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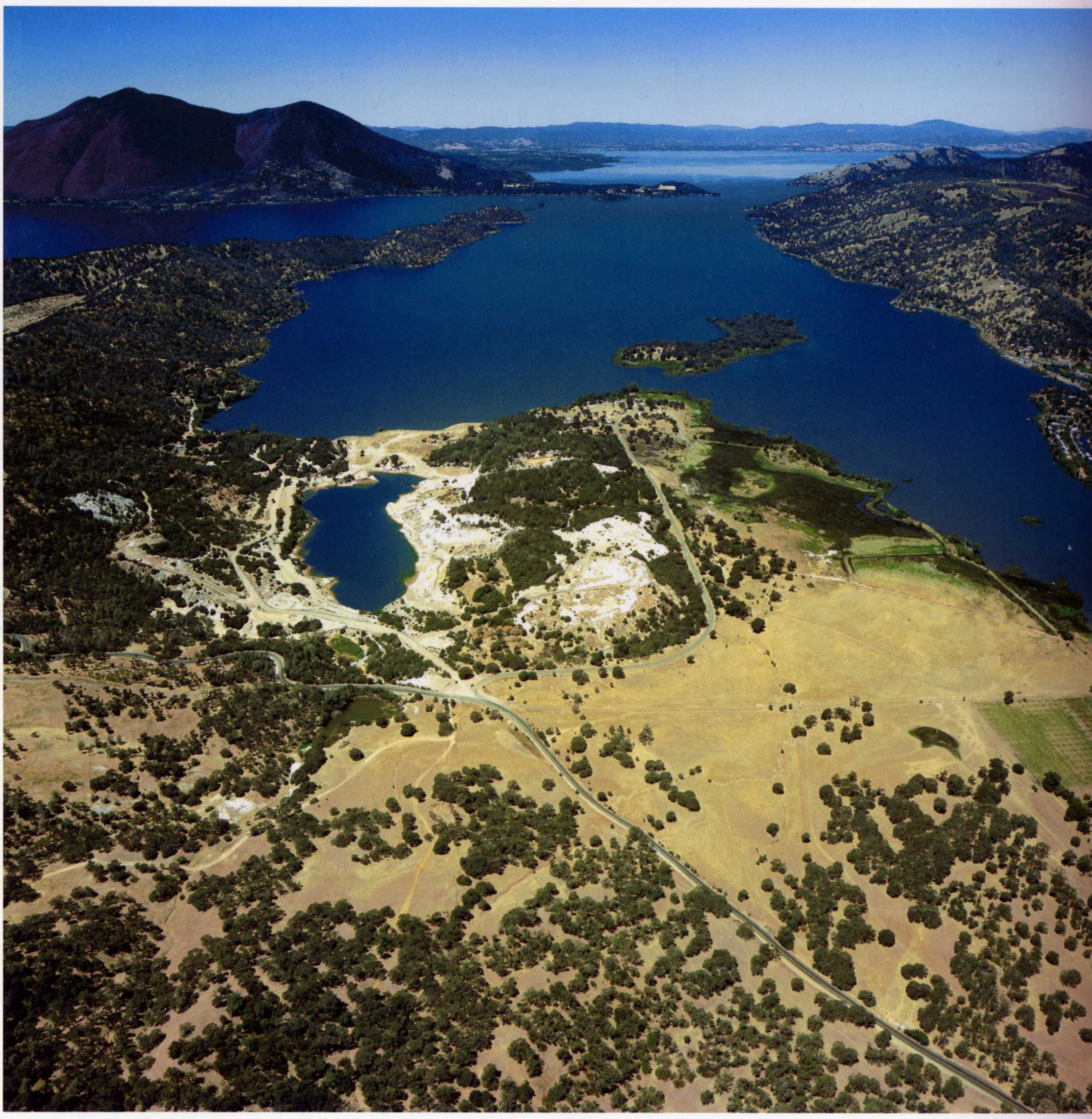

Mercury Cycling and Bioaccumulation in Clear Lake

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MINE-DERIVED MERCURY: EFFECTS ON LOWER TROPHIC SPECIES IN CLEAR LAKE, CALIFORNIA

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Abstract. Considerable ecological research on mercury (Hg) has focused on higher trophic level species (e.g., fishes and birds), but less on lower trophic species. Clear Lake, site of the abandoned Sulphur Bank Mercury Mine, provides a unique opportunity to study a system influenced by mine-derived Hg. An exponentially decreasing gradient of total Hg (TotHg) away from the mine allowed us to evaluate Hg bioaccumulation in planktonic and benthic invertebrates and evaluate population- and community-level parameters that might be influenced by Hg. Studies from 1992–1998 demonstrated that TotHg in lower trophic species typically decreased exponentially away from the mine, similar to trends observed in water and sediments. However, a significant amount of invertebrate TotHg (~60% for sediment-dwelling chironomid insect larvae) likely derives from Hg-laden particles in their guts. Spatially, whole-body methylmercury (MeHg) did not typically exhibit a significant decrease with increasing distance from the mine. Temporally, TotHg concentrations in plankton and chironomids did not exhibit any short-term (seasonal or annual) or long-term (multiyear) trends. Methylmercury, however, was elevated during late summer/fall in both plankton and chironomids, but it exhibited no long-term increase or decrease during this study. Although data from a 50-yr monitoring program for benthic chaoborid and chironomid larvae documented significant population fluctuations, they did not demonstrate population-level trends with respect to Hg concentrations. Littoral invertebrates also exhibited no detectable population- or community-level trends associated with the steep Hg gradient. Although sediment TotHg concentrations (1–1200 mg/kg dry mass) exceed sediment quality guidelines by up to 7000 times, it is notable that no population- or community-level effects were detected for benthic and planktonic taxa. In comparison with other sites worldwide, Clear Lake's lower trophic species typically have significantly higher TotHg concentrations, but comparable or lower MeHg concentrations, which may be responsible for the discrepancy between highly elevated TotHg concentrations and the general lack of observed population- or community-level effects. These data suggest that MeHg, as well as TotHg, should be used when establishing sediment quality guidelines. In addition, site-specific criteria should be established using the observed relationship between MeHg and observed ecological responses.

Key words: benthic invertebrates; chironomid; Clear Lake, California, USA; crayfish; mercury; mining; oligochaete; plankton; sediment quality criteria; sediment quality guidelines; Sulphur Bank Mercury Mine.

INTRODUCTION

This evaluation of mercury (Hg) in the lower trophic 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 abandoned Hg mine, through the abiotic (sediment and water) matrices, to lower trophic level species (benthic invertebrates and plankton) to higher trophic level species (e.g., fish, birds, and mammals). In addition to describing the spatial and temporal variability of Hg in the lower trophic species, it provides foundational data that are used in several other papers in this Special Issue, especially those that deal directly with the higher trophic level species such as fish and birds.

For contaminants such as Hg that biomagnify, concentrations in lower trophic level species can drive ultimate effects in higher level consumers such as fishes, birds, and mammals, including humans. But lower trophic level species can be affected directly by contaminants as well. Besides outright mortality, effects

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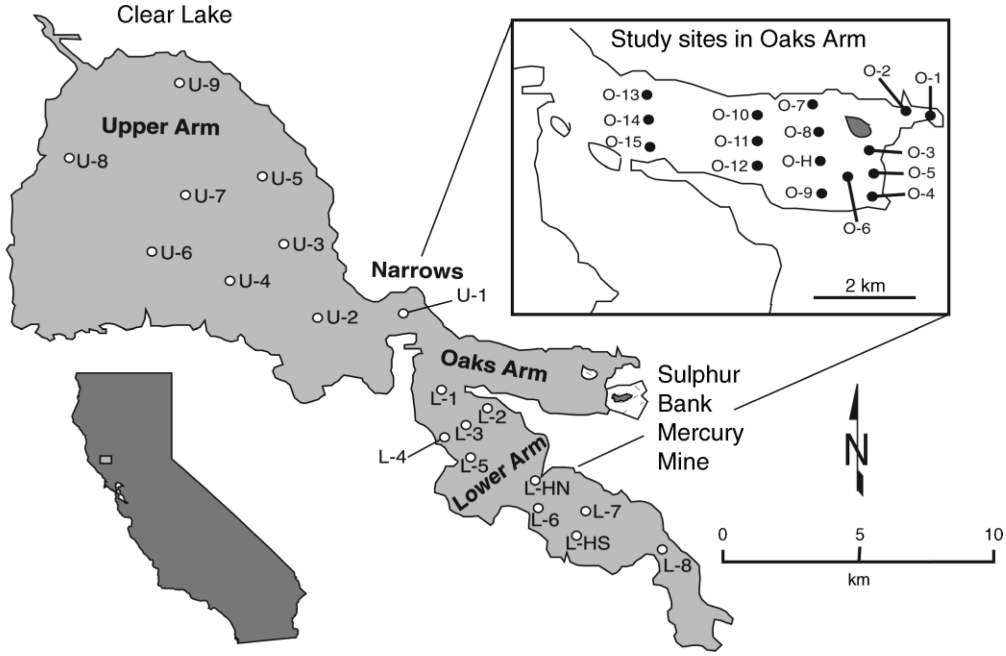

FIG. 1. Location of Sulphur Bank Mercury Mine and collection sites at Clear Lake during the preliminary lake survey in fall 1992.

of Hg on invertebrates can include malformations (Wiederholm 1984, Warwick 1991), reproductive impairment (Weiderholm and Dave 1989), and heterozygote deficiencies (Woodward et al. 1996). For example, in euryhaline crabs, Hg negatively affects active transport processes and disturbs the Na^+/K^+ pump and Cl^- channels in gill membranes (Pequeux et al. 1996). For freshwater species, brine shrimp (*Artemia*) raised in a lifetime 5 μg/L Hg environment had increased birth size and growth rates, but their lifespan was reduced (Sarabia et al. 1998). Crayfish have a 30-d exposure LC_{50} (the lethal concentration of a contaminant that causes 50% mortality in the test group) of 2.0 μg/L Hg in water, whereas the lifetime exposure LC_{50} for *Daphnia* is 1.3–1.8 μg/L Hg (U.S. EPA 1980). Higher level population- and community-level effects from Hg contamination have also been documented (Suchanek et al. 1995, 2000*a*, Horne et al. 1999).

A legacy of Hg mining at Clear Lake has resulted in ~100 Mg of Hg entering this aquatic ecosystem (see Suchanek et al. [1998, 2003, 2008*b*, *c*] for an overview and background). Mercury is moved in particulate and dissolved form from a point source, the abandoned Sulphur Bank Mercury Mine, to all regions of the lake by wind-driven currents (Rueda et al. 2008), producing an exponential decline of total Hg (TotHg) and methylmercury (MeHg) in sediments and water with increasing distance from the mine (Suchanek et al. 2008*b*).

Here we document Hg concentrations in Clear Lake plankton and benthic invertebrates from 1992 to 1998, compare those concentrations with other systems worldwide, relate them to Hg sources in the abiotic matrices of Clear Lake (e.g., sediments, water, and suspended particulate matter), and provide a summary of potential Hg effects on Clear Lake profundal and littoral invertebrate species. In addition, we present a 50-year (1954–2003) data set of relative abundance in two profundal invertebrates (benthic chaoborids and chironomids) and evaluate their fluctuations in relation to distance from the mine (as a proxy for Hg concentrations).

METHODS

This study was conducted at Clear Lake, California, site of the abandoned Sulphur Bank Mercury Mine, a U.S. Environmental Protection Agency (U.S. EPA) Superfund Site since 1990 (Suchanek et al. 2008*c*).

Most of the samples were collected from all three arms of Clear Lake from 1992 to 1998. Plankton and benthic invertebrates were collected: (1) during a single campaign in September/October of 1992 designated as the preliminary lake survey (PLS; see Fig. 1); (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 for studies from 1994 to 1998 are shown in Fig. 2. 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*b*, *c*, Shipp and Zierenberg 2008), were collected from August 1996 to March 1998. All samples were analyzed for TotHg and most for MeHg.

