site. Sample splits were also collected at a 5% frequency. Prior to sampling, and between sampling runs, all non-disposable sampling equipment was decontaminated with 10% nitric acid and rinsed with deionized water. Sediments from all stations were analyzed for total Hg, grain size and TOC. Sediments from a subset of stations (18 of 35 total) were also analyzed for methyl Hg.

In order to more easily compare grain size data among sites and apply statistics, we computed a 'mean grain size index', with the value spanning a theoretical range of 0.0 (100% clay particles) to 3.0 (100% gravel or larger). The four grain size categories analyzed were assigned values as follows: clay = 0, silt range = 1, sand range = 2, and gravel = 3. To obtain a mean grain size the values for each sample were multiplied by the corresponding percentages found for each of the four grain size ranges (USDA System): clay (< 2 μm), silt (2–50 μm), sand (50–200 μm), gravel (> 200 μm). The resulting index is reasonably linear with respect to the percentage of clay sized particles within each sample.

Because wind and surface currents generally keep Clear Lake's shallow water column unstratified and well mixed (Goldman and Horne, 1983), little horizontal small-scale spatial variability of the water column was expected. There is a diurnal pattern of wind, with strong afternoon breezes leading to typical current velocities in the range of 5–20 cm sec⁻¹ (Lynch, 1996). Thus, water sampling was conducted at a reduced number of stations (= water blocks, see Figure 1).

Water samples were collected using the 'ultra-clean' techniques of Gill and Bruland (1990) and Watras *et al.* (1991). At each station, surface samples were collected in acid-boiled, double-bagged Teflon™ bottles just below the surface and another about 1 meter off the bottom. Deep water samples were collected using a peristaltic pump fitted with acid-cleaned, weighted, non-adsorptive Teflon™ tubing. Aqueous Hg analyses for each sample site and depth included total Hg and

methyl Hg in both a raw (unfiltered) water sample and a filtered ($< 0.45 \mu\text{m}$) fraction. There are undoubtedly particles and colloids (to which Hg can bind) smaller than the $0.45 \mu\text{m}$ filter size we have used, so the filtered samples do not represent a truly dissolved fraction. Total organic carbon (TOC) and total suspended solids (TSS) were also determined for both raw and filtered water from each sample.

We collected profiles at meter intervals for the following limnological parameters that may influence Hg methylation: dissolved oxygen, conductivity, temperature, pH, and redox potential (using a HydrolabTM) as well as bottom depth and Secchi depth.

All sediment and water samples were sent to contract analytical laboratories for analysis. All water filtration was conducted at the contract lab upon arrival (within 24–48 hrs of collection). Sediment grain size was analyzed (by Weyerhaeuser Analytical, Seattle, WA) using EPA method D 422-63. Organic carbon was analyzed (by Chem-Tech Consulting, Englewood, NJ) in water using EPA Method 415.1 (combustion) and in lake sediment by modified SW-846 Method 9060A utilizing a TOC analyzer. TSS (analyzed by Century Testing, Bend, OR) was determined gravimetrically, dried at 103–105 °C. Total Hg in lake sediments was analyzed (by Wadsworth/Alert Labs, North Canton, OH) using standard cold vapor atomic absorption (CVAA) methodology. Total Hg in water was analyzed (by Brooks Rand Ltd., Seattle, WA) using dual amalgamation/cold vapor atomic fluorescence spectrometry (Bloom and Crecelius, 1987). Methyl Hg in water and sediment samples was analyzed (by Brooks Rand Ltd., Seattle, WA) using aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection (Bloom, 1989). Both field and laboratory blanks were used throughout the study. Minimum detection limits for Hg were: sediments (total Hg = $100 \mu\text{g kg}^{-1}$; methyl Hg = $0.16 \mu\text{g kg}^{-1}$), water (total Hg = 0.47 ng L^{-1} ; methyl Hg = 0.008 ng L^{-1}).

Exploratory plotting and regression modeling were accomplished using JMP (SAS Institute, Inc.). Variables not normally distributed were transformed using either a \log_{10} transformation for normal variables (used for all total Hg values), or a logit (logistic) transformation for proportions (used for all ratio values).

Partition coefficients (K_d 's) are a measure of the relative binding of aqueous Hg to suspended particulates at the different sites. Particulate-specific partition coefficients were calculated using Hg concentrations in deep (near bottom) water associated with Hg in particulate material within that water column. These standard proportions were calculated as the ratio of (ng kg^{-1} Hg in particulates): (ng L^{-1} Hg in filtered water).

3. Results

3.1. SEDIMENTS

Typical Clear Lake surficial sediments are dark brown to dark gray or black muds, with a soft, flocculent texture, a water content of 80–90%, and a dry organic matter content of ca. 10–20% at the sediment/water interface. Clear Lake is a highly eutrophic lake dominated by extensive cyanobacterial blooms each summer, which contribute significantly to organic loading. Sediments were dominated at most stations by clay and silt sized particles; however, the stations nearest the mine (O-1 through O-6; grain size range = 0.96–1.40), at L-8 (mean grain size = 1.91), and the beach samples (grain size estimated at 2) were quite gravelly. In both the Oaks Arm and the Lower Arm clay proportions increased and sand proportions declined at stations nearer the Narrows. The grain size distribution of surficial sediments exhibited a gradual exponential decline ($P < 0.001$) with distance from the mine in the Oaks and Upper Arm, but exhibited an opposing trend at Lower Arm stations (Figure 3A).

Sediment TOC levels were quite high throughout Clear Lake, varying from ca. 24,900–610,000 mg kg⁻¹ (=2.5 to 61%), but showed no clear distributional differences other than a general increase in the deeper central regions of each arm (Figure 3B). The outlier datum at Station L-7 (double the next highest datum) remains unexplained. Neither clay nor silt percentages correlated with TOC, but sand percentage yielded a negative relationship. Grain size correlates weakly with depth unless coarse beach samples are included.

Total Hg concentrations in sediment ranged from a high of 183 mg kg⁻¹ (dry weight) near the mine to ca. 1 mg kg⁻¹ at sites furthest from the mine (Figure 3C, points above dashed line), calculated as distance by shortest water route. Individual data points plotted in Figure 3 are mean values of two replicate samples. On average, inter-replicate variability for total Hg was about 25% in the Oaks Arm, about 21% in the Upper Arm and 14% in the Lower Arm. Methyl Hg levels declined from 15.9 µg kg⁻¹ (Station O-6) to below detection (Station L-8) (Figure 3C), points below dashed line). Methyl:total Hg ratios varied from ca. 0.0001–0.003 (= 0.01–0.3%).

