# IS CLEAR LAKE METHYLMERCURY DISTRIBUTION DECOUPLED FROM BULK MERCURY LOADING?

Thomas H. Suchanek,[1,3] Collin A. Eagles-Smith,[1,4] and E. James Harner[2]

[1]*Department of Wildlife, Fish and Conservation Biology, University of California, Davis, California 95616 USA*
[2]*Department of Statistics, West Virginia University, Morgantown, West Virginia 26506 USA*

*Abstract.* Clear Lake is the site of the abandoned Sulphur Bank Mercury Mine, active periodically from 1873 to 1957, resulting in ~100 Mg of mercury (Hg) being deposited into the lake's ecosystem. Concentrations of total (primarily inorganic) Hg (TotHg) in Clear Lake are some of the highest reported worldwide for sediments (up to $4.4 \times 10^5$ ng/g [ppb dry mass]) and water (up to $4 \times 10^{-1}$ µg/L [= ppb]). However, the ratio of methylmercury (MeHg) to TotHg at Clear Lake indicates that the methylation process is mostly decoupled from bulk inorganic Hg loading, with Hg in lower trophic level biota significantly less than anticipated compared with other Hg-contaminated sites worldwide. This may be due to several factors, including: (1) reduced bioavailability of Hg derived from the mine (i.e., cinnabar, metacinnabar, and corderoite), (2) the alkaline nature of the lake water, (3) the shallow depth of the lake, which prevents stratification and subsequent methylation in a stratified hypolimnion, and (4) possible dilution of MeHg by a highly productive system. However, while bulk inorganic Hg loading to the lake may not contribute significantly to the bioaccumulation of Hg, acid mine drainage (AMD) from the mine likely promotes Hg methylation by sulfate-reducing and iron-reducing bacteria, making AMD a vehicle for the production of highly bioavailable Hg. If Clear Lake were deeper, less productive, or less alkaline, biota would likely contain much more MeHg than they do presently. Comparisons of MeHg:TotHg ratios in sediments, water, and biota from sites worldwide suggest that the highest production of MeHg may be found at sites influenced by chloralkali plants, followed by sites influenced by gold and silver mines, with the lowest production of MeHg observed at cinnabar and metacinnabar Hg mines. These data also suggest that the total maximum daily load (TMDL) process for Hg at Clear Lake, as currently implemented to reduce contamination in fishes for the protection of wildlife and humans, may be flawed because the metric used to implement Hg load reduction (i.e., TotHg) is not directly proportional to the critical form of Hg that is being bioaccumulated (i.e., MeHg).

*Key words: chironomids; Clear Lake, California, USA; fish; invertebrates; management; mercury; methylmercury; sediments; total maximum daily load (TMDL); water; zooplankton.*

## INTRODUCTION

This comparison of total mercury (TotHg) vs. methylmercury (MeHg) in Clear Lake is one component of a larger ecosystem-level study that traces the origin and pathways of mercury (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). This paper uses data from several other contributions in

this Special Issue to highlight a prominent feature of this mine-dominated ecosystem, which has received an enormous load of inorganic Hg input from the mine, yet compared to other sites worldwide has surprisingly lower production of MeHg than comparable or less contaminated sites. These comparisons provide the basis for preliminary generalizations about MeHg concentrations in both abiotic and biotic components of various types of Hg-contaminated systems.

Globally, most research on Hg contamination has focused on sources derived from atmospheric deposition, and those sources are typically from industrial power plants. Considerably less attention and research has been focused on mining sources and especially Hg mining (Hylander and Meili 2003). As a result of Hg mining practices, Clear Lake, California, USA, is one of the most Hg-contaminated aquatic ecosystems in the world, with up to 438 mg/kg (ppm) of TotHg in surficial sediments (Suchanek et al. 2008*a*), nearly 1200 mg/kg documented in near-surface sediments (CVRWQCB 1987), and aqueous TotHg concentrations sometimes

exceeding 350 ng/L (pptr) in regions of the lake near the abandoned Sulphur Bank Mercury Mine Superfund Site (Suchanek et al. 2008a, d). Total mercury in unfiltered water from non-contaminated sites typically ranges from ~0.3 to 8.0 ng/L, whereas sites influenced by Hg mining or industrial pollution typically exhibit TotHg concentrations of 10–40 ng/L (Wiener et al. 2003). Thus, Clear Lake is exceptional in its extremely high TotHg concentrations. Despite elevated TotHg in sediment and water, MeHg concentrations in sediment, water, and biota are considerably lower than might be expected based on the bulk Hg contamination compared with other systems (Suchanek et al. 2008a, b, c).

In accordance with Section 303(d) of the Clean Water Act (CWA), states must adopt assessment criteria for priority toxic pollutants. This process involves establishing a total maximum daily load (TMDL) process to set the maximum amount of a toxic substance that can enter a water body from all sources without affecting the designated uses of that water body. More than 6000 sites within the United States, 64 of which are in California, have implemented TMDL reduction programs based on Hg contamination. Based on elevated Hg concentrations in fish tissues, Clear Lake was placed on California's 303(d) list of impaired water bodies in 1988, and the Central Valley Regional Water Quality Control Board (CVRWQCB) subsequently implemented a TMDL program to reduce Hg loading to Clear Lake (CVRWQCB 2002a, b). The regulatory approach to implementing reductions in Hg loading through the TMDL process involves reducing TotHg loading to the system. However, MeHg (not TotHg) is the critical toxic form that bioaccumulates most efficiently. And at Clear Lake, a highly contaminated system because of an abandoned cinnabar mine, the production rate of MeHg from inorganic Hg appears to be significantly less efficient than at other less contaminated or non-contaminated sites (Suchanek et al. 2008d).

In some systems, such as controlled laboratory experiments, MeHg production can be predicted directly from the addition of specific quantities of inorganic Hg as shown by Rudd et al. (1983), but this often does not hold for natural systems. Over the past few decades, several investigators have suggested that MeHg concentrations are weakly related or unrelated to TotHg concentrations. Working at a site contaminated with Hg from a chlor-alkali plant, Jackson and Woychuk (1980, 1981) identified several factors (such as pH, nutrients, and microbial activity, but not TotHg) that correlated well with sediment MeHg concentrations. Kelly et al. (1995), working in the more pristine environment of the Experimental Lakes Area in northwestern Ontario, Canada, also found no relationship between TotHg and MeHg concentrations.

Acid volatile sulfides (AVS) have been shown to enhance sulfide binding to trace metals that can reduce their relative bioavailability and potential toxicity (Di Toro et al. 1990, Hare et al. 1994, Ankley et al. 1996).

The ratio of simultaneously extractable metals (SEM) to AVS (SEM:AVS) provides one measure of sulfide binding that can influence bioavailability and toxicity (Ankley et al. 1994, Berry et al. 1996). Values >1.0 suggest weak sulfide binding and increased bioavailability (and subsequent increased toxicity), whereas values <1.0 suggest lowered bioavailability (with reduced toxicity). Although sulfide binding has been shown to reduce MeHg concentrations and therefore bioavailability (Bowles et al. 2003), it is questionable whether SEM:AVS ratios accurately predict Hg toxicity (Haines et al. 2003).

Benoit et al. (2003) provide an overview of Hg methylation in different ecological systems worldwide, suggesting that the range of methylation rates across ecosystems is greater than the range of Hg deposition rates. For relatively uncontaminated sites, they report a close relationship between inorganic Hg loading and MeHg production, but for more contaminated sites with TotHg greater than ~0.5 mg/kg in sediments, such a relationship is not apparent. And, for the more contaminated sites, it appears that sediments in rivers have higher MeHg:TotHg ratios than those in lakes.

The objective of this study was to determine whether there is a linkage or a decoupling between inorganic Hg loading and MeHg in Clear Lake, a system highly contaminated with inorganic Hg as a result of Hg mining. We provide comparisons of TotHg to MeHg concentrations in Clear Lake water, sediments, and biota in relation to those same parameters at other sites worldwide and identify several factors that likely limit or inhibit the production and/or bioaccumulation of MeHg at this cinnabar mine site relative to other systems. We also discuss the implications of these characteristics on the management of Clear Lake and the establishment of a Hg TMDL for highly contaminated systems like Clear Lake.

## Materials and Methods

Data and comparisons presented in this paper were derived in part from results reported in Suchanek et al. (2008a, b, c). Brief descriptions of the analytical methods used to obtain those data are presented here, but more detailed methods for those collections and analyses for the appropriate matrices can be obtained directly from those papers in this Special Issue. For water, sediments, and lower trophic level species, data were collected during fall (September/October) of 1992 (identified as the Preliminary Lake Survey [PLS]) and during multiple seasons from 1994 to 1998 (identified as the Long-term Lake Study [LLS]). Fig. 1 provides locations of water, sediment, plankton, and invertebrate sampling sites.