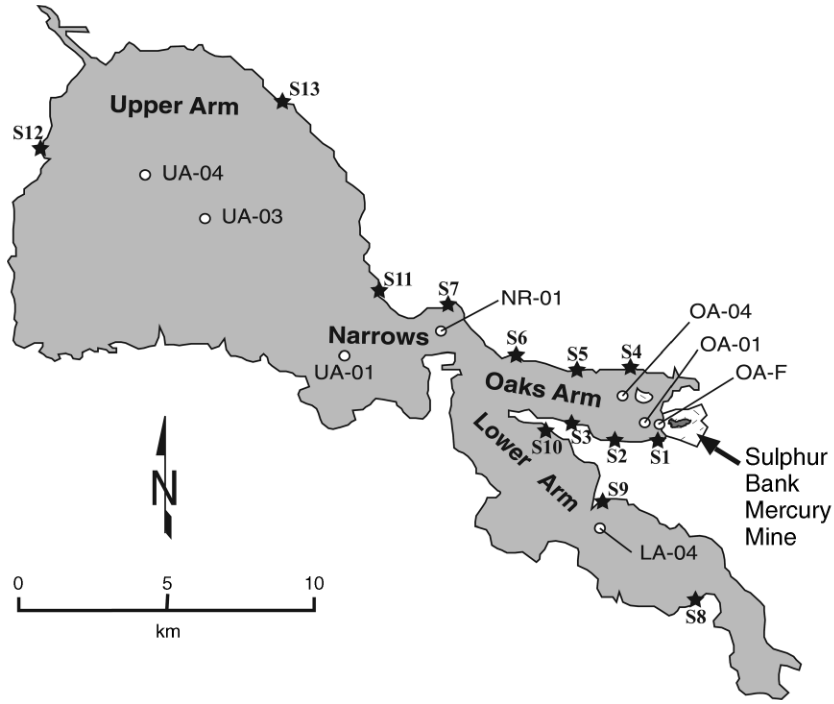

FIG. 2. Location of Sulphur Bank Mercury Mine and study sites at Clear Lake for the period 1993–1998. Stars represent littoral habitat collecting sites in 1993. Open circles are profundal collecting sites for the time series studies.

Plankton

A 25-cm diameter Nitex plankton net (80 μm mesh; SEFAR America, Briarcliff Manor, New York, USA) was towed behind a 6.69-m research vessel for two to four minutes at slow speed to collect total plankton samples. Clear Lake is a eutrophic lake with abundant cyanobacterial blooms; a large proportion of the plankton samples was comprised of cyanobacteria, primarily *Anabaena*, *Aphanizomenon*, and *Microcystis* (see Richerson et al. 1994). For zooplankton, a subset of each total plankton sample was washed carefully through a 300-μm Nitex screen with distilled water, eliminating the majority of the cyanobacteria mass. Total plankton and zooplankton were dried at 50°C until a constant mass was achieved (typically 24–48 h) and ground with mortar and pestle to a fine powder. Dried samples of both total plankton (all net plankton) and zooplankton were analyzed for TotHg and MeHg. A single sample from a large bloom of the cyanobacteria *Aphanizomenon* was also collected in July 1995 from the Oaks Arm, processed in the manner described above, and analyzed for Hg.

Benthic invertebrates

From 1954 to 2003, populations of benthic chironomid and chaoborid larvae were monitored (using an ~15-cm Ekman dredge) in surficial sediments from all three arms of Clear Lake (Upper Arm, 28 sites; Oaks Arm, 12 sites; Lower Arm, 18 sites). Collection sites for these benthic species were distributed uniformly throughout a band within ~0.8 km from shore along all three arms of the lake. These population data were used to evaluate relationships between population abundance and distance from the mine (as a proxy for sediment Hg concentrations). See Suchanek et al. (2008*b*) for the relationship between distance from the mine and Hg concentrations in sediments and water.

In a separate series of collections during the fall of 1992 and from 1994 to 1998, profundal invertebrates (primarily oligochaete worms, chironomid insect larvae, and leeches) were sampled from Clear Lake surficial sediments using an ~15-cm Ekman dredge. Oligochaete worms were analyzed for TotHg and MeHg from the fall of 1992 only. There are >10 species of oligochaetes in Clear Lake sediments, but we identified them only to Oligochaeta. This may have influenced the calculated benthic community structure indices by eliminating variance at the genus or species level. Chironomid insect larvae (*Chironomus* spp.) were analyzed for TotHg and MeHg from the entire collection period.

Littoral invertebrates were sampled at 13 sites around Clear Lake in November 1993 (see collection sites in Fig. 2). Representatives from four groups were collected for Hg analysis: leeches (*Mooreobdella tetragon*), case-making caddisflies (*Nectopsyche* sp.), amphipods (*Hyalella azteca*), and mixed snail species. In addition, littoral population and community samples (from water depths $\leq$ 35 cm) were collected from six replicates of 50×50 cm quadrats (sampling unit) at each of the 13 sites. Quadrat placement was haphazard at each site. Individuals ≥ 1 mm in size were identified to the lowest feasible taxonomic unit and counted. In order to provide equivalent comparisons to invertebrate community indices for other Clear Lake benthic species by Suchanek et al. (1995), Shannon-Wiener diversity and Pielou's evenness indices (Pielou 1975) were calculated to evaluate potential effects of Hg on population- and community-level parameters. Although another diversity index (Simpson's index) is not as sensitive (i.e., gives relatively less weight) to rarer species, both indices have shown virtually identical results for Clear Lake benthic fauna (Suchanek et al. 1995).

In 1994, opportunistic collections were made at several shoreline locations of two macroinvertebrate species: *Anodonta nuttalliana* (the winged floater mussel, an indigenous littoral bivalve) and *Corbicula fluminea* (the introduced, highly invasive Asiatic clam). These two species were analyzed for soft-tissue TotHg. *Procambarus clarkii*, the introduced Louisiana crayfish (red swamp crayfish), were collected using minnow traps at several locations around Clear Lake from 1992 to 1999 and analyzed for tail muscle TotHg.

Analytical Procedures

For the preliminary lake survey (1992)

Total mercury and MeHg were analyzed by Brooks Rand (Seattle, Washington, USA). Tissue samples were analyzed for TotHg (method detection limit [MDL] = 0.005 μg/g) using the methods of Roesijadi (1982). Samples were digested with an $HNO_3/HClO_4$ acid mixture. Mercury ions in the digestate were reduced by acidic $SnCl_2$ to TotHg and concentrated on a gold foil trap by purging with nitrogen. The gold foil trap was heated, and the released Hg was measured by atomic absorption. Tissue samples were analyzed for MeHg using the methods of Bloom (1989), following initial digestion and extraction in KOH/methanol. For both TotHg and MeHg analyses, method blanks and spikes were used with each set of samples analyzed. The range of spike recovery was within 75–125%.

For studies in 1994 and beyond

Aquatic invertebrate tissue samples, except as noted below, were analyzed by Battelle Marine Science Laboratory (Sequim, Washington, USA) using the methods previously described (see *For the preliminary lake survey (1992)*). Bivalves and crayfish were analyzed for TotHg (MDL = 0.005 μg/g) by digesting tissues in hot sulfuric/nitric acid and potassium permanganate under pressure in a two-stage process (see Slotton et al. [1995] for more details on methods). Digests were then analyzed using standard cold-vapor atomic absorption (CVAA) using a stannous chloride reductant. Method blanks, certified reference materials, and spikes were used with each set of samples analyzed. The range of spike recovery was within 85–115%. Results are presented in either dry mass (DM) or wet mass (WM) values.

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 lower trophic species. Spatial analyses were linear regressions of $\log_{10}$(TotHg [or MeHg]) concentrations vs. distance from the mine (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.

Temporal analyses were more complex. Two types of models were fit: a linear regression model of $\log_{10}$(TotHg) (and $\log_{10}$(MeHg), and in some cases $\log_{10}$(MeHg:TotHg)) by year within each site and corresponding analyses of covariance that incorporated sites into the models for lower trophic species. The linear regression models, computed within each site, were done to visualize the possible effects of a year × site interaction. The tests were not equivalent to the year × 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 used year as the covariant and site as the factor. Models were fit with and without the year × site interaction term. If the interaction term was not significant, then the additive model, containing only year and site, was appropriate. However, multiple comparisons tests were performed 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 using site as the 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 test is a weaker form of protection against spurious significant statistical outcomes. However, for completeness the LSD was run 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. By bracketing a range of conservatism, the two approaches provide a bounding analysis for the statistical significance assessment.

Site effects were also evaluated within each sample year. As with the trend analysis within sites, the site analysis within years provides information on the possible year × site interaction. The nested trend and

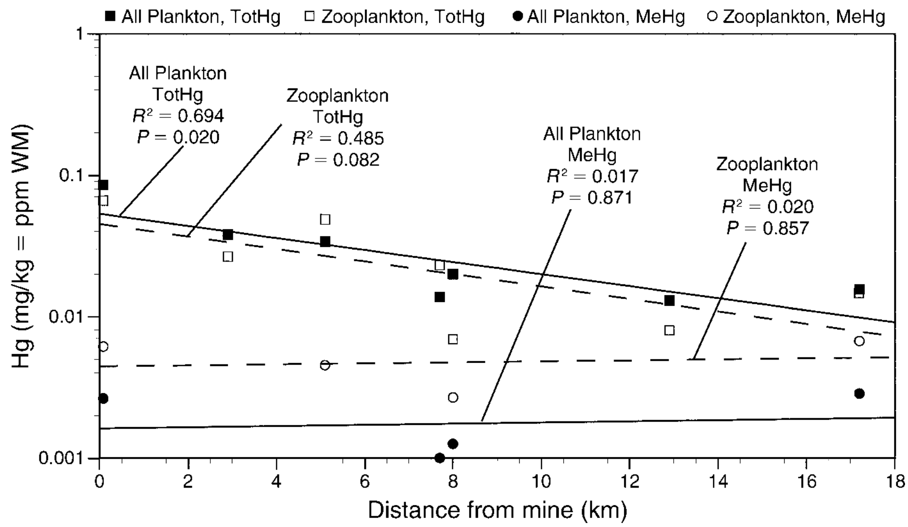

FIG. 3. Total mercury (TotHg) and methylmercury (MeHg) in plankton (both All Plankton group and Zooplankton group) as a function of distance from the Sulphur Bank Mercury Mine from the preliminary lake survey (PLS) study (fall 1992; "WM" indicates wet mass). The R^2 values are adjusted for potentially small sample sizes. The curve fits are exponential.

site analyses were most useful in interpreting a significant year × site interaction. Significance levels in this study were defined as a probability value of $P < 0.05$.

RESULTS

Spatial trends

Mercury in plankton.—Mercury was analyzed for all plankton (all net plankton, including masses of several species of cyanobacteria) and zooplankton only. The proportion of each sample that was zooplankton varied among samples depending mostly on the presence of large masses of cyanobacteria. Total mercury was higher in zooplankton at some sites and higher in all plankton at other sites, but no uniform proportional trends between these two plankton groups emerged for all sites or as a function of distance (Fig. 3). Total mercury ranged from 0.01 to 0.09 mg/kg WM in the all-plankton group and from 0.01 to 0.07 mg/kg WM in the zooplankton-only group; both declined as a function of distance from the mine, but only the all-plankton group exhibited a statistically significant decreasing trend ($P = 0.020$), whereas the zooplankton group was close to significance at $P = 0.082$ (linear regression). No significant difference was recorded for TotHg between the all-plankton group and the zooplankton group as a function of distance from the mine ($P = 0.949$, ANCOVA). For MeHg, the all-plankton group (0.001–0.003 mg/kg WM) were typically lower than the zooplankton group (0.003–0.007 mg/kg WM) and neither exhibited any significant trends as a function of distance from the mine ($P = 0.871$ and $P = 0.857$, respectively; linear regression; Fig. 3), and the two data sets were not significantly different ($P = 0.984$, ANCOVA).