Total and methyl Hg in surficial sediments exhibited clear exponential declines as a function of distance from the mine ($P < 0.001$, Figure 3C), although several Lower and Upper Arm stations yielded methyl Hg concentrations somewhat higher than expected for the fitted curve for the data set. Because methyl Hg concentrations did not decline as steeply as total Hg concentrations, the ratio of methyl:total Hg (using a simple linear regression model) increased exponentially ($P < 0.001$) with distance from the mine (Figure 3D). This last trend is strongly significant in spite of a unimodal relationship with distance evident in the Lower Arm stations.

Using a multiple regression model, total Hg was significantly influenced by distance from the mine ($P < 0.001$) and bottom water D.O. ($P < 0.01$), confirming the trend evident in Figure 3C (Table I). Methyl Hg concentration is slightly more

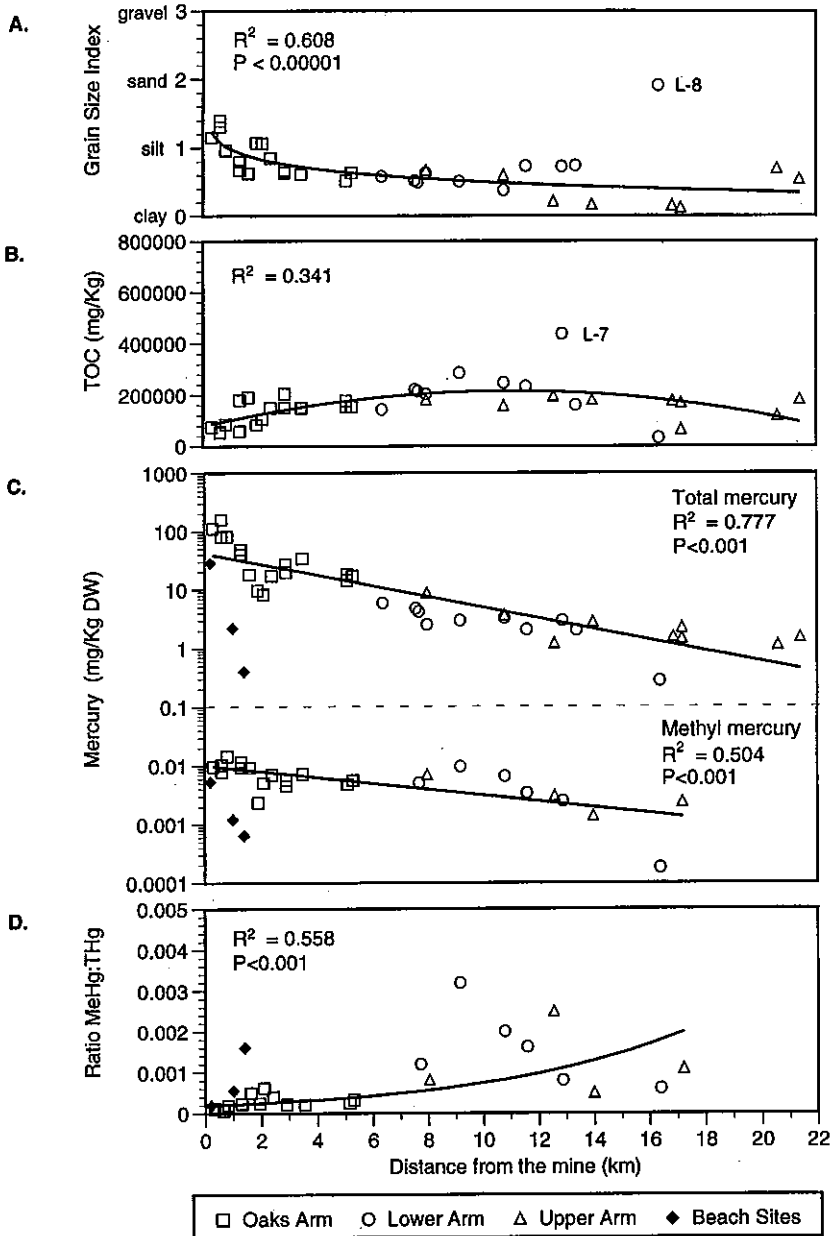


Figure 3. Mean surficial sediment values for (A) grain size index, (B) total organic carbon, (C) total Hg and methyl Hg, [Note log scale -- the dashed line separates data points for total Hg from those for methyl Hg], and (D) the ratio of methyl Hg to total Hg plotted as a function of distance from the mine. All plots are shown with 'best fit' curves, which were exponential curves fits for all, except for the TOC Data which were fit best by a second degree polynomial. Curve fits do not include beach sites. R^2 values are shown.

strongly correlated with sediment total Hg at the same site ($P < 0.001$; Table D) than with distance, and no multiple models improved the fits. The ratio of methyl:total Hg was most strongly related to distance from the mine ($P < 0.001$). When distance was removed as an independent variable (to ascertain whether any other variables might be influential in determining the ratio) grain size proved to be the only variable that showed a significant ($P < 0.01$) relationship to the ratio (Table I). Thus, the relatively low methyl:inorganic ratio in the eastern part of the Lower Arm may be due to coarse sediments supporting little methylation or retaining little methyl Hg. Using either simple or multiple regression, none of the limnological parameters tested (temperature, pH, D.O., redox potential, conductivity) were significantly related to the ratio at the $P < 0.05$ level.

3.2. WATER

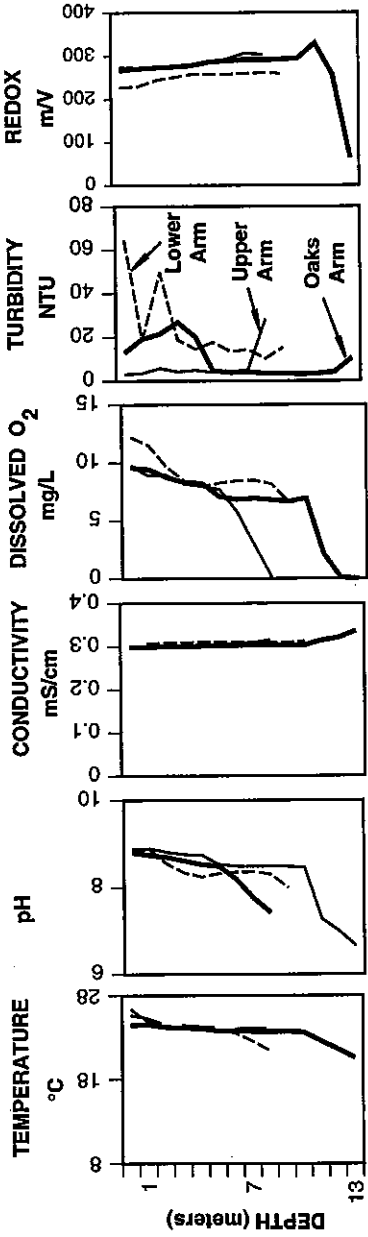
Limnological conditions for typical summer (July) and winter (January) conditions within each of the three basins are represented in Figure 4. These data were selected from a more extensive limnological database and are intended to represent the extent of seasonal variability and stratification during the two extreme periods of the year.

