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MERCURY IN ABIOTIC MATRICES OF CLEAR LAKE, CALIFORNIA: HUMAN HEALTH AND ECOTOXICOLOGICAL IMPLICATIONS

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Abstract. Mercury (Hg) from Hg mining at Clear Lake, California, USA, has contaminated water and sediments for over 130 years and has the potential to affect human and environmental health. With total mercury (TotHg) concentrations up to 438 mg/kg (dry mass) in surficial sediments and up to 399 ng/L in lake water, Clear Lake is one of the most Hg-contaminated lakes worldwide. Particulate Hg in surface water near the mine ranges from 10 000 to 64 000 ng/g; TotHg declines exponentially with distance from the Sulphur Bank Mercury Mine. From 1992 to 1998, no significant long-term trends for TotHg or methylmercury (MeHg) in sediments or water were observed, but peaks of both TotHg and MeHg occurred following a 1995 flooding event. Sediments and water exhibit summer/fall maxima and winter/spring minima for MeHg, but not TotHg. Sediment TotHg has not declined significantly a decade after remediation in 1992. At the mine site, aqueous TotHg reached 374 000 ng/L in unfiltered groundwater. Pore water sulfate in sediments varies seasonally from 112 mg/L in summer/fall (when Hg methylation is highest) to 3300 mg/L in winter. While TotHg is exceptionally high in both sediments and water, MeHg is substantially lower than would be expected based on the bulk Hg loading to the lake and in comparison with other sites worldwide.

Total mercury in Clear Lake water does not exceed the Safe Drinking Water Act criteria, but it sometimes greatly exceeds human health criteria established by the Great Lakes Initiative, U.S. Environmental Protection Agency water quality guidelines, and the California Toxics Rule criterion. Methylmercury concentrations exceed the Great Lakes Initiative criterion for MeHg in water at some sites only during summer/fall.

Relative to ecological health, Clear Lake sediments greatly exceed the National Oceanic and Atmospheric Administration's benthic fauna Sediment Quality Guidelines for toxic effects, as well as the more concensus-based Threshold Effects Concentration criteria. Based on these criteria, Hg-contaminated sediments and water from Clear Lake are predicted to have some lethal and sublethal effects on specific resident aquatic species. However, based on unique physical and chemical characteristics of the Clear Lake environment, MeHg toxicity may be significantly less than anticipated from the large inorganic Hg loading.

Key words: acid mine drainage; Clear Lake, California, USA; ecotoxicology; human health; mercury; methylmercury; mining; sediment quality criteria; Sulphur Bank Mercury Mine; water quality criteria.

Introduction

This evaluation of mercury (Hg) in the abiotic compartments of Clear Lake, California, USA, is one component of a larger ecosystem-level study that traces the origin and pathways of Hg from the ore body at an abandonded Hg mine through the abiotic (sediment and water) matrices to lower trophic level species (benthic invertebrates and plankton) and to higher trophic level species (e.g., fish, birds, and mammals). In addition to describing the spatial and temporal variability of Hg in the abiotic compartments of the ecosystem, this paper provides Hg data in sediments and water that are used in numerous other papers to elucidate the manner in which Hg is transformed, transported, bioaccumulated, and stored in this system.

Mercury has been identified as a significant threat to human and environmental health. Typically, Hg exists in very low concentrations in the environment, but in some regions, especially those altered by human activities (e.g., Hg, gold, and silver mining sites, chloralkali plants), it can occur at relatively high concentrations. Considerable research has focused on Hg contamination from atmospheric sources, but much less has addressed

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Hg sources from mining (Wiener and Suchanek 2008). Even in low concentrations in water or sediment, Hg can bioaccumulate through the food web to toxic levels in humans or wildlife. But at sites with high Hg concentrations, this risk may be even greater.

Because of nearly a century (1873–1957) of intermittent Hg mining along the shoreline of Clear Lake and subsequent erosion and intentional dumping of residual waste rock and tailings piles into the lake, with an estimated 100 Mg of Hg cycling through the aquatic ecosystem (Chamberlin et al. 1990), the abiotic matrices of this ecosystem contain some of the highest Hg concentrations of any lentic system reported to date (Suchanek et al. 2000*b*, 2003, 2008*e*). In addition to being one of the most popular bass-fishing sites in California, Clear Lake also serves as a drinking water source for the communities that surround the lake. Furthermore, the North Wetland region of the lake is used for cattle grazing and as a source of fish, tules, and other resources utilized by the Elem Pomo Indian Tribe.

Some have speculated that elevated Hg concentrations in Clear Lake have origins in the abundant geothermal springs emanating from the lake bed, with an insignificant contribution from anthropogenic mining activities (e.g., Varekamp and Waibel 1987). This hypothesis has its origins in deep (20–28 m) cores that exhibit some peaks of total Hg (TotHg) during prehistoric times (e.g., at ~3600, 7400, 9500, 18 000, and 34 000 years before present [ybp]) that likely originated from natural processes such as volcanic and/or tectonic events within the Clear Lake Basin (Sims and White 1981). Mercury plots from these deep cores and an analysis of historic and prehistoric Hg deposition into the lake are provided in Suchanek et al. (2008*d*), and Hg profiles of additional dated cores collected in 1996 and 2000 are given in Richerson et al. (2008). Although TotHg in water and sediment decreases exponentially as a function of distance from the mine and the highest Hg peaks in dated cores are found closest to the mine during time periods (calculated from ^{210}Pb dating) associated with extensive Hg mining (Richerson et al. 2008, Suchanek et al. 2008*d*), it is still important to evaluate whether geothermal springs contribute significantly to Hg loading within the lake.

Despite the overwhelming inventory of inorganic Hg in Clear Lake, the biological/ecological components of this system have considerably less methylmercury (MeHg) than might be expected based on the total inorganic Hg loading to the system (Suchanek et al. 2008*a*). Furthermore, despite the proportionately low MeHg concentrations in biota, the concentrations of Hg within the abiotic matrices often exceed wildlife toxicity thresholds and human sediment or water quality criteria (Suchanek et al. 2008*b*). Therefore, it is useful to describe the relationship between the spatial and temporal variability of Hg in the abiotic matrices of this system to better understand how Hg is distributed and bioaccumulated into the biological/ecological components and how that might affect human or environmental health. Because the mine site received substantial remediation by the U.S. Environmental Protection Agency (U.S. EPA) in 1992 (Suchanek et al. 2008*e*), it is also important to document whether there have been any significant trends in the Hg concentrations of abiotic matrices of the system in the years following that event. This study documents the distribution of Hg in sediments and water within the Clear Lake aquatic ecosystem over space and time primarily from 1992 to 1999.

Methods

Study site

This study was conducted at Clear Lake, California (39°3′ N, 122°49′ W), site of the abandoned Sulphur Bank Mercury Mine, a U.S. EPA Superfund Site since 1990. Suchanek et al. (2003, 2008*e*) provide historical information on Clear Lake in the context of a significant mining site within the California Coast Range Hg mining belt, which contains nearly 300 abandoned Hg mines and prospects (Churchill 2000), most of which are releasing various residual Hg compounds to the environment. Some of these products, along with other Hg compounds derived from the Sierra Nevada gold and silver mines, travel downstream and eventually reach the San Francisco Bay-Delta ecosystem, where an interdisciplinary effort is underway to address Hg contamination in that system (Wiener et al. 2003*a*, Domagalski et al. 2004, Alpers et al. 2005, Wiener and Suchanek 2008).

The bulk of the samples were collected from the three arms of Clear Lake from 1992 to 1998. Water and sediment were collected (1) during a single campaign in the fall (September/October) of 1992 designated as the preliminary lake survey (PLS), (2) from May 1994 through November 1996 at approximate intervals of six to eight weeks, and (3) thereafter through 1998 at approximate intervals of three to seven months. Sampling sites are shown in Fig. 1. Samples from the Oaks Arm site, where acid mine drainage (AMD) from the mine discharges into Clear Lake (at site OA-F [the floc site]; see Suchanek et al. 2000*a*, 2008*e*, Shipp and Zierenberg 2008), were collected from August 1996 to March 1998. Site location and relocation was accomplished using visual triangulation, Loran-C, and a global positioning system (GPS); the level of precision achieved for relocating sites was ~10–15 m.

Additional samples were collected occasionally from the mine site in: (1) Herman Pit and the Basalt Pit, remnants of open-pit mining on the site; (2) a series of test wells on the mine site installed by the U.S. EPA; and (3) the North Wetland (immediately north of the mine), which also receives AMD from the waste rock piles located between the wetland and the Herman Pit (see site locations in Fig. 2). A pile of waste rock from the mine had been dumped in the North Wetland during mining operations, and the concentrations of TotHg in

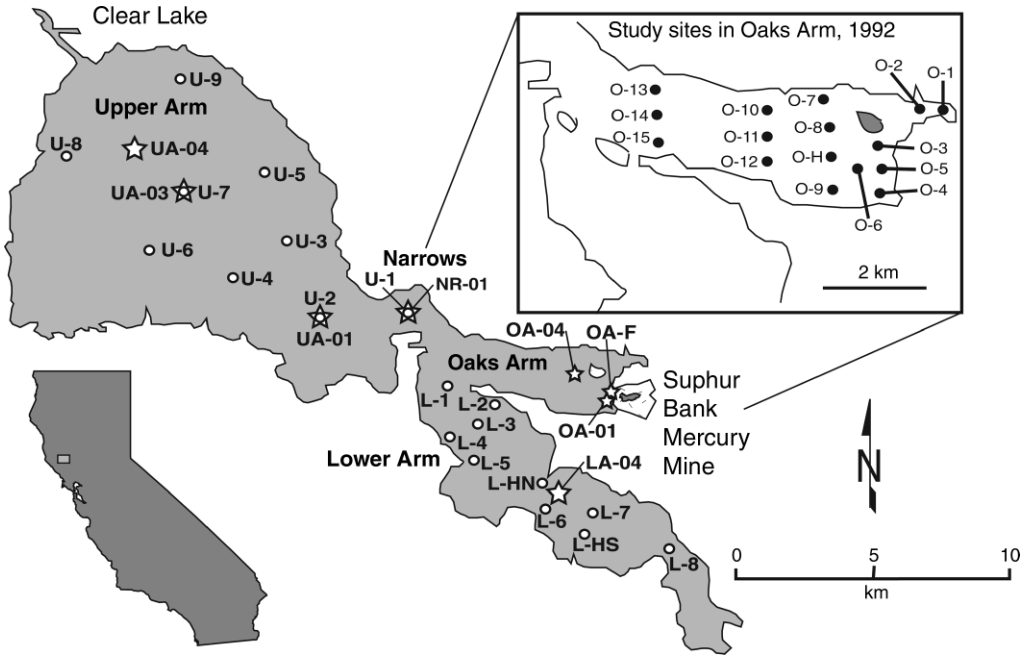

FIG. 1. Location of the Sulphur Bank Mercury Mine and Clear Lake collection sites in California, USA, for the preliminary lake survey (PLS) in fall 1992 (circles) and the long-term lake study (LLS) from 1994 to 1999 (stars). Note that some sites are identical in the two studies.

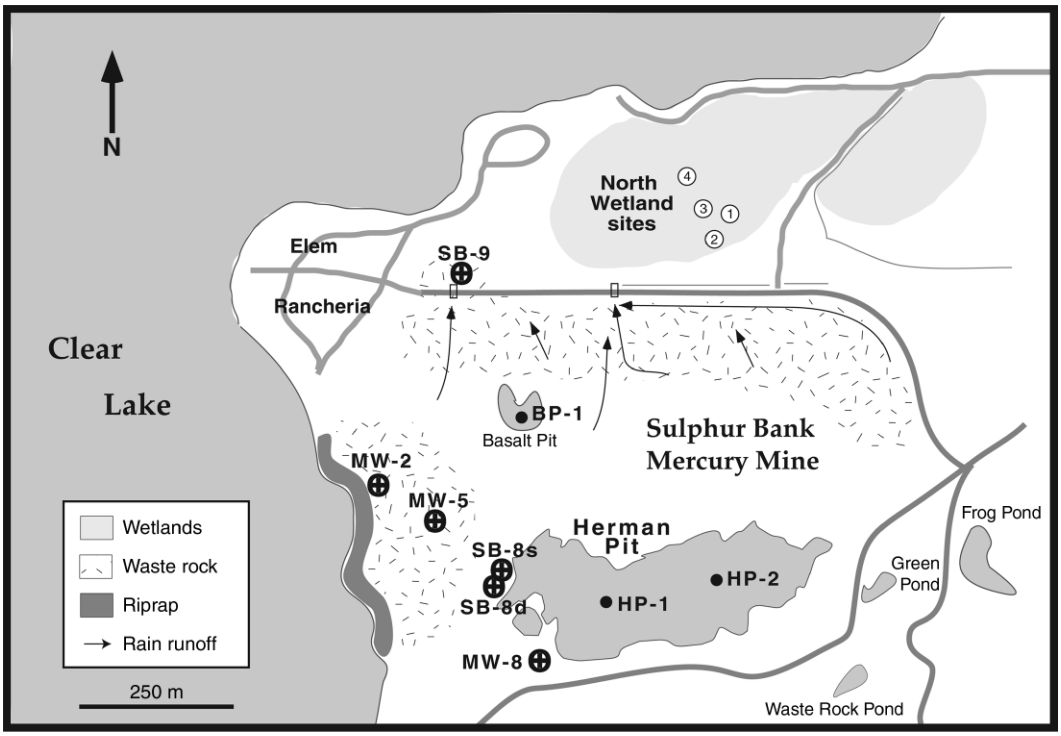

FIG. 2. Sampling sites in the Herman Pit (HP sites), Basalt Pit (BP), the monitoring wells (MW and SB sites), and the North Wetland (NW) region north of the Sulphur Bank Mercury Mine. Replicates (A and B) were collected at several NW sites.

that soil reached 1230 mg/kg, with an average of 850 mg/kg. This pile was partially excavated in 1992 and capped and revegetated, yet the North Wetland still receives AMD and remains a site of ongoing Hg contamination to the local environment.

Sediments

Sediments were collected from a 6.7 m long research vessel using a 15.24-cm Ekman dredge from which an aliquot of the top 1 cm of sediment was removed, homogenized, and placed into replicate borosilicate jars on ice. Samples for MeHg were analyzed on a wet-mass basis. Moisture percentage was determined for each sample at the time of analysis for dry-mass conversions. Samples for TotHg were dried to constant mass at 50°C (typically 24–48 h) and ground to a fine powder prior to analysis.

Sediment samples collected in 1992 were analyzed for TotHg at Wadsworth/Alert Laboratories (Research Triangle Park, North Carolina, USA), with subsequent analyses through 2002 performed by Battelle Marine Science Laboratory (Sequim, Washington, USA). Sediment collections in May 2003 were analyzed for TotHg by the UC Davis Environmental Mercury Laboratory (Davis, California, USA). All three laboratories utilized standard cold-vapor atomic absorption spectrophotometric technique based on U.S. EPA standard method 245.5.

The 1992 sediment samples were analyzed for MeHg by Brooks Rand (Seattle, Washington, USA), with analyses in later years performed by Battelle Marine Science Laboratory. Both laboratories analyzed sediment MeHg using aqueous distillation combined with the aqueous ethylation/cold-vapor atomic fluorescence spectroscopy methods of Bloom (1989). Samples were distilled by reacting an aliquot of sediment in water with sulfuric acid and potassium chloride, then heating the distiller to 125°C (Horvat et al. 1993) and collecting the distillate in a Teflon (Dupont, Wilmington, Delaware, USA) receiving vial.

Because of an identified artifact in the distillation method for analyzing MeHg in sediments that created spurious MeHg results (Liang et al. 1996, Bloom et al. 1997), original MeHg concentrations analyzed using the distillation method were corrected to reflect results obtained from an alternative method (extraction) that is believed to reduce or eliminate the artifact. Using the extraction method, an aliquot of sediment was reacted with acidic potassium bromide solution and copper sulfate and extracted into methylene chloride. The sample is allowed to react for an hour, then shaken vigorously for an hour to move all the MeHg into the methylene chloride phase. The methylene chloride is then back-extracted into deionized water for analysis. Both preparation techniques put the MeHg into a clean dionized water matrix that was quantified by the same analytical technique, U.S. EPA Method 1630 (draft). An ethylating agent is added to the distillate/extract to form a volatile methyl-ethylmercury derivative, then purged onto graphitized carbon traps as a means of preconcentration and interference removal. Samples were then isothermally chromatographed, pyrolitically broken down to elemental Hg, and quantified using a cold-vapor atomic fluorescence detector. The quantification method is based upon the emission of 254-nm radiation by excited Hg atoms in an inert gas stream at an intensity directly proportional to the amount of Hg in the gas stream. Typical detection limits for the method are 0.005 ng/g by distillation and 0.02 ng/g by extraction. We collected a variety of surficial sediment samples from all three arms of the lake and analyzed them using both distillation and extraction methods and obtained a correction factor that was applied to our earlier distillation data.