For limnological data and water, samples were collected typically at up to seven sites from May 1994 through May 1997. A Hydrolab model H2O-BT water sampler (Hach Environmental, Loveland, Colorado, USA) was used to obtain limnological data for surface water (within 1 m of the air–water interface) and bottom
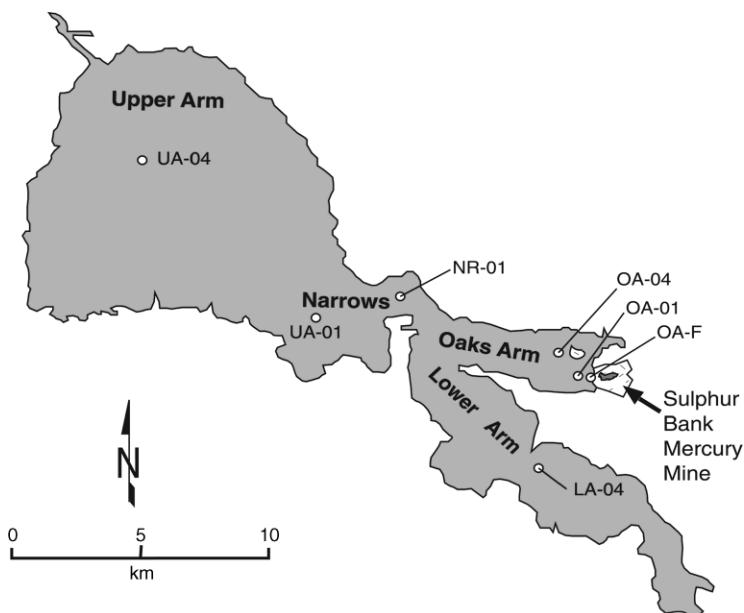
Fɪɢ. 1.   Sampling sites in Clear Lake, California, USA. Water distances from the Sulphur Bank Mercury Mine: OA-F, 0.1 km; OA-01, 0.6 km; OA-04, 2.9 km; NR-01, 8 km; LA-04, 11 km; UA-01, 12 km; UA-04, 19 km.

water (within 1 m of the sediment–water interface) for the following parameters: temperature, pH, specific conductivity, total dissolved solids, dissolved oxygen, turbidity, and reduction-oxidation (redox) potential. Surface and bottom unfiltered water was also collected at these sites using ultraclean protocols (Gill and Fitzgerald 1985, 1987). Acid-washed Teflon tubing (Dupont, Wilmington, Delaware, USA) was used in conjunction with a peristaltic pump to collect water samples into acid-washed Teflon bottles with no headspace and chemically analyzed for total organic carbon (TOC), humic acids, total suspended solids (TSS), sulfate, TotHg, and MeHg. Filtered water passed through a 0.45-μm filter was analyzed for dissolved organic carbon (DOC), TotHg, and MeHg. Total organic carbon and DOC were analyzed by Analytical Resources (Seattle, Washington, USA). Organic carbon was converted to carbon dioxide by wet chemical oxidation and quantified using an infrared detector following EPA Method 415.1 (U.S. EPA 1979). Sulfate was analyzed by Analytical Resources using EPA method 375.2 (U.S. EPA 1979). Total suspended solids (TSS) were quantified by Analytical Resources following EPA Method 160.2 (U.S. EPA 1979). For humic substances, water samples were centrifuged to remove particulate matter. The level of humic substances (HS) was determined by measuring the fluorescence emission at 440 nm resulting from excitation at 360 nm (Senesi et al. 1991) using a Perkin-Elmer fluorescence spectrometer (Perkin-Elmer, Wellesley, Massachusetts, USA). The method was standardized using the sodium salt of humic acid (Aldrich Chemical, Milwaukee, Wisconsin, USA).

Total mercury and MeHg were analyzed by Battelle Marine Sciences Laboratory (Sequim, Washington, USA). Total mercury was analyzed using the bromine monochloride oxidation, stannous chloride reduction, and cold vapor atomic fluorescence analytical methods of Bloom and Crecelius (1983), now EPA Method 1631. Methylmercury was analyzed using the distillation, aqueous phase ethylation and cold vapor atomic fluorescence methods of Bloom (1989) and Horvat et al. (1993), now EPA Method 1630-draft.

Sediments were collected from the same vessel identified above 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 TotHg analysis were dried to constant mass at 50°C (typically 24–48 h) and ground to a fine powder, prior to analysis. Total mercury samples were analyzed by Battelle Marine Sciences Laboratory, utilizing a standard cold vapor atomic absorption (CVAA) spectrophotometric technique based on EPA standard method 245.5. Methylmercury was analyzed using aqueous distillation combined with the aqueous ethylation/cold vapor atomic fluorescence spectroscopy methods of Bloom (1989). Because of an identified artifact in the distillation method for analyzing MeHg in sediments (Liang et al. 1996, Bloom et al. 1997), original MeHg concentrations were corrected to reflect results obtained from an alternative method (extraction) that is believed to reduce or eliminate the artifact. See Suchanek et al. (2008a) for details.

Acid volatile sulfides (AVS) and simultaneously extractable metals (SEM) in sediments were analyzed
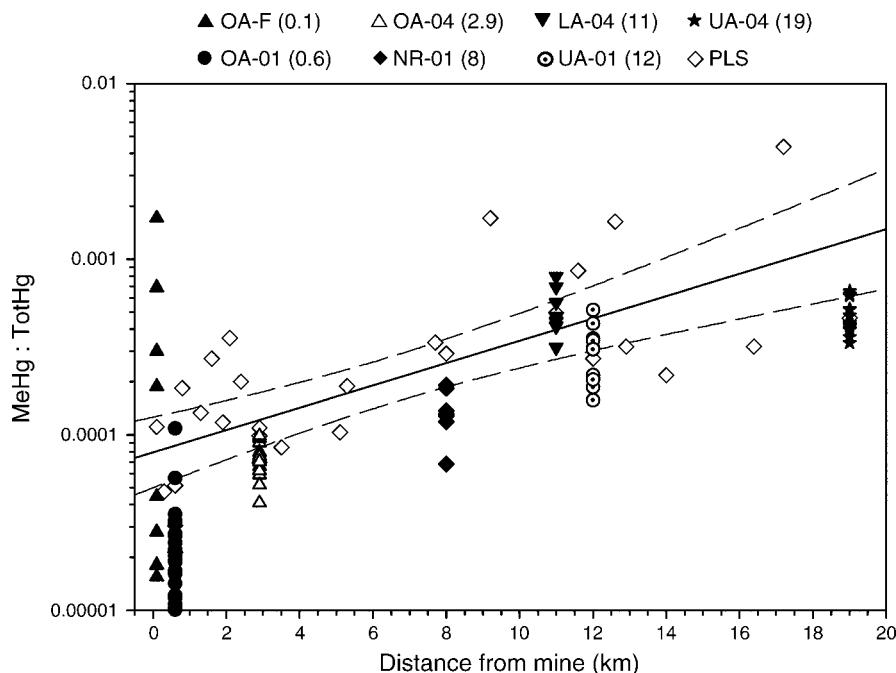
Fig. 2. The ratio of methylmercury to total mercury (MeHg:TotHg) in Clear Lake sediments as a function of distance from the Sulphur Bank Mercury Mine from 1992 to 1998 (data from Suchanek et al. [2008a]). The curve fit is exponential ($R^2 = 0.536$). The Preliminary Lake Survey (PLS) data points are from multiple sites throughout the lake during the fall of 1992 (see key). All other data are from the Long-term Lake Study (LLS), which includes all seasons from 1994 to 1998. Confidence intervals are 95% of the geometric means for each site. The numbers in parentheses in the key represent distances (km) from the mine.

by Battelle Marine Sciences Laboratory. The AVS analyses followed Cutter and Oatts (1987). Briefly, this method employed selective generation of hydrogen sulfide, cryogenic trapping, gas chromatographic separation, and photoionization detection. A known mass of sediment was reacted with a known volume of 1 mol/L HCl, and the evolved $H_2S$ was quantified to determine the AVS concentration. The SEM analyses followed the methods of U.S. EPA (1991) and Bloom and Crecelius (1983) by analyzing the metals content of the filtered acid/sediment slurry produced during the AVS analysis. The SEM extract was analyzed for Cd, Cu, Ni, Pb, and Zn by inductively coupled plasma mass spectrometry (ICP-MS) (U.S. EPA 1991) and for Hg by cold-vapor atomic fluorescence (CVAF).

For tissue samples, TotHg and MeHg were analyzed by Battelle Marine Sciences Laboratory, using the methods of Roesijadi (1982) for TotHg and using the methods of Bloom (1989), following initial digestion and extraction in potassium hydroxide (KOH)/methanol for MeHg.

## RESULTS

### Sediments

Sediments in Clear Lake are highly contaminated with inorganic Hg (Suchanek et al. 2008a). There are likely several sources of Hg to Clear Lake, the most significant of which derive from the Sulphur Bank Mercury Mine

along the shoreline of the lake (Suchanek et al. 2008a, d). Historically, these sources have included contaminated soils and mine wastes intentionally dumped into the lake or eroded from the mine site during storms. In Clear Lake sediments, the ratio of MeHg:TotHg (often used as a relative proxy for bioavailability) increases as a function of distance from the mine (Fig. 2).

The MeHg:TotHg ratios at PLS sites in the fall of 1992 were generally higher than the remainder of the pooled data set in Fig. 2. This is consistent with the fact that late summer/early fall is a period when the greatest methylation takes place (Mack 1998), and this is reflected in the higher MeHg concentrations (Suchanek et al. 2008a) as well as an increased ratio of MeHg:TotHg in the sediments.