Mercury in profundal invertebrates.—The most common profundal benthic invertebrates (chironomid insect larvae and oligochaete worms) also exhibited decreasing TotHg as a function of distance from the mine (see Figs. 4 and 5 for data from the PLS study only). For data from the multiyear temporal study (see Fig. 12) chironomid TotHg ranged from 4.47 mg/kg WM (at OA-01, the closest site) to 0.01 mg/kg WM (at site LA-04, about a third of the distance down the Lower Arm) with a significant decline as a function of distance from the mine ($P = 0.020$).

Because chironomids consume particles at the sediment–water interface, Hg bound to sediments in the gut may significantly influence the measured concentration of Hg in the whole organism. Our data, however, represent Hg values for chironomids without purging their guts because our study was focused on what the next higher trophic level would consume and potentially assimilate. To test the potential influence of gut contents on Hg concentrations, we conducted a gut-purging experiment. Four samples of ~50 chironomids each were collected using an Ekman dredge in December 1998 from site UA-03 (Fig. 2). Sediments at this site contained ~2.0 mg/kg DM TotHg and 0.001 mg/kg DM MeHg (Suchanek et al. 2008*b*). The four samples were separated into two treatments: purged guts and unpurged guts. Chironomids from the unpurged gut treatment were sacrificed immediately, dried, and analyzed for Hg. Chironomids from the purged gut treatment were held in beakers containing lake water (from the same site) in the laboratory for 48–72 h until their digestive tracts were purged of sediment, at which time they were dried and analyzed. Because of the small biomass, the two samples within each treatment were composited to obtain enough biomass to analyze. The composited sample of chironomids with unpurged guts

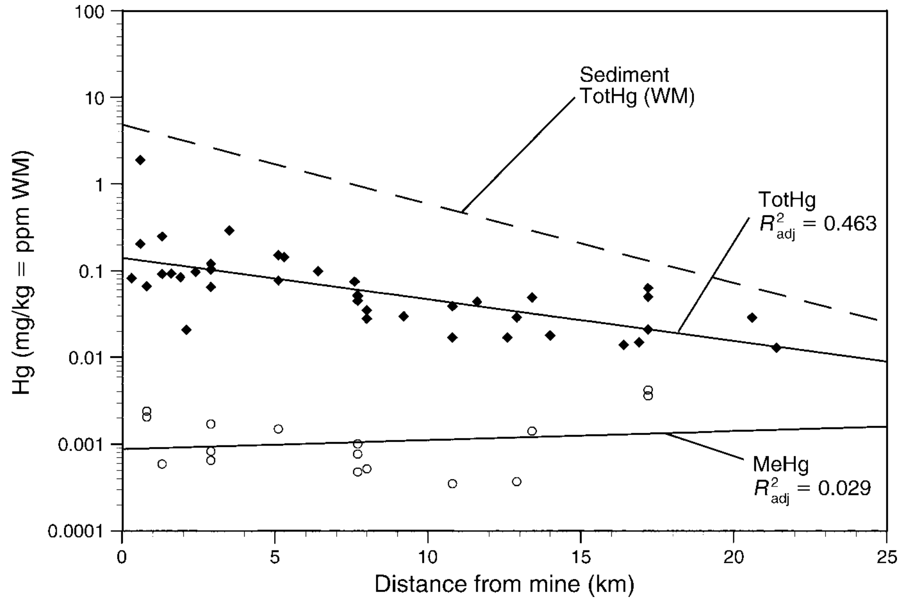

FIG. 4. Total mercury (TotHg) and methylmercury (MeHg) in chironomid insect larvae as a function of distance from the Sulphur Bank Mercury Mine during the preliminary lake survey study (fall 1992; "WM" indicates wet mass). The R^2 values are for chironomids and are adjusted for potentially small sample sizes. The dashed line is a curve fit for sediment TotHg (here represented as wet mass) from Suchanek et al. (2008*b*). The curve fits are all exponential.

yielded a TotHg concentration of 0.763 mg/kg DM, whereas the sample of chironomids with purged guts was 0.288 mg/kg DM TotHg. These limited data suggest that Hg in sediments within the gut (at least at site UA-03) likely contributes ~62% of the TotHg body burden in these organisms. This percentage may be different at other sites within the lake. Interestingly, MeHg in the unpurged treatment group was 0.031 mg/kg DM whereas those with purged guts had 0.067 mg/kg DM MeHg. This is likely due to the fact that a chironomid with a purged gut is significantly lighter than one with a full gut. Thus, assuming the sediments in the gut contained primarily inorganic Hg (~2000 times higher than the MeHg concentrations), the same mass of MeHg in the lighter body tissue mass of the purged chironomids would increase the concentration. The dry-to-wet Hg concentration conversion for chironomids is 0.068 (i.e., 6.8% solids). To demonstrate the relationship between chironomid TotHg and sediment TotHg, Fig. 4 also contains an additional fitted curve of sediment TotHg as a function of distance from the mine taken from data in Suchanek et al. (2008*b*). Methylmercury in

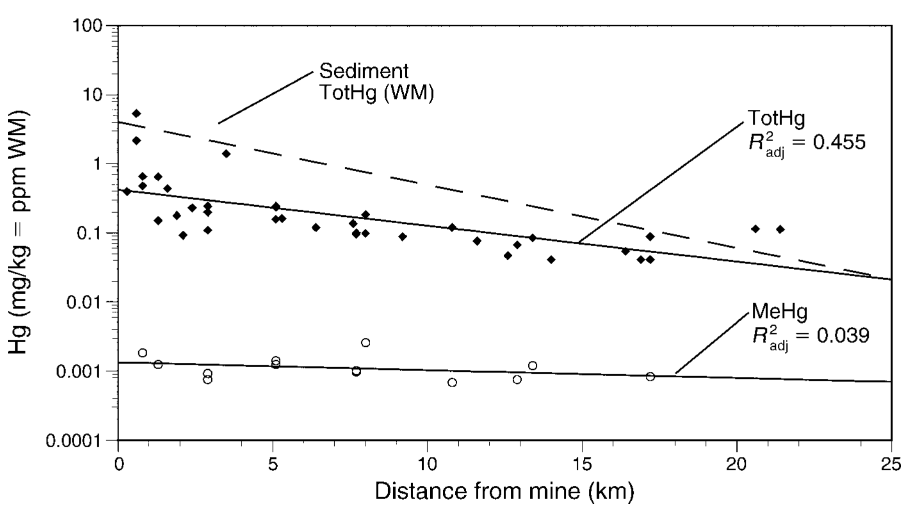

FIG. 5. Total mercury (TotHg) and methylmercury (MeHg) in oligochaete worms as a function of distance from the Sulphur Bank Mercury Mine during the preliminary lake survey (PLS) study (fall 1992; "WM" indicates wet mass). The R^2 values are adjusted for potentially small sample sizes. The dashed line is a curve fit for sediment TotHg (wet mass) from Suchanek et al. (2008*b*). The curve fits are exponential.

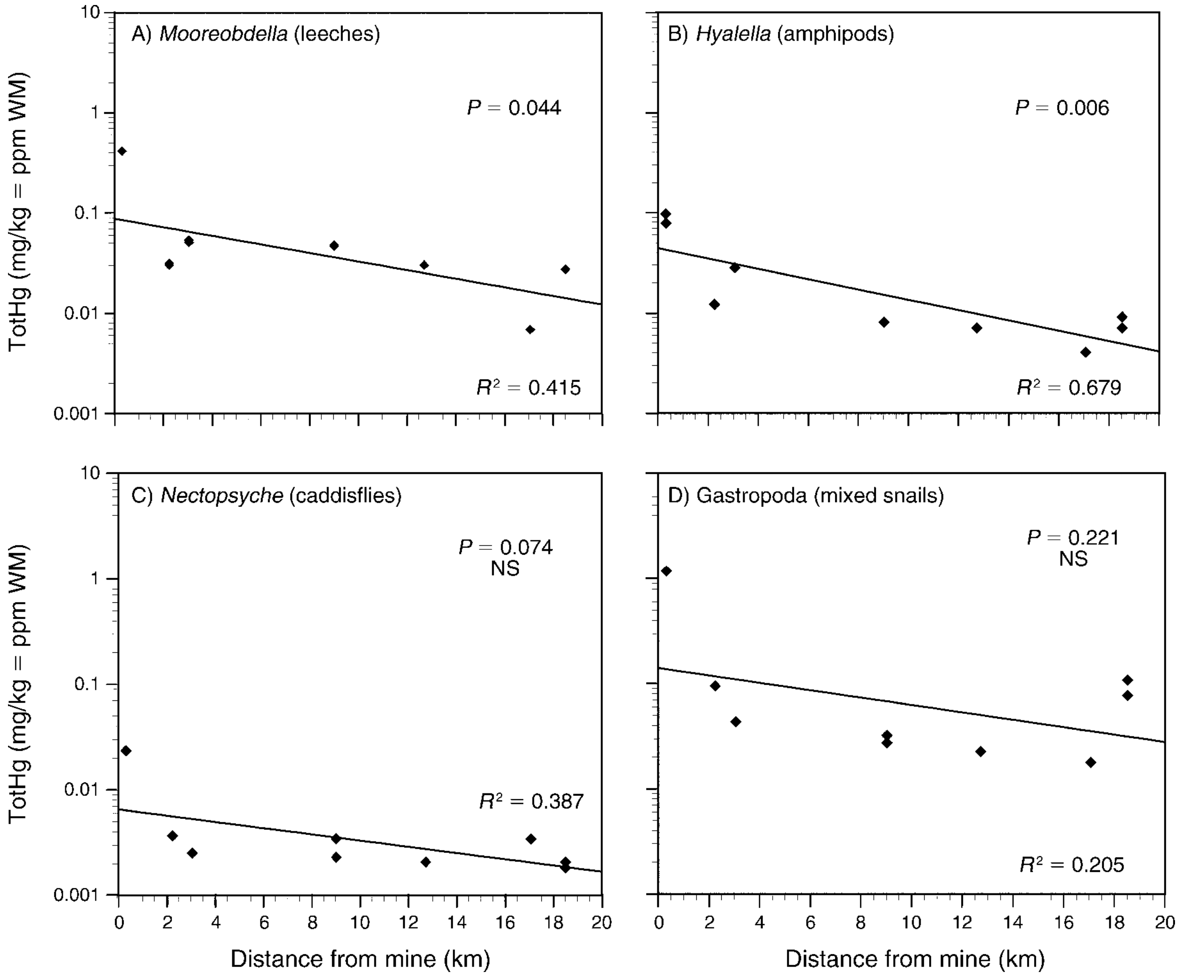

FIG. 6. Total mercury (TotHg) in four groups of littoral invertebrates as a function of distance from the Sulphur Bank Mercury Mine in November 1993. All curve fits are exponential (NS, not significant).

chironomids was one to two orders of magnitude lower than TotHg and did not exhibit any significant trend as a function of distance from the mine ($P = 0.857$).

In 1992, TotHg in oligochaetes ranged from 0.041 mg/kg WM (at several sites distant from the mine) to 5.38 mg/kg WM at O-3 (Fig. 5), the same site where TotHg in chironomids reached its maximum (Fig. 4), which is also the site with the highest TotHg concentrations in sediment. Oligochaete guts were not purged. As in the other biotic components, TotHg in oligochaetes also decreased significantly ($P < 0.0001$) as a function of distance from the mine. As with chironomids, MeHg in oligochaetes exhibited no significant decline with distance ($P = 0.249$; Fig. 5).

Mercury in littoral invertebrates.—Four invertebrate taxa collected during the November 1993 littoral survey were collected in sufficient abundance to analyze for Hg. Total mercury exhibited a significant decline with distance from the mine in the amphipod *Hyalella* ($P = 0.006$) and the leech *Mooreobdella* ($P = 0.044$; Fig. 6). However, while there was some decline in TotHg in the caddisfly *Nectopsyche* and mixed snails with distance from the mine (see Fig. 6), this relationship was not significant ($P = 0.074$ and $P = 0.221$, respectively).