Some studies have also identified a positive relationship between the magnitude of the MeHg artifact and inorganic TotHg in the sample (e.g., Bloom et al. 1997, Hammerschmidt and Fitzgerald 2001). However, we found no significant relationship between the MeHg artifact and TotHg for our samples (linear regression, $P = 0.06$, $R^2 = 0.189$, $n = 20$). Thus, we applied an average correction factor to the original distillation values as follows: $\mathrm{MeHg}_{(\mathrm{Extr})} = \mathrm{MeHg}_{(\mathrm{Dist})} \times 0.53$.

Water

Water samples were collected in Clear Lake from the same research vessel identified above using ultra-clean protocols (Gill and Fitzgerald 1985, 1987) from shallow (within 1 m of the surface) and bottom (within 1 m of the bottom) depths. Acid-washed Teflon tubing was used in conjunction with a peristaltic pump to collect water samples into acid-washed Teflon bottles. Samples were kept on ice in the dark and shipped within 24 h to the analytical laboratory. Unfiltered and filtered (to 0.45-μm pore size) water samples were analyzed for TotHg and typically for MeHg. Parallel sampling was conducted for total suspended solids and sulfate in unfiltered water. Pore water sulfate was extracted from sediment samples by centrifugation of 50-cm^3 samples with no airspace, followed by decantation into sample bottles with no airspace that were shipped to the analytical laboratory within 24 h of collection.

In the preliminary lake survey (1992), aqueous TotHg and MeHg were analyzed by Brooks Rand. Later collections were analyzed by Battelle Marine Sciences Laboratories. For TotHg, both laboratories utilized bromine monochloride oxidation, stannous chloride reduction, and cold-vapor atomic fluorescence analytical methods of Bloom and Crecelius (1983), now U.S. EPA Method 1631. For MeHg, the laboratories utilized distillation, aqueous phase ethylation, and cold-vapor atomic fluorescence methods of Bloom (1989) and Horvat et al. (1993), now U.S. EPA Method 1630 (draft).

Sulfate in water and pore water was analyzed by Analytical Resources (Seattle, Washington, USA) using

U.S. EPA method number 375.2 (U.S. EPA 1983). Total suspended solids (TSS) were analyzed by Century Testing (Bend, Oregon, USA) using a standard filtration-based multiple weighing technique.

Quality assurance and quality control

Quality assurance and quality control were based on adherence to ultra-clean collection and laboratory protocols, together with the extensive use of equipment blanks, reference standards, certified matrix reference materials, matrix spikes, field duplicates, and laboratory replicates in each analytical run. Data accuracy was monitored by analyzing reference standards with certified concentrations at least every 20 samples and equipment blanks during each run. Precision was monitored by analyzing laboratory replicates at least every 10 samples. Absolute variability in excess of 25% triggered reanalysis and/or flagging of data points.

Statistical analysis

Statistical analyses using the models and procedures described below were performed using JMP Statistical Software version 5.1 for the Macintosh (SAS Institute, Cary, North Carolina, USA). Models were fit and hypotheses were tested to assess both spatial and temporal trends of Hg in Clear Lake. The spatial analyses were simple linear regressions of $\log_{10}$(TotHg) or $\log_{10}$(MeHg) concentrations on distance from the mine (measured in kilometers). In some cases, the regressions were run separately for each arm (Oaks, Lower, and Upper) to determine whether the drop-off rates from the mine were equivalent. For some analyses, adjusted R^2 values were reported for potentially small sample sizes.

Temporal analyses, which were run on sediment samples as well as bottom and surface water samples, were more complex. Two types of models were fit: a simple regression model of $\log_{10}$(TotHg) (and MeHg) on year within each site and corresponding analyses of covariance that incorporated sites into the models. The simple regression models, computed within each site, were done to visualize the possible effects of a year $\times$ site interaction. The tests are not equivalent to the year $\times$ site interaction, which was tested in the more complex covariance model, since the error terms are not pooled across sites. However, these tests of significance provide information on the consistency of trends over years among the sites.

Analysis of covariance models had year as the covariant and site as the factor. Models were fit with and without the year $\times$ site interaction term. If the interaction term was not significant, then the additive model, containing only year and site, was appropriate. However, multiple testing was done on sites even if the interaction was significant, primarily for consistency and the fact that the interaction was rarely significant.

Multiple comparisons were used to evaluate site effects, i.e., tests were performed on the site main effect, which is equivalent to averaging over years. The liberal Fisher's least significant difference (LSD) and the more conservative Tukey's honest significant difference (HSD) tests were used. The HSD test controls the overall error rate for the inflation caused by multiple testing, whereas the LSD was used if the overall F for the site term was significant, which is a weaker form of protection. However, the LSD test was used whether or not the overall test was significant, i.e., the tests are equivalent to running multiple t tests with an error term pooled over sites. Therefore, caution should be exercised when interpreting the LSD; but, on the other hand, the HSD is probably more conservative than necessary. Together, these two approaches provide a reasonably complete view of statistical significance.

Results and Discussion

Clear Lake spatial trends

Sediments.—In Clear Lake proper, TotHg concentrations in surficial sediments ranged from 0.3 mg/kg at a site in the Lower Arm (L-8) during the PLS phase (1992) to 425 mg/kg at Oaks Arm site OA-01 during the time series study (1994–1998; see Fig. 1) and a maximum of 438 mg/kg at Oaks Arm site O-5 in 2003 (Suchanek et al., *in press*). Both TotHg and MeHg decline precipitously as a function of distance from the mine ($P < 0.0001$ for both), with TotHg decreasing more sharply, with nearly three orders of magnitude difference between sites near the mine and those at more distant sites in the Upper and Lower Arms (Fig. 3). Close to the mine, MeHg is four to five orders of magnitude lower than TotHg, but this is reduced to only approximately three orders of magnitude at a distance of ~20 km from the mine. Note that there is also a high degree of variability in TotHg concentrations at the two sites closest to the mine: OA-01, one of the long-term monitoring stations, and OA-F, a site also influenced heavily by AMD (see Shipp and Zierenberg 2008). Fig. 4 provides the coefficient of variation for surficial sediment Hg, indicating the high degree of patchiness near the mine and significantly less variability with distance from the mine. This is almost certainly heavily influenced by the historical practice of bulldozing mine wastes into the nearshore region of Clear Lake and subsequent remobilization and transport of Hg-laden particles further from these sites of origin by wind-driven currents (Rueda et al. 2008), with heavier/coarser particles dropping out closer to the mine. The ultimate source of this variability is likely to have had several causes. First, as mentioned above, during the period of active mining, waste rock and tailings were intentionally bulldozed and/or dumped into the nearshore regions of the lake at the face of the mine (Chamberlin et al. 1990), resulting in highly contaminated sediments and patchy Hg concentrations in this nearshore area. Second, erosion of steeply sloped waste rock piles along the shoreline yielded soils highly contaminated with Hg,

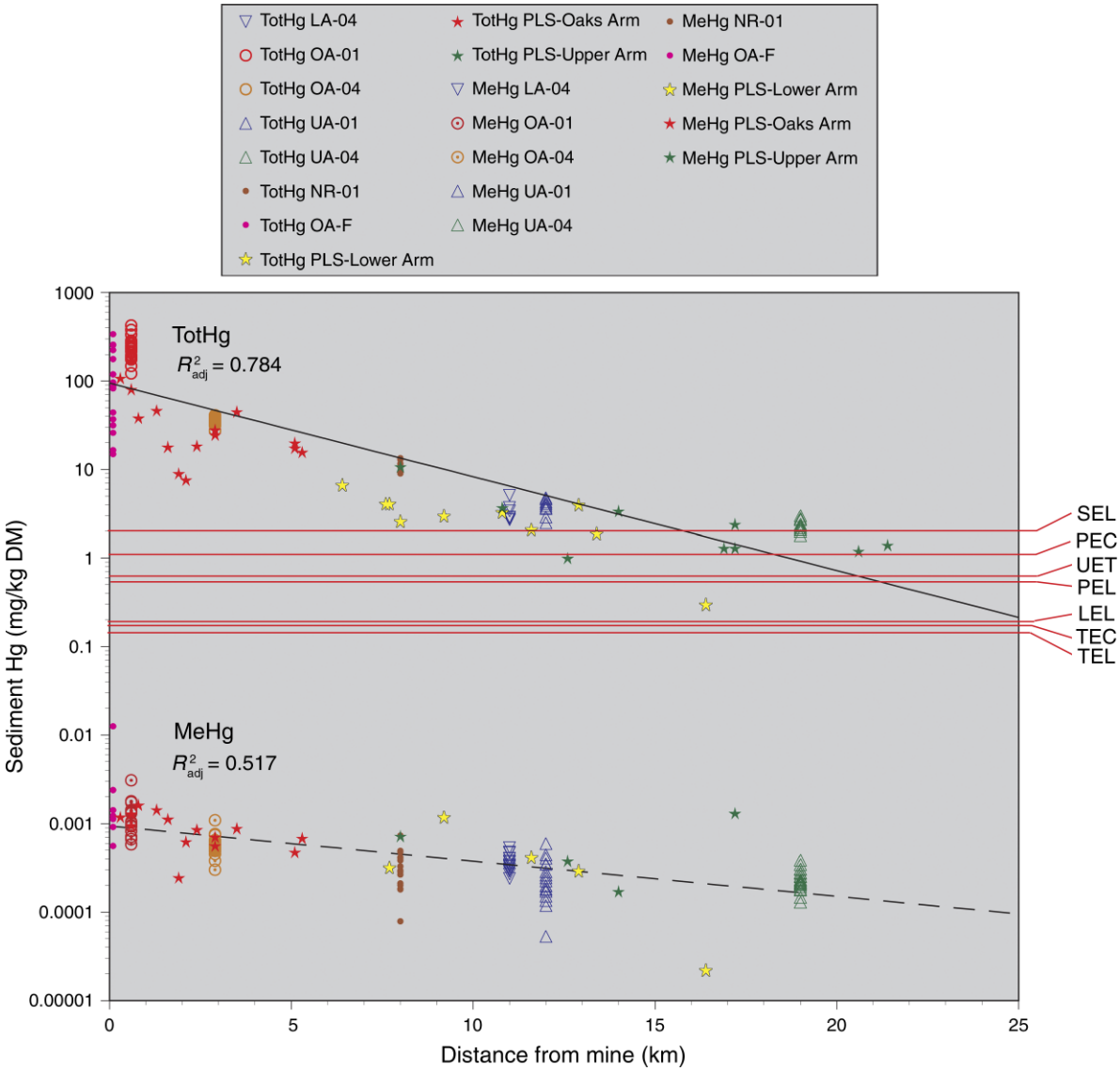

FIG. 3. Distribution of total mercury (TotHg; solid line; DM, dry mass) and methylmercury (MeHg; dashed line) in surficial sediments as a function of distance from the Sulphur Bank Mercury Mine at Clear Lake sites sampled from 1992 to 1998. The preliminary lake survey (PLS) samples from 1992 are shown as stars. All other data are from time series data collected from 1994 to 1998. Curve fits are exponential. The R^2 values are adjusted for potential effects of small sample sizes. Site abbreviations are: OA, Oaks Arm sites; UA, Upper Arm sites; LA, Lower Arm sites; NR, Narrows site. See Fig. 1 for site locations. Horizontal red lines represent sediment quality criteria: SEL, severe effect level; PEC, probable effects concentration; UET, upper effects threshold; PEL, probable effects level; LEL, lowest effect level; TEC, threshold effects concentration; TEL, threshold effects level.

which were deposited in the nearshore areas to the mine, especially during winter storms with extreme precipitation events. Third, Clear Lake sites OA-01 and OA-F are also sites of active AMD leaching from the mine into the nearshore environment (see Shipp and Zierenberg 2008, Suchanek et al. 2000*b*, 2008*e*), which is derived in part from the Herman Pit, which has water pH ~3.0, water sulfate concentrations of 1700–2900 mg/L, and sediment pore water sulfate concentrations of 2600–4700 mg/L.

Sediment Hg (derived from the mine) also declines more quickly as a function of distance from the mine into the Lower Arm than into the Upper Arm (ANCOVA, $P < 0.0001$, df = 5) (Fig. 5). Because west-to-east wind-driven currents move surface water toward the mine, the return current along the bottom entrains Hg-laden particles from the mine site and transports them first to the Upper Arm, then down to the Lower Arm (see Rueda et al. 2008). Thus, for sites with equivalent distances from the mine, those in the Lower Arm tend to have lower Hg concentrations than those in the Upper Arm because Hg-laden particles have had to travel farther to get there and some particles will

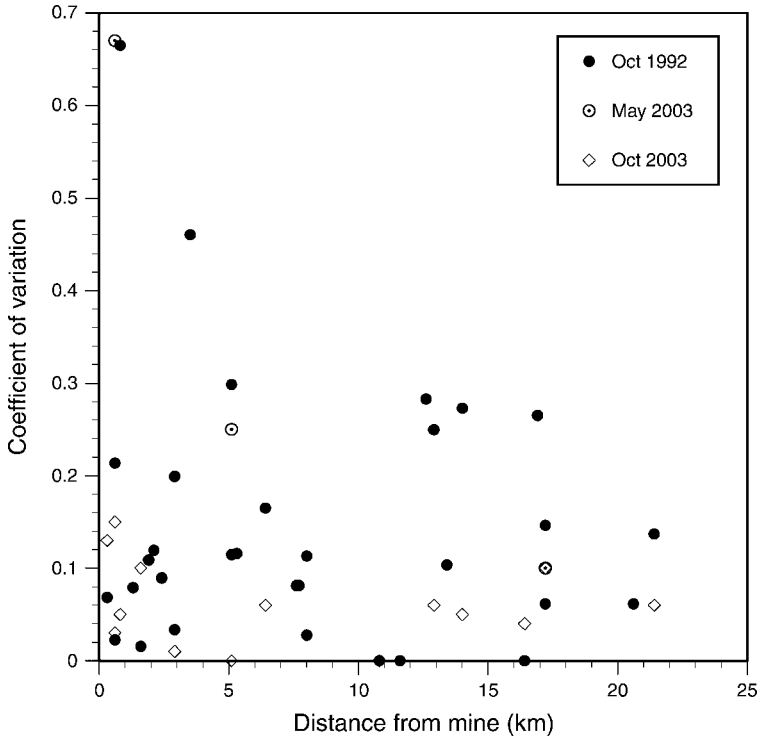

FIG. 4. Coefficient of variation in sediment total mercury (TotHg) concentrations from replicate samples as a function of distance from the Sulphur Bank Mercury Mine using combined data from 1992 and 2003 samples ($N = 44$).

have a higher likelihood of being deposited earlier along that pathway.

Methylmercury increases as a function of TotHg and, thus, with proximity to the mine (Fig. 6). However, the magnitude of that relationship changes dramatically with distance. At distant sites (e.g., UA-04, UA-01), the MeHg:TotHg ratio is $\sim 10^{-3}$, whereas at sites close to the mine (e.g., OA-01) that value decreases significantly to nearly 10^{-5}. The rate of this changing relationship with increasing TotHg at Clear Lake is entirely consistent with a more general analysis of the relationship between MeHg and TotHg in sediments from multiple habitat types including freshwater wetlands, marine and estuarine systems, lakes, and rivers present-

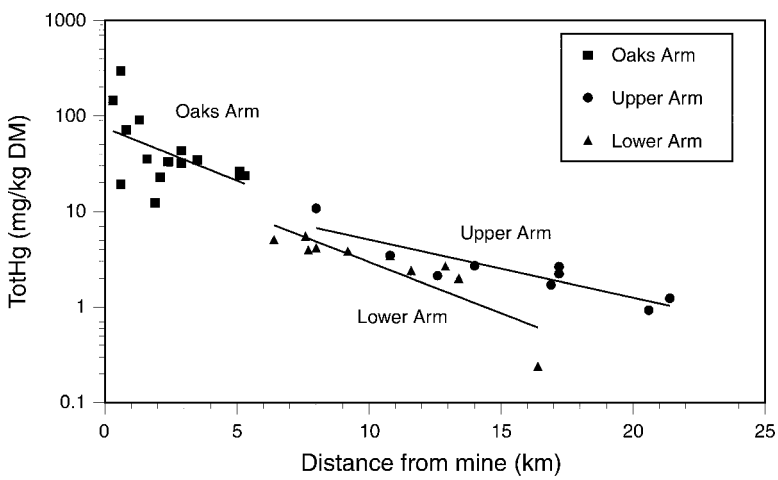

FIG. 5. Surficial sediment mean total mercury (TotHg) concentrations (DM, dry mass) at 34 sites in 2003 as a function of distance from the Sulphur Bank Mercury Mine, plotted for each arm of Clear Lake. The fitted curves are exponential.