Interestingly, in the LLS data set in Fig. 2, site LA-04 (at 11 km from the mine) exhibited some of the highest MeHg:TotHg ratios in the lake for that subset of data. This site is located in the Lower Arm, which, because of water movements in the lake related to wind-driven currents (Rueda et al. 2008), is the furthest "effective distance" from the mine (with respect to water/particle transport) and the last to receive water with entrained particles derived and transported from the mine (see Suchanek et al. [2008a, d] and Fig. 6 for comparable data for TotHg). This is another line of evidence that suggests that generally the greater the influence of the
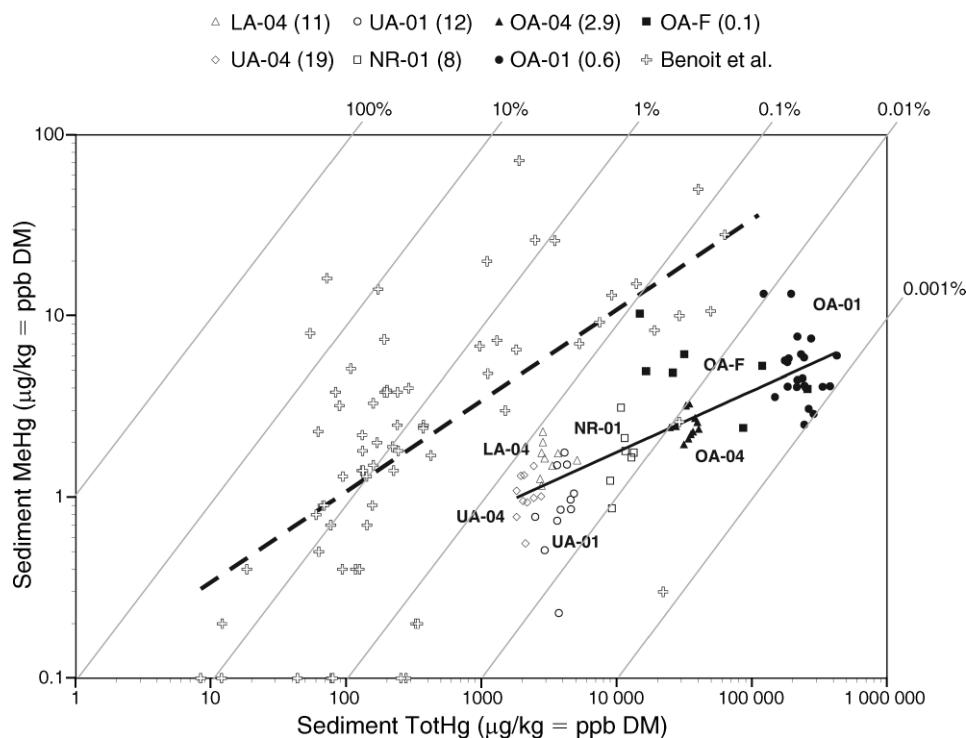
FIG. 3. Total mercury (TotHg) and methylmercury (MeHg) (µg/kg = ppb dry mass [DM]) in sediments from seven sites in Clear Lake over all seasons from 1992 to 1998 (data from Suchanek et al. [2008a]). The solid line (power fit, $R^2 = 0.632$) represents a fitted line for all Clear Lake data. The numbers in parentheses in the key are distances (km) from the Sulphur Bank Mercury Mine. The dashed line (power fit, $R^2 = 0.414$) and all open cross symbols represent the worldwide trend for data from several ecosystems (freshwater wetlands, marine and estuaries, lakes, rivers) from Benoit et al. (2003). The gray diagonal lines represent isoclines for percentages of MeHg:TotHg.

mine, the lower the relative bioavailability of Hg. Exceptions to this generality are hot spots of upwelling acid mine drainage (AMD) immediately in front of the mine at sites such as OA-F (Fig. 2), where elevated concentrations of MeHg (that are likely more bioavailable) have been documented previously (Suchanek et al. 2000a, b).

When viewed on a lake-wide basis, Clear Lake sediments exhibit a pattern of increasing MeHg with increasing TotHg, typically correlated with increasing proximity to the mine (Fig. 3), and the sites with the highest MeHg are, indeed, closest to the mine (Suchanek et al. 2008a). Although it appears that the relative bioavailability of Hg (ratio of MeHg:TotHg) in sediments decreases with proximity to the mine (Fig. 2), absolute MeHg concentrations in sediments increase with increasing proximity to the mine (Suchanek et al. 1998, 2000a, b, 2008a). This is almost certainly due to the overwhelmingly large inventory of inorganic Hg available from mine wastes for methylation in the sediments at and near the mine site. Even though a much lower percentage of the Hg may be methylated near the mine, the absolute amount of MeHg produced is still large in comparison with other regions of the lake. In a review of factors affecting methylation, Ullrich et al. (2001) note that MeHg concentrations in sediments typically range from ~1% to 1.5% of the TotHg concentrations and even less (typically <0.5%) in estuarine and marine environments. Benoit et al. (2003) have evaluated the relationship between MeHg and TotHg in sediments from a variety of ecosystems worldwide, with the percentage of MeHg typically ranging from ~0.01% to 10% of TotHg concentrations. Benoit's values are also plotted with the Clear Lake values in Fig. 3, and it is clear that the percentage of MeHg in Clear Lake sediments (0.001–0.1%) falls at the low end of, and up to an order of magnitude below, the typical range for the other worldwide sites presented by Benoit et al. (2003). It is evident that Clear Lake has some of the highest sediment TotHg concentrations, yet exhibits some of the lowest MeHg values compared with other sites worldwide at those same TotHg concentrations.

Acid volatile sulfides in lake bed sediments are highest near the mine and decrease significantly with distance from the mine (linear regression: $P = 0.0001$, $R^2 = 0.26$, $N = 44$, Fig. 4A). However, the flocculent precipitate (floc) produced from acid mine drainage hot spots immediately in front of the mine (Suchanek et al. 2000a) exhibits extremely low AVS concentrations. With the exception of the floc, the SEM:AVS ratio (also a proxy for relative potential toxicity) exhibits a generally
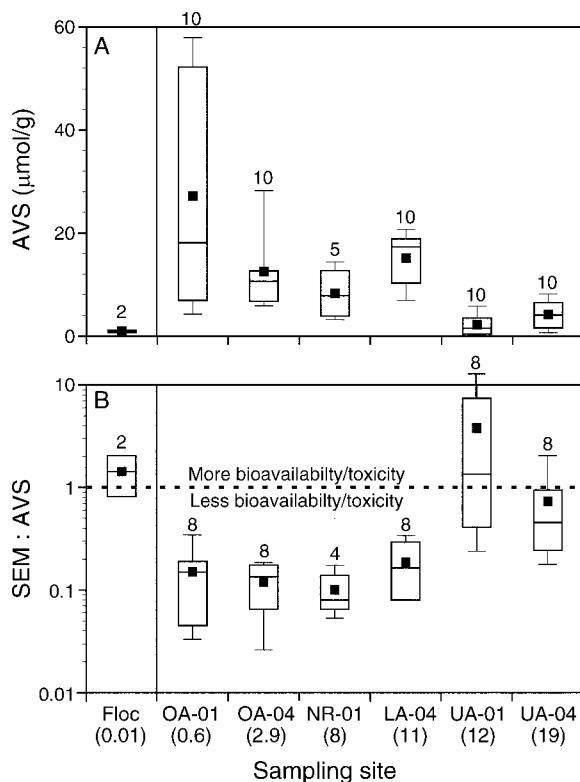
FIG. 4. Box plots of acid volatile sulfides (AVS) and simultaneously extractable metals (SEM) at sediment collection sites in Clear Lake. (A) Sediment AVS at sites along a distance gradient away from the Sulphur Bank Mercury Mine. (B) Ratio of SEM:AVS along the same distance gradient indicating relative Hg bioavailability/toxicity of sediment samples as a function of their relative position above or below a ratio of 1.0. The solid squares are means; the tops and bottoms of boxes and horizontal lines through boxes represent the 75th and 25th percentiles and medians, respectively; the top and bottom whiskers represent 90th and 10th percentile (outlier caps), respectively. The numbers above whiskers are sample sizes. The numbers in parentheses below site codes are distances (km) from the mine (see Fig. 1 for locations of sites).

increasing trend with distance from the mine (linear regression of ln[SEM:AVS vs. distance]: $P = 0.001$, $R^2 = 0.22$, $N = 44$, Fig. 4B). Based on interpretations of SEM:AVS ratios from other studies (Di Toro et al. 1992, Ankley et al. 1996, Haines et al. 2003) the influence of sulfides in binding Hg in sediments yields SEM:AVS ratios that suggest significantly lowered Hg bioavailability and potential toxicity to biota below a ratio of 1.0, i.e., within ~10–12 km of the mine (Fig. 4B). Lowered AVS concentrations (and thus lowered Hg binding to sulfides) in regions distant from the mine (e.g., the Upper Arm) yield SEM:AVS ratios that suggest greater potential Hg bioavailability and toxicity (Fig. 4B). Interestingly, floc produced from acid mine drainage exhibits SEM:AVS ratios suggesting higher bioavailability and toxicity.

*Water*

Water quality data (original data, plus minimum, maximum, and mean values for each site) collected from the Hydrolab water sampler and chemical analyses are provided in the Supplement. One parameter that has been identified as particularly influential in regulating methylation is dissolved organic matter (DOM). In our study we measured TOC, DOC, and humic acids; for Clear Lake, humic acids make up 80% ± 13% (mean ± SE) of TOC.