Opportunistic collections of littoral bivalves (*Corbicula* and *Anodonta*) in November 1994 provided an opportunity to evaluate Hg bioaccumulation as a function of proximity to the mine. Mercury in bivalves (which can be long lived) can be influenced by both shell length (which can be used as a proxy for age) as well as distance from a contaminant source, so it is important to define how each of those variables is related to Hg body burdens. Both bivalve species exhibited similar trends in Hg concentrations with respect to both shell length and distance from the mine (Fig. 7). For both *Anodonta* and *Corbicula*, Hg concentrations were not significantly correlated with shell length (Fig. 7A, C), but Hg concentrations in both species decreased significantly as a function of distance from the mine ($P = 0.013$ and $P < 0.0001$, respectively; Fig. 7B, D). While no other samples were collected between 0 and 4 km distance, those closest to the mine were consistently higher in

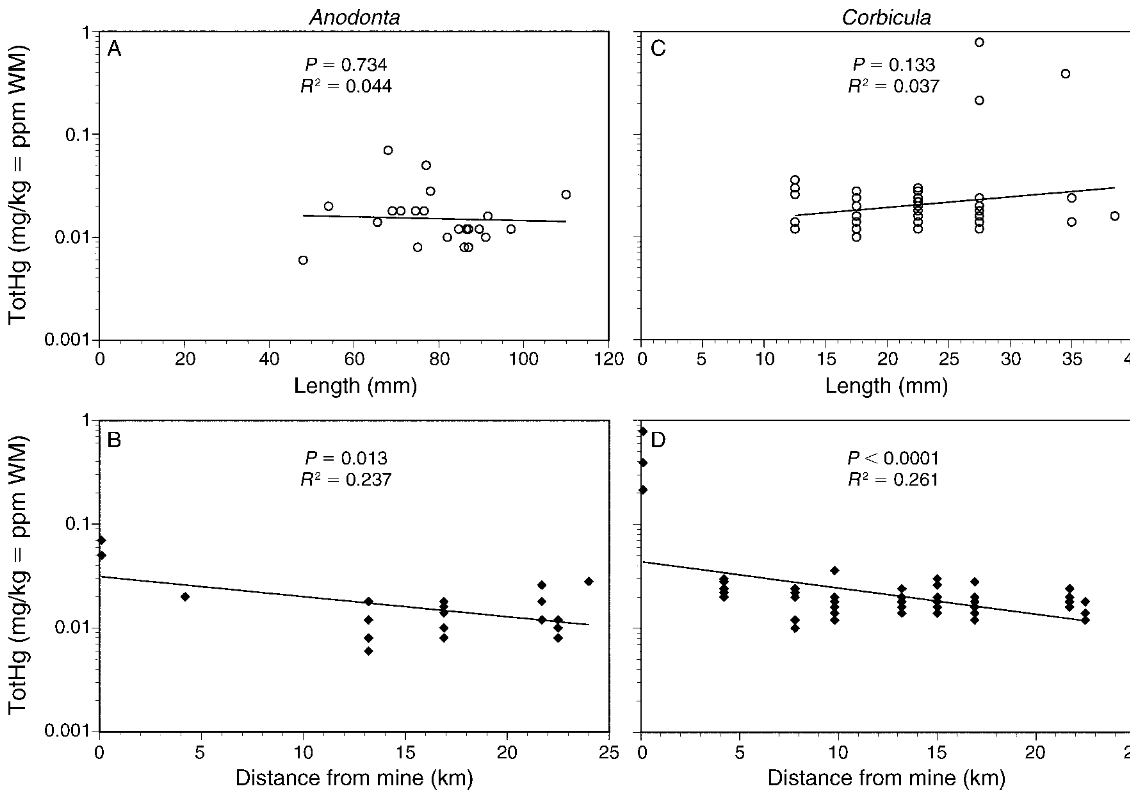

FIG. 7. Total mercury (TotHg) in the littoral bivalves *Anodonta* and *Corbicula* in November 1994. (A) *Anodonta* Hg vs. shell length, (B) *Anodonta* Hg vs. distance from the Sulphur Bank Mercury Mine, (C) *Corbicula* Hg vs. shell length, and (D) *Corbicula* Hg vs. distance from the mine. The R^2 values are adjusted for potentially small sample sizes. The curve fits are exponential.

TotHg by an order of magnitude or more. The difference in the trends of Hg concentrations between sediment-dwelling bivalves and surface-dwelling insect larvae (Figs. 4 and 5) or littoral fauna (Fig. 6) may be related to the life history of the latter group deriving food from water-based sources as opposed to sediment-based sources for the former.

Both TotHg and MeHg in *Procambarus* crayfish collected from 1992 to 1999 also decreased significantly with distance from the mine ($P = 0.001$ and $P = 0.006$, respectively), with concentrations ranging over more than two orders of magnitude at some sites (Fig. 8). Size was similarly noninfluential in determining Hg concentrations at any particular site.

Population- and community-level parameters

Profundal invertebrates.—Abundance of chironomid and chaoborid larvae in all three arms of Clear Lake were monitored for 50 years (from 1954 to 2003), the longest continuous data set for any organisms in Clear Lake (Fig. 9). Several anthropogenic events may have influenced population fluctuations in these species during that period (see Suchanek et al. 2003). While populations of chironomids exhibited less variability over the 50-year study (with some noticeable increases since the 1980s), chaoborid populations underwent dramatic temporal fluctuations (Fig. 9). Temporal data from Richerson et al. (2008) indicate that lake bed sediment TotHg has generally declined throughout Clear Lake since about the 1950s, but it is impossible to determine whether population fluctuations of chaoborids or chironomids over the past 50 years have been influenced by changing sediment Hg concentrations. Other factors may have been much more influential. *Chaoborus astictopus* (the non-biting mosquito-like "Clear Lake gnat") was a nuisance pest and, in an attempt to reduce numbers of the adult winged form by controlling its benthic/planktonic larval populations, large quantities of dichlorodiphenyldichloroethane (DDD) were applied to the lake in 1949, 1954, and 1957 (see discussion in Suchanek et al. 2003). Additional control was attempted using lakewide applications of methyl parathion from 1962 to 1975. Furthermore, deliberate and/or accidental introductions of several alien planktivorous species, (1) inland silversides (*Menidia beryllina*) in 1967, (2) threadfin shad (*Dorosoma petenense*) in 1985, and (3) the predaceous plankter *Leptodora kindtii* in 1985, may have altered their populations significantly (see Eagles-Smith et al. 2008). Nonetheless, this long-term data set provides an excellent opportunity to evaluate whether there is a

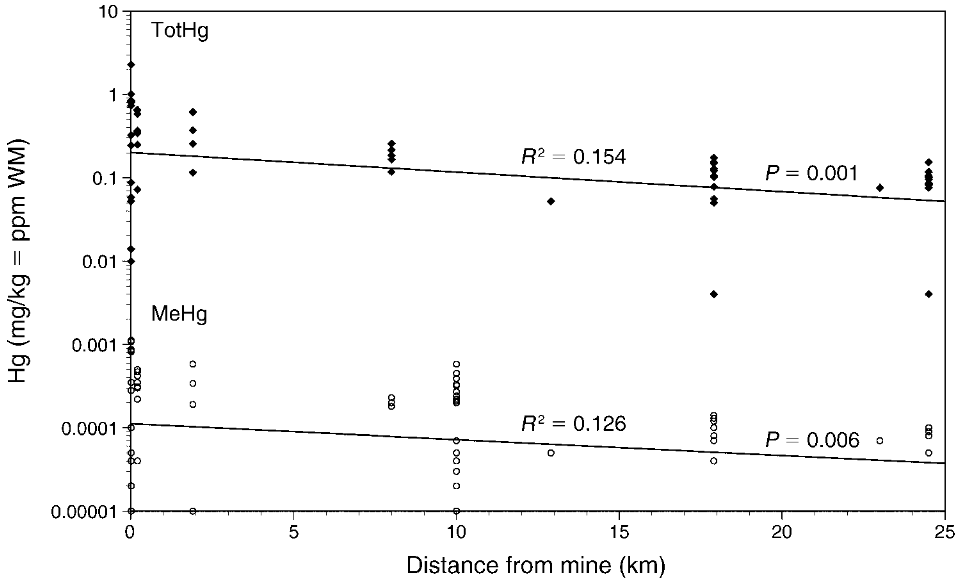

FIG. 8. Total mercury (TotHg) and methylmercury (MeHg; wet mass) in *Procambarus* crayfish as a function of distance from the Sulphur Bank Mercury Mine throughout the entire study. The curve fits are exponential.

relationship between chironomid and chaoborid populations vs. Hg in Clear Lake.

Population data for benthic chaoborids and chironomids (from 1988 to 1994, the years for which data from the widest distribution of sites is available) are plotted for each site as a function of distance from the mine in Fig. 10 (as a proxy for sediment Hg concentrations; see Suchanek et al. 2000*b*, *c*, 2008*b*). Linear regression analysis of log of abundance vs. distance from the mine indicates no significant relationship for chaoborids ($P = 0.51$, $n = 78$), but chironomids show significantly increasing abundance with distance ($P = 0.02$, $n = 203$). Other sources of variability may be influencing these distribution patterns on a lake-wide basis.

Littoral invertebrates.—Clear Lake littoral invertebrate communities, sampled at 13 sites in November 1993, yielded 21 taxa (Table 1). An analysis of individual population numbers and biomass for each of the 21 taxa of littoral invertebrates for the six replicates at each of the 13 sites yielded only nine species that had sufficient abundance on which to perform statistical analyses. Of those nine, only three showed significant relationships with distance from the mine (as a proxy for Hg concentrations at each of those sites). *Tinodes* and *Petrophila* exhibited significant declines in both numerical abundance and biomass as a function of distance from the mine (i.e., increasing abundance closer to the mine; Table 2). Larval chironomids (Chironominae) were the only taxonomic group that exhibited significant increases with distance (i.e., lower densities closer to the mine). The community indices Shannon-Wiener diversity (H') and Pielou's evenness (J') yielded no significant trends with distance from the mine. Horne et al. (1999) also found no consistent patterns of population densities for specific species of benthic fauna in response to point sources of pollutants such as Hg and polychlorinated biphenyls (PCBs), but did report shifts in the proportions of surface vs. subsurface feeders as a function of proximity to the contaminant source.