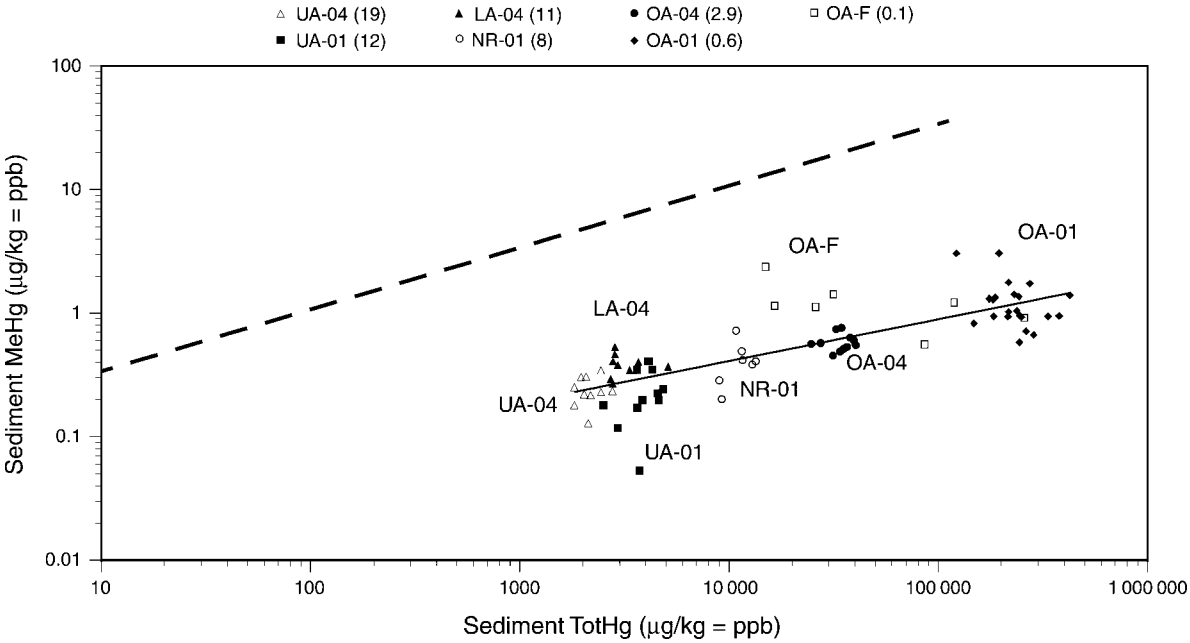

FIG. 6. Methylmercury (MeHg; μg/kg dry mass) as a function of total mercury (TotHg; μg/kg dry mass) in Clear Lake sediments for all seasons from 1992 to 1998. The fitted lines are power curves. The numbers in parentheses in the key represent distances (km) from the Sulphur Bank Mercury Mine. The dashed line represents the worldwide average for all types of aquatic systems from Benoit et al. (2003). See Suchanek et al. (2008*a*) for a more complete comparison of these data to those of Benoit et al. (2003). See Fig. 1 for site locations.

ed by Benoit et al. (2003). The dashed line in Fig. 6 represents the worldwide average of all systems documented by Benoit et al. (2003). While the TotHg concentrations found at Clear Lake are among the highest reported worldwide, MeHg:TotHg ratios from Clear Lake (Fig. 6) fall entirely below the worldwide average and significantly below most lake sites, indicating a much lower potential to produce MeHg in comparison with most other systems, especially lake systems. Suchanek et al. (2008*a*) also show that this ratio declines along a gradient from pristine to contaminated sites.

Compared with other lentic and lotic systems, Clear Lake contains some of the most Hg-contaminated sediments in the world, up to 438 mg/kg in surficial sediments in this study, but ~1000–1200 mg/kg TotHg documented in Oaks Arm near-surface sediments reported by CVRWQCB (1986), with exponentially declining concentrations with distance from the mine. The only site found in the literature that has comparable sediment TotHg concentrations (ranging up to 1610 mg/kg) is the Carson River/Lahontan Reservoir site in Nevada, a gold/silver mining site (Gustin et al. 1994). Sites associated primarily with atmospheric deposition of Hg ranged up to a maximum of 0.31 mg/kg, those with chloralkali plants ranged up to 85.4 mg/kg, and those with mining (gold, silver, Hg) ranged to 1610 mg/kg (see Table 1).

Water.—Data from 11 water collection sites in fall 1992 indicate that TotHg in unfiltered surface water (collected from within 1 m of the air–water interface) declines significantly as a function of distance from the mine ($P = 0.036$), but this decline is even more significant ($P = 0.018$) for bottom water (collected from within 1 m of the sediment–water interface) in which TotHg can be up to approximately five times higher than in surface water (Fig. 7A, B). Similarly, MeHg in both surface and bottom unfiltered water declines significantly ($P = 0.003$ and $P = 0.002$, respectively) as a function of distance from the mine (Fig. 7C, D).

In general, water from unfiltered samples exhibits significantly higher TotHg and MeHg concentrations than their filtered water counterparts (Fig. 7), suggesting that the majority of Hg in the lake is bound to particles. These particles are likely sediment or floc (produced from the mine; see Suchanek et al. 2000*a*, 2008*e*) remobilized from the lake bed. In particular, water produced from a high-volume lake bed spring at the Narrows was shown to contain significantly elevated TotHg and MeHg in unfiltered water, but when filtered this water did not exhibit any higher Hg than ambient concentrations for water in that region of the lake (Fig. 7A), indicating that these elevated Hg concentrations were found primarily on nearby surficial sediment particles entrained by the turbulent upwelling spring water, not originating from the spring water itself. In addition, Hg concentrations in water collected at three other major lake bed springs (found at sites O-H, L-HN, and L-HS; see Fig. 1 for locations) that do not exhibit turbulent upwelling show no localized elevated Hg

TABLE 1. Comparison of mercury concentrations in sediments from Clear Lake, California, USA, and other contaminated and uncontaminated lake sites worldwide.

Sediments	Location	Source of Hg†	Range of TotHg (mg/kg = ppm DM)	Range of MeHg (μg/kg = ppb DM)	Reference‡
Clear Lake sites					
Surficial	Oaks Arm	M	7.6–438	1.1–53.9	1, 2
Surficial	Upper Arm	M	0.9–10.8	0.2–5.7	1, 2
Surficial	Lower Arm	M	0.3–6.7	0.1–5.1	1, 2
3 m deep cores	Oaks Arm	M	3.8–109.0	0.05–3.3	3
3 m deep cores	Upper Arm	M	0.13–4.88	0.01–1.16	3
3 m deep cores	Lower Arm	M	0.41–9.41	0.02–1.10	3
Surficial	North Wetland	M	5.1–60.6	1.2–12.8	1
Surficial	acidic mine pits	M	61–1940	0.83–84.3	1
Shallow cores	Oaks Arm	M	90–1180		4
Other contaminated sites					
Surficial	California, USA	M	0.2–87.2		5
Surficial	Nevada, USA	G	0.1–1610		6
Surficial	Oregon, USA	G	0.2–0.4		7
Surficial	Oregon, USA	M	1–4		7
Surficial	New York, USA	C	0.84–85.4	0.39–14.6	8, 9, 10
Surficial	Ontario, Canada	C/P	2.20		11
Surficial	Northwest Territories, Canada	G	1.30		11
Surficial	British Columbia, Canada	M	0.03		11
Surficial	Sweden	C	0.2-5.3		12
Surficial	Slovenia	P	0.053–0.166	0.05–6.22	13
Cores	Oregon, USA	G	0.2–7.2		7
Cores	Oregon, USA	M	1–20.5		7
Cores	Ontario, Canada	C/P	2–67		14
Cores	Ontario, Canada	C/P	2–11		11
Cores	Northwest Territories, Canada	G	0.2–2.4		11
Cores	British Columbia, Canada	M	0.01–0.16		11
Non-contaminated sites					
Surficial	Wisconsin, USA	NK	0.028–0.398	0.1–12.2	15
Surficial	Manitoba, Canada	NK	0.014–0.28	0–0.034	16
Surficial	Newfoundland, Canada	A	0.01–0.08		17
Surficial	Siberia, Russia	A	0.05–0.27		18
Surficial	Ontario, Canada	A	0.03–0.31		19
Surficial	Wisconsin, USA	A	0.001–0.14	0.00001–0.01	20

Notes: Abbreviations are: TotHg, total mercury; MeHg, methylmercury; DM, dry mass.

† Key to sources of mercury: M, mercury mining; G, gold/silver mining; C, chloralkali plant; C/P, chloralkali plant/paper mill; P, coal-fired power plant; NK, no known local source; A, atmosphere.

‡ Referecnes: 1, this study; 2, Suchanek et al. (*in press*); 3, Richerson et al. (2008); 4, CVRWQCB (1986); 5, D. G. Slotton (*personal communication*); 6, Gustin et al. (1994); 7, Ambers and Hygelund (2000); 8, Effler et al. (1998); 9, PTI (1993); 10, Henry et al. (1995); 11, Lockhart et al. (1995); 12, Lindeström (2001); 13, Kotnik et al. (2002); 14, Jackson and Woychuk (1980); 15, Watras et al. (1998); 16, Jackson (1988); 17, French et al. (1999); 18, Blais et al. (1999); 19, Wong et al. (1997); 20, Gilmour and Riedel (1995).

signal from those sites (independent of the influence of distance from the mine; see Fig. 7), confirming that, in general, lake bed springs do not represent a significant independent source of Hg loading to Clear Lake. In addition to the data from the four major lake bed springs sampled in this study, Goff and Janik (1993) demonstrated that lake bed springs are highly variable and often emit large volumes of carbon dioxide and/or methane, but very little H_2S and virtually no Hg. Except for those springs at the mine itself, geothermal waters in the Clear Lake region generally contain very low to non-detectable Hg (Goff et al. 2001).

Although TotHg in unfiltered water exhibits a highly significant relationship with distance from the mine, filtered water samples exhibit a much weaker relationship with distance for surface and bottom water ($P = 0.055$ and $P = 0.810$, respectively) that are not significant. This difference almost certainly is due to the fact that the Hg-laden particles are driving the Hg–distance relationship and the majority of these are removed by filtration.

While MeHg in unfiltered water declines significantly as a function of distance from the mine, this decline is also found in both surface and bottom filtered water ($P = 0.039$ and $P = 0.049$, respectively), suggesting that MeHg does not have as close an association to particles as does the more abundant inorganic fraction. As with sediments, MeHg in both unfiltered and filtered water increases as a power function of increasing TotHg ($\text{MeHg} = e^{(-4.35)} \times \text{TotHg}^{(0.62)}$, $R^2 = 0.73$, $n = 41$). This trend of increasing MeHg with TotHg is also consistent with the relationship described by Benoit et al. (2003) for freshwater sediments throughout the world.

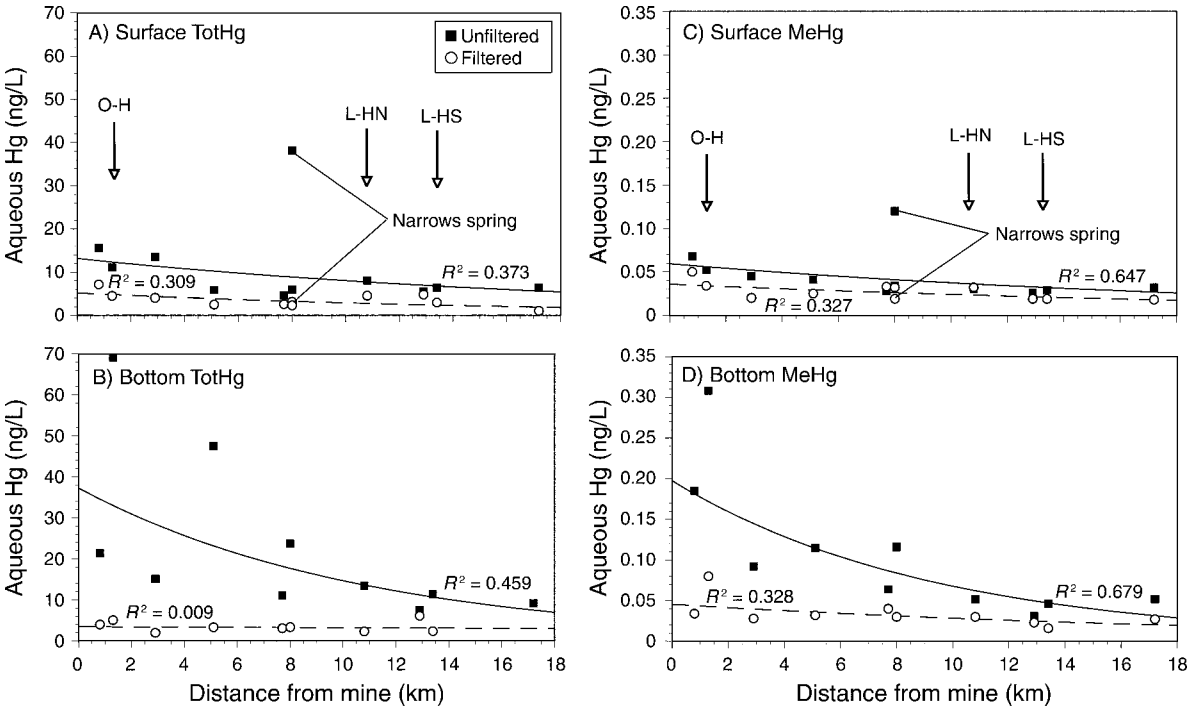

FIG. 7. Total mercury (TotHg) and methylmercury (MeHg) in unfiltered and filtered water samples from Clear Lake during September 1992 as a function of distance from the Sulphur Bank Mercury Mine: (A) TotHg in surface water, (B) TotHg in bottom water, (C) MeHg in surface water, (D) MeHg in bottom water. Curve fits are exponential; the solid lines represent unfiltered water, and the dashed lines represent filtered water. The R^2 values are adjusted for potential effects of small sample sizes. For surface water, R^2 values exclude the Narrows Spring data. The locations of other lake bed spring sites are indicated in panels (A) and (C): site O-H = 1.3 km, site L-HN = 10.8 km, and site L-HS = 13.4 km from the mine. See Fig. 1 for site locations.

Limited data from a few other studies suggests that Clear Lake contains among the highest TotHg concentrations in filtered water worldwide, up to 19.9 ng/L in the Oaks Arm. The maximum value for Onondaga Lake (a chloralkali plant site) was 12 ng/L and Mono Lake was similar at 12.6 ng/L; several remote Wisconsin lakes reached up to 4.69 ng/L and other gold/silver/Hg-mining sites ranged up to 3.4 ng/L (Table 2).