The ratio of MeHg:TotHg (data from Suchanek et al. [2008a]) exhibits a significant increase (suggesting increasing Hg bioavailability) with distance away from the mine for both surface and bottom waters (Fig. 5). Methylmercury in Clear Lake unfiltered water typically exhibits a maximum during late summer or early fall (Suchanek et al. 2008a). And, within any one season, there appears to be a strong significant positive relationship ($P < 0.0001$) between aqueous MeHg and TotHg (Fig. 6A). Data for Fig. 6A were collected during the PLS survey in fall 1992 (Suchanek et al. 2008a), but data for Fig. 6B were collected throughout all seasons and all years during the study period from 1992 to 1998, and this relationship is significant at $P = 0.045$. Because there is significant variability in MeHg production during different seasons (Suchanek et al. 2008a, b, d), combining data from all seasons masks the static and pronounced relationship between MeHg and TotHg at any instant in time (Fig. 6B). Thus, it may be misleading to interpret a larger data set from an entire site or system without first considering the significance of seasonal drivers of methylation.

Ullrich et al. (2001) report that MeHg is typically <5% of TotHg in estuarine and marine waters, but up to 30% in freshwater lakes, and Bloom (1989) has reported 37% MeHg in the anoxic bottom waters of a stratified pristine lake. Clear Lake waters, on the other hand, are in the very lower end of this range, with MeHg percentages in the range of 0.003–10%. Schaefer et al. (2004:4304) evaluated the percentage of TotHg as MeHg in surface waters worldwide for a variety of ecosystems, including lakes, rivers, wetlands, and estuaries, and identified the "MeHg accumulation paradox," which could be explained by the quantitative induction of bacterial enzymes. Fig. 7 illustrates the relationship between the percentage of TotHg as MeHg for Clear Lake unfiltered surface waters throughout the duration of our study in relation to the worldwide trend line for all ecosystems, and lakes in particular, identified by Schaefer et al. (2004). Not only do all of the Clear Lake data fall below Schaefer's global trend line for all ecosystems, but nearly all the data (with the exception of a few points in the Upper Arm furthest away from the mine) fall below the worldwide data for lakes.

Methylmercury in Clear Lake water was further compared with other contaminated and non-contaminated sites worldwide. This comparison indicated that the proportion of MeHg in Clear Lake water is lower
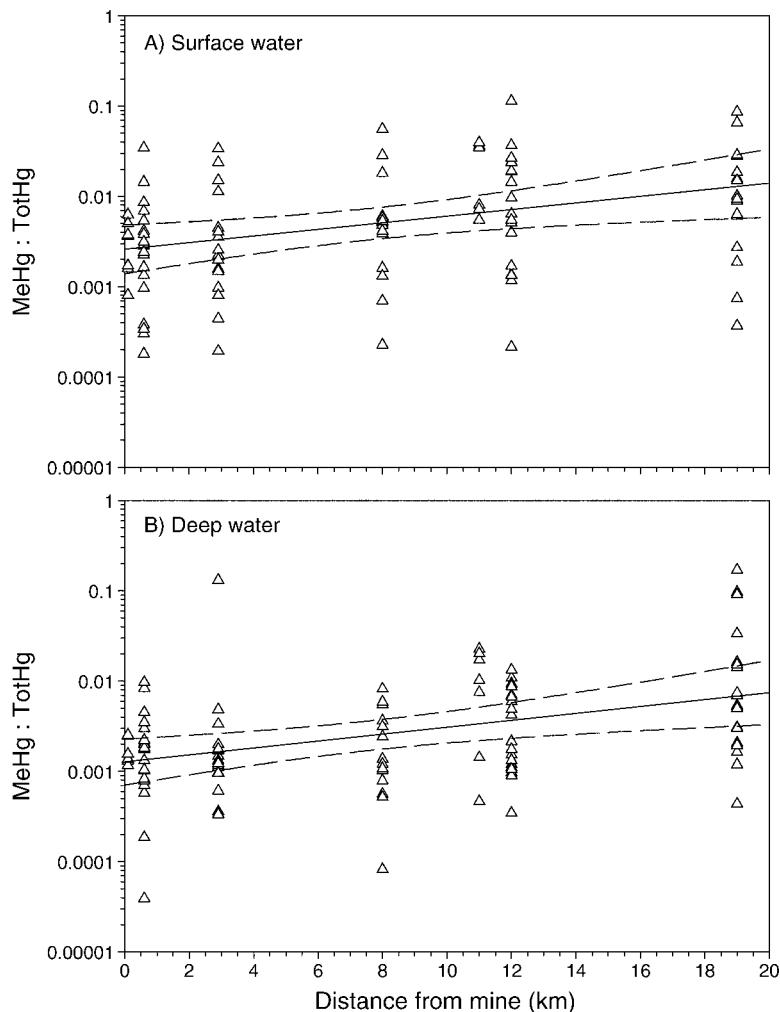
FIG. 5. The ratio of methylmercury to total mercury (MeHg:TotHg) in surface and deep unfiltered Clear Lake water samples as a function of distance from the Sulphur Bank Mercury Mine, including data for all seasons from 1992 to 1998 (data from Suchanek et al. [2008a]). The line fits are exponential with 95% confidence intervals. (A) Surface water, $R^2 = 0.127$, linear regression significant at $P = 0.001$; (B) deep water, $R^2 = 0.177$, linear regression significant at $P = 0.007$.

than most other contaminated and non-contaminated sites for which both TotHg and MeHg data were available (Fig. 8). Interestingly, Clear Lake has the widest range of both aqueous TotHg as well as the MeHg:TotHg ratio. One striking aspect of these data is that waters from the vicinity of two chloralkali plants (Fig. 8: boxes 9A, B and 10A, B) typically contain only moderate concentrations of TotHg, yet exhibit the highest MeHg concentrations when compared with waters from Hg-, gold-, and silver-mining sites such as Clear Lake, Lahontan Reservoir in Nevada, USA, and Wanshan, China. A site in Canada influenced by municipal wastes (Fig. 8: box 6) is quite similar to Clear Lake, with high concentrations of TotHg, but relatively low MeHg. Interestingly, waters from the gold- and silver-mining sites at Lahontan Reservoir (Fig. 8: box 8) can reach up to 5–10 times the MeHg concentrations than those at a Hg-mining site in China and as high as

two orders of magnitude higher than Clear Lake. This may be a reflection of the relatively more bioavailable Hg source (Hg°) at gold/silver-mining sites vs. the more abundant, yet refractory, cinnabar (HgS) source contaminating Hg-mining sites (see Bloom et al. [2003] for a discussion of methylation potential for various forms of Hg).

These data are consistent with the concept that the chemical form of Hg being released from different types of sites (e.g., from Hg mines vs. gold or silver mines or from chloralkali plants) has a dramatic influence on how bioavailable that Hg will be for methylation and how efficiently it will bioaccumulate throughout the ecosystem. Other factors undoubtedly also influence bioavailability (see *Discussion*), but our data suggest that the chemical nature of the source Hg appears to be one very important driver.
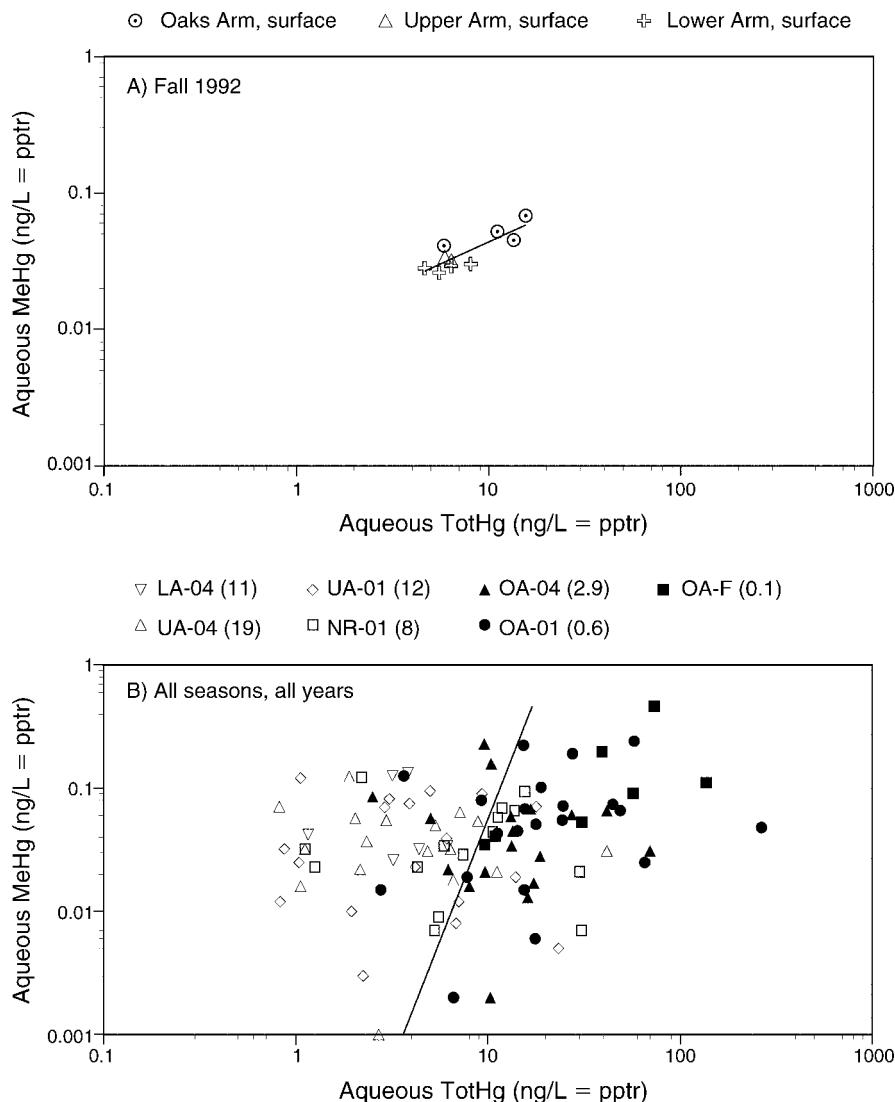
FIG. 6.    Total mercury (TotHg) and methylmercury (MeHg) from unfiltered surface waters at Clear Lake (pptr, parts per trillion). (A) Data from fall 1992 only (during the Preliminary Lake Survey). The fitted line is a power curve ($R^2 = 0.722$; linear regression on log-transformed data is significant at $P < 0.0001$). (B) Data for all seasons from 1992 to 1998. Note log scales on both plots comparing "single season" data (A) vs. "multi-season, multi-year" data (B). The fitted line is a power curve ($R^2 = 0.05$; linear regression on log-transformed data is significant at $P = 0.04$). In (B) the solid symbols represent data from the Oaks Arm; the open symbols represent data from non-Oaks Arm sites. The numbers in parentheses in the key are distances (km) from the Sulphur Bank Mercury Mine.