Temporal trends

Plankton.—Time series data indicate that TotHg in zooplankton ranged from 0.004 mg/kg WM (at site LA-04 in November 1995) to 0.145 mg/kg WM (at site OA-01 in March 1998), with the range of values for any one sampling date spanning about one order of magnitude between sites with the highest and lowest Hg concentrations (Fig. 11). Similar to trends in abiotic matrices (sediments and unfiltered water; Suchanek et al. 2008*b*), zooplankton TotHg also declined as a function of distance from the mine. Although most sites varied together over time, there were no consistent peaks of TotHg seasonally. In addition, linear regression analyses indicate that there were no long-term unidirectional trends (increases or decreases) in TotHg for zooplankton at any site from 1992 to 1998 ($P > 0.05$). Methylmercury in zooplankton, which ranged from ~0.001 to 0.031 mg/kg WM, also exhibited no long-term unidirectional trends at any sites during the study period ($P > 0.05$), but did exhibit clear peaks during summer periods (Fig. 11). The highest value was recorded during a single sampling event at OA-F (the floc site) in August 1998. The MeHg:TotHg ratio in zooplankton varied by nearly two orders of magnitude and exhibited a trend of increasing values as a function of distance from the mine (Fig. 11). Some sites (OA-01, OA-04, and LA-04) did show significantly increasing trends in the MeHg:TotHg ratio over time ($P < 0.0001$,

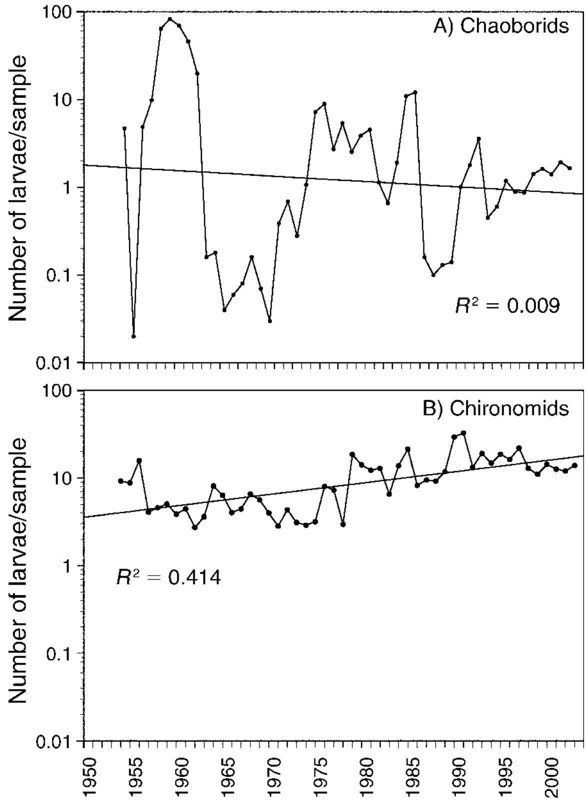

FIG. 9. Population fluctuations in benthic chaoborid and chironomid larvae in Clear Lake sediments as reflected in the mean number of larvae per Ekman grab sample per year from 1954 to 2003. Data are annual averages from all three arms of Clear Lake with 696 Ekman samples collected per year. The curve fits are exponential.

$P = 0.013$, and $P = 0.041$, respectively). Although quite variable, peaks of the MeHg:TotHg ratio occurred more often in summer/fall and minimal values occurred more often in winter.

Tukey's HSD and Fisher's LSD tests suggest that zooplankton throughout the Oaks Arm (the arm closest to the mine) have mostly comparable TotHg, but as a group are differentiated from zooplankton throughout the rest of Clear Lake (Table 3). For MeHg, Tukey's HSD test suggests that all sites are comparable; but the more liberal Fisher's LSD test suggests more finely defined differences among sites, but still retains significant differences between Oaks Arm and other sites in Clear Lake. The ratio of MeHg:TotHg shows similar patterns, indicating higher level differences between Oaks Arm and other sites within Clear Lake. Multiple comparisons tests for differences by year yielded mixed results. For TotHg and the MeHg:TotHg ratio, there were significant differences among sites in 1994 and 1995, but not for 1996. Insufficient data were available for tests in 1997. For MeHg, no differences among sites were documented for any year.

Profundal invertebrates.—Chironomid midge larvae exhibited spatial patterns of TotHg concentrations that decreased as a function of distance from the mine, with concentrations ranging over more than two orders of magnitude from a minimum of 0.01 mg/kg WM at site LA-04 in September 1994 to a maximum of 4.47 mg/kg WM at site OA-01 in June 1994 (Fig. 12).

Chironomid guts were not purged in the seasonal samples, thus a substantial portion of the Hg concentrations reported here could have been related to the sediments contained within their digestive tract. Thus, for comparison, the TotHg, MeHg, and MeHg:TotHg ratio values for sediments (plotted on a wet mass basis) from OA-01 (from Suchanek et al. 2008*b*) have been plotted on the panels depicting temporal changes in Fig. 12. It appears that some, but not all, of the variability in chironomid TotHg, MeHg, and MeHg:TotHg ratios may be due to the sediments within their guts.

Linear regression analysis verified that there were no long-term unidirectional temporal changes in chironomid TotHg, MeHg, or the MeHg:TotHg ratio (Table 4 and Fig. 12). Tukey's HSD and Fisher's LSD tests indicate that for chironomid TotHg there were strong differences among virtually all sites. For MeHg, however, only OA-01 (the site closest to the mine) was significantly different (higher) than all other sites, which had very similar fluctuating trends over time. The MeHg:TotHg ratio more closely resembled the differences in time series trends exhibited by MeHg (Fig. 12), but with some similarities within groups of sites (see

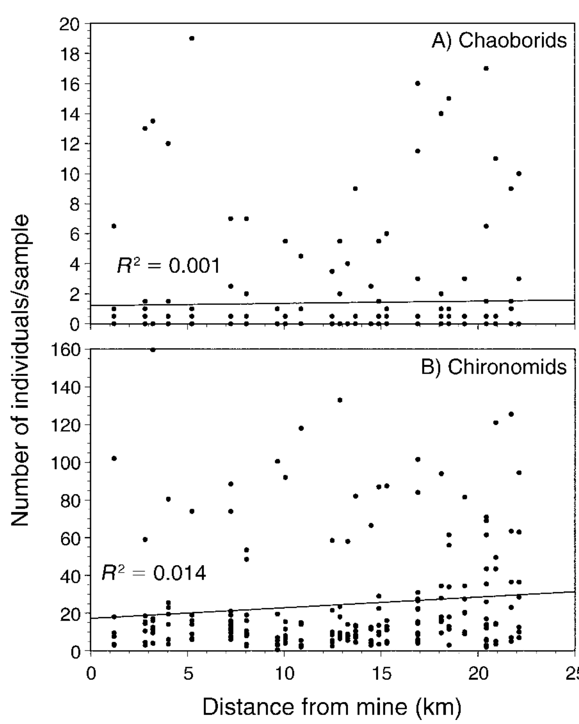

FIG. 10. Population data for chaoborids and chironomids per Ekman grab sample per year from 1988 to 1994 plotted as a function of distance from the Sulphur Bank Mercury Mine. The fitted lines are both linear. Note different ordinate scales.

TABLE 1. List of taxa identified in the littoral survey, November 1993.

Phylum/Class/Order/Family Genus and species	Common name	Trophic status
Arthropoda/Insecta/Trichoptera/Leptoceridae *Nectopsyche* sp.	case-building caddisfly larva	omnivore
Arthropoda/Insecta/Trichoptera/Psychomyiidae *Tinodes* sp.	net-spinning caddisfly larva	herbivore
Arthropoda/Insecta/Ephemeroptera/Caenidae *Caenis* sp.	mayfly nymph	collector-gatherer
Arthropoda/Insecta/Heteroptera/Corixidae *Corisella decolor*	water boatman	herbivore
Arthropoda/Insecta/Hemiptera/Naucoridae *Ambrysus mormon*	creeping water bug	predator
Arthropoda/Insecta/Diptera/Chironomidae unknown species	chironimid larva	collector-gatherer
Arthropoda/Insecta/Diptera/Orthocladinae unknown species	dipteran larva	collector-gatherer
Arthropoda/Insecta/Odonata/Coenagrionidae *Enallagma* sp.	damselfly nymph	predator
Arthropoda/Insecta/Lepidoptera/Pyralidae *Petrophila confusalis*	aquatic moth larva	grazer/herbivore
Arthropoda/Insecta/Coleoptera/Elmidae *Dubiraphia* sp.	riffle beetle	herbivore
Arthropoda/Amphipoda/Malacostraca/Hyalellidae *Hyalella azteca*	amphipod	detritivore
Arthropoda/Arachnoidea/Hydracarina unidentified mite	red mite	
Mollusca/Gastropoda/Basommatophora/Lymnaeidae *Physa* sp.	snail	grazer
Mollusca/Gastropoda/Basommatophora/Lymnaeidae *Lymnaea* sp.	snail	grazer
Mollusca/Gastropoda/Basommatophora/Planorbidae *Gyraulus* sp.	snail	grazer
Mollusca/Bivalvia/Veneroida/Corbiculidae *Corbicula fluminea*	Asiatic clam	filter feeder
Annelida/Oligochaeta unknown species	oligochaete worm	detritivore
Annelida/Hirudinea/Pharyngobdellida/Arhychobdellida *Mooreobdella tetragon*	leech	predator
Annelida/Hirudinea/Rhyncobdellida/Glossiphoniidae *Helobdella papillata*	leech	predator
Helobdella triserialis	leech	predator
Helobdella stagnalis	leech	predator

Table 4). Multiple comparisons tests for TotHg and the MeHg:TotHg ratio indicate significant differences among sites in all years where enough data were available for testing. For MeHg, only 1995 showed significant differences among sites.

DISCUSSION

Spatial trends (Fig. 3) and, to a lesser extent, temporal trends (Fig. 11) for TotHg in zooplankton followed patterns very similar to those of sediments (see Figs. 4 and 5), with declining concentrations as a function of distance from the mine. However, the decline in sediment Hg (a factor of ~100 across the lake) is much steeper than that for zooplankton (a factor of ~10). Methylmercury in zooplankton, however, did not exhibit comparable spatial/temporal patterns to those of sediments. Zooplankton at most sites had very similar MeHg concentrations that typically peaked in summer/fall (Fig. 11). This was likely due to MeHg concentrations on particles that they were consuming within the water column throughout the year. Methylmercury in Clear Lake sediments exhibits distinct seasonal patterns, with maxima in summer/fall and minima in winter/spring (Suchanek et al. 2008*b*). With Hg-laden particles (both biotic and abiotic) being remobilized from the

TABLE 2. Significance (P) values from linear regression analyses for abundance and biomass of littoral invertebrates (shown in Table 1; $N = 78$ for all analyses).

Genus	Abundance	Biomass
Tinodes	(−) 0.025	(−) 0.048
Nectopsyche	0.146	0.133
Petrophila	(−) 0.012	(−) 0.007
Chironominae	(+) 0.005	(+) 0.007
Orthocladinae	0.186	0.208
Hyalella	0.267	0.197
Physa	0.324	0.602
Helobdella	0.195	0.119
Mooreobdella	0.054	0.272

Notes: Shannon-Wiener diversity (H') for abundance = 0.309 and for biomass = 0.204. Pielou's evenness (J') as a function of distance from the mine for abundance = 0.099 and for biomass = 0.270.