As might be expected from the data presented for unfiltered and filtered water, most of the Hg, both TotHg and MeHg, is held in the particulate fraction of the water column, not the dissolved fraction. Particle-bound Hg (Fig. 8) decreased exponentially as a function of distance from the mine (similar to the patterns seen for sediments and unfiltered water) and had nearly one order of magnitude higher concentrations near the sediment–water interface than near the air–water interface. In the PLS in fall 1992, particulate TotHg ranged from a minimum of 730 ng/g in surface water at site L-7 far down in the Lower Arm to a maximum of ~64 000 ng/g in bottom water at site O-H closer to the mine in the middle of the Oaks Arm. One study that came the closest to the maximum value documented particulate Hg in two flooded reservoirs at 200–900 ng/g and in four natural lakes in northern Quebec at 150–490 ng/g (Plourde et al. 1997; Table 3). Total mercury on bottom water particles (entrained in currents originating primarily from the mine; Rueda et al. 2008) showed a significant decrease ($P = 0.05$) with distance from the mine, whereas TotHg on surface water particles (entrained in currents that originate primarily from the low-Hg Upper Arm; Rueda et al. 2008) also appears to have decreased as a function of distance from the mine, but this relationship is not statistically significant ($P = 0.128$). Particulate MeHg ranged from a minimum of "non-detectable" in surface water at sites L-3 and L-HN in the Lower Arm to a maximum of 228 ng/g on particles in bottom water at site O-H. Methylmercury on both surface and bottom water particles decreased significantly as a function of distance from the mine ($P = 0.050$ and $P = 0.005$, respectively).

Clear Lake temporal trends

Sediments.—Clear Lake surficial sediments sampled in 1992 and from 1994 to 1998 maintained relatively comparable TotHg concentrations at each site. Consistent with the spatial patterns shown in the pooled data in Fig. 3, TotHg concentrations were highest (averaging ~200–300 mg/kg) close to the mine (site OA-01) and about two orders of magnitude lower (averaging ~2 mg/kg) at sites furthest from the mine (e.g., UA-04, LA-04; Fig. 9). Total mercury declined monotonically along the following gradient of sites (with distance from the mine in parentheses): OA-01 (0.01 km) → OA-04 (2.9

TABLE 2. Comparison of mercury concentrations in filtered water from Clear Lake and other contaminated and uncontaminated lake sites worldwide.

Matrix: filtered water	Location	Source of Hg†	Range of TotHg (ng/L = pptr)	Range of MeHg (ng/L = pptr)	MeHg (%)	Reference‡
Clear Lake sites						
Surface	Oaks Arm	M	0.30–19.90	0.002–0.227	0.13–45.58	1
Surface	Upper Arm	M	0.02–3.17	0.001–0.188	0.60–>100	1
Surface	Lower Arm	M	0.07–1.59	0.002–0.159	0.13–>100	1
Bottom	Oaks Arm	M	0.04–16.90	0.001–0.332	0.02–>100	1
Bottom	Upper Arm	M	0.01–3.34	0.001–0.611	0.23–87.91	1
Bottom	Lower Arm	M	0.11–0.94	0.002–0.220	6.42–99.55	1
Water column	North Wetland	M	1.4–52.3	0.02–5.37		1
Water column	mine site groundwater	M	0.31–84 100	0.01–11.6		1
Water column	acidic mine pits	M	13.8–1890	0.02–0.94		1
Other contaminated sites						
Water column	California, USA	G	2.8–3.4			2
Water column	New York, USA	C	2–12	0.21–5.74		3
Water column	Nevada, USA	G	3–56	0.13–0.15		4
Non-contaminated sites						
Water column	California, USA	NK	11.2–12.6			2
Water column	Wisconsin, USA	NK	0.38–4.69	0.02–0.73		5
Water column	Lake Michigan, USA	NK		0.005–0.042		6
Epilimnion	Finland	NK		0.058–0.88		7
Hypolimnion	Finland	NK		0.50–1.16		7

Notes: Water samples were collected in Clear Lake using ultra-clean protocols from "surface" (within 1 m of the surface) and "bottom" (within 1 m of the bottom) depths. Abbreviations are: TotHg, total mercury; MeHg, methylmercury; pptr, parts per trillion.

† Key to sources of mercury: M, mercury mining, G, gold/silver mining; C, chloralkali plant; NK, no known local source.

‡ References: 1, this study; 2, Gill and Bruland (1990); 3, Bloom and Effler (1990); 4, Bonzongo (1996); 5, Watras et al. (1998); 6, Sullivan and Mason (1998); 7, Verta and Matilainen (1995).

km) → NR-01 (8.0 km) → UA-01 (12.0 km) → LA-04 (11.0 km) → UA-04 (19.0 km). Site OA-F (closest to the mine) yielded highly variable Hg concentrations with a 24-fold range (14–339 mg/kg), but this reflects extreme patchiness in Hg concentrations closest to the mine where both bulldozing of waste rock and tailings occurred, as well as upwelling AMD from sediments (see Fig. 4 and Shipp and Zierenberg 2008), rather than any specific temporal changes in the Hg concentrations. Small-scale sampling in this region (especially at and near site OA-F) indicates that sediment TotHg concentrations may vary more than an order of magnitude over less than a 1-m distance (D. C. Nelson, *personal communication*).

Sediment MeHg ranged from a low of 0.095 μg/kg (at site L-8 during the PLS in 1992) to 54.0 μg/kg (at site OA-0F in May 1997). Like TotHg, MeHg in sediments also declined along this same distance gradient from the mine, although the differences between sites for MeHg were not as dramatic as for TotHg (Fig. 9). For the sediment MeHg time series data, there is some indication of seasonal increases during summer and/or fall. The ratio of MeHg:TotHg, often used as an indicator of the relative bioavailability of Hg in ecological systems, spanned nearly two orders of magnitude and increased consistently as a function of distance from the mine, a trend opposite to that of absolute concentrations for both TotHg and MeHg (Fig. 9). There do not appear to be significant seasonal trends present for this parameter.

Table 4 summarizes results of statistical analyses for temporal trends in sediment Hg. Linear regression analysis confirms that no long-term temporal trends (increases or decreases) in sediment TotHg and MeHg concentrations or the ratio of MeHg:TotHg were documented for the six sites (excluding OA-F) sampled during the time series study from 1994 to 1998 (Fig. 9). The one exception to this, OA-F, appears to increase in TotHg over time. However, as noted above, sampling that site on a regular basis commenced in May 1996, and, because subsequent sampling was not always conducted at the exact same location, the high degree of patchiness in the Hg concentrations in this localized region caused increased variability.

Tukey's HSD test (more conservative) and the Fisher's LSD test (more liberal), analyzing for differences between sites for TotHg, MeHg, and the ratio of MeHg:TotHg over time, showed very similar results. For TotHg, there was almost no similarity between individual sites. For MeHg, and to a lesser extent the ratio of MeHg:TotHg, some similarities exist between sites NR-01, UA-01, UA-04, and LA-04 (the most distant sites).

Surficial sediment pore water sulfate, a potentially important driver of Hg methylation, was monitored from May 1994 through March 1998. Pore water sulfate concentrations ranged over three orders of magnitude with sites distant from the mine averaging 1–10 mg/L to sites OA-01 and OA-F (the two sites closest to the mine) reaching extremely high concentrations nearing 3500

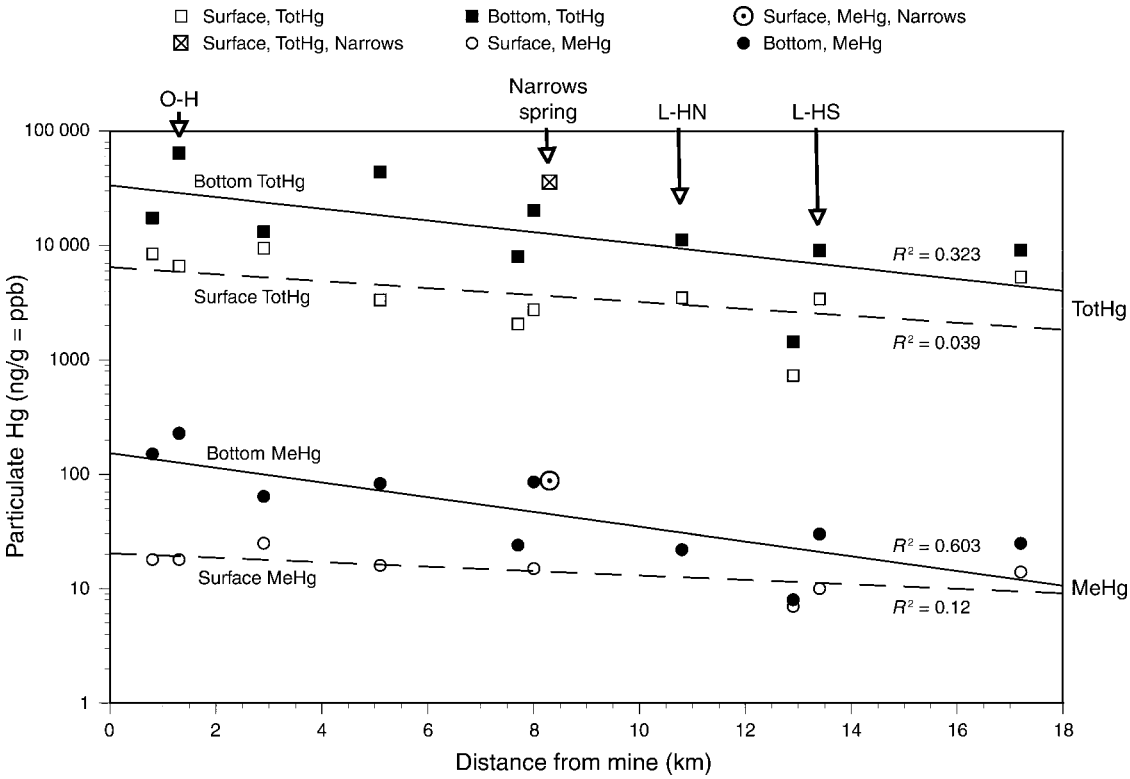

FIG. 8. Particle-bound total mercury (TotHg) and methylmercury (MeHg; ng/g = ppb) in surface and bottom water samples from Clear Lake during September 1992 as a function of distance from the mine. Curve fits are exponential; the solid lines and symbols represent bottom water data, and the dashed lines and open symbols represent surface water data. The location of the Narrows turbulent lake bed spring and other non-turbulent lake bed springs are shown at the top of the figure with arrows. All R^2 values are adjusted for small sample sizes.

mg/L (Fig. 10). The heavy rain year of 1995 (with an overflow from the Herman Pit) yielded the highest pore water sulfate concentrations. Reduced rainfall in subsequent years, resulting in reduced AMD flow from the mine, yielded lower annual peaks of pore water sulfate. Sediment pore water sulfate concentrations in Clear Lake proper at these sites close to the mine represent some of the highest values found in any lake or stream environment, even exceeding marine pore water sulfate concentrations generally considered to be quite high at ~2800 mg/L (Stumm and Morgan 1981).

A dramatic seasonal trend was observed in pore water sulfate concentrations, with the highest concentrations in winter months being drawn down by the process of bacterial sulfate reduction throughout the summer across the entire lake (Mack 1998). Thus, by late summer/early fall, sediment pore water sulfate concentrations converge to a very narrow range (1–5 mg/L) everywhere except immediately adjacent to the mine (site OA-F), where some factor (e.g., low pH and/or high advective flux of sulfate) limits the ability of sulfate-reducing bacteria to significantly deplete sulfate. Linear regression analysis indicates that only one site exhibited any significant long-term trend in pore water sulfate concentrations, a highly significant ($P < 0.0001$) increase at site OA-04 (Table 5). The reason for this increase is unclear. As shown in Fig. 10, and Tukey's HSD and Fisher's LSD tests confirm, site OA-01 had significantly elevated pore water sulfate, and there were no discernable differences in this parameter among all other sites monitored for long-term changes, except OA-F. Multiple comparisons tests confirm that site OA-01 was significantly different from all other sites (Table 5).

Water.—Mercury in unfiltered and filtered water was monitored in 1992 and from 1994 to 1998 at the same seven sites where sediment Hg samples were collected. The range of TotHg concentrations for all parameters reported in water (surface unfiltered, surface filtered, bottom unfiltered, and bottom filtered) varied over approximately two orders of magnitude (Fig. 11) and followed the same trend as the sediments with decreasing Hg concentrations as a function of distance from the mine (Fig. 9). For unfiltered water, TotHg concentrations ranged from ~1–100 ng/L, whereas for filtered water, TotHg concentrations typically ranged an order of magnitude lower at ~0.1–10 ng/L. Generally, for unfiltered and filtered water, TotHg concentrations from bottom and surface samples varied together at most sites. The most typical pattern for both surface and bottom unfiltered water was for TotHg maxima in the

TABLE 3. Comparison of mercury concentrations in water column particulates from Clear Lake, California, USA, and other contaminated and uncontaminated lake sites worldwide.

Matrix: water column particulates	Location	Source of Hg†	Range of TotHg (ng/g = ppb)	Range of MeHg (ng/g = ppb)	MeHg (%)	Reference‡
Clear Lake sites						
Surface	Oaks Arm	M	188–60 252	0.91–67.5	0.06–3.3	1
Surface	Upper Arm	M	23–4303	1.04–28.3	1.0–6.9	1
Surface	Lower Arm	M	83–2120	1.9–71.2	2.2–3.9	1
Bottom	Oaks Arm	M	1585–29 752	2.9–554	0.01–1.11	1
Bottom	Upper Arm	M	671–5633	1.7–135	0.11–1.88	1
Bottom	Lower Arm	M	602–2035	13.6	0.11–0.12	1
Other contaminated sites						
Surface particles	Quebec, Canada	FR	250–900	10–110	3–24	2
Non-contaminated sites						
Epilimnion	Finland	NK		0.007–0.20		3
Hypolimnion	Finland	NK		0.20–1.67		3
Epilimnion	Lake Michigan, USA	NK	0.08–0.28			4
Hypolimnion	Lake Michigan, USA	NK	0.05–0.30			4
Surface particles	Quebec, Canada	NK	150–490	2.5–20	2–6	2

Note: Water samples were collected in Clear Lake using ultra-clean protocols from "surface" (within 1 m of the surface) and "bottom" (within 1 m of the bottom) depths. Abbreviations are: TotHg, total mercury; MeHg, methylmercury.

† Key to sources of mercury: M, mercury ming; FR, flooded reservoir; NK, no known local source.

‡ References: 1, this study; 2, Plourde et al. (1997); 3, Verta and Matilainen (1995); 4, Sullivan and Mason (1998).

summer/fall, with minima occurring in winter/spring. In contrast, surface and bottom filtered water exhibited the opposite trend, with maxima often occurring in the winter/spring and minima occurring in the summer/fall, but this trend was much weaker. The seasonal variation in Hg content of filtered water is similar to the sulfate profile.

The percentage of TotHg in the dissolved fraction exhibited striking seasonal trends at all sites with maxima in winter/spring and minima in summer/fall (Fig. 12), similar to those trends in sediment pore water sulfate (Fig. 10). Especially dramatic was the increase in percentage of dissolved fraction in the winter of 1994–1995 when extreme rainfall events in January and March of 1995 caused an overflow from the Herman Pit into Clear Lake. This can also be seen in the plot of TotHg in surface and bottom filtered water at all sites, but especially at OA-01 and OA-04 (closest to the mine) during the winter of 1994–1995 (Fig. 11C, D). This overflow event, with concomitant increases in TotHg and MeHg in Oaks Arm water near the mine, was also reflected in increased Hg in juvenile largemouth bass (*Micropterus salmoides*) during the summer following that event (see Suchanek et al. 2008*c*). The floc site, OA-F (see Suchanek et al. 2000*b*), also receives large volumes of AMD upwelling through sediments from the mine (Shipp and Zierenberg 2008). This, in turn, results in the precipitation/deposition of Hg into these nearshore sediments, producing significantly elevated sediment Hg concentrations at OA-F, a typical "hot spot" of AMD and dissolved Hg input to Clear Lake. Cumulatively, these data are consistent with the hypothesis that the mine site is leaching dissolved Hg during winter/spring rainy periods when a stronger hydraulic head forces Hg-laden AMD fluids from the mine site into and under Clear Lake.

Aqueous MeHg concentrations also varied over about two orders of magnitude, with surface and bottom unfiltered and filtered water ranging from ~0.001 to 0.6 ng/L and with the highest concentrations in the Upper Arm, followed by the Oaks Arm and the Lower Arm (Fig. 13, Tables 2 and 6). Bottom and surface MeHg concentrations in unfiltered water varied together at most sites, but generally had little or no correspondence between sites for filtered water. Temporal trends for unfiltered (but not filtered) water yielded maxima in summer/fall and minima in winter/spring. During MeHg peak periods (summer/fall), sites closer to the mine generally had higher MeHg than those further away, but during winter/spring periods, no such trends were observed. No distinct seasonal trends were observed in time series data for MeHg in filtered water, which were about one order of magnitude lower than MeHg in unfiltered water. This suggests that the seasonal cycles seen in unfiltered water are driven by MeHg adhered to particles in the water column. The seasonal trend for unfiltered MeHg is also consistent with the seasonal cycle of MeHg production stimulated during the summer/fall, which is consistent with the same seasonal cycles seen in both plankton and benthic invertebrates (see Suchanek et al. 2008*b*).