Neither organic carbon in raw or filtered water, nor TSS in raw water, exhibited differences between surface and deep samples or any trend with distance from the mine. Most TOC levels in raw water samples were in the range of 30–50 mg L⁻¹, with some as low as 6 to 8 mg L⁻¹. Filtered water samples were considerably lower in TOC, with values consistently in the range of ca. 6 to 20 mg L⁻¹. TSS exhibited a similar distribution that ranged from ca. 5 to 20 mg L⁻¹. Unlike previous investigators (Allan, 1986; Chamberlin *et al.*, 1990) we have never observed a nepheloid layer or sediment blanket above the normal sediment-water interface. Our work coincided with years of unusually low cyanobacterial biomass, and hence of relatively low delivery of organic matter to the sediments (Richerson *et al.*, 1994), which could be linked to production of methyl Hg.

Total Hg in raw surface and deep water exhibited an exponential decline away from the mine, with values as high as ca. 16 ng L⁻¹ for surface water and ca. 70 ng L⁻¹ for deep water close to the mine (Figure 5). Filtered samples for both surface and deep water yielded considerably lower values (as high as ca. 6–7 ng L⁻¹ for both) which is comparable to the limited data collected earlier by Gill and Bruland (1990) for Clear Lake filtered surface water during April 1987 (which yielded values of ca. 4 to 12 ng L⁻¹). Other filtered surface water samples collected by Gill and Bruland (1990) during February 1987 indicated much higher concentrations (14–104 ng L⁻¹), which may be a function of the relative mixing of bottom water higher into the water column during a more stormy season. During our study, however, we were not able to test water concentrations as a function of season.

In unfiltered water samples, total Hg (almost entirely inorganic Hg) in both surface and deep water ranged from ca. 5–70 ng L⁻¹. Other than the surface sample from the Narrows active spring site, which had anomalously high Hg levels, deep

Summer Limnological Data



Winter Limnological Data

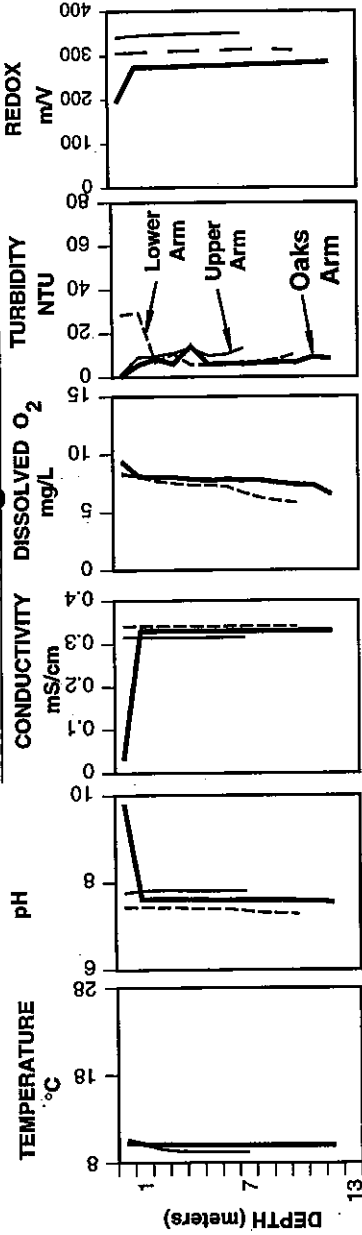
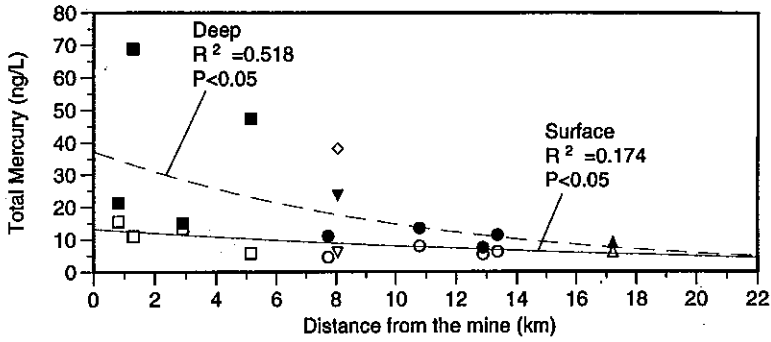
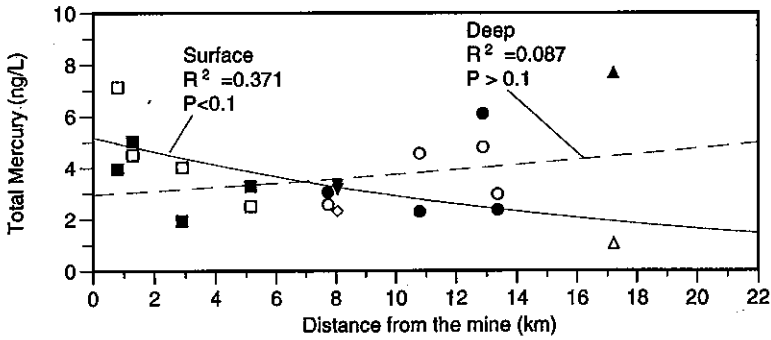


Figure 4. Typical summer and winter limnological conditions at Clear Lake. The dashed line represents data from the Lower Arm; the thin line represents data from the Upper Arm; the bold line represents data from the Oaks Arm.

A. Raw water



B. Filtered water



C. Particulate fraction (raw water minus filtered water)

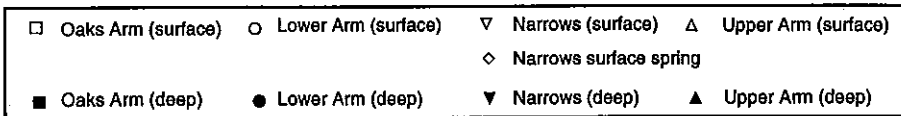
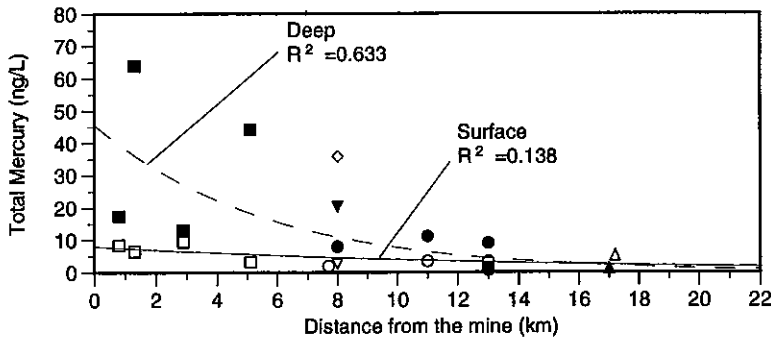