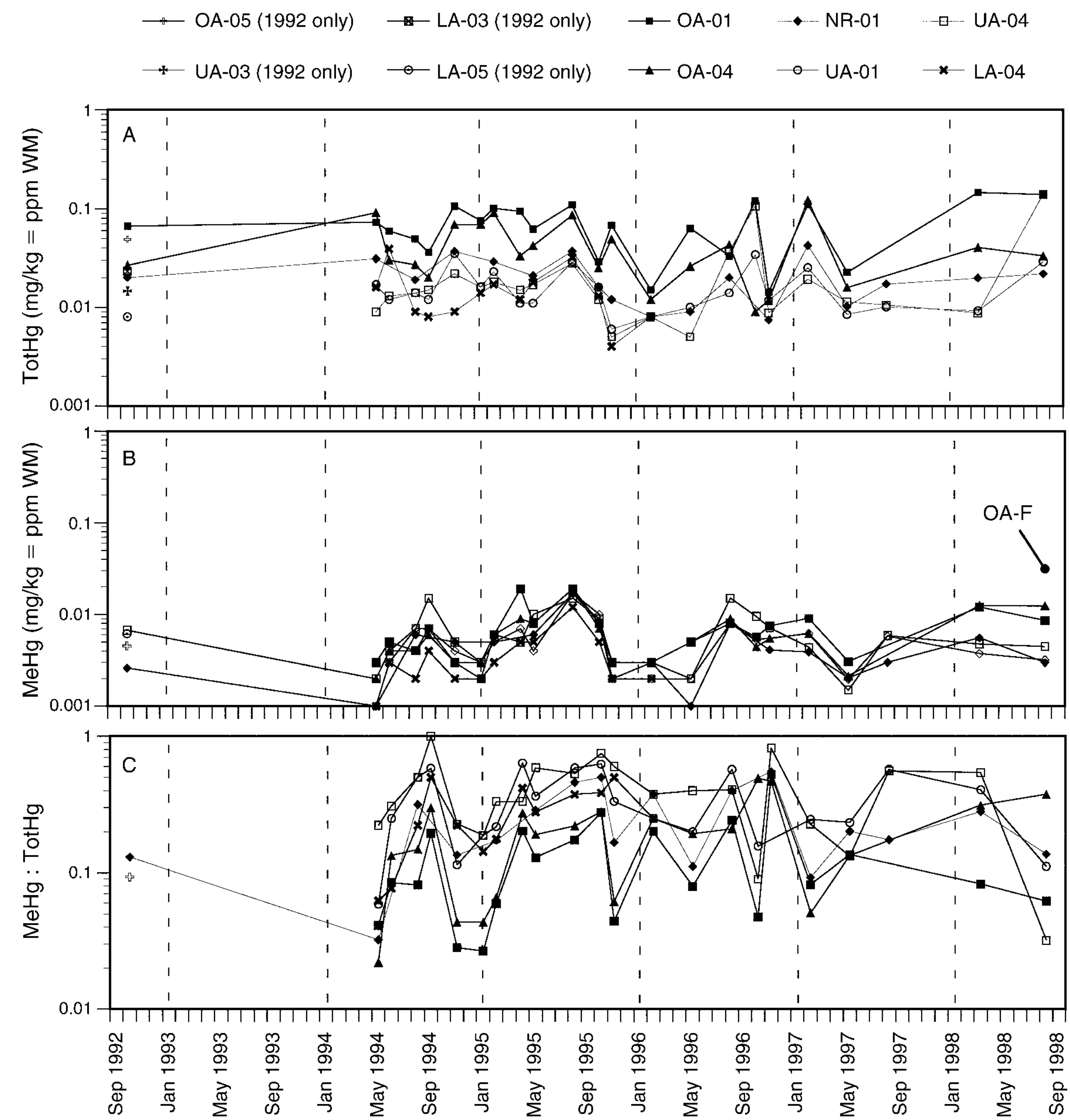

FIG. 11. Temporal trends for mercury in zooplankton by collection site. See Figs. 1 and 2 for locations of collection sites.

sediment–water interface by wave action and currents and subsequent active transport of these particles (Rueda et al. 2008), zooplankton likely consume significant quantities of Hg transported on particles from the mine and thereby reflect the MeHg characteristics of sediments throughout the seasonal cycle. This summer/fall maximum in zooplankton MeHg is consistent with other studies from softwater lakes in northeastern Minnesota, USA (Monson and Brezonik 1998), but notably different from other systems (e.g., Lake Superior), where the maximum MeHg occurs in the spring and is lowest in the summer/fall (Back et al. 2003). Slotton et al. (1995) also demonstrated striking peaks in zooplankton Hg in late fall and early winter, with minima in spring/summer at a gold-mining site reservoir in California near Clear Lake. Interestingly, those sites where MeHg peaks occur in winter are deep-water lakes typically greater than 15–20 m depth (the depth at which a hypolimnion typically develops) and that experience turnover in the fall. The sites where MeHg peaks occur in the summer/fall are shallow-water lakes (<15 m depth) such as Clear Lake and the Canadian Shield lakes in northern Minnesota, which do not undergo significant summer stratification and sequestration of MeHg at depth and thus do not turn over seasonally. Since the MeHg produced in the sediments of deep-water lakes is not mobilized up into the epilimnion until the fall turnover, the increase in

TABLE 3. Statistical analysis results for zooplankton mercury time series data.

Site	Long-term temporal trends	Differences between sites: Tukey's HSD test	Differences between sites: Fisher's LSD test
TotHg			
OA-01	no	A	A
OA-04	no	A	B
NR-01	no	B	C
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	AB
NR-01	no	A	BC
UA-01	no	A	BC
UA-04	no	A	B
LA-04	no	A	C
MeHg:TotHg			
OA-01	no	C	D
OA-04	significant increase	BC	CD
NR-01	no	AB	BC
UA-01	no	AB	AB
UA-04	no	A	A
LA-04	significant increase	AB	ABC

Notes: Long-term temporal trends were determined by linear regression. Different letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test outputs indicate significant differences between data generated from those sites.

zooplankton Hg concentrations is delayed relative to non-stratified lakes.

Chironomid TotHg exhibits no consistent seasonal trends at all sites, although chironomids at OA-01, the site closest to the mine, appear to exhibit peaks during the summers of 1994, 1995, and 1996, but not 1997 or 1998 (Fig. 12). Chironomid Hg at other sites appears variable during the five years of relatively consistent data collection (1994–1998).

Methylmercury in chironomids, however, exhibits a summer/fall peak comparable to that found for MeHg in raw water (Fig. 9) and zooplankton (Fig. 11), suggesting that MeHg on particles remobilized into the water column is the source of the MeHg in chironomids as well as zooplankton. The results of the chironomid gut-purging experiment suggests that a significant proportion (~60–65%) of the TotHg measured in chironomids was due to sediment held within the digestive tract. However, there are likely to be significant differences in this proportion among sites throughout the lake as a result of the different TotHg concentrations in sediment by site. The increased MeHg concentrations in purged chironomids also suggests that the mass of sediment in the gut may significantly dilute MeHg concentrations (when reported on a mass/mass basis), and when purged, these concentrations more accurately reflect those MeHg concentrations in the chironomid tissues themselves.

Compared with other lentic and lotic systems, Clear Lake sediments are some of the most Hg-contaminated in the world (Suchanek et al. 2008*a*, *b*, *c*). In contrast, TotHg concentrations in Clear Lake plankton are fairly comparable to those found at other contaminated, non-contaminated, and flooded reservoir sites (Table 5); the ranges are very broad for all these types of sites. In general, TotHg in Clear Lake plankton ranges from ~0.004 to 0.140 mg/kg WM, whereas plankton from non-contaminated or flooded reservoir sites reported in the literature typically range from ~0.003 to 0.200 mg/kg WM (wet mass values were converted from dry mass values; see Table 5). One other highly contaminated mining site (Davis Creek Reservoir; Slotton et al. 1995) in the vicinity of Clear Lake exhibited even higher Hg concentrations in plankton, ranging from ~0.040 to 0.540 mg/kg WM. Only one study (Chen et al. 2000) reported highly elevated TotHg (up to ~2.9 mg/kg WM in plankton from two out of 18 New England lakes in which there was no known local Hg source). Planktonic MeHg was also comparable between Clear Lake and other lakes reported in the literature regardless of whether they were contaminated (Table 5). While the percentage of MeHg increased with distance from the mine (see Table 5 and Suchanek et al. 2008*a*), the Oaks Arm exhibited the lowest percentage, the Upper Arm the highest percentage, and the Lower Arm had an intermediate range (Table 5).

TABLE 4. Statistical analysis results for chironomid mercury time series data.

Site	Long-term temporal trends	Differences between sites: Tukey's HSD test	Differences between sites: 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	DE	DE
LA-04	no	E	E
MeHg			
OA-01	no	A	A
OA-04	no	B	BC
NR-01	no	B	BC
UA-01	no	B	B
UA-04	no	B	BC
LA-04	no	B	C
MeHg:TotHg			
OA-01	no	D	D
OA-04	no	C	C
NR-01	no	BC	C
UA-01	no	A	AB
UA-04	no	A	A
LA-04	no	AB	B

Notes: Long-term temporal trends were determined by linear regression. Different letters in the Tukey's honest significant difference (HSD; more conservative) and Fisher's least significant difference (LSD; more liberal) test outputs indicate significant differences between data generated from those sites.

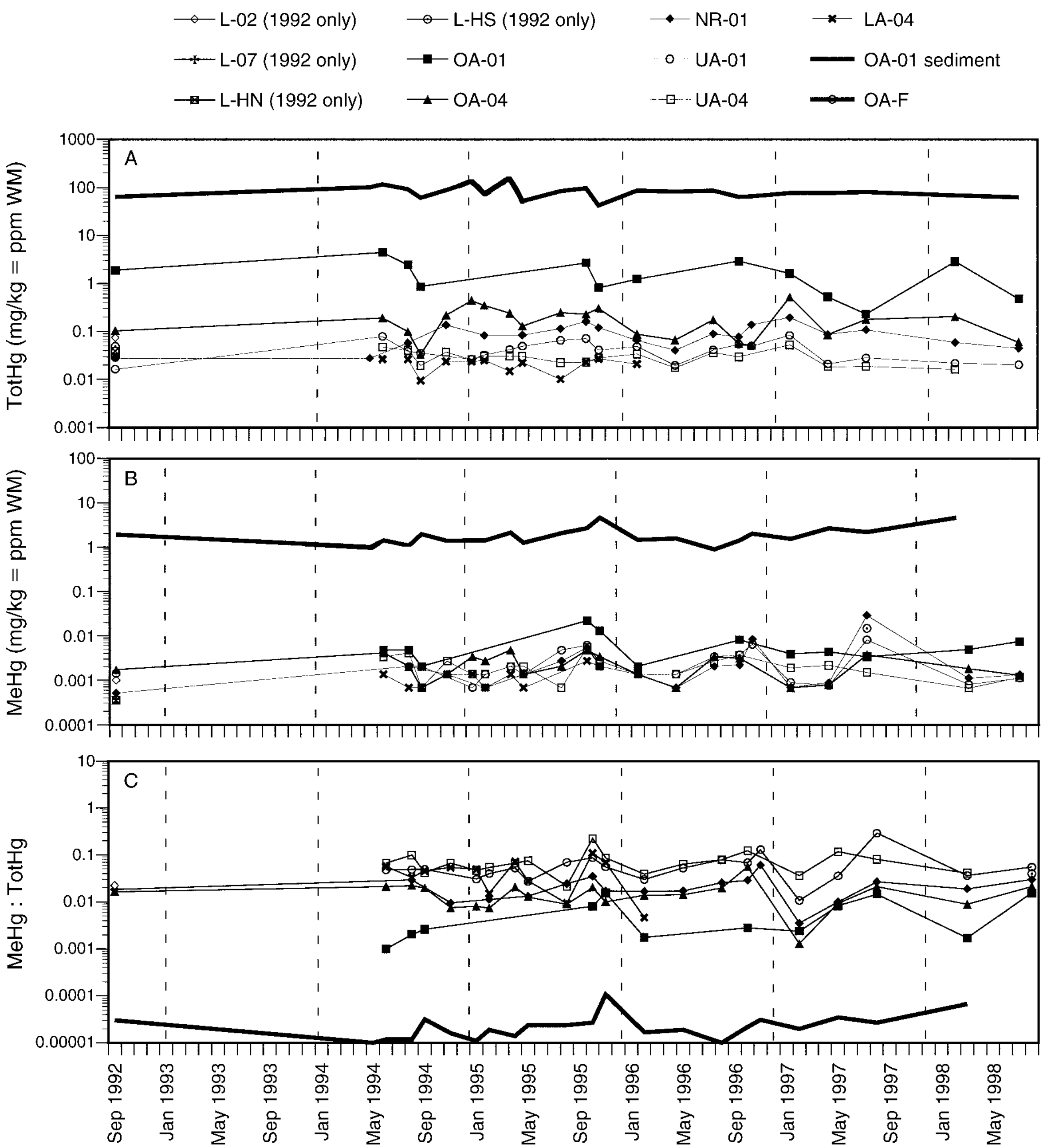

FIG. 12. Temporal trends for mercury (wet mass) in chironomids. The solid black line (without symbols) represents comparable sediment Hg data (plotted as wet mass) from site OA-01, taken from Suchanek et al. (2008*b*). See Figs. 1 and 2 for locations of collection sites.

Benthic invertebrates from Clear Lake exhibited equivalent or higher concentrations of TotHg than those from other contaminated and non-contaminated sites (Table 6). This is likely due, in large part, to the fact that a substantial amount of the Hg in benthic invertebrates may derive from Hg-contaminated sediments in their guts. Other than the experiment to purge chironomid guts, none of the other benthic invertebrates reported in our study were purged of their gut contents before analyzing for Hg. Only one other study was found, from 15 remote lakes in Wisconsin (Watras et al. 1998), that reported MeHg in benthic invertebrates (in this case chironomids) which, when converted to wet-mass values, MeHg concentrations were equivalent to those found in the least contaminated arm (Lower Arm) of Clear Lake (Table 6). The percentage of MeHg in Clear Lake chironomids exhibited similar trends as those for plankton, with the lowest values (0.5–2.9%) being found in the Oaks Arm, the highest values (3.8–14.7%) in the Upper Arm, and intermediate

TABLE 5. Comparison of mercury concentrations in plankton from Clear Lake, California, USA, and from other sites worldwide.