### Biota

As observed in sediments and water, on a lakewide basis, MeHg increases with increasing TotHg for both zooplankton and chironomids (Fig. 9). For pooled zooplankton (even when incorporating all seasons over all years), although the data were highly variable ($R^2 = 0.151$), MeHg does exhibit a significantly positive relationship to TotHg (linear regression: $P = 0.0198$). Pooled chironomid data are somewhat less variable ($R^2 = 0.238$), and the regression relationship between TotHg and MeHg is highly significant at $P < 0.0001$.

*Percentage of MeHg in biota.*—Plankton and benthic invertebrates (oligochaetes and chironomids) were evaluated for percentage of MeHg as a function of distance from the mine. As observed for both sediment and water matrices, the ratio of MeHg:TotHg in lower trophic level biota also increase significantly with distance from the mine (Fig. 10, zooplankton; Fig. 11, chironomids). Because invertebrate MeHg varies significantly by season, with higher percentages in the late summer and fall (Suchanek et al. 2008b), it is important to include a temporal component when evaluating relationships between the percentage of MeHg and distance. Suchanek et al. (2008b) provide additional seasonal data for both zooplankton and chironomids, showing that for
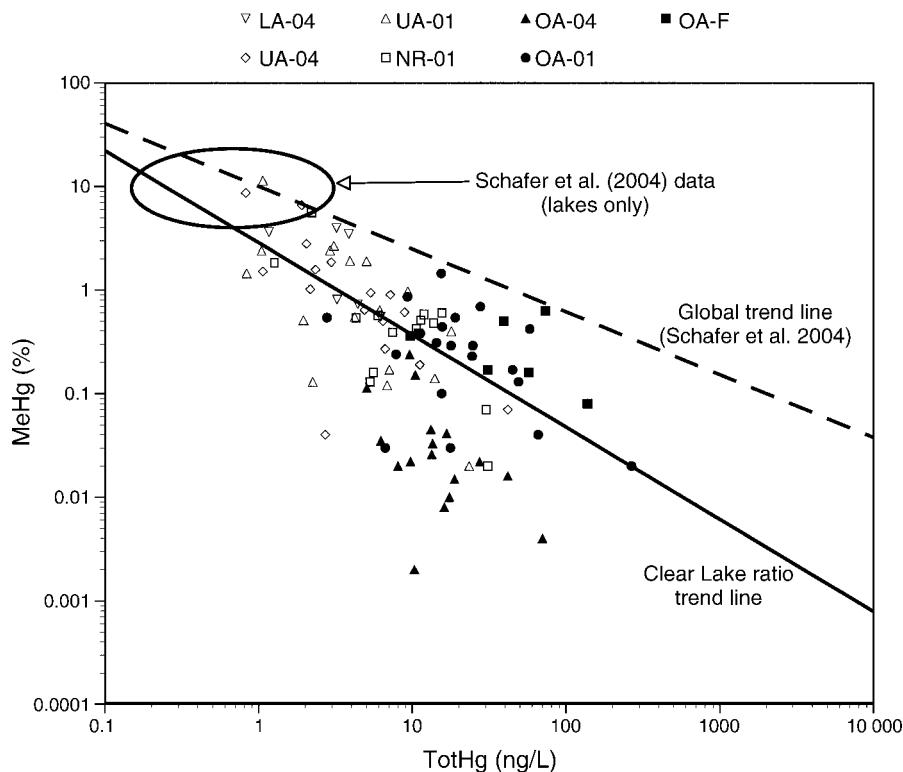
FIG. 7. Percentage of methylmercury (MeHg) as a function of total mercury (TotHg) concentrations in unfiltered surface waters for Clear Lake (symbols) in comparison with data from Schaefer et al. (2004) for lakes and a variety of other ecosystems worldwide. The dashed line represents Schaefer's global trend line for all ecosystems, and the solid line is a power curve fit for all the Clear Lake data.

any point in time, the percentage of MeHg increases predictably with distance from the mine at the six long-term sampling sites. But this relationship could be lost with pooled data.

The ratio of MeHg:TotHg in zooplankton was evaluated on a site-specific basis (Fig. 10). Zooplankton ranged from ~3% to 99% MeHg, with the majority of values >10%, and exhibited a highly significant positive relationship with distance from the mine (linear regression, $P < 0.0001$).

The ratio of MeHg:TotHg in chironomids, which are benthic detritivores, also increases significantly (linear regression, $P < 0.001$) with increasing distance from the mine (Fig. 11), with the minimum value of 0.1% found at OA-01 (the site closest to the mine) and the maximum value of 22.4% occurring at UA-04 (the site furthest from the mine). In comparison, chironomids from flooded hydroelectric reservoirs in northern Quebec ranged from ~20% to 25% MeHg (Tremblay et al. 1996).

*Comparisons of biotic TotHg and MeHg to other sites worldwide.*—Suchanek et al. (2008b) documented TotHg and MeHg in lower trophic species for several other studies worldwide. Here we plot TotHg vs. MeHg for Clear Lake in relation to those values from other sites for zooplankton (Fig. 12) and chironomids (Fig. 13). As was observed with sediment and water, Clear Lake