In contrast to aqueous TotHg, Clear Lake MeHg concentrations were significantly lower than at other contaminated sites (Tables 2 and 6). Aqueous MeHg at other non-contaminated sites has been reported in the range of 0.04–0.8 ng/L, but can reach up to 8.5–12 ng/L at some chloralkali plant sites (Parks et al. 1989, Henry et al. 1995, Wiener et al. 2003*b*).

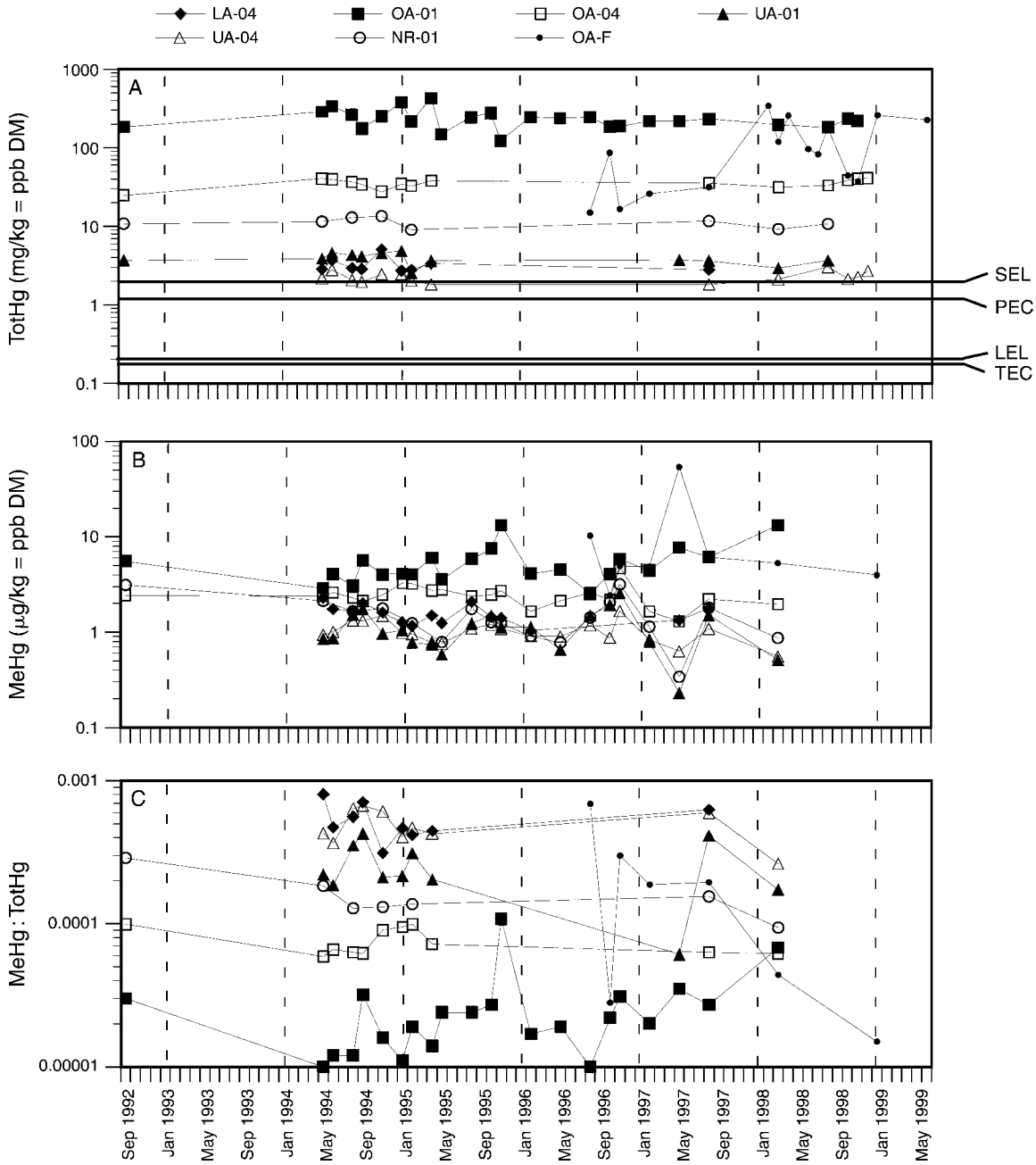

FIG. 9. Temporal trends of mercury in surficial sediments in Clear Lake from 1992 (preliminary lake survey) and 1994–1998 (the time series study): (A) total mercury (TotHg; DM, dry mass), (B) methylmercury (MeHg), (C) ratio of MeHg:TotHg. Sediment quality criteria abbreviations are: SEL, severe effects level; PEC, probable effects concentration; LEL, lowest effect level; and TEC, threshold effects concentration. See Fig. 1 for site locations.

The ratio of MeHg:TotHg (Fig. 14), which is believed to represent a measure of Hg bioavailability, spanned one to two orders of magnitude during any one sampling period and exhibited temporal trends that are related to the peaks of MeHg in unfiltered water (Fig. 13). As with MeHg, maxima for the ratio in unfiltered (but not filtered) water occurred during the summer/fall periods, whereas minima occurred during the winter/spring. Spatially, although the data show considerable variability, sites closest to the mine had the lowest ratios, whereas those furthest away had the highest ratios. These trends are also consistent with another index of bioavailability, the ratio of simultaneously extractable metals to acid volatile sulfides (SEM:AVS), which generally shows the lowest metal bioavailability near the mine and the highest at sites distant from the mine (Suchanek et al. 2008*a*).

TABLE 4. Statistical analysis results for mercury time series data in sediments.

Site	Long-term temporal trends	Differences between sites	
		Tukey's HSD test	Fisher's LSD test
TotHg			
OA-01	no	A	A
OA-04	no	B	B
NR-01	no	C	C
UA-01	no	D	D
UA-04	no	E	F
LA-04	no	D	E
MeHg			
OA-01	no	A	A
OA-04	no	B	B
NR-01	no	CD	C
UA-01	no	D	D
UA-04	no	D	D
LA-04	no	CD	C
MeHg:TotHg ratio			
OA-01	no	D	D
OA-04	no	C	C
NR-01	no	B	B
UA-01	no	B	B
UA-04	no	A	A
LA-04	no	A	A

Notes: Long-term temporal trends were determined by linear regression. Identical letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test columns indicate no significant differences between sites; different letters indicate significant differences between data generated from those sites. See Fig. 1 for site locations. Other abbreviations are: TotHg, total mercury; MeHg, methylmercury.

Linear regression analysis indicates that no significant long-term increases or decreases were observed during the study period (1994–1998) for TotHg or MeHg in either surface or bottom water (Table 7). Differences between sites analyzed by Tukey's HSD and Fisher's LSD multiple comparisons tests indicate that for TotHg in unfiltered water (both surface and bottom) there were two basic groupings of sites: (1) those in the Oaks Arm (sometimes including the nearby Narrows site) and (2) those in all other parts of the lake. This same basic relationship existed for TotHg in surface filtered water, but not for bottom filtered water. However, MeHg generally exhibited no (or minimal) statistically significant differences between sites throughout the lake, with the one exception of some differences (similar to the groupings identified above) in bottom unfiltered water. There were also no significant differences between sites for both TotHg and MeHg in bottom filtered water.

Particulate Hg (Fig. 15) exhibited temporal trends similar to sediments and unfiltered water and, with only one exception, no significant long-term increases or decreases during 1994–1998 (Table 8). During the time series study, particulate Hg remained exceptionally high, with particles in the Oaks Arm exhibiting maxima of 29 800 ng/g in water near the sediment–water interface and 60 300 ng/g in water near the air–water interface. These values, together with those from the PLS, were the highest reported values worldwide (see Table 3). Consistently high concentrations in the bottom water samples are undoubtedly due to a thick "nepheloid"

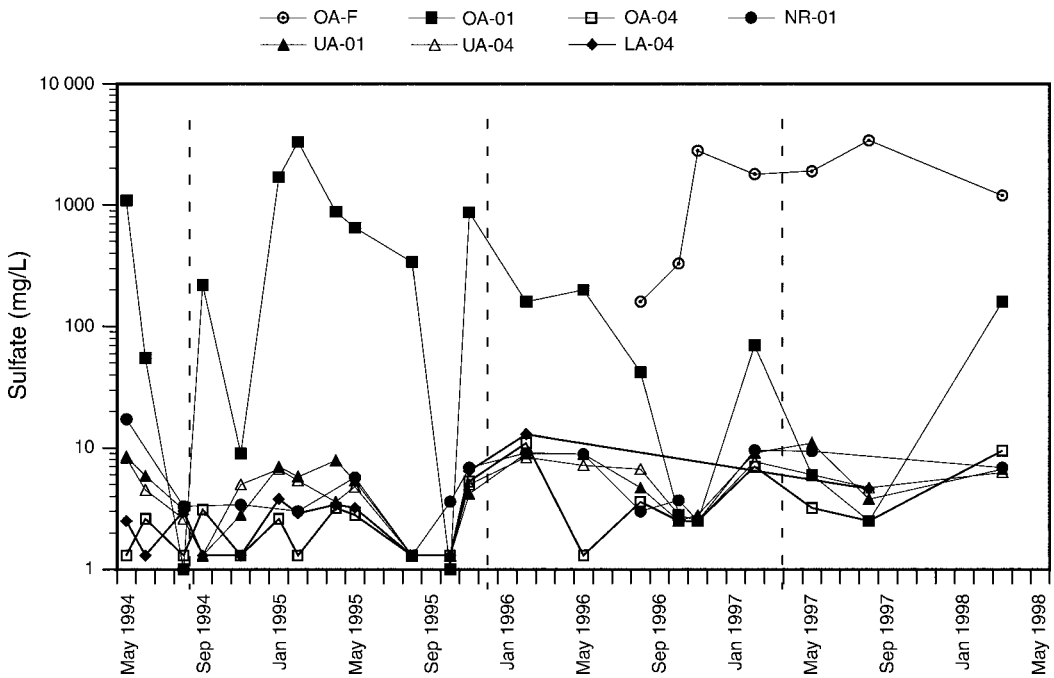

FIG. 10. Temporal fluctuations in surficial sediment pore water sulfate from 1994 to 1998 in Clear Lake sediments. See Fig. 1 for site locations.

layer at the sediment–water interface that keeps much of the loose, unconsolidated sediments resuspended in the water column of Clear Lake, holding much of the Hg inventory with it.

For unfiltered water, Clear Lake exhibits some of the highest TotHg concentrations (up to 399 ng/L) of any lake worldwide, exceeded (similar to the trend for sediments) only by the Lahontan Reservoir, which had a maximum of 1580 ng/L (Table 6; Bonzongo et al. 1996). Yet Hg in unfiltered water from North Wetland sites exceeded Clear Lake proper by two- to 10-fold (reaching 827 ng/L TotHg) and groundwater from test wells at the mine were the highest recorded anywhere at 374 000 ng/L TotHg. Maximum concentrations reported for sites influenced only by atmospheric deposition ranged from 0.7 to 5.3 ng/L, sites impacted by chloralkali plants ranged from 26 to 80 ng/L, and those in the vicinity of mining sites ranged from 2 to 1580 ng/L (Table 6).

North Wetlands

Sediments.—Total mercury and MeHg were also sampled periodically from April 1997 to September 1998 in sediments and water from the North Wetland just north of the mine, which receives AMD from the waste rock piles in that vicinity of the site (Fig. 2). Sediment TotHg was typically <10 mg/kg dry mass, except for both replicates at site NW-1, which exhibited significantly elevated concentrations at ~60 mg/kg on a single sampling event in May 1997 (Appendix A). These concentrations are roughly equivalent to those in sediments at Clear Lake sites that are ~5–10 km from the mine. Methylmercury in North Wetland sediments remained variable (5–10 μg/kg) throughout the sampling period, but with no predominant trends.

Water.—Water in the North Wetland was also sampled at roughly the same frequency as sediments. Total mercury in wetland unfiltered water (Appendix B) typically ranged from ~10 to 100 ng/L, about an order of magnitude higher than corresponding surface water samples within Clear Lake, but were very comparable to bottom water samples during the same time periods (Fig. 11). Total mercury in wetland filtered water was also typically an order of magnitude higher than comparable samples in Clear Lake proper. Generally, ~25–50% of the TotHg in wetland water samples was in dissolved form, with no striking trends with respect to subsite or season (Appendix B).

Methylmercury in North Wetland unfiltered water, typically ~1–10 ng/L (tabular data in Appendix B), was generally one to two orders of magnitude higher than comparable surface and bottom water samples within Clear Lake (see Fig. 13). Methylmercury in North Wetland filtered water was also one to two orders of magnitude higher than comparable samples in Clear Lake proper. Typically, 25–80% of the MeHg in wetland samples was in dissolved form, with no obvious trends with respect to site or season.

TABLE 5. Statistical analysis results for pore water sulfate data.

Site	Long-term temporal trends	Differences between sites	
		Tukey's HSD test	Fisher's LSD test
OA-01	no	A	A
OA-04	yes, <0.0001	B	B
NR-01	no	B	B
UA-01	no	B	B
UA-04	no	B	B
LA-04	no	B	B

Notes: Long-term temporal trends were determined by linear regression. Identical letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test columns indicate no significant differences between sites; different letters indicate significant differences between data generated from those sites. See Fig. 1 for site locations.

Sulphur Bank Mercury Mine site

Sediments.—Sediments in the Herman Pit and Basalt Pit were analyzed for TotHg and MeHg (Appendix C). Although samples were collected only occasionally, the data indicate relatively consistent Hg concentrations at each site over time for TotHg, with the Basalt Pit having the highest values at ~800–1000 mg/kg and the Herman Pit about an order of magnitude lower. Methylmercury, however, was quite similar between the two sites and exhibited summer/fall peaks similar to those observed in Clear Lake proper.

Water.—Water samples were also collected from the following locations at the mine site from October 1996 to December 1998: (1) monitoring wells MW-2, MW-5, MW-8, SB-8s (shallow), SB-8d (deep), and SB-9, (2) the Basalt Pit, and (3) the Herman Pit (see Fig. 2 for locations).