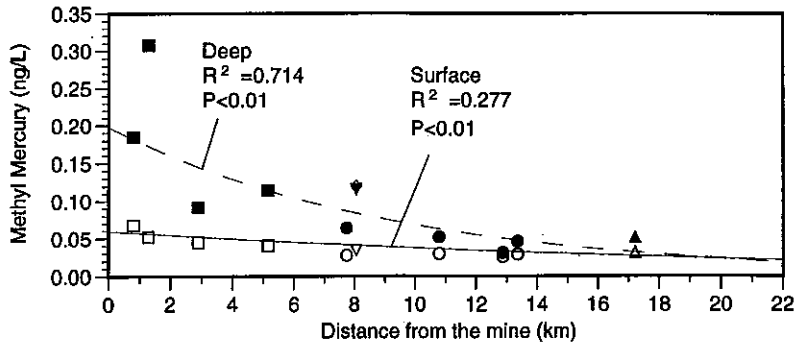
Figure 5. Total Hg in: (A) raw water; (B) filtered water; (C) the particulate fraction (raw minus filtered water). Curve fit for each data set is exponential. Note different scales on A and B.

unfiltered water samples had much higher levels of inorganic Hg and methyl Hg than either unfiltered surface samples or any filtered samples (surface or deep). Hg concentrations from filtered water samples were about an order of magnitude lower than from raw water samples. Filtering removed the clear distinction between surface and deep water samples and brought the values for the Narrows active spring site (anomalously high in raw water Hg) in line with other filtered water samples (Figure 5A and 5B), indicating substantial resuspension of Hg-laden particles to the surface waters at this site due to upwelling of water and gases (see Figure 5C). Total Hg in the particulate fraction (especially for deep particles) declined exponentially as a function of distance from the mine, corresponding to the same trend as sediments (Figure 5C). The particulate fraction contained about 33-94% of the inorganic Hg and about 25-78% of the methyl Hg in the water column (Figures 5 and 6).

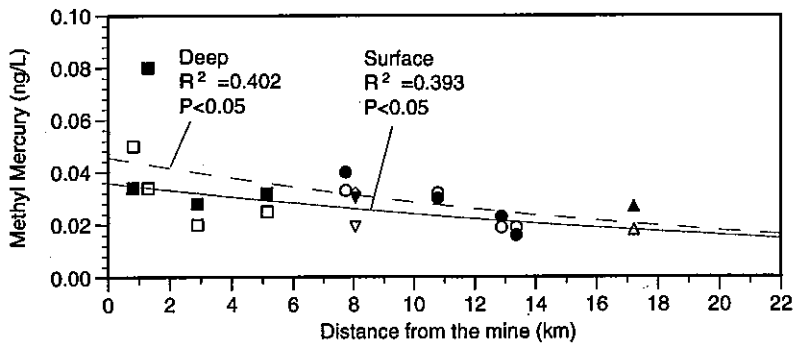
Filtered Hg concentrations in water exhibited more gradual declines as a function of distance from the mine than did those in sediments. Total Hg in both surface and deep raw water showed a statistically significant exponential decline ($P < 0.05$) away from the mine (Figure 5A). In contrast, total Hg in deep filtered water showed no decline with distance, and in surface filtered water only a weak decline ($0.05 < P < 0.10$, Figure 5B). Methyl Hg in raw water exhibited a trend similar to total Hg with higher levels and steeper decreases near the mine for deep water samples (0.31 ng L^{-1} at O-H), relatively lower levels (from $0.03\text{--}0.07 \text{ ng L}^{-1}$) in the surface samples, and a singular high level (0.12 ng L^{-1}) at the Narrows active spring site (Figure 6A).

Methyl Hg concentrations were higher in deep water samples than in surface samples in unfiltered water, but not in filtered water, indicating it is more significant loading on deep particles. Methyl Hg in unfiltered water (for both deep and surface samples) was highest close to the mine, yielding a significant ($P < 0.01$) negative relationship with distance from the mine (Figure 6A). However, unlike total Hg, methyl Hg in all filtered water samples showed a gradual, but statistically significant, decline ($P < 0.05$) as a function of distance from the mine (Figure 6B). Particles in deep water (compared with shallow water) also showed higher concentrations of methyl Hg and exhibited an exponential decline away from the mine (Figure 6C). Nevertheless, the trend in the methyl:total Hg ratio (for both raw and filtered water) as a function of distance from the mine (Figure 7A and 7B) was not significant. Methyl:inorganic Hg ratios in unfiltered water ranged from ca. 0.002 to 0.009 (0.2-0.9%), whereas filtered water values were roughly twice as high and more variable, ranging from ca. 0.004 to 0.016 (0.4-1.6%). Note that both ratios indicate methyl Hg is much higher (relative to inorganic Hg) in water as compared to sediments near the mine. The ratio of methyl:total Hg in water (ca. 10^{-3} to 10^{-2}) is relatively consistent with published ratios from most other highly Hg contaminated sites (e.g. Jackson *et al.*, 1982; Bloom, 1989; Gustin *et al.*, 1994). The methyl:inorganic ratio for sediments (and for particles) increases away from the mine, but is virtually constant in water (compare Figure 3D with Figure 7C).