Matrix	Location	Source of Hg†	TotHg range	MeHg range	MeHg (%)	Reference‡
Clear Lake						
Total plankton	Oaks Arm	M	0.034–0.086 WM	0.003 WM	3.1–4.1	1
Total plankton	Upper Arm	M	0.016–0.020 WM	0.001–0.003 WM	18.2–19.3	1
Total plankton	Lower Arm	M	0.013–0.014 WM	0.001 WM	6.2–7.3	1
Zooplankton	Oaks Arm	M	0.009–0.145 WM	0.002–0.031 WM	2.2–52.3	1
Zooplankton	Upper Arm	M	0.005–0.140 WM	0.001–0.017 WM	3.2–100	1
Zooplankton	Lower Arm	M	0.004–0.040 WM	0.001–0.012 WM	6.3–50.0	1
Aphanizomenon cyanobacteria	Upper Arm	M	0.177 DM	0.004 DM	1.9	1
Other contaminated sites						
Zooplankton, >80 μm	New York, USA	C	0.036–0.140 WM§	0.026–0.065 WM§		2
Zooplankton	California, USA	G	0.4–5.4 DM			3
Bulk zooplankton	Lake Superior, USA	NP	0.022–0.135 DM	0.012–0.045 DM	30–55	4
Non-contaminated sites						
Plankton, >10 μm	Manitoba, Canada	NK	0.320–2.100 DM			5
Plankton, >73 μm	Manitoba, Canada	NK	0.020–0.880 DM			5
Plankton, >250 μm	Wisconsin, USA	NK	0.100–0.700 DM			6
Zooplankton	Wisconsin, USA	NK	0.036–0.092 WM§	0.012–0.028 WM§	29	7
Zooplankton	Wisconsin, USA	NK	0.049–0.089 WM§	0.052–0.056 WM§	91	7
Zooplankton	Quebec, Canada	NK	0.165–0.405 DM	0.056–0.170 DM	14–70	8
Zooplankton	Quebec, Canada	NK	0.225–1.130 DM	0.115–0.845 DM	46–83	8
Plankton, >300 μm	Minnesota, USA	NK	0.053–0.300 DM			9
Plankton, >80 μm	Ontario, Canada	NK	0.060–0.191 DM	0.011–0.054 DM		10
Plankton, >80 μm	Ontario, Canada	NK	0.171–1.173 DM	0.029–0.692 DM		10
Total zooplankton	Wisconsin, USA	NK	0.033–0.206 DM	0.060–0.161 DM		11
Small zooplankton, 45–202 μm	northeast USA	NK	0.026–29.400 DM			12
Large zooplankton, >202 μm	northeast USA	NK	0.028–7.480 DM			12
Macrozooplankton, >190 μm	Quebec, Canada	NK	0.075–0.180 DM	0.020–0.140 DM		13
Macrozooplankton, >190 μm	Quebec, Canada	NK	0.190–0.320 DM	0.130–0.225 DM		13
Bulk zooplankton, >112 μm	Isle Royale, USA	NK	0.151–0.307 DM	0.032–0.075 DM		14

Notes: Mercury concentrations (mg/kg = ppm) are reported on a dry mass (DM) or wet mass (WM) basis, depending upon the units reported in the source publication. For comparison purposes, a typical conversion for zooplankton dry-to-wet mass Hg concentration is 0.10. Abbreviations are: TotHg, total mercury; MeHg, methylmercury.

† Key: M, mercury mine; C, chloralkali plant; G, gold/silver mine; NP, non-point source; NK, no known local source.

‡ References: 1, this study; 2, E. Henry, *personal communication*; 3, Slotton et al. (1995); 4, Back et al. (2002, 2003); 5, Jackson (1988); 6, Meili and Parkman (1988); 7, Watras and Bloom (1992); 8, Plourde et al. (1997); 9, Monson and Brezonik (1998); 10, Paterson et al. (1998); 11, Watras et al. (1998); 12, Chen et al. (2000); 13, Kainz and Lucotte (2002); 14, Gorski et al. (2003).

§ Assumes [Hg-wet mass] = 0.2[Hg-dry mass].

values (1.4–4.0%) in the Lower Arm. These chironomid percentages were closest to data reported from Watras et al. (1998; values between 4% and 5%) for 15 remote lakes in Wisconsin, but significantly lower than the 26% MeHg reported from a chloralkali plant at Onondaga Lake, New York (Table 6). Oligochaete MeHg percentages followed the same trends in Clear Lake, but no comparable data were found in the literature.

The relationship between some profundal invertebrate populations and communities vs. sediment Hg in Clear Lake from preliminary data collected in 1992 was reported by Suchanek et al. (1995). While other factors (e.g., sediment grain size, total organic carbon, water depth) can often play a significant role in regulating these benthic populations, some trends related to Hg concentrations emerged. Results of stepwise multiple regression analyses from the earlier study suggest that Hg, grain size, and depth were influential in defining distribution patterns of several benthic invertebrate species. Populations of *Procladius* chironomid midges exhibited a significant increase and *Placobdella* leeches exhibited a significant decline with increasing sediment Hg concentrations. In fact, *Placobdella* was virtually absent at Hg concentrations greater than ~10 mg/kg DM. A series of multivariate analyses indicated that there may be significant population effects above a threshold of sediment Hg concentration (Suchanek et al. 1995). In addition, community-level parameters (Shannon-Wiener diversity H' and Pielou's evenness J') declined with increasing sediment Hg concentrations, but with considerable variation at low Hg levels. However, these results need to be interpreted with some caution because of the influence of other factors on their distribution. In Clear Lake, for example, sediments near the mine in the Oaks Arm are coarser grained than at other locations around the lake and that may help to drive some of the patterns observed. Further discussion of the combined influence of grain size, depth, and total organic carbon on profundal benthic invertebrate populations and communities from 1992 data can be found in Suchanek et al. (1995).

While very few of the littoral invertebrate populations analyzed here showed any significant relation to distance from the mine (as a proxy for Hg concentrations), some

TABLE 6. Comparison of mercury concentrations in benthic invertebrates from Clear Lake, California, USA, and from other sites worldwide.

Matrix	Location	Source of Hg†	TotHg range	MetHg range	MeHg (%)	Reference‡
Clear Lake						
Chironomids	Oaks Arm	M	0.021–4.47 WM	0.001–0.022 WM	0.5–2.9	1
Chironomids	Upper Arm	M	0.013–0.197 WM	0.001–0.029 WM	3.8–14.7	1
Chironomids	Lower Arm	M	0.010–0.099 WM	0.000–0.001 WM	1.4–4.0	1
Oligochaetes	Oaks Arm	M	0.092–5.38 WM	0.001–0.002 WM	0.03–0.9	1
Oligochaetes	Upper Arm	M	0.041–0.184 WM	0.001–0.003 WM	1.4–2.0	1
Oligochaetes	Lower Arm	M	0.054–0.137 WM	0.001–0.001 WM	0.9–1.3	1
Mooreobdella leeches	Oaks Arm	M	0.030–0.415 WM			1
Mooreobdella leeches	Upper Arm	M	0.027 WM			1
Mooreobdella leeches	Lower Arm	M	0.007–0.300 WM			1
Hyalella amphipods	Oaks Arm	M	0.008–0.097 WM			1
Hyalella amphipods	Upper Arm	M	0.004–0.007 WM			1
Hyalella amphipods	Lower Arm	M	0.007–0.009 WM			1
Nectopsyche caddisflies	Oaks Arm	M	0.003–0.023 WM			1
Nectopsyche caddisflies	Upper Arm	M	0.002–0.003 WM			1
Nectopsyche caddisflies	Lower Arm	M	0.002 WM			1
Mixed snails	Oaks Arm	M	0.027–1.179 WM			1
Mixed snails	Upper Arm	M	0.077–0.108 WM			1
Mixed snails	Lower Arm	M	0.018–0.023 WM			1
Other contaminated sites						
Chironomids	New York, USA	C	0.350–1.90 DM		26	2
Non-contaminated sites						
Chironomids	Wisconsin, USA	NK	0.095–0.133 DM	0.003–0.007 DM	4–5	3
Chironomids	Manitoba, Canada	NK	0.018–0.208 WM§			4
Oligochaetes	Manitoba, Canada	NK	0.043–0.696 WM§			4
Bivalves	Manitoba, Canada	NK	0.016–0.306 WM§			4
Chironomids	Ontario, Canada	A	0.097–0.177 DM			5
Oligochaetes	Ontario, Canada	A	0.164 DM			5
Gastropods	Ontario, Canada	A	0.609–0.939 DM			5
Chironomus	Sweden	A	0.001–0.007 DM			6

Note: Mercury concentrations (mg/kg = ppm) are reported on a dry mass (DM) or wet mas (WM) basis, depending upon the units reported in the source publication.

† Key: M, mercury mine; C, chloralkali plant; NK, no known local source; A, atmospheric.

‡ References: 1, this study; 2, Becker and Bigham (1995); 3, Watras et al. (1998); 4, Jackson (1988); 5, Wong et al. (1997); 6, Parkman and Meili (1993).

§ Chironomid guts were purged before analysis.

of the same factors identified above may play important roles in controlling the abundance and/or biomass of these species, but no additional data on those parameters were collected for the present study (primarily post-1992). Horne et al. (1999) also found no consistent patterns of population densities for specific species of benthic fauna in response to point sources of pollutants such as Hg and polychlorinated biphenyls (PCBs), but did report shifts in the proportions of surface vs. subsurface feeders as a function of proximity to the contaminant source.

To date there have been no specific studies to evaluate the effects of Hg on Clear Lake benthic invertebrates at the level of the individual. However, because Clear Lake sediments range from ~1 to 1200 mg/kg DM TotHg, they exceed ecological health guidelines for benthic invertebrates (Suchanek et al. 2008*b*). These guidelines include the National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQuiRTs) to assess toxicity of contaminants to benthic fauna: threshold effects level (TEL), probable effects level (PEL), and upper effects threshold (UET) (Buchman 1999). For TotHg, these concentrations are: 0.174, 0.486, and 0.560 mg/kg DM for the TEL, PEL, and UET, respectively. Clear Lake sediments distant from the mine exceed the TEL for Hg by ~10 times and exceed the PEL and the UET for Hg by factors of approximately two to three, whereas those sediments near the mine exceed those toxic criteria by factors of ~1000–7000 (see Suchanek et al. 2008*b*). Using a consensus-based "weight-of-evidence" approach, MacDonald et al. (2000) established a threshold effects concentration (TEC; contaminant concentrations at which threshold effects are observed) and probable effects concentration (PEC; contaminant concentrations at which probable effects are expected) to assess potential toxic effects to benthic fauna, which, for TotHg, are 0.18 and 1.06 mg/kg DM, respectively. Clear Lake sediments exceed the TEC by ~1–1100 times and the PEC by ~5–6500 times, exceeding the TEC and PEC at virtually all sites and all times (Suchanek et al. 2008*b*). Although Suchanek et al. (1995) did find population and community effects for some profundal species at Clear Lake, the chironomids, oligochaetes, and chaoborids evaluated in the present

PLATE 6. A structure that is likely a brick Scott furnace, with associated large condenser.

study did not exhibit population- or community-level trends related to Hg concentrations. Thus, given the exceedances shown above to current sediment quality guidelines, it is possible that toxic effects are experienced by some benthic invertebrate fauna in Clear Lake sediments. Thus, further studies using site-specific sediment toxicity tests should be conducted on individual taxa to evaluate these potential effects.