Total mercury concentrations in unfiltered water spanned over five orders of magnitude among the sites, with monitoring wells SB-8s, MW-5, and MW-2 sometimes exceeding 100 000 ng/L (374 000 ng/L for SB-8s; Appendix D). These concentrations are approximately three to four orders of magnitude higher than comparable water samples in Clear Lake (Fig. 11). All three of these monitoring wells are in the direct path of down-gradient AMD flow from the Herman Pit to Clear Lake (see Shipp and Zierenberg 2008, Suchanek et al. 2008*e*). This path empties into Clear Lake at the precise location (site OA-F) where the highest accumulation of white floc precipitate has been documented previously (Suchanek et al. 2000*b*). Total mercury in the Basalt Pit and Herman Pit was somewhat lower and ranged from ~200 to 2000 ng/L in unfiltered water and from ~10 to 1000 ng/L in filtered water, which represent concentrations ~20–200 times higher for unfiltered water samples, but 10–1000 times higher than comparable filtered water samples in Clear Lake proper. However, a U.S. EPA-funded study (with a detection limit of 50 ng/L; G. Reller, *personal communication*) reported finding no

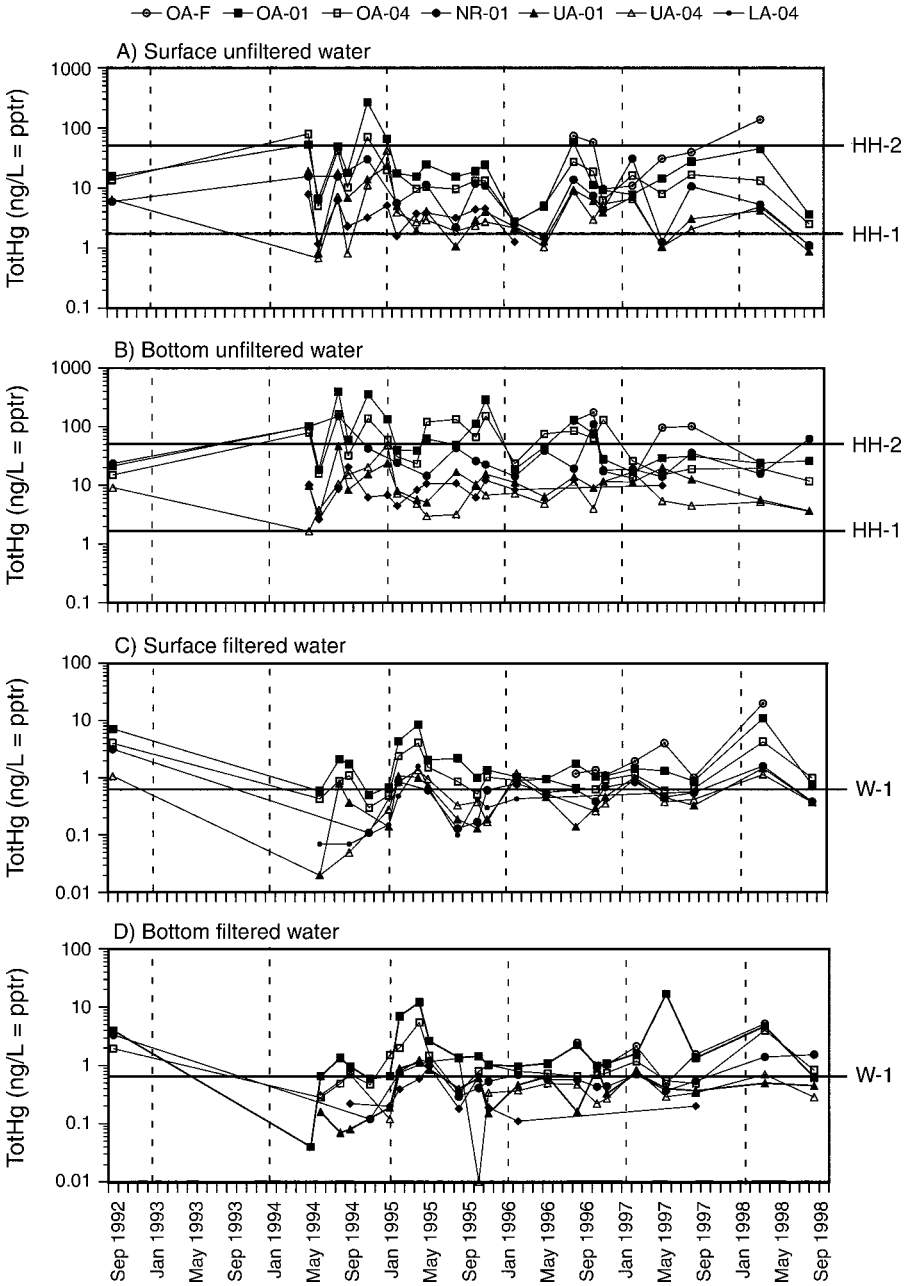

FIG. 11. Temporal trends in total mercury (TotHg; pptr, parts per trillion) concentrations in unfiltered and filtered surface and bottom water from Clear Lake stations from 1992 and 1994–1998. Human Health Criteria: HH-1, Great Lakes Initiative Mercury Criterion; HH-2, California Toxics Rule criterion. Ecological Health Criterion: W-1, U.S. Environmental Protection Agency wildlife criterion. See Fig. 1 for site locations.

detectable Hg in Herman Pit water samples collected in 2000 (Jewett et al. 2000).

For TotHg in filtered water, there were also striking (five orders of magnitude) differences between the SB-8s and SB-8d wells, which is surprising because they are co-located companion wells differing only in the depth at which the intake screens are located (Appendix D). This suggests that at this particular location, more leaching of Hg from the surrounding waste rock is occurring in the shallow zone than at depth. The average percentage of TotHg in the dissolved fraction varied tremendously between samples (Appendix D). Further seasonal analysis indicates that TotHg in the dissolved form never exceeds ~20% in the Basalt Pit, whereas in Herman Pit it varies seasonally from ~5–10% in winter to 100% in late fall. Herman Pit exhibited a significantly higher average percentage of TotHg in the dissolved fraction (~67%) than the Basalt Pit (~8%), which has a

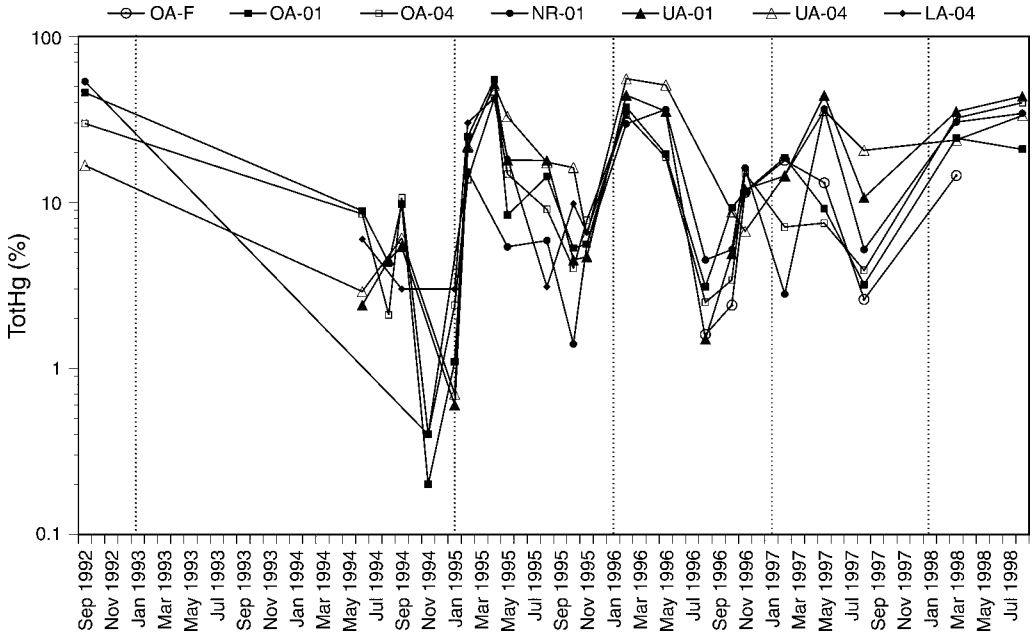

FIG. 12. Temporal trends in the percentage of total mercury (TotHg) in the dissolved fraction of water samples from 1992 and 1994–1998. See Fig. 1 for site locations.

very shallow water depth and likely experiences greater sediment resuspension than does the Herman Pit. Of particular interest is the monitoring well SB-8s, where TotHg was found primarily in the dissolved fraction (~75%), vs. SB-8d, where almost none was in the dissolved fraction (<1%). Monitoring wells SB-8s, MW-5, and MW-2 (on the direct hydrologic downslope gradient to Clear Lake) all exhibited exceptionally high percentages (~75–95%) of dissolved TotHg, which apparently can easily leach from the mine site into the lake. No prominent seasonal trends were observed for TotHg concentrations from these sites for either unfiltered or filtered water samples.

Methylmercury in unfiltered water exhibited the same trends as TotHg, with the three monitoring wells (SB-8s, MW-5, and MW-2) exhibiting the highest concentrations, ranging from ~1 to 42 ng/L (Appendix D). Methylmercury in filtered water was nearly as high, with concentrations from ~1 to 12 ng/L. The other sites had values generally <1 ng/L. Collectively, these values are only slightly higher than those found in Clear Lake proper.

Human health criteria

The primary Hg-related human health issues affecting Clear Lake are dermal exposure, particulate intake through inhalation, and, most importantly, consumption of aquatic biota. Results of a 1992 Hg-related health survey of Native Americans residing on and off the Elem Pomo Indian Tribe Rancheria, located directly adjacent to the Sulphur Bank Mercury Mine and the Oaks Arm of Clear Lake, recorded elevated levels of blood Hg at 15.6 μg/L (mean) and 38.8 μg/L (maximum) that were significantly higher than that in the average U.S. population (see Suchanek et al. [2008*e*] for further details). Here we address specific data on Hg concentrations in the abiotic components of the Clear Lake environment as they relate to relevant human sediment and water quality criteria.

Sediments.—The California Code of Regulations established a "hazardous waste criterion" for Hg at concentrations >20 mg/kg wet mass. Sediment Hg concentrations plotted in Figs. 3 and 9 are given in dry mass, but because Clear Lake surficial sediments are typically ~88% moisture, the 20 mg/kg wet mass criterion is equivalent to 167 mg/kg dry mass. For TotHg, ~110 000 m^2 (0.1% of Clear Lake lake bed and roughly 1% of the Oaks Arm) contain surficial sediment Hg at levels that exceed 160 ppm (dry mass) TotHg, roughly equivalent to the California hazardous waste criterion (Suchanek et al., *in press*).

Water.—

1. *Total mercury*.—The federal Safe Drinking Water Act requires public water systems to limit Hg concentrations in water to 2 μg/L (2000 ng/L). At concentrations of ~1–400 ng/L, Clear Lake never exceeds this limit. However, the California Toxics Rule (Code of Federal Regulations: 40 CFR 131, Water Quality Standards) has established a safe concentration of TotHg in unfiltered water (i.e., total recoverable Hg) for the protection of human health (from the consumption of water and organisms) at 50 ng/L. Furthermore, the Great Lakes Initiative Mercury Criterion for the protection of human health was established at 1.8 ng/L.

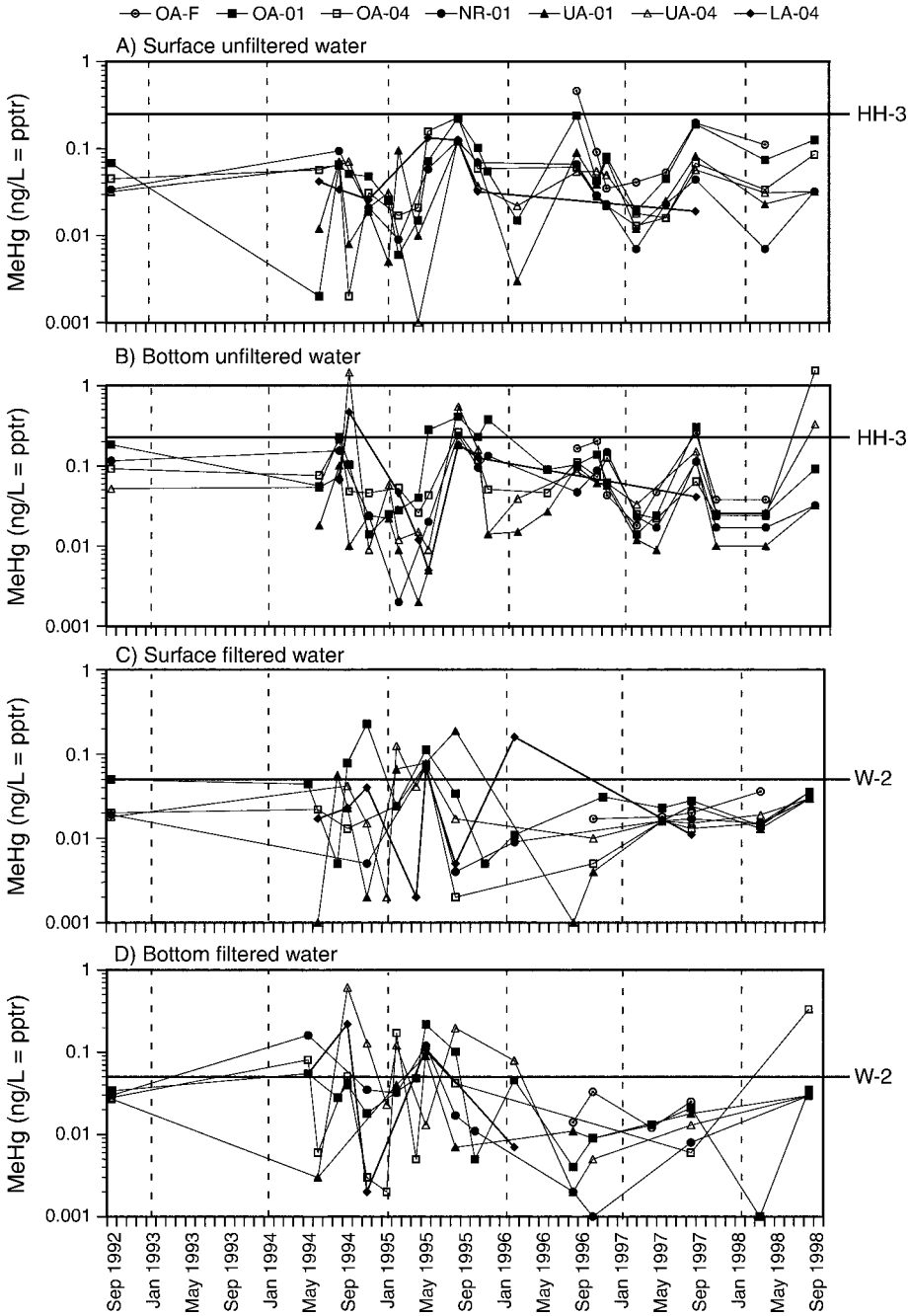

FIG. 13. Temporal trends in aqueous methylmercury (MeHg; pptr, parts per trillion) in unfiltered and filtered surface and bottom water from Clear Lake stations from 1992 and 1994–1999. Human Health Criterion: HH-3, Great Lakes Initiative Human Health Criterion. Ecological Health Criterion: W-2, U.S. Environmental Protection Agency wildlife criterion. See Fig. 1 for site locations.

Clear Lake waters exceed the California Toxics Rule criterion approximately one-third of the time and exceed the Great Lakes Initiative criterion almost continuously at all sites.

2. *Methylmercury*.—The Great Lakes Human Health Criterion for MeHg in unfiltered water has been set at 0.24 ng/L. Clear Lake waters range from ~0.002 to 2.0 ng/L MeHg, exceeding this criterion mostly at deep-water sites only during summer months (Fig. 13).

Ecological health criteria

Sediments.—Clear Lake surficial sediment concentrations of TotHg vary from ~1 to 400 mg/kg. While no formal regulatory criteria exist for toxicity of contam-

TABLE 6. Comparison of mercury concentrations in unfiltered water from Clear Lake, California, USA, and other contaminated and uncontaminated lake sites worldwide.

Matrix: unfiltered water	Location	Source of Hg	Range of TotHg (ng/L = pptr)	Range of MeHg (ng/L = pptr)	MeHg (%)	Reference
Clear Lake site						
Surface	Oaks Arm	M	2.8–257	0.002–0.463	0.08–3.45	1
Surface	Upper Arm	M	0.7–41.6	0.001–0.125	0.02–11.39	1
Surface	Lower Arn	M	1.1–30.8	0.019–0.133	0.55–3.96	1
Bottom	Oaks Arm	M	11.8–399	0.014–1.55	0.01–13.15	1
Bottom	Upper Arm	M	1.65–151	0.002–1.46	0.01–17.13	1
Bottom	Lower Arm	M	2.63–20.6	0.005–0.468	0.05–2.27	1
Water column	North Wetland	M	1.2–827	0.17–25.6		1
Water column	mine site groundwater	M	7.13–374 000	0.02–42.2		1
Water column	acidic mine pits	M	145–1730	0.03–1.04		1
Water column	Oaks Arm	M	12–104			2
Water column	Upper Arm	M	4–18			2
Other contaminated sites						
Water column	California, USA	G	2.74–44.2			3
Water column	California, USA	M	8.8			2
Water column	Nevada, USA	G	57–1582	0.4–0.5		4
Epilimnion	New York, USA	C	3–21.7	0.18–1.4		5, 6
Hypolimnion	New York, USA	C	5–24	0.2–12		5, 6
Water column	Ontario, Canada	C/P	5–80	1.8–2.8		7
Surface	Ontario, Canada	C/P		0.2–8.5		8
Hypolimnion	Ontario, Canada	C/P	3–76	1–28		8
Water column	Saskatchewan, Canada	U	15–510	0.07–0.11		9
Water column	St. Lawrence Estuary	C	0.36–1.56			10
Water column	St. Lawrence Estuary	C	0.08–2.64			11
Water column	China	M	550–1500	0.04–0.77		12
Water column	Slovenia	P	0.2–2.7	0.020–0.086		13
Non-contaminated sites						
Water column	California, USA	NK	20–21.6			2
Water column	California, USA	NK	0.48–0.60			2
Water column	Montana, USA	NK	0.35–2.85	0.01–0.10	4 ± 2	14
Water column	Wisconsin, USA	NK	0.15–4.80	0.04–2.20	14 ± 10	15
Water column	Wisconsin, USA	NK	0.52–4.19	0.04–0.83		16
Water column	Lake Michigan, USA	NK	0.008–0.72			17
Water column	Minnesota, USA	NK	0.20–3.20	0.04–0.34		18
Water column	New York, USA	NK	0.8–5.3	0.07–0.61		19
Water column	Ontario, Canada	A	0.304–0.438			20
Water column	Nova Scotia, Canada	A	0.50–6.23			21
Water column	Ontario, Canada	NK		0.18–0.38		8
Water column	Sweden	NK		0.12–0.41		22
Water column	Sweden	NK		0.12–0.41		22

Note: Water samples were collected in Clear Lake using ultra-clean protocols from "surface" (within 1 m of the surface) and "bottom" (within 1 m of the bottom) depths.