A. Raw water



B. Filtered water



C. Particulate fraction (raw water minus filtered water)

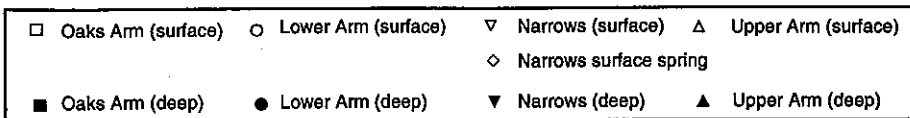
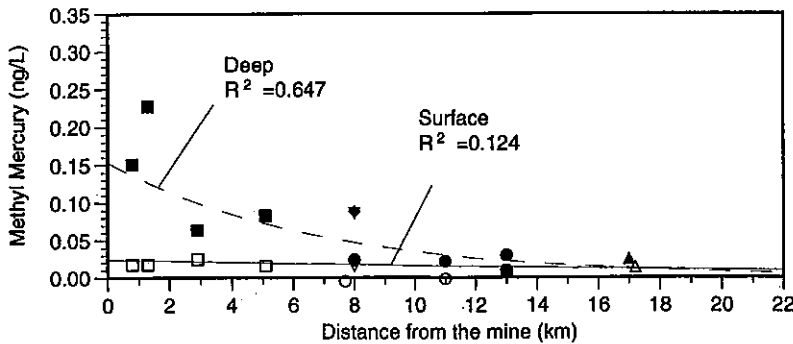
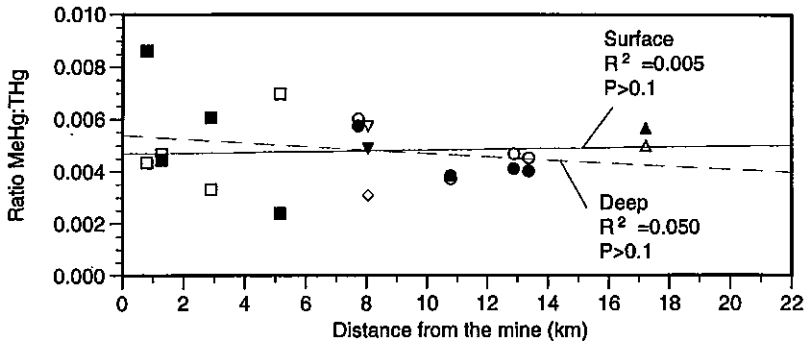
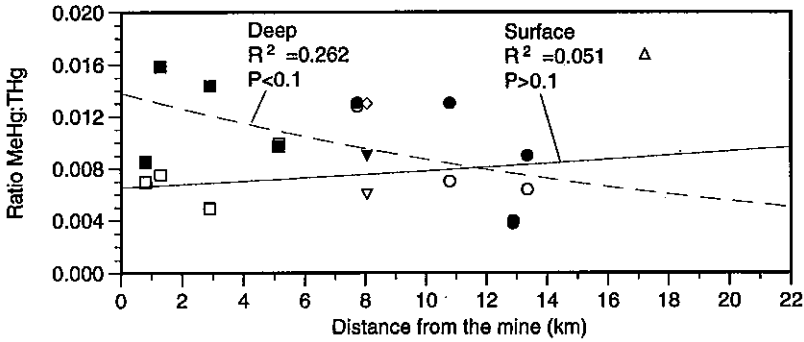


Figure 6. Methyl Hg in: (A) raw water; (B) filtered water; (C) the particulate fraction (raw minus filtered water). Curve fit for each data set is exponential. Note different scales on A and B.

A. Raw water



B. Filtered water



C. Particulate fraction (raw water minus filtered water)

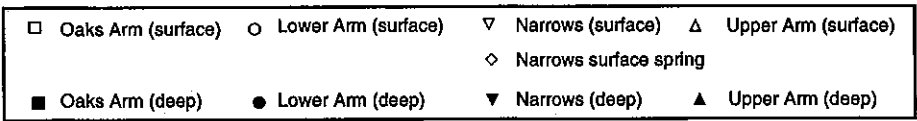
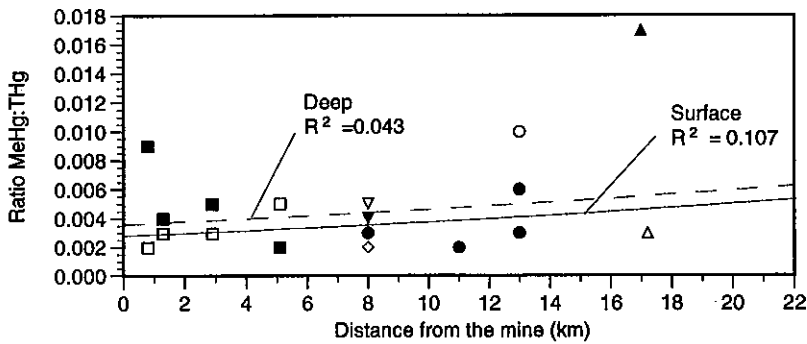


Figure 7. Ratio of methyl Hg to total Hg in: (A) raw water; (B) filtered water; (C) the particulate fraction (raw minus filtered water). Curve fit for each data set is exponential. Note different scales on A and B.

These observations suggest greater down-gradient transport of methyl Hg in the water column (see Discussion).

Several pairwise regression of water column Hg species on sediment concentrations of total and methyl Hg and other variables are also significant, but given the colinearity of distance and sediment concentrations, the additional variation explained by combinations of variables in multiple regressions is small and insignificant (Table I).

3.3. MERCURY PARTITIONING

Aqueous Hg data were also analyzed with respect to their partitioning relationship, or K_d , between suspended particulate matter and the 'dissolved' (= filtered < 0.45 μm) phase. K_d relationships for both aqueous total Hg and aqueous methyl Hg are provided in Figure 8. In general, partition coefficients for total Hg and methyl Hg in deep (near bottom) waters exhibited a significant decline with distance from the mine, and were of comparable magnitudes for both (10^5 - 10^6). Surface waters did not exhibit this same trend, yet exhibited consistently lower K_d s, about an order of magnitude lower than those for deep waters.

4. Discussion and Conclusions

4.1. SEDIMENTS

The concentrations of total Hg in surficial sediments found in this study are consistent with historical data collected at Clear Lake (summarized in CVRWQCB, 1987). However, the distribution of total Hg in the Oaks Arm is very patchy, indicating that pockets with comparable historical levels would likely have been found with more intense sampling (subsequent sediment sampling in this region in the Oaks Arm during 1994 and 1995 has yielded values in excess of 300 mg kg^{-1} near the mine; unpublished data). And, preliminary data from one core taken in the Oaks Arm near the mine indicate elevated levels of inorganic Hg (near 100 mg kg^{-1}) likely associated with increased episodes of Hg mining, but these samples have not been accurately dated.

Table II presents a comparison of data from our study with sediment and water data from a variety of contaminated and uncontaminated sites worldwide. Total Hg concentrations in Clear Lake sediments are high but fairly typical of highly contaminated sites found in the vicinity of Hg recovery plants (e.g. Johnston *et al.*, 1991) and gold mining sites (e.g. Gustin *et al.*, 1994; Wayne *et al.*, 1995), but considerably lower than levels (ca. 10,000 mg kg^{-1}) found at a former chlor-alkali plant (e.g. Berman and Barths, 1986). At 2-15 $\mu\text{g kg}^{-1}$, our sediment methyl Hg concentrations were considerably lower than have been reported from other Hg contaminated sites, which range from ca. 50-2,700 $\mu\text{g kg}^{-1}$ (e.g. Berman and Bartha, 1986; Johnston *et al.*, 1991). The ratio of methyl:total Hg for Clear Lake

Table II
Comparison of Clear Lake data with studies of other contaminated and non-contaminated systems. '-' indicates no data available