zooplankton typically exhibit concentrations of MeHg that are at the low end of the range for any given concentration of TotHg observed for other sites worldwide (Fig. 12). In addition, the range of zooplankton TotHg in Clear Lake is the broadest of any site, and, with the exception of the flooded peatland reservoir in Quebec, the range of MeHg is the largest as well. The percentage of MeHg in Clear Lake zooplankton appears to be more similar to pristine than contaminated sites. Remote lakes in Wisconsin, USA (Fig. 12: box 2; Watras and Bloom 1992, Watras et al. 1998), and natural lakes in Quebec, Canada (Fig. 12: box 4A; Plourde et al. 1997, Kainz and Lucotte 2002), contained zooplankton that had about the same concentrations of MeHg as the highest values found in Clear Lake. Yet, when those lakes were altered (e.g., flooded or acidified), they yielded zooplankton with nearly an order of magnitude higher MeHg than highly contaminated Clear Lake. Interestingly, when those lakes were altered, zooplankton increased not only in MeHg, but in TotHg as well. Bulk zooplankton from Lake Superior, a relatively non-polluted oligotrophic lake, exhibited both TotHg and MeHg concentrations that were at the low to mid-range of those in Clear Lake (Fig. 12: box 3; Gorski et al. 2003). By far the highest concentrations of MeHg in zooplankton (specifically daphnids) were documented in Onondaga Lake, USA, site of a chloralkali plant (E.
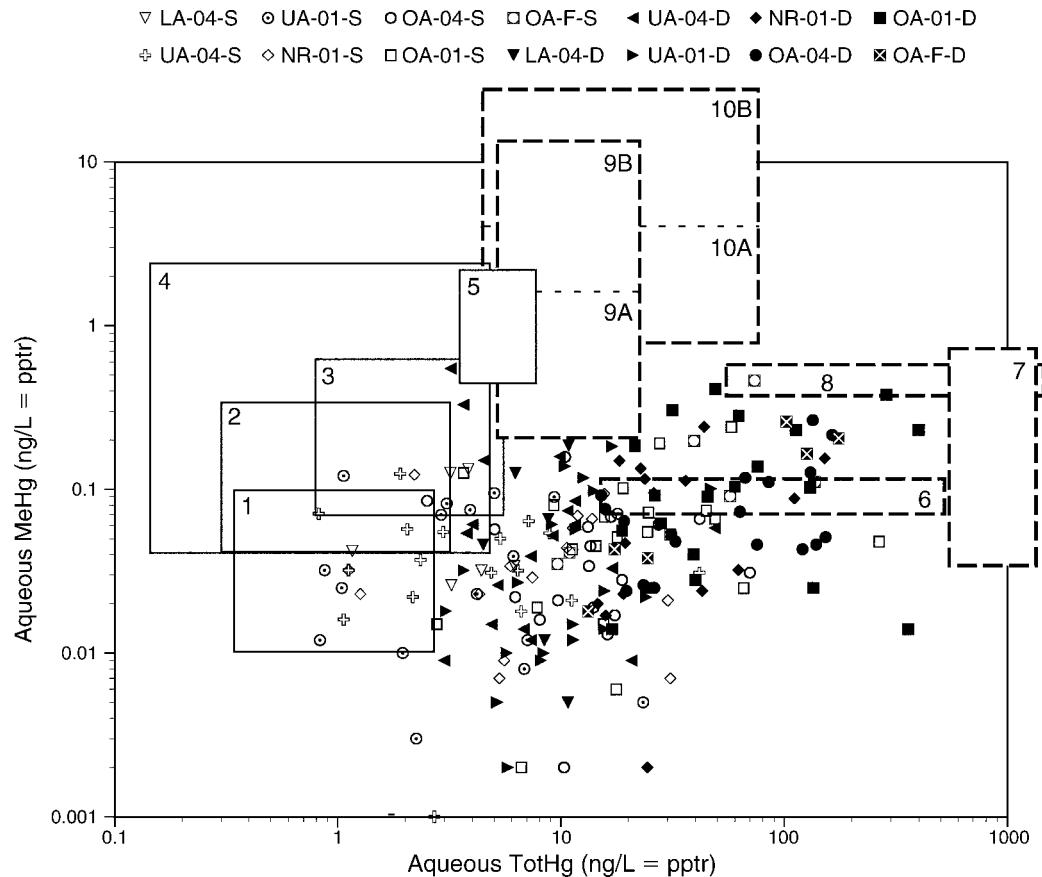
Fig. 8. Methylmercury (MeHg) vs. total mercury (TotHg) from unfiltered Clear Lake water (symbols; pptr, parts per trillion) compared to the range of aqueous TotHg and MeHg concentrations at five non-contaminated and five contaminated sites worldwide (boxes). For Clear Lake data, open symbols are shallow-water samples (S in key); solid symbols are deep-water samples (D in key). Areas within boxes represent minimum and maximum values for both TotHg and MeHg from the cited studies. Non-contaminated sites (solid boxes): 1, 12 pristine lakes in Montana, USA (Watras et al. 1995a); 2, 12 lakes in northeast Minnesota, USA (Monson and Brezonik 1998); 3, remote lakes in New York, USA (Driscoll et al. 1994); 4, 23 remote lakes in Wisconsin, USA (Watras et al. 1995b, 1998); 5, three small lakes in Finland (Verta et al. 1994). Contaminated sites (dashed boxes): 6, eutrophic lake influenced by urban sources in Saskatchewan, Canada (urban wastes; Jackson 1986); 7, reservoir and pond in Wanshan, China (Hg mining; Horvat et al. 2003); 8, Lahontan Reservoir, Nevada, USA (gold/silver mining; Bonzongo et al. 1996); 9, Onondaga Lake, New York (chloralkali plant; Henry et al. 1995, Jacobs et al. 1995; 9A, maximum for epilimnion; 9B, maximum for hypolimnion); 10, Clay Lake, Ontario (chloralkali plant; Parks et al. 1989; 10A, maximum for epilimnion; 10B, maximum for hypolimnion). The bold dashes define minimum/maximum potential space for each site; the minor dashes within boxes 9 and 10 define maxima for epilimnion.

Henry, *personal communication*), nearly one to two orders of magnitude higher than bulk zooplankton at Clear Lake with a cinnabar mine as the Hg source.

Benthic chironomid insect larvae exhibited MeHg concentrations (Fig. 13) very similar to those of zooplankton (Fig. 12). However the TotHg concentrations found in the chironomids were roughly one to two orders of magnitude higher than for zooplankton. And, like the trend in zooplankton, chironomid TotHg and MeHg in Clear Lake varied much more widely than at other sites. When compared with other sites worldwide, Clear Lake chironomids exhibited significantly higher TotHg, but generally lower MeHg and significantly lower MeHg percentage. Methylmercury concentrations in chironomids from flooded hydroelectric reservoirs

(Fig. 13: box 2; Tremblay et al. 1996) were at the high end of Clear Lake values, and chironomids from Onondaga Lake, a site contaminated by a chloralkali plant, exhibited the highest MeHg percentages (Fig. 13: box 1; Becker and Bigham 1995).

Taken together, these MeHg:TotHg ratios suggest that the Hg-mine-dominated Clear Lake aquatic ecosystem does not produce and/or bioaccumulate MeHg at nearly the efficiency of other systems worldwide. For example, the MeHg:TotHg ratios for most parameters typically resemble more pristine or non-contaminated sites. For unfiltered water (Fig. 8), remote lakes appear to produce as much MeHg as Clear Lake, but from approximately one to two orders of magnitude lower TotHg. The site influenced by urban waste in Saskatch-
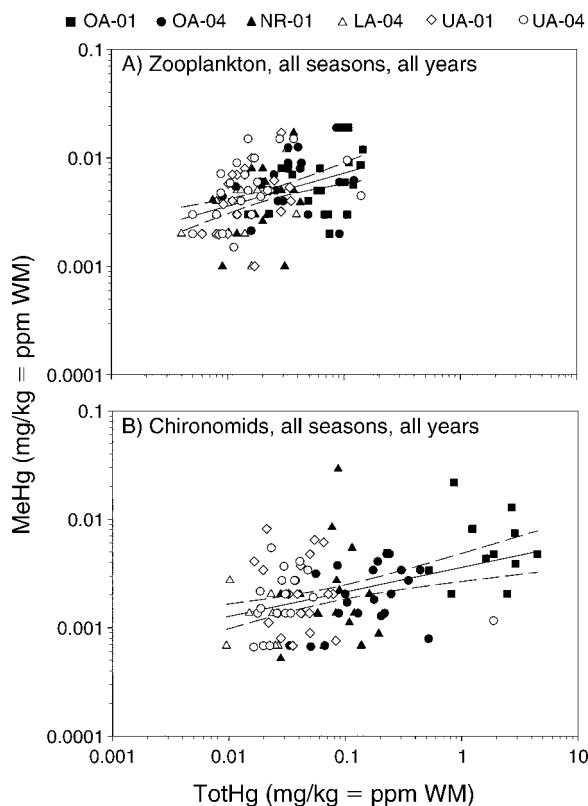
FIG. 9. Methylmercury (MeHg; WM, wet mass) vs. total mercury (TotHg) for Clear Lake planktonic and benthic invertebrates during all seasons and all years from 1992 to 1998: (A) zooplankton ($P = 0.0005$), (B) chironomids ($P < 0.0001$). The fitted lines are power curves. Data are from Suchanek et al. (2008b). The dashed lines represent 95% confidence intervals.

ewan, Canada, and the other mining sites had roughly comparable ratios to those from Clear Lake. However, those sites contaminated by chloralkali plants exhibited exceptionally high MeHg concentrations at comparable TotHg values, with hypolimnion water typically about an order of magnitude higher in MeHg than epilimnion water.

Clear Lake fishes also exhibit relatively low Hg (primarily MeHg) concentrations that, for adult predatory largemouth bass, range from ~0.5 to 2.0 µg/g (Suchanek et al. 2008c). Comparable fishes from other sites impacted by Hg contamination have much higher concentrations. Wiener et al. (2003) provide a range of maximum Hg concentrations for fishes from a series of sites variously influenced by chlor-alkali plants (2–15 µg/g wet mass), newly flooded reservoirs (2–6 µg/g wet mass), South Florida wetlands (2–4 µg/g wet mass), and low-alkalinity lakes (1–3 µg/g wet mass).

DISCUSSION

Is there linkage or a decoupling between inorganic Hg loading and biotic Hg in Clear Lake? Over the past 130 years, an estimated 100 Mg or more of Hg have been deposited into the Clear Lake aquatic ecosystem from the Sulphur Bank Mercury Mine (Chamberlin et al. 1990, Suchanek et al. 2003, 2008d), with ongoing loading from the mine estimated at ~322–331 kg/yr (Suchanek et al. 2008a, d; Suchanek et al., in press). Yet Clear Lake exhibits significantly lower MeHg relative to TotHg concentrations in sediments, water, and biota than might be expected based on the massive bulk loading of inorganic Hg in comparison with other
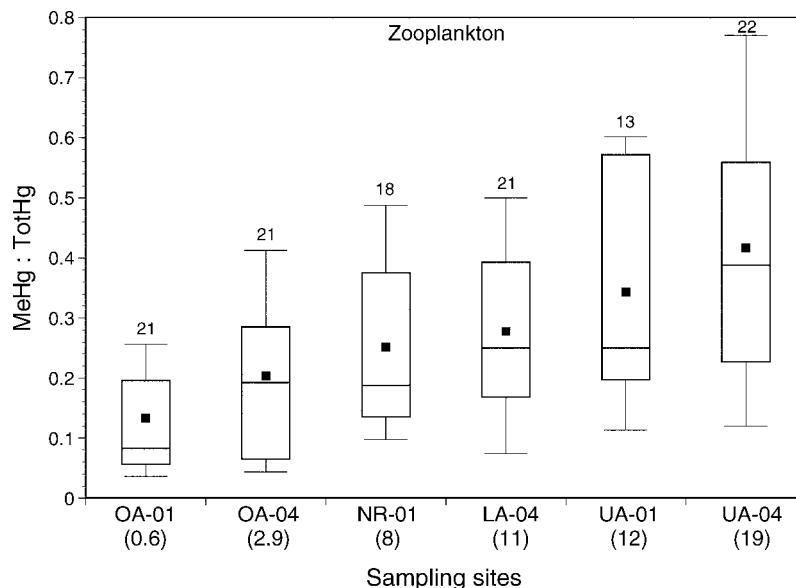