† Key to sources of mercury: M, mercury mining; G, gold/silver mining; C, chloralkali plant; C/P, chloralkali plant/paper mill; U, urban sources; P, coal-fired power plant; NK, no known local source; A, atmosphere.

‡ References: 1, this study; 2, Gill and Bruland (1990); 3, Gill and Bruland (1992); 4, Bonzongo et al. (1996); 5, Henry et al. (1995); 6, Jacobs et al. (1995); 7, Bloom and Effler (1990); 8, Parks et al. (1989); 9, Jackson (1986); 10, Cossa and Gobeil (2000); 11, Quemerais et al. (1999); 12, Horvat et al. (2003); 13, Kotnik et al. (2002); 14, Watras et al. (1995*a*); 15, Watras et al. (1995*b*); 16, Watras et al. (1998); 17, Sullivan and Mason (1998); 18, Monson and Brezonik (1998); 19, Driscoll et al. (1994); 20, Wong et al. (1997); 21, Vaidya and Howell (2002); 22, Lee and Hultberg (1990).

inants to benthic fauna in freshwater sediments, the National Oceanic and Atmospheric Administration (NOAA) has developed a series of screening quick reference tables (SQuiRTs) as informal interpretive tools for the National Status and Trends Program to evaluate the "safe" concentrations of contaminants below which adverse effects are not likely and above which adverse effects are more likely (Buchman 1999). The SQuiRTs have been used for a variety of purposes, including establishing preliminary target remediation objectives (Ingersoll et al. 2001), although they were not designed for that purpose. From a series of studies in which toxic effects were documented for various concentrations of TotHg in freshwater sediments, the following SQuiRTs were developed. Threshold effects levels (TEL) are those concentrations below which adverse effects are expected to occur only rarely. Probable effects levels (PEL) are those concentrations above which adverse effects are frequently expected. Upper effects threshold (UET) levels (for Hg, it is based on a Microtox bioassay test [Microbics, Carlsbad, California, USA]) are those concentrations above which adverse biological impacts would always be expected. The TEL, PEL, and UET values for TotHg in freshwater sediments are 0.174,

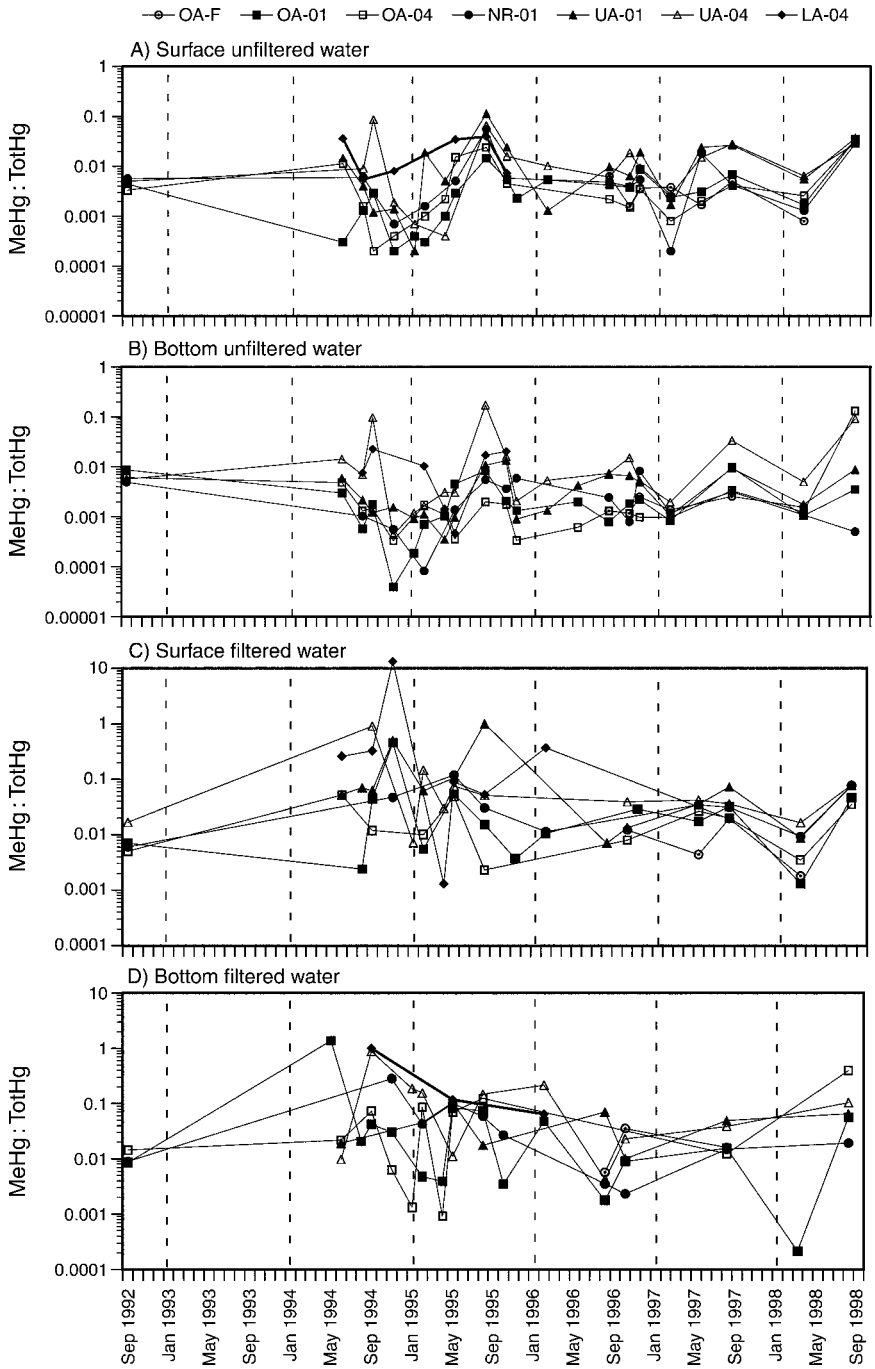

FIG. 14. Temporal trends in methylmercury : total mercury ratios (MeHg:TotHg) in unfiltered and filtered surface and bottom water from Clear Lake stations from 1992 to 1999. See Fig. 1 for site locations.

0.486, and 0.560 mg/kg, respectively. Clear Lake sediments at sites far distant from the mine, with TotHg concentrations of ~1 mg/kg or less, exceed the TEL by ~10 times and exceed the PEL and UET toxic criteria by a factor of approximately two to three. Sediments near the mine, which have been measured as high as ~438 mg/kg in our study and up to 1200 mg/kg previously (CVRWQCB 1986), exceed those toxic criteria values by factors of ~1000–7000 times. See Fig. 4 for a comparison of SQuiRTs in comparison to the range of Clear Lake sediment TotHg concentrations.

MacDonald et al. (2000) combined results from a wide variety of toxicity studies in the literature to develop a consensus-based "weight-of-evidence" thresh-

TABLE 7. Results of statistical analysis for mercury time series data in water.

Site	Long-term temporal trends	Differences between sites	
		Tukey's HSD test	Fisher's LSD test
Surface, unfiltered			
TotHg			
OA-01	no	A	A
OA-04	no	A	AB
NR-01	no	A	B
UA-01	no	B	C
UA-04	no	B	C
LA-04	no	B	C
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	no	A	A
Surface, filtered			
TotHg			
OA-01	no	A	A
OA-04	no	AB	A
NR-01	no	BC	B
UA-01	no	C	B
UA-04	no	C	B
LA-04	no	C	B
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	no	A	A
Deep, unfiltered			
TotHg			
OA-01	no	A	A
OA-04	no	A	AB
NR-01	no	A	B
UA-01	no	B	C
UA-04	no	B	C
LA-04	no	B	C
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	AB	AB
UA-01	no	B	B
UA-04	no	AB	A
LA-04	no	AB	AB
Deep, filtered			
TotHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	no	A	A
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	no	A	A

Notes: Long-term temporal trends were determined by linear regression. Identical letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test columns indicate no significant differences between sites; different letters indicate significant differences between data generated from those sites. See Fig. 1 for site locations. Other abbreviations are: TotHg, total mercury; MeHg, methylmercury.

old effects concentration (TEC; contaminant concentrations at which threshold effects were observed) and a probable effects concentration (PEC; contaminant concentrations at which probable effects are expected). The consensus-based TEC and PEC concentrations for TotHg were determined to be 0.18 and 1.06 mg/kg, respectively. Clear Lake sediments, with a range of ~1–1200 mg/kg TotHg, are ~1–1100 times the PEC and ~5–6500 times the TEC. The TEC and PEC values are provided in Fig. 3 for comparison with the SQuiRTs and again in Fig. 9 in relation to the concentrations of TotHg in Clear Lake sediments over the entire time series study. Total mercury in Clear Lake sediments exceeds both the TEC and the PEC at virtually all sites and all times (with the exception of two individual samples for TotHg collected during the PLS that were located at distant sites in the Upper Arm and Lower Arm; Fig. 3). Because these consensus-based criteria are

TABLE 8. Results of statistical analysis for Hg time series data for particulate mercury.

Site	Long-term temporal trends	Differences between sites	
		Tukey's HSD test	Fisher's LSD test
Surface			
TotHg			
OA-01	no	A	A
OA-04	no	A	AB
NR-01	no	AB	BC
UA-01	no	B	D
UA-04	no	B	D
LA-04	no	B	CD
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	no	A	A
Bottom			
TotHg			
OA-01	no	A	A
OA-04	no	A	B
NR-01	no	B	C
UA-01	no	BC	D
UA-04	yes	D	E
LA-04	no	CD	E
MeHg			
OA-01	no	A	A
OA-04	no	A	A
NR-01	no	A	A
UA-01	no	A	A
UA-04	no	A	A
LA-04	...†	A	A

Notes: Long-term temporal trends were determined by linear regression. Identical letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test columns indicate no significant differences between sites; different letters indicate significant differences between data generated from those sites. See Fig. 1 for site locations. Other abbreviations are: TotHg, total mercury; MeHg, methylmercury.

† Not enough data were available for a linear regression test.

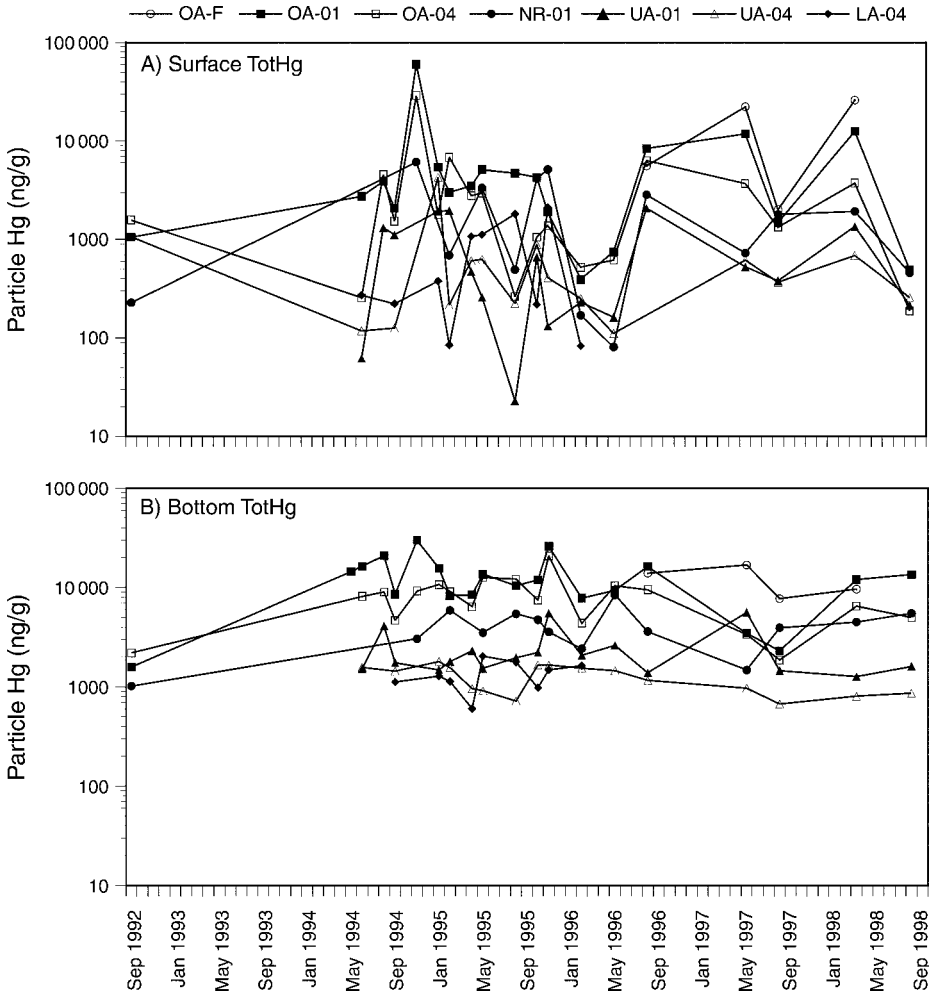

FIG. 15. Temporal trends in particulate mercury (total mercury [TotHg] and methylmercury [MeHg]) in surface and bottom water for Clear Lake sites from 1992 to 1998. See Fig. 1 for site locations.

very similar to the SQuiRTs, the range of exceedances for Clear Lake sediments are virtually identical to those discussed here for the SQuiRTs.

Efroymson et al. (1996) provided preliminary remediation goals for TotHg in freshwater sediments relative to ecological endpoints at 0.70 mg/kg, which Clear Lake sediments exceed by a range of factors from ~1 to 1700 times. The Ontario Ministry of Environment and Energy has also established a set of Provincial Sediment Quality Guidelines (PSQGs) specifically to evaluate and establish allowable fill quality or cleanup goals for sediments (Persaud et al. 1993). Their lowest effect level (LEL) indicates a concentration that has no effect on the majority of sediment-dwelling organisms; this sediment could be clean to marginally polluted. Their severe effect level (SEL) indicates a contaminant concentration that is likely to affect the health of sediment-dwelling organisms and would represent a grossly polluted environment. For Hg, their LEL and SEL levels are 0.2 mg/kg (dry mass) and 2.0 mg/kg (dry mass), respectively. Approximately 80% of Clear Lake exceeds the SEL criterion as a grossly polluted environment and would, under the PSQG guidelines, be evaluated further for contaminant control or removal.

Water.—Clear Lake's TotHg in unfiltered and filtered water ranges from ~1 to 400 ng/L and from 0.01 to 10 ng/L, respectively (Fig. 11). Fitzgerald (1979) published a value for typical "background" concentrations of TotHg in unfiltered water at 10 ng/L, which is exceeded approximately half the time in Clear Lake proper.

From an ecological perspective, Rudd (1995) interpreted a concentration of 0.1 ng/L MeHg as being representative of pristine environments. Since Clear Lake MeHg concentrations in unfiltered water range from ~0.001 to 0.5 ng/L (Fig. 13), it would not be considered highly contaminated with respect to MeHg under Rudd's criterion.