Matrix	Location	Source of Hg	Range of total Hg (mg kg ⁻¹)	Range of methyl Hg (μg kg ⁻¹)	Ratio methyl:Total Hg	Methyl Hg as a percentage of Total Hg	References
sediment	Clear Lake, CA, U.S.A.	Hg mine	0.5-83	0.2-15	0.7-32 E-04	0.007-0.32	this study
sediment	Wisconsin, U.S.A.	pristine seepage lakes	0.001-0.14	0.00001-0.01	1.6-7.9 E-02	1.6-7.9	Gilmour and Riedel, 1995
sediment	Onondaga Lake, NY, U.S.A.	chloralkali & sewage plant	1.08-49.5	3.7-10.6	0.2-4.5 E-03	0.02-0.45	Henry <i>et al.</i> , 1995
sediment	Finland	stratified forest lakes	134-277	<0.3-8	<0.1-5.97 E-02	<0.1-5.97	Verta and Matilainen, 1995
sediment	Carson River basin, U.S.A.	gold mining	0.1-1,610	-	-	-	Gustin <i>et al.</i> , 1994
sediment	Sweden	remote lakes	0.013-0.3	-	-	-	Parkman and Meili, 1993
sediment	Brazil	gold mining	0.01-19.8	-	-	-	Pfeiffer <i>et al.</i> , 1993
sediment	Wisconsin, U.S.A.	seven seepage lakes	nd-0.27	-	-	-	Rada <i>et al.</i> , 1993
sediment	U.S. & Can. lakes and res.	varied	0.2-0.9	0.007-0.055	0.875-30 E-05	0.0009-0.03	Gilmour and Henry, 1991
sediment	Germany	chlor-alkali plant	2-59	50-2,700	2.5-9.6 E-02	2.5-9.6	Wilkin and Hintelman, 1991
sediment	New Jersey, U.S.A.	chlor-alkaline plant	10,000	10-209	1.0-20.9 E-06	0.0001-0.0021	Berman and Bertha, 1986
sediment	Wabigoon River, Can	wood treatment plant	1.5-3	5.3-11	3.0-7.33 E-03	0.3-0.73	Jackson and Woychuck, 1980
raw water	Clear Lake, CA, U.S.A.	Hg mine	(ng L ⁻¹) 5-700	(ng L ⁻¹) 0.03-0.30	0.4-6 E-02	4-6	this study
raw water	NW Ontario, Can	wetland: prior to flooding	-	0.05-0.28	-	-	Rudd, 1995
raw water	NW Ontario, Can	wetland: after flooding	-	2.3	-	-	Rudd, 1995
raw water	Strait of Gibraltar	varied	-	0.003-0.078	-	-	Cossa <i>et al.</i> , 1994a
raw water	Carson River basin, U.S.A.	mining	10-354	0.4-22	1.06-6.23 E-02	1.1-6.2	Gustin <i>et al.</i> , 1994
raw water	Wisconsin, U.S.A.	seven seepage lakes	0.7-2.1	0.05-0.33	6-19 E-02	6-19	Warras <i>et al.</i> , 1994
raw water	Clear Lake, CA, U.S.A.	mining	3.6-104	-	-	-	Gill and Bruland, 1990
raw water	other CA lakes U.S.A.	varied	0.5-8.8	-	-	-	Gill and Bruland, 1990
raw water	Sweden	three remote lakes	-	0.12-0.41	-	-	Lee and Hultberg, 1990
raw water	Wabigoon, River, Can	wood treatment plant	3-26.5	0.18-1.4	1.58-7.88 E-02	1.6-7.9	Parks and Hamilton, 1987
filtered water	Clear Lake, CA, U.S.A.	Hg mine	2-8	0.02-0.08	4-16 E-03	0.4-1.6	this study
filtered water	Finland	stratified forest lakes	-	0.58-1.20	-	-	Verta and Matilainen, 1995
filtered water	Strait of Dover	natural	0.12-1.34	-	-	-	Cossa <i>et al.</i> , 1994b
filtered water	Clear Lake, CA, U.S.A.	mining	1.1-1.5	-	-	-	Gill and Bruland, 1990
filtered water	other CA lakes, U.S.A.	varied	0.4-3.4	-	-	-	Gill and Bruland, 1990

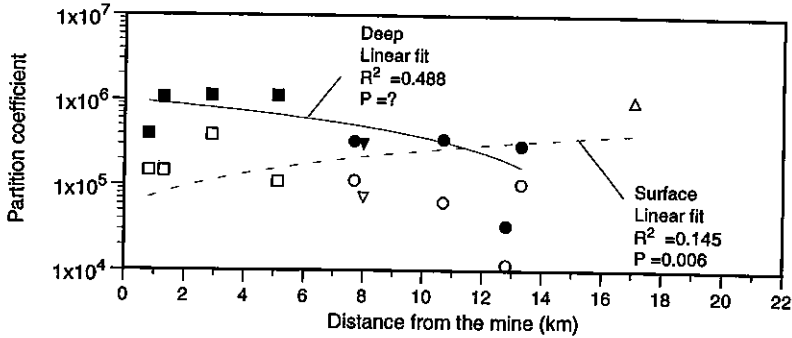
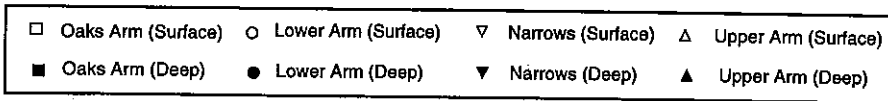
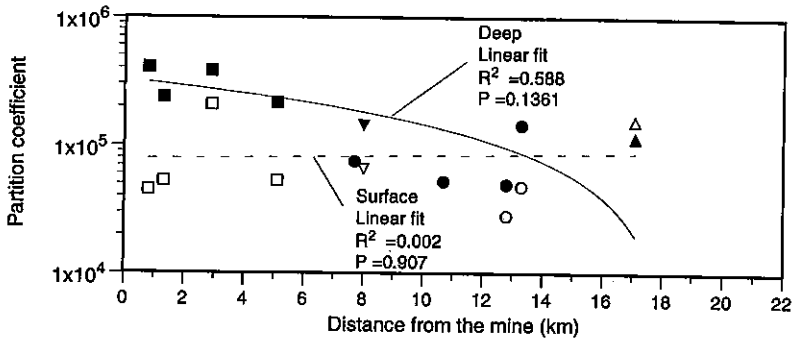
A. Total mercury**B. Methyl mercury**

Figure 8. Partition coefficients (ratio of Hg in suspended particles to aqueous Hg) for total and methyl Hg in water. All curves are linear fits.

sediments was ca. 10^{-4} to 10^{-3} . Since other reported values for this ratio range from 10^{-6} to 10^{-2} for a variety of contaminated and uncontaminated sites (e.g. Berman and Bertha, 1986; Gilmour and Henry, 1991; Wilkin and Hintelman, 1991) it is difficult to make a meaningful comparison of this ratio with previous studies other than to note that our results do not exhibit any unusual trends with respect to this ratio. However, it should be noted that the exceptionally low ratio values found at the extremely contaminated chlor-alkali site (Berman and Bartha, 1986) were associated with sediments high in sulfides.

Contaminant levels typically decline exponentially with distance from a point source, with the gradient's steepness determined by the contaminant's mobility. The striking exponential decline of sediment total Hg with distance from the mine, and the results from multiple regressions, strongly indicate that the overwhelmingly

significant source of total Hg (< 99% inorganic Hg) in Clear Lake sediments is the mine. Methyl Hg in sediments, exhibiting a more gradual decline with distance than does total Hg (1) may not be dependent upon the mine's point source of total Hg, (2) may be related to an additional point or non-point source away from the mine, and (3) appears more mobile than total Hg.