FIG. 10. Box and whisker plots of methylmercury to total mercury ratios (MeHg:TotHg) in zooplankton for pooled data from 1992 to 1998 (all seasons) at six long-term sampling stations (with increasing distance from the Sulphur Bank Mercury Mine [km] in parentheses). The numbers above whiskers are sample sizes. See Fig. 4 for interpretation of box and whisker plots. Data are from Suchanek et al. (2008b).
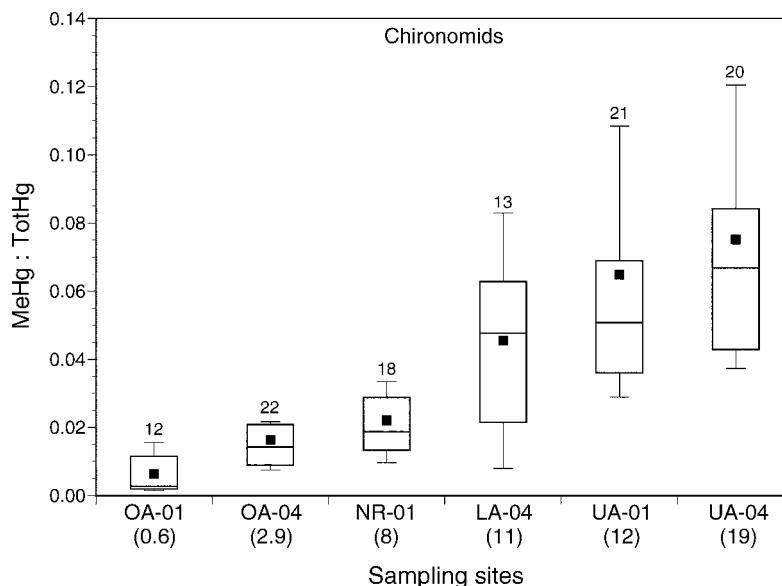
FIG. 11.   Box and whisker plots of methylmercury to total mercury ratios (MeHg:TotHg) in chironomids from 1992 to 1998 (all seasons) at six long-term sampling stations (with increasing distance from the Sulphur Bank Mercury Mine [km] in parentheses). The numbers above whiskers are sample sizes. See Fig. 4 for interpretation of box and whisker plots. Data are from Suchanek et al. (2008b).

contaminated and non-contaminated systems worldwide. Aqueous MeHg can represent up to ~30% of the TotHg in lakes and reservoirs (Fig. 7; Meili 1997, Schaefer et al. 2004) whereas at Clear Lake, that value barely reaches 10% (Fig. 7). For most freshwater systems, sediment MeHg is typically 1–5% of TotHg and is often much lower (<0.5%) in estuarine and marine environments, but can also reach up to ~30% (Fig. 3; Ullrich et al. 2001, Benoit et al. 2003). Yet at Clear Lake, sediment MeHg only ranges from ~0.01% to 0.1% (Fig. 3). Thus, Clear Lake water and sediments exhibit two to three orders of magnitude lower percentage of MeHg than other lake or reservoir systems.

Over the past two decades, significant progress has been made in understanding those factors that either enhance or inhibit methylation and bioaccumulation (Ullrich et al. 2001, Wiener et al. 2003, 2007). Some of the factors suggested to have the greatest influence include: (1) amount and concentration of inorganic source Hg, (2) chemical form of the source Hg, (3) presence and condition of methylating bacteria, (4) temperature, (5) pH, (6) reduction/oxidation (redox) state of environmental media, (7) a source of labile carbon, (8) concentration of sulfate, (9) concentration of sulfides, (10) complexation with dissolved organic matter (DOM), and (11) dilution by primary production. Each of these factors is discussed relative to its potential applicability to Clear Lake.

1. *Amount and concentration of inorganic source Hg.*— With the legacy of at least 100 Mg of Hg deposited into Clear Lake, there is no lack of bulk source material for methylation. Concentrations of inorganic Hg in Clear Lake sediments near the mine reach as high as 438 mg/kg dry mass (DM) in surface sediments (Suchanek et al. 2008a) and 1220 mg/kg DM in near-surface sediments (CVRWQCB 1987). These concentrations decline exponentially to nearly regional soil background levels (~0.5 mg/kg DM) at the furthest distances in the lake from the mine (Suchanek et al. 2008a).

2. *Chemical form of the source Hg.*—Using X-ray absorption spectroscopy, the chemical composition of the Hg from soils and mine wastes at the Sulphur Bank Mercury Mine has been identified as: 46% metacinnabar (HgS [cub]), 34% corderoite ($Hg_3S_2Cl_2$), and 20% cinnabar (HgS [hex]) (Kim et al. 2000). In recent years, there also have been advances in relating the various forms of Hg from mining sites and other contaminant sources to their methylation potential. Through a series of selective chemical extractions, Bloom et al. (2003) found that cinnabar and metacinnabar, two of the predominant forms of Hg in the mine wastes, are significantly less bioavailable than other chemical forms of Hg. This result is in agreement with the literature findings summarized by Ullrich et al. (2001). Thus, it is likely that the massive bulk loading of sediment-derived cinnabar and metacinnabar from the terrestrial part of the mine is largely refractory and may not contribute nearly as much as would be expected based on its mass. However, because that mass is so enormous, even a very low methylation rate on such a large source would still produce a substantial amount of MeHg to be distributed throughout the ecosystem.
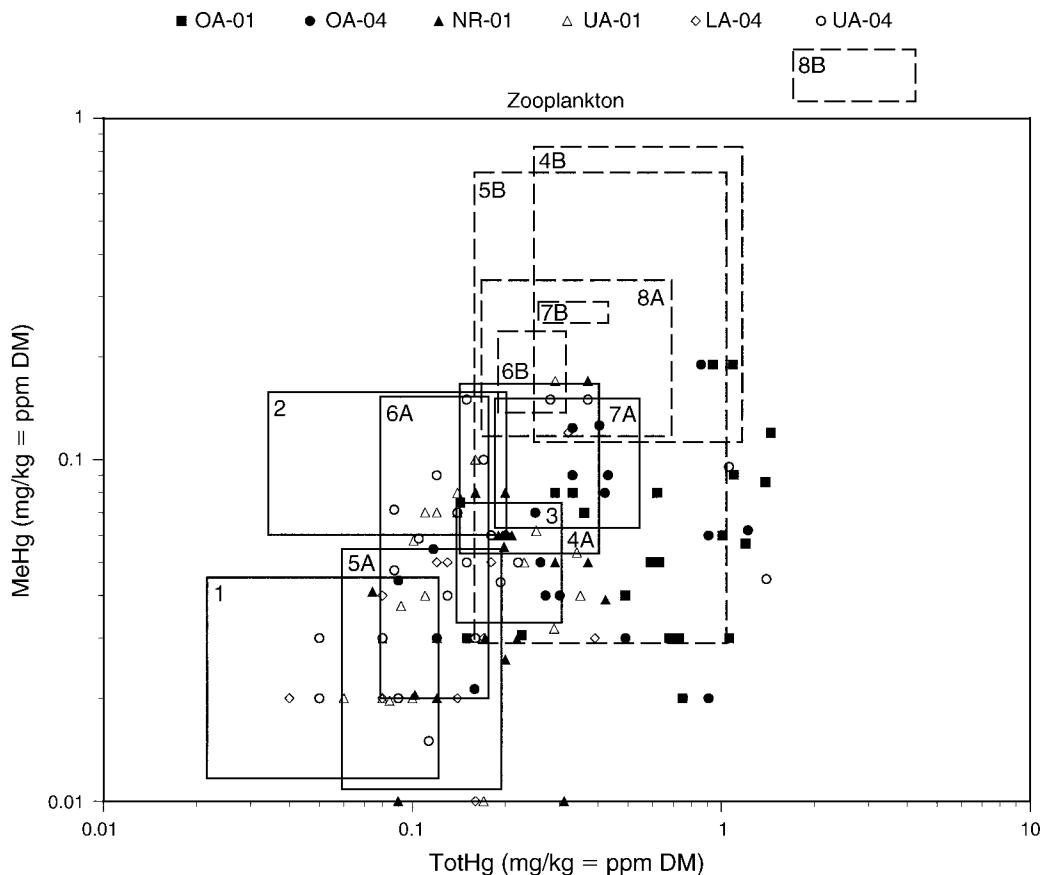
FIG. 12. Methylmercury (MeHg) vs. total mercury (TotHg) in zooplankton (ppm dry mass [DM]) from Clear Lake (1992–1998 represented by solid and open symbols) compared to the range of TotHg and MeHg concentrations at several other sites worldwide (represented by large rectangles). Natural or reference lakes are shown with solid lines; flooded, acidified, or contaminated lakes are shown with dashed lines. For Clear Lake data, solid symbols are closest to the Sulphur Bank Mercury Mine, and open symbols are farthest from the mine. Areas within boxes represent minimum and maximum values for both TotHg and MeHg from the cited studies. Sites: 1, bulk zooplankton from Lake Superior (Back et al. 2003); 2, total plankton from 15 remote lakes in Wisconsin, USA (Watras et al. 1998); 3, bulk zooplankton from two lakes on Isle Royale National Park, Lake Superior (Gorski et al. 2003); 4, zooplankton from several lakes in Quebec, Canada (Plourde et al. 1997; 4A, four natural lakes; 4B, two flooded reservoirs); 5, 80-μm net zooplankton from a peatland reservoir in northwest Ontario, Canada (Paterson et al. 1998; 5A, before flooding; 5B, after flooding); 6, zooplankton from northern Quebec, La Grande Reservoir system (Kainz and Lucotte 2002; 6A, from a series of undisturbed natural lakes; 6B, from a flooded reservoir); 7, individual *Daphnia* from Little Rock Lake, Wisconsin (Watras and Bloom 1992; 7A, from reference basin; 7B, from acidified basin); 8, plankton from Onondaga Lake, New York, USA (chloralkali plant; E. Henry, *personal communication*; 8A, bulk zooplankton; 8B, daphnids). The daphnid data from Lake Onondaga in box 8B represent the highest MeHg values reported in the literature and are plotted to an accurately extended log scale of the figure that is out of the data field to save space and enhance the spread of the Clear Lake data in comparison with other sites.