CONCLUSIONS

Spatially, TotHg in all lower trophic level biota (both profundal and littoral) from Clear Lake exhibited trends comparable to those found in the abiotic components of the lake described by Suchanek et al. (2008*b*), with significantly decreasing concentrations as a function of distance from the mine, although the slope of declining TotHg in sediments is steeper than that for chironomids and oligochaetes. For chironomids, >60% of the TotHg measured in whole-body analyses could be accounted for by sediment in their digestive tract, from at least one site (UA-03). Methylmercury in crayfish also declined with distance from the mine, but this trend was not observed in chironomids or plankton.

Data from a 50-year monitoring effort showed no significant population-level effects experienced by benthic chaoborid and chironomid larvae with increasing sediment Hg concentrations towards the mine. However, Suchanek et al. (1995) found some significant population-level effects on chironomids with increasing TotHg when analyzed using spatial comparisons. In the 50-year data set, community-level parameters (species diversity and evenness) in littoral invertebrate communities exhibited no significant response to increased TotHg concentrations in water and sediment near the mine. Thus, although there were some indications of responses to individual species, this did not appear to translate into measurable differences in benthic community metrics investigated in this study.

Temporally, TotHg concentrations in plankton and chironomids did not exhibit any short-term (seasonal or annual) or long-term (multiyear) trends. Methylmercury, however, was elevated during late summer or fall in both plankton and chironomids.

In comparison with other contaminated and noncontaminated sites worldwide, lower trophic species (plankton and chironomids) in Clear Lake typically have elevated TotHg concentrations but comparable or lower MeHg concentrations. A discussion of possible reasons for this trend is included in Suchanek et al. (2008*a*).

The results of this study indicate that concentrations of TotHg in sediment alone are not good indicators of the site-specific biological effects of Hg. As such, generic sediment quality guidelines or criteria should not be used in isolation to assess potential or magnitude of harm at Clear Lake. Assessments should consider instead both the inorganic and organic forms of Hg found at the site of toxic action (tissue level) that exhibit a spatial trend similar to the pattern of biological response.

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Literature Cited

Back, R. C., P. R. Gorski, L. B. Cleckner, and J. P. Hurley. 2003. Mercury content and speciation in the plankton and benthos of Lake Superior. Science of the Total Environment 304:349–354.

Back, R. C., J. P. Hurley, and K. R. Rolfhus. 2002. Watershed influences on the transport, fate and bioavailability of mercury in Lake Superior: field measurements and modeling approaches. Lakes and Reservoirs: Research and Management 7:201–206.

Becker, D. S., and G. N. Bigham. 1995. Distribution of mercury in the aquatic food web of Onondaga Lake, New York. Water, Air and Soil Pollution 80:563–571.

Bloom, N. S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. Canadian Journal of Fisheries and Aquatic Sciences 7:1131–1140.

Buchman, M. F. 1999. NOAA screening quick reference tables. NOAA HAZMAT Report 99-1. Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, Seattle, Washington, USA.

Chen, C. Y., R. S. Stemberger, B. Klaue, J. D. Blum, P. C. Pickhardt, and C. L. Folt. 2000. Accumulation of heavy metals in food web components across a gradient of lakes. Limnology and Oceanography 45:1525–1536.

Eagles-Smith, C. A., T. H. Suchanek, A. E. Colwell, N. L. Anderson, and P. B. Moyle. 2008. Changes in fish diets and food web mercury bioaccumulation induced by an invasive planktivorous fish. Ecological Applications 18(Supplement): A213–A226.

Gorski, P. R., L. B. Cleckner, J. P. Hurley, M. E. Sierszen, and D. E. Armstrong. 2003. Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. Science of the Total Environment 304:327–348.

Horne, M. T., N. J. Finley, and M. D. Sprenger. 1999. Polychlorinated biphenyl- and mercury-associated alterations on benthic invertebrate community structure in a contaminated salt marsh in southeast Georgia. Archives of Environmental Contamination and Toxicology 37:317–325.

Jackson, T. A. 1988. Accumulation of mercury by plankton and benthic invertebrates in riverine lakes of Northern Manitoba (Canada): importance of regionally and seasonally varying environmental factors. Canadian Journal of Fisheries and Aquatic Sciences 45:1744–1757.

Kainz, M., and M. Lucotte. 2002. Can flooded organic matter from sediments predict mercury concentrations in zooplankton of a perturbed lake? Science of the Total Environment 293:151–161.

MacDonald, D. D., C. G. Ingersoll, and T. A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines. Archives of Environmental Contamination and Toxicology 39:20–31.

Meili, M., and H. Parkman. 1988. Seasonal mercury accumulation patterns in mesoplankton. International Association of Theoretical and Applied Limnology 23:1639–1640.

Monson, B. A., and P. L. Brezonik. 1998. Seasonal patterns of mercury species in water and plankton from softwater lakes in northeastern Minnesota. Biogeochemistry 40:147–162.

Parkman, H., and M. Meili. 1993. Mercury in macroinvertebrates from Swedish forest lakes: influence of lake type, habitat, life cycle, and food quality. Canadian Journal of Fisheries and Aquatic Sciences 50:521–534.

Paterson, M. J., J. W. M. Rudd, and V. St. Louis. 1998. Increases in total and methylmercury in zooplankton following flooding of a peatland reservoir. Environmental Science and Technology 32:3868–3874.

Pequeux, A., A. Bianchini, and R. Gilles. 1996. Mercury and osmoregulation in the euryhaline crab *Eriocheir sinensis*. Comparative Biochemistry and Physiology 113C(2):149–155.

Pielou, E. C. 1975. Ecological diversity. John Wiley and Sons, New York, New York, USA.

Plourde, Y., M. Lucotte, and P. Pichet. 1997. Contribution of suspended particulate matter and zooplankton to MeHg contamination of the food chain in midnorthern Quebec (Canada) reservoirs. Canadian Journal of Fisheries and Aquatic Sciences 54:821–831.

Richerson, P. J., T. H. Suchanek, and S. J. Why. 1994. The causes and control of algal blooms in Clear Lake. Clean Lakes Diagnostic/Feasibility Study for Clear Lake, California. U.S. Environmental Protection Agency, Region IX, San Francisco, California, USA.

Richerson, P. J., T. H. Suchanek, R. A. Zierenberg, D. A. Osleger, A. C. Heyvaert, D. G. Slotton, C. A. Eagles-Smith, and C. E. Vaughn. 2008. Anthropogenic stressors and changes in the Clear Lake ecosystem as recorded in sediment cores. Ecological Applications 18(Supplement):A257–A283.

Roesijadi, G. 1982. Uptake and incorporation of mercury into mercury-binding proteins of gills of *Mytilus edulis* as a function of time. Marine Biology 66:151–152.

Rueda, F. J., S. G. Schladow, and J. F. Clark. 2008. Mechanisms of contaminant transport in a multi-basin lake. Ecological Applications 18(Supplement):A72–A87.

Sarabia, R., A. Torreblanca, J. J. Del Ramo, and J. Diaz-Mayans. 1998. Effects of low mercury concentration exposure on hatching, growth and survival in the *Artemia* strain La Mata parthenogenetic diploid. Comparative Biochemistry and Physiology A(1):93–97.

Shipp, W. G., and R. A. Zierenberg. 2008. Pathways of acid mine drainage to Clear Lake: implications for mercury cycling. Ecological Applications 18(Supplement):A29–A54.

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

Suchanek, T. H., C. A. Eagles-Smith, and E. J. Harner. 2008*a*. Is Clear Lake methylmercury distribution decoupled from bulk mercury loading? Ecological Applications 18(Supplement):A107–A127.

Suchanek, T. H., C. A. Eagles-Smith, D. G. Slotton, E. J. Harner, and D. P. Adam. 2008*b*. Mercury in abiotic matrices of Clear Lake, California: human health and ecotoxicological implications. Ecological Applications 18(Supplement):A128–A157.

Suchanek, T. H., B. A. Lamphere, L. H. Mullen, C. E. Woodmansee, P. J. Richerson, D. G. Slotton, L. A. Woodward, and E. J. Harner. 2000*a*. Mercury in lower trophic levels of the Clear Lake aquatic ecosystem, California. Pages 249–268 *in* G. Fogg, D. Hinton, M. Johnson, and K. Scow, editors. The integrated assessment of ecosystem health. Ann Arbor Press, Chelsea, Michigan, USA.

Suchanek, T. H., L. H. Mullen, B. A. Lamphere, P. J. Richerson, C. E. Woodmansee, D. G. Slotton, E. J. Harner, and L. A. Woodward. 1998. Redistribution of mercury from contaminated lake sediments of Clear Lake, California. Water, Air and Soil Pollution 104(1/2):77–102.

Suchanek, T. H., D. C. Nelson, R. Zierenberg, A. L. Bern, W. Shipp, P. King, and K. McElroy. 2000*b*. Influence of acid mine drainage from the abandoned Sulphur Bank Mercury Mine on methyl mercury production in Clear Lake (CA). Pages 218–224 *in* Proceedings: assessing and managing mercury from historic and current mining activities, 28 November 2000. U.S. Environmental Protection Agency, Office of Research and Development, Ada, Oklahoma, USA.

Suchanek, T. H., P. J. Richerson, J. R. Flanders, D. C. Nelson, L. H. Mullen, L. L. Brister, and J. C. Becker. 2000*c*. Monitoring inter-annual variability reveals sources of mercury contamination in Clear Lake, California. Environmental Monitoring and Assessment 64:299–310.

Suchanek, T. H., P. J. Richerson, L. J. Holts, B. A. Lamphere, C. E. Woodmansee, D. G. Slotton, E. J. Harner, and L. A. Woodward. 1995. Impacts of mercury on benthic invertebrate populations and communities within the aquatic ecosystem of Clear Lake, California. Water, Air and Soil Pollution 80:951–960.

Suchanek, T. H., et al. 2003. Evaluating and managing a multiply stressed ecosystem at Clear Lake, California: a holistic ecosystem approach. Pages 1239–1271 *in* D. J. Rapport, W. L. Lasley, D. E. Rolston, N. O. Nielsen, C. O. Qualset, and A. B. Damania, editors. Managing for healthy ecosystems. Lewis, Boca Raton, Florida, USA.

Suchanek, T. H., et al. 2008*c*. The legacy of mercury cycling from mining sources in an aquatic ecosystem: from ore to organism. Ecological Applications 18(Supplement):A12–A28.

U.S. EPA [U.S. Environmental Protection Agency]. 1980. Ambient water quality criteria for mercury. Report 440/5-80-058. National Technical Information Service, Springfield, Virginia, USA.

Warwick, W. F. 1991. Indexing deformities in ligulae and antennae of Procladius larvae (Diptera: Chironomidae): application to contaminant-stressed environments. Canadian Journal of Fisheries and Aquatic Sciences 48:1151–1166.

Watras, C. J., R. C. Back, S. Halvorsen, R. J. M. Hudson, K. A. Morrison, and S. P. Wente. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment 219:183–208.

Watras, C. J., and N. S. Bloom. 1992. Mercury and methylmercury in individual zooplankton: implications for bioaccumulation. Limnology and Oceanography 37:1313–1318.

Wiederholm, T. 1984. Incidence of deformed chironomid larvae (Diptera: Chironomidae) in Swedish lakes. Hydrobiologia 109:243–249.

Wiederholm, T., and G. Dave. 1989. Toxicity of metal polluted sediments to *Daphnia magna* and *Tubifex tubifex*. Hydrobiologia 176/177:411–417.

Wong, A. H. K., D. J. McQueen, D. D. Williams, and E. Demers. 1997. Transfer of mercury from benthic invertebrates to fishes in lakes with contrasting fish community structures. Canadian Journal of Fisheries and Aquatic Sciences 54:1320–1330.

Woodward, L. A., M. Mulvey, and M. C. Newman. 1996. Mercury contamination and population-level responses in chironomids: Can allozyme polymorphism indicate exposure? Environmental Toxicology and Chemistry 15:21–28.