The trends in sediment methyl Hg distribution and the increase in methyl:total Hg ratio as a function of distance from the mine may be due to: (1) increasing bioavailability (to methylating bacteria) of inorganic Hg as a function of distance from the mine, (2) increased activity by methylating bacteria, producing higher net methylation at sites distant from the mine, (3) a threshold phenomenon for a Michaelis-Menton or similar functional relationship of methylation relative to total Hg concentrations, and/or (4) increased or preferential transport of methyl Hg-complexed particles away from their source at the mine. Increased bioavailability or microbe activity at sites distant from the mine may also be related to an excess of either inorganic Hg or sulfides or other competing metals near the mine site. Studies currently underway will help to evaluate the first three alternatives. The likelihood of alternative (4) depends upon whether smaller, highly mobile particles tend to have high methyl:total Hg ratios. Our ongoing field observations (Lynch, 1996) and a particle transport model of Clear Lake circulation (A. Bale, unpublished data) both indicate that a significant bottom current runs from the Oaks Arm to the Upper Arm, counterbalancing the typical NW wind-driven surface currents, which will presumably carry fine particles via a deep water pathway toward the Upper Arm. The grain size distribution of the Oaks Arm is consistent with the predictions of the model, with larger grain sizes near the mine, smaller ones near the Narrows, and mostly fines in the Upper Arm. Clay, however, which forms the smallest particles, has also been reported to inhibit methylation by binding with inorganic Hg, making it unavailable for methylation (Rudd *et al.*, 1983). This could result in lower methyl:total Hg ratios in the smallest, most mobile particles (i.e. those sediments rich in clay), making alternative (4) less likely, although methyl Hg could later migrate to fine particles.

Resuspension of sediment, rather than actual Hg release from sediment, also explains the anomalously high concentrations of total and methyl Hg in raw water samples at the Narrows active spring site. Upwelling of gases and water at subsurface spring sites like the Narrows entrains sediments into the water column, contaminating the water column above the site. If the spring at the Narrows represented a separate source of soluble Hg, filtered water samples as well as sediment samples should also show elevated Hg levels. Since (1) filtration removed the sediment contamination and (2) comparison with nearby sites fit the exponential decline as well as others, the high Hg levels at the Narrows spring site are probably not due to Hg emission, but to resuspension into the water column of Hg-associated sediment particles that had originated from the mine.

4.2. WATER

Although Gustin *et al.* (1994) reported exceptionally high values of total Hg (up to 35,400 ng L⁻¹) in water from the Carson River Superfund Site (Nevada), other studies (e.g. Parks *et al.*, 1986; Bloom, 1989 and Gustin *et al.*, 1994) show that total Hg levels in Clear Lake waters are roughly comparable to the levels observed at most other contaminated sites.

The greater concentrations of Hg found in raw as compared with filtered samples indicate that most total and methyl Hg in the water column was associated with particulates. This association also explains the higher total Hg levels in deep raw (as compared to filtered) water samples. Since deeper water samples were collected closer to the sediments, which are a rich source of relatively contaminated particles, they contained high levels of Hg-associated sediment particles. These particles can then be transported by wind-generated currents to sites distant from the source.

The low concentrations of aqueous Hg in the < 0.45 μm filtered fraction likely reflect the strong affinity of Hg for larger particles as illustrated by its high K_d (10^4 – 10^5 for methyl Hg and 10^5 – 10^7 for total Hg), especially at sites close to the mine. As most Hg in the water column was associated with particles large enough to be filtered, processes affecting particle transport are presumably of great importance in overall methyl:inorganic Hg dynamics in sediments and water.

Total and methyl Hg levels in water appear to depend primarily upon Hg concentrations in sediments and limnological characteristics affecting Hg transfer, making the mine an indirect point source of Hg to water as well. The less extreme spatial gradient of Hg in water (relative to sediments) indicates that wind-driven currents, waves and possibly springs and other processes resuspend sediment particles, resulting in down-gradient transport. From a mass balance perspective, our current and dye studies (Lynch, 1996) and preliminary calculations indicate that reintrained particle transport originating from the Oaks Arm near the mine can account for the transport of methyl and inorganic Hg and resulting concentrations in sediments of the Upper Arm.

The collection of data for this study in the late summer and early fall may have skewed the results toward lower aqueous Hg levels. Clear Lake's dry, relatively storm-free summers likely minimize sediment resuspension, lowering Hg levels in water and inhibiting transport of Hg-laden particles down-gradient. Moreover, the fall 1992 sample period was initiated during the sixth year of drought conditions in California, when the previous several winters had produced well-below average storm activity and associated rains. Hence, it is possible that these results may not necessarily be typical of Clear Lake within an annual cycle or among years. However, factors lowering aqueous total Hg may have been counteracted to some degree by seasonal changes in methylation. Several studies have found seasonal variations in Hg concentrations and methylation rates, with higher methyl Hg levels found in late summer and declining rapidly in fall (e.g. Korthals and Winfrey, 1987).

In comparison with other sites worldwide (Table II), it is noteworthy that methyl

Hg in raw water from Clear Lake is roughly comparable to other contaminated and non-contaminated sites worldwide. For methyl Hg in filtered water ('dissolved' component), few published studies provide these values, but Clear Lake waters contaminated from the mine appear to be 1–2 orders of magnitude lower than those reported from relatively pristine stratified lakes in Finland (Verta and Matilainen, 1995).

4.3. MERCURY PARTITIONING

Partition coefficients are a measure of the relative binding of aqueous Hg to suspended particulates at each site. The K_d data do not indicate what types of particulates or what binding mechanisms are involved, and it is likely that the relationships for methyl Hg are dominated by different mechanisms than those for the more prevalent Hg(II), which constitutes the bulk of the total Hg. However, the K_d data from this preliminary study provide general information on the relative importance of particulate binding of Hg, both between and among sites, and suggest potential areas for future investigation.

The aqueous Hg partitioning values for total Hg in Clear Lake (ca. 10^6 – 10^7) are one to three orders of magnitude higher than those presented in summertime studies of contaminated Canadian lakes (3.9×10^3 to 9.3×10^5 ; Jackson *et al.*, 1982; Parks *et al.*, 1986). Methyl Hg K_d 's (all ca. 10^5) are similar to K_d 's in samples collected in early summer (2.2×10^6 ; Jackson *et al.*, 1982; Verta and Matilainen, 1995). Data from Jackson *et al.* (1982) show that total Hg K_d 's declined an order of magnitude and methyl Hg K_d 's dropped below detection from May to September, making the high levels in our late September samples more remarkable. While differences in climate between their study sites and Clear Lake probably account for much of the difference in September K_d , it is reasonable to believe that K_d 's may have been even higher had we sampled in early summer.