Aquatic life criteria.—While there are currently no

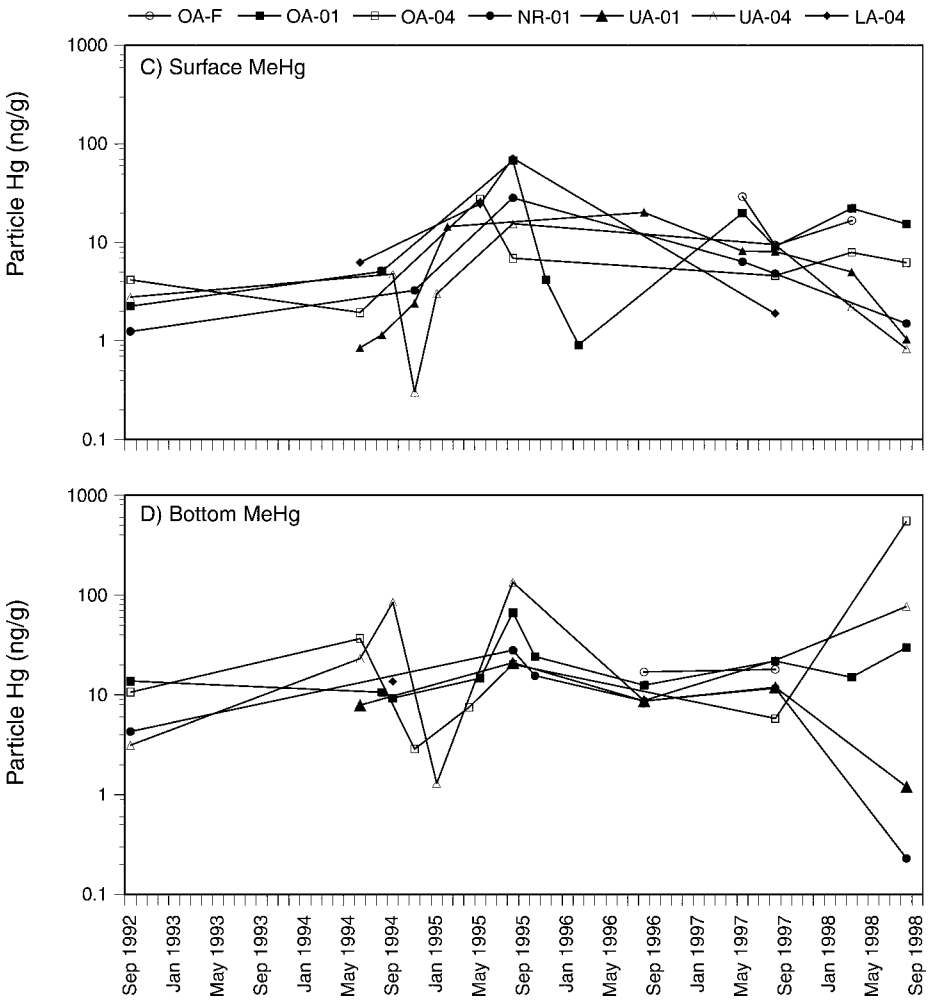

FIG. 15. Continued.

aquatic life criteria established for Hg specifically for California, there are U.S. EPA-established aquatic life criteria with which to compare Clear Lake values. In 1995, the U.S. EPA established chronic and acute aquatic life criteria, expressed as total recoverable (unfiltered) Hg. The chronic exposure criterion (highest average four-day concentration, not to be exceeded more than once every three years) was 908 ng/L, and the acute criterion (highest average one-hour concentration, not to be exceeded more than once every three years) was 1694 ng/L. In 2002, these criteria were revised by the U.S. EPA so as to be expressed as total dissolved (filtered) Hg, with a chronic exposure value of 770 ng/L and an acute exposure value of 1440 ng/L. Mercury concentrations in Clear Lake water, both filtered and unfiltered, are well below the U.S. EPA criteria designed to protect aquatic life.

Wildlife criteria.—The U.S. EPA also established Hg criteria designed to protect piscivorous wildlife. For the Great Lakes Initiative (GLI) in 1995, the U.S. EPA determined a wildlife criterion of 1.3 ng/L, expressed as total recoverable Hg in water. This value was based on exposure estimates for avian species. In the 1997 Mercury Study Report to Congress (MSRC), the U.S. EPA developed national wildlife criteria guidance based on dissolved MeHg (U.S. EPA 1997). The final wildlife criterion from this effort was 0.05 ng/L MeHg and was based on exposure estimates for mammalian species. Based on U.S. EPA assumptions about the relative proportions of dissolved MeHg to dissolved TotHg and total recoverable Hg, the 0.05 ng/L criterion corresponds to values of 0.641 ng/L (dissolved TotHg) and 0.910 ng/L (total recoverable Hg). The total recoverable criteria from both the GLI (1.3 ng/L) and MSRC (0.910 ng/L) are exceeded in Clear Lake virtually throughout the year at all sites. The MSRC total dissolved Hg criterion (0.641 ng/L) is exceeded in Clear Lake at the majority of sites a majority of the time.

Potential impacts to aquatic organisms

In addition to lethality, and its ability to act as a mutagen, teratogen, and carcinogen, Hg can have

PLATE 4. Parrot Pit at Sulphur Bank Mercury Mine during the era of open pit mining showing steam shovel and dump trucks, ca. 1939 (courtesy of California Geological Survey, Department of Conservation).

sublethal effects on aquatic organisms, including inhibition of reproduction, reduced growth rate, increased frequency of tissue histopathology, impairment of ability to capture prey, reduced olfactory receptor function, alterations in blood chemistry and enzyme activities, and disruption of thyroid function and chloride secretion (see review by Eisler 2000). Documented effects of various Hg concentrations in sediments and water on aquatic organisms are reviewed here in relation to typical Hg concentrations found in Clear Lake.

While relatively few studies have evaluated the effects of Hg on invertebrates, the vast majority of research has focused on vertebrates, especially fish and birds. Most aquatic organisms are exposed to non-dietary Hg through contact with sediments or water.

Sediments.—From a series of laboratory studies involving Hg contamination in freshwater sediments, Birge et al. (1979) observed an 11% reduction in rainbow trout (*Oncorhynchus mykiss*) egg survival at TotHg sediment concentrations of 0.18 mg/kg, a 29% reduction at sediment Hg concentrations of 1.05 mg/kg, and a 46% reduction at sediment Hg concentrations of 12.1 mg/kg. Teratic larvae were also observed at 5%, 13%, and 20%, respectively, for each of the sediment Hg concentrations identified above. Survival through 10 days post-hatch was reduced by 26%, 52%, and 76%, respectively, for those same sediment Hg concentrations. Clear Lake sediments exceed the Hg concentrations at which these effects could occur in trout by ~10–2400 times. While rainbow trout no longer reside in Clear Lake (they became extinct in the lake before 1963 [Moyle 2002]), this evidence suggests that they could be dramatically affected by Hg if they were reintroduced.

Water.—Lethal concentrations of aqueous Hg to different species of aquatic organisms range from ~100 to 200 000 ng/L (Eisler 2000). Total mercury in Clear Lake unfiltered water ranges from ~1 to 400 ng/L (Fig. 12). Birge et al. (1979) provided data on the toxic effects of Hg in water on rainbow trout indicating that eight days of continuous exposure to a mean concentration of 100–140 ng/L of TotHg yielded 100% mortality to embryos and larvae. Thain (1984) also documented reduced hatching success in the zebrafish (*Brachydanio rerio*) at TotHg concentrations of 100 ng/L. In a flow-through experimental system, Birge et al. (1979) also determined a TotHg 10-day LC_{50} (the concentration at which 50% of individuals die after 10 days of exposure) of <100 ng/L for embryos and larvae of the rainbow trout and 300 ng/L for channel catfish (*Ictalurus punctatus*), one of the most common fish species in Clear Lake. Because TotHg in Clear Lake unfiltered water is often above 100 ng/L (Fig. 12), some fish species could be experiencing lethal effects in Clear Lake, especially in the Oaks Arm. This is consistent with the data presented by Suchanek et al. (2008*c*), indicating

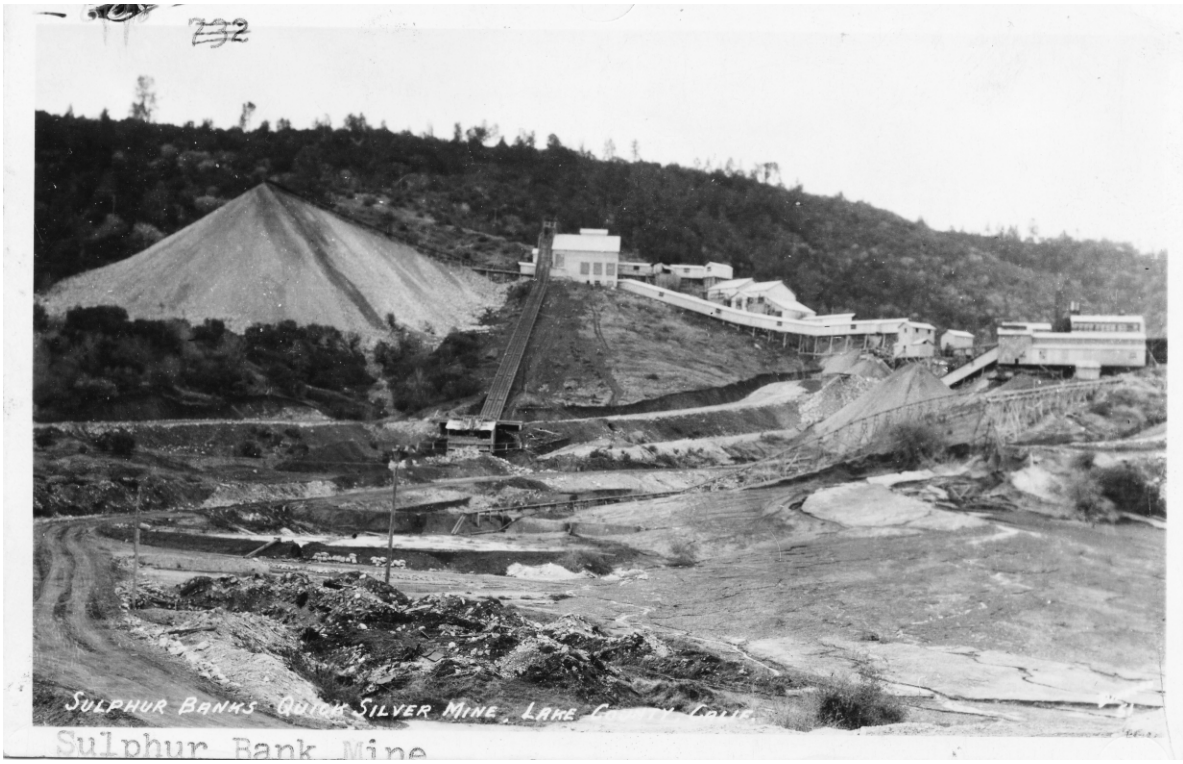

PLATE 5. Sulphur Bank Mercury Mine operations during large-scale production, with massive tailings pile on left, shortly before the end of the mining era ca. 1946 (courtesy of Lakeport Historic Courthouse Museum).

reduced population sizes in the Oaks Arm for several species of Clear Lake fishes.

Actual impacts to aquatic organisms?

Based on the numerous sediment and water criteria derived from the literature on TotHg concentrations discussed above, with some Clear Lake values exceeding various criteria for probable ecotoxicological effects by 1000–7000 times, it would appear that there is a significant potential for toxic impacts to be realized by Clear Lake biota. Because no formal toxicity studies have been performed on biota from Clear Lake, it is uncertain whether these projections would be accurate. However, because of a combination of factors present at Clear Lake, the relative production and/or bioaccumulation of MeHg may be significantly diminished from what might be expected based on the vast inorganic Hg loading (Suchanek et al. 2008*a*). These factors include: (1) a Hg source derived largely from refractory cinnabar, (2) the shallow nature of Clear Lake, preventing the development of a well-developed hypolimnion where the production of MeHg could be accelerated, (3) the slightly alkaline nature of Clear Lake water, (4) a generally positive reduction-oxidation (redox) environment, (5) abundant sulfides near the Hg source at the mine, (6) a low ratio of simultaneously extractable metals to acid volatile sulfides (SEM:AVS) in a large region of the lake, suggesting lowered toxicity, (7) potential complexation of Hg with dissolved organic matter, and (8) potential dilution of Hg by high organic productivity. With diminished MeHg production and the potential for sulfides to bind with Hg, it is possible that both the uptake and toxicity of MeHg at Clear Lake might be significantly lower than that observed in other systems in which many of the sediment and water criteria identified here were developed.

CONCLUSIONS

Clear Lake exhibits some of the highest sediment Hg concentrations of any lake system worldwide, with up to 483 mg/kg in surficial sediments and ~1200 mg/kg in near-surface sediments. Total mercury in sediments, water, and particles exhibits a classic point source distribution, with dramatically decreasing concentrations as a function of distance from the mine, both into the Upper Arm and the Lower Arm, although Hg concentrations are significantly higher in the Upper Arm compared with the Lower Arm, consistent with prevailing currents. For the time series data (1992–1998), there were no detectable long-term unidirectional trends of increasing or decreasing sediment or water TotHg. Methylmercury in both sediments and unfiltered water, however, exhibited seasonal increases in summer/fall periods at most sites in Clear Lake, but also no long-term trends up or down.

Mercury concentrations in water from monitoring wells at the mine site do not vary greatly over time, but the highest concentrations of aqueous Hg (~100 000 ng/L in unfiltered water) are found in three wells that are in a direct pathway to Clear Lake where large accumulations of AMD-generated floc have been reported previously (Suchanek et al. 2000*a*, *b*).

Only ~0.1% of the lake (1% of the Oaks Arm) sediment surface exceeds the California hazardous waste criterion for TotHg (20 mg/kg wet mass = 167 mg/kg dry mass), although aquatic organisms can experience deleterious effects at much lower concentrations. Relative to effects on benthic fauna, Clear Lake sediments exceed the PEC (0.18 mg/kg) and TEC (1.06 mg/kg) at virtually all sites and at all times, in some locations reaching as high as 1100 times the PEC and 6500 times the TEC.

Clear Lake water (at ~1–400 ng/L TotHg) is well below the federal Safe Drinking Water Act criterion of 2000 ng/L, but often exceeds the California Toxics Rule safe criterion of 50 ng/L and almost always exceeds the Great Lakes Initiative Mercury Criterion of 1.8 ng/L for the protection of human health. While TotHg in Clear Lake unfiltered water is well below the U.S. EPA's 2002 Water Quality Criteria for chronic exposure (770 ng/L) and acute exposure (1440 ng/L) for the protection of aquatic life, it does exceed the Hg criterion (0.641 ng/L in filtered water) for the protection of avian wildlife approximately half of the time. Clear Lake water also exceeds the TotHg criterion established by the Clean Water Act for the protection of aquatic life (12 ng/L) most of the time and the Hg criterion established in the Final Water Quality Guidance for the Great Lakes System for the protection of wildlife (1.3 ng/L) nearly always.

However, despite the significant inorganic Hg loading from the mine, a more complete understanding of the factors that foster or inhibit MeHg production, bioaccumulation, and toxicity suggests that the unique physical and chemical characteristics of Clear Lake may result in an aquatic ecosystem less impacted by MeHg toxicity than would be expected based on the TotHg concentrations alone (Suchanek et al. 2008*a*). These results suggest that an evaluation of potential ecotoxicological impacts vs. actual toxic effects should be a consideration for all studies of Hg contamination that involve varying chemical sources of Hg as well as other physical and chemical characteristics of the environment.

As of this writing (2007) the U.S. EPA Region IX Superfund program is currently undergoing further investigations at the mine and in Clear Lake to determine the best options for remediating ongoing Hg loading to Clear Lake from the Sulphur Bank Mercury Mine.

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APPENDIX A

Mercury in surficial sediments at North Wetland sites from August 1997 to September 1998 (*Ecological Archives* A018-076-A1).

APPENDIX B

Total mercury (TotHg) and methylmercury (MeHg) in unfiltered and filtered water from North Wetland sites from April 1997 to September 1998 (*Ecological Archives* A018-076-A2).

APPENDIX C

Total mercury (TotHg) and methylmercury (MeHg) in sediments within the Basalt Pit and two sites within the Herman Pit (Sulphur Bank Mercury Mine) (*Ecological Archives* A018-076-A3).

APPENDIX D

Aqueous total mercury (TotHg) and methylmercury (MeHg) in the Herman Pit, Basalt Pit, and monitoring wells at the Sulphur Bank Mercury Mine (*Ecological Archives* A018-076-A4).