The high K_d 's indicate that total Hg and, to a lesser extent, methyl Hg have a stronger affinity to particulate matter in Clear Lake than in other studied systems. As a result, the filtered fraction of water contains relatively little of the Hg in the water column. This is consistent with the sediment data, which indicate that the bulk of the Hg in Clear Lake is bound in particulate form. Neither the spatial trend nor the high autumn level in K_d can be attributed to variation in the concentration of total suspended solids, which showed no significant relationship to either distance from the mine or Hg K_d values. It is possible, however, that the composition of the aqueous particulates was different between surface and bottom water, as algal blooms in surface water significantly affect surface water TOC and TSS. As with sediment, Hg-binding in particulates may be determined by sulfate, Fe oxides, or Mn oxides, possibilities being examined in ongoing studies.

4.4. METHYL MERCURY PRODUCTION/TRANSPORT

One of the most interesting questions raised by Hg contaminated sites like Clear

Lake is how methyl Hg is produced and/or potentially transported away from the source of inorganic Hg contamination (in this case the mine). At Clear Lake, some species of fish regularly have concentrations of methyl Hg in their muscle tissue in excess of 1 mg kg^{-1} . Human consumers and fish eating birds are exposed to levels of methyl Hg that cause concern. The objective of the EPA Superfund project at Clear Lake is to determine whether there are ways to reduce the methyl Hg concentration in fish to levels half or less than currently measured, possibly by sediment capping or some other means. The relationship between production and transport is critical to this determination.

At Clear Lake there has clearly been some transport of inorganic Hg down-gradient away from the source of contamination, but the gradient of methyl Hg in sediment and water as a function of distance is much flatter than for inorganic Hg. This relationship could be due to (1) in-situ production of methyl Hg at sites distant from the source or (2) the production of methyl Hg as a more or less linear function of sediment inorganic concentrations near the source, with subsequent transport of methyl Hg to other parts of the lake. If the latter scenario is correct and if methyl Hg is lost or sequestered relatively rapidly (time scale of ca 1 year), then remediating a relatively small area of sediment (near the source) would eventually reduce fish body burdens of methyl Hg. Or, if the methylation process has some non-linear relationship to inorganic concentration, such as a saturating relationship with an asymptote at 5 or 10 mg kg^{-1} in sediments, then treating a much larger area of sediments would be necessary. Alternatively, methylation would be a complex process jointly controlled by inorganic Hg concentration and many other variables, such as sulfate and organic matter supply.

The data presented here suggest either (1) differential down-gradient transport of methyl Hg or (2) preferential production of methyl Hg at sites distant from the mine. The concentration of methyl Hg relative to inorganic Hg is much greater in the water column compared to sediments in the source region near the mine, and most of that exists in the particulate fraction. For much of the year, cyanobacterial 'algal' blooms represent the largest fraction of that water column biomass. In any event, either these biotic particles or other abiotic particles that are forced by wave/current movements, have the ability to differentially transport methyl Hg from areas near the mine to far distant regions such as the Upper Arm. In fact, recent observations of a white flocculent material originating from the Sulphur Bank Mercury Mine (derived from acid mine drainage) may provide the source material that is carried by wind-driven currents to sites distant from the mine. In terms of total mass in the region near the mine, the water column concentration of about 0.1 ng L^{-1} methyl Hg ($0.1 \text{ } \mu\text{g m}^{-3}$) is equivalent to about $1 \text{ } \mu\text{g m}^{-2}$ in a 10 m water column. Sediment concentrations of methyl Hg near the mine of around 1 ng g^{-1} in wet weight (surficial sediments are approximately 90% water by weight) yield an estimated 1 mg m^{-3} , or roughly $100 \text{ } \mu\text{g m}^{-2}$ in the top 10 cm of sediment exposed to bioturbation. The equivalent calculation for inorganic Hg is approximately 30 ng L^{-1} in the water column, equivalent to $300 \text{ } \mu\text{g m}^{-2}$

in the 10 m water column, versus 40 mg kg^{-1} in sediments or $4 \times 10^6 \mu\text{g m}^{-2}$ in the top 10 cm of sediment. The 100 fold larger fraction of the total stock of methyl Hg in the water column relative to inorganic mercury means that methyl Hg will be transported down gradient in the water column much more efficiently than inorganic Hg. This calculation is qualitatively in agreement with the rising ratio of methyl:inorganic Hg in sediments away from the mine. Methyl Hg can diffuse from sediments comparatively efficiently, is dispersed by water movements, and can re-enter the less contaminated sediments far from the mine. Core data from sites distant from the mine shown higher concentrations at the surface than at depth, indicating net loading at the surface and bioturbation downwards, whereas those near the mine appear to be approximately in equilibrium.

While extensive data do not exist on chlorophyll concentrations of phytoplankton with which to evaluate methyl Hg in different regions and seasons of Clear Lake as a function of primary productivity, there do exist data on the distribution of cyanobacterial blue-green 'algae' versus diatoms. Primarily because of prevailing NW winds, cyanobacterial bluegreens (mostly positively buoyant) become differentially transported by wind to the Oaks Arm and the Lower Arm, leaving a higher proportion of diatoms versus bluegreens in the Upper Arm (Richerson *et al.*, 1994). And, since zooplankton prefer diatoms (because bluegreens are large and of poor nutritional quality – Elser and Goldman, 1991), the trophic transfer of methyl Hg in the Upper Arm may be more efficient than in other arms of Clear Lake, yielding higher methyl:total Hg ratios in this region.

Nevertheless, data we present here are not sufficient to determine specifically what area of sediments is a net producer of methyl Hg. Quantitative data on methylation rates as a function of inorganic Hg, DOC, and SO_4 concentrations, demethylation rates, and a quantitative understanding of transport processes would be required to produce a quantitative estimate of the area of contaminated sediments responsible for any given fraction of the methyl Hg supply to the system. Efforts to combine existing models of Hg dynamics, literature values for processes, and our descriptive data have not yielded quantitative estimates which warrant high confidence (Bale, 1995). This state of affairs is undesirable for practical purposes. Ideally, accurate answers to the question of what area of sediments to remediate should be possible from a knowledge of the basic ecotoxicology of Hg combined with a relatively inexpensive characterization of a given site. Although much is known about Hg ecotoxicology, it is still not sufficient to translate even a relatively detailed characterization of a system, such as we conducted, into sound quantitative recommendations to regulators faced with challenging remediation tasks. The aim of future investigations should be to develop our knowledge of Hg ecotoxicology to the point that relatively simple studies are sufficient to guide remediation. This level of practical knowledge of process exists for such aquatic ecosystem stresses as excessive oxygen demand and eutrophication due to phosphorus loading (e.g. Sas, 1989; Cooke *et al.*, 1993), and should be the target for studies of Hg ecotoxicology.

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