Another potential source of ongoing Hg contamination entering Clear Lake is in dissolved form ($Hg^{2+}$) derived from acid mine drainage from the mine (see Shipp and Zierenberg 2008). Because sulfate reduction, which produces sulfide anions as a waste product, is important in Clear Lake, one expects the resultant formation of highly insoluble mercuric sulfide (HgS) to strongly limit the availability of $Hg^{2+}$ at neutral pH (Ullrich et al. 2001). However, further evidence suggests that dissolved $HgS^0$ has the ability to be transported across bacterial membranes and that the aqueous concentration of this compound correlates strongly with methylation rates in pure culture studies (Benoit et al. 2001).

3. *Presence and condition of methylating bacteria.*— Active production of monomethyl Hg in slurries of Clear Lake sediments amended with $HgCl_2$ and incubated under anaerobic conditions indicates that there are large populations of bacteria that can catalyze this process (Mack 1998). A significant part of the methylation activity, as shown by molybdate inhibition experiments, is due to the activity of sulfate-reducing bacteria (Mack 1998). Surprisingly, the majority of methylation activity is not due to this group of bacteria (Mack 1998), and recent studies with the first pure culture of an iron-reducing bacterium derived from Clear Lake (Fleming et al. 2006) show that the per-cell methylation rate by this type of bacterium could exceed
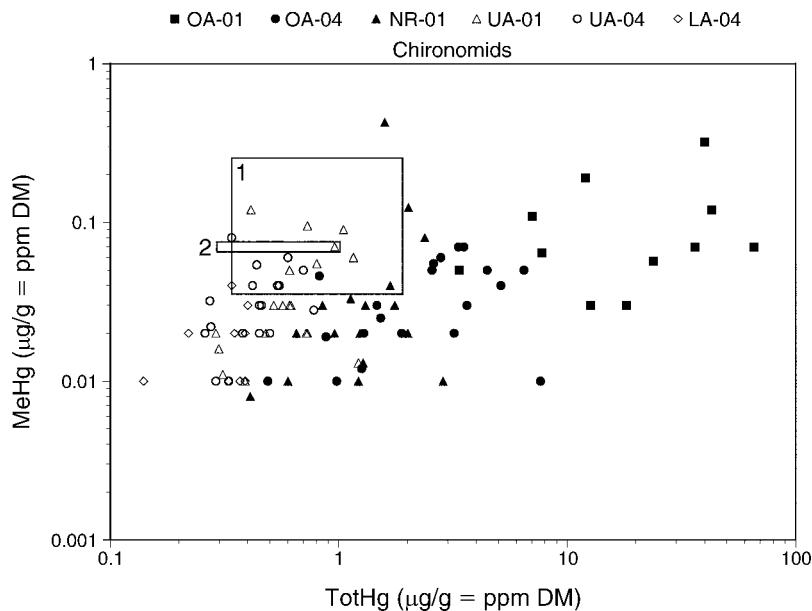
FIG. 13. Methylmercury (MeHg) vs. total mercury (TotHg) in chironomid insect larvae from Clear Lake sites (1992–1998) compared to the range of TotHg and MeHg concentrations at other sites. For Clear Lake data, solid symbols are closest to the Sulphur Bank Mercury Mine, and open symbols are farthest from the mine. Comparison sites: 1, Onondaga Lake, New York, USA (chloralkali plant; PTI 1993); 2, Le Grande hydroelectric reservoirs (14 years post-flooding), Quebec, Canada (Tremblay et al. 1996).

that of sulfate-reducers. Determinations of the most probable number have shown that there are at least $10^8$ (culturable) iron reducers per gram of Clear Lake sediment, which, in turn, suggests that this group may be very significant contributors to methylation in this lake that receives high input of oxidized iron, the oxidant required for this group of facultatively anaerobic bacteria (Fleming et al. 2006).

4. *Temperature.*—As is true for most biological systems, temperature will increase the metabolism of microorganisms, including sulfate- and iron-reducing bacteria. Elevated temperatures have been shown to increase methylation, whereas lowered temperatures enhance demethylation, resulting in significant increases in MeHg production in summer as compared with winter (Bodaly et al. 1993, Ramlal et al. 1993). The summary of annual sulfate reduction rates and Hg methylation potential for Clear Lake sediments (Mack 1998) is completely consistent with this pattern. In Clear Lake, elevated temperatures in late summer and early fall (see Supplement; Suchanek et al. 2008d) also contribute to the production of large masses of "blue-green algae" (cyanobacteria) and increase the production of MeHg, which appears seasonally elevated in sediments, water, and lower trophic level biota (Suchanek et al. 2008a, b, d).

5. *pH.*—One of the significant correlates of elevated methylation rates is lowered pH (Ullrich et al. 2001). The exact mechanism(s) by which pH may regulate methylation rates in natural systems remains unknown. However, a wide variety of hypotheses have emerged to

suggest why methylation increases at lowered pH, including the influence of pH on: (1) DOC–Hg interactions (Winfrey and Rudd 1990), (2) the balance between populations of methylating and demethylating bacteria (Steffan et al. 1988, Ramlal et al. 1993), (3) loss of volatile Hg species from water surfaces (Ullrich et al. 2001), and (4) a facilitated mechanism by which Hg (II) is taken up by aquatic bacteria (Kelly et al. 2003).

Although acid mine drainage from the Sulphur Bank Mercury Mine ranges in pH from 2.5 to 3.5, it is soon mixed with a large-volume lake with water that ranges in pH from ~7.5 to 9.0 (see data in Supplement), leaving the zone of significantly lowered pH limited to a region quite close to the mine (Shipp and Zierenberg 2008). The alkaline nature of the majority of Clear Lake waters may also contribute to lowered production of MeHg throughout most of the lake. However, close to the mine, conduits of acid rock drainage emanate from sediment "hot spots" (Shipp and Zierenberg 2008), where MeHg production is much higher than in the remainder of Clear Lake. Experiments with intact sediment cores (Mack 1998; T. H. Suchanek, *unpublished data*) have demonstrated that net efflux of MeHg into the overlying water is highest at these hot spots, probably due to enhanced solubility of Hg species.

6. *Reduction/oxidation (redox) state of environmental media.*—Sulfate-reducing bacteria (the agent most frequently identified as the primary Hg methylators in aquatic systems), although able to survive transient exposure to oxic conditions, require fully anoxic conditions for growth and metabolism, including Hg

methylation (Compeau and Bartha 1985, Gilmour and Henry 1991). Most deep lakes will stratify vertically during summer months, developing a steep temperature and oxygen demarcation between upper oxic (epilimnion) and lower less oxic or near anoxic (hyoplimnion) zones. Lakes that are typically deeper than ~15 m will develop a strong thermocline with nearly anoxic water below. This deeper hypolimnetic water often develops high concentrations of MeHg (see data table in Suchanek et al. [2008a]). A number of bacteria can also perform demethylation reactions (generally oxidizing $Hg^{2+}$ in MeHg to $Hg^0$), which are generally found to be much more significant under oxic conditions (Ullrich et al. 2001), and the depression of these reactions contributes to anoxic buildup of MeHg. When these types of lakes undergo mixing during the fall/winter "turnover" period, this deep MeHg-charged water is remobilized upwards from the bottom and becomes available to be bioaccumulated throughout the water column. However, lakes that do not stratify rarely develop oxygen-depleted bottom waters and thus rarely develop elevated MeHg in the hypolimnion.

Lakes with an Osgood index (mean depth [in meters] divided by the square root of the lake area [in kilometers]) of three to four or less are polymictic (undergo frequent vertical mixing). Clear Lake's Osgood index is ~0.06, it is shallow (<10 m depth for most of its area), and, with the exception of a few limited deeper regions to ~15 m, the lake does not stratify for any extended periods of time (Richerson et al. 1994, Rueda et al. 2008). Stratification, if it does occur, has been observed for one to two days in localized areas (during summer periods) before disintegrating. This lack of stratification reduces the ability by sulfate-reducing and iron-reducing bacteria to build up a large inventory of methylated Hg in a stratified hypolimnion or in sediments below the hypolimnion. And, since it is not produced, MeHg is ultimately unavailable to the ecosystem during lake turnover. Thus, MeHg burdens in benthic invertebrates, zooplankton, and fish should be much lower in lakes that do not stratify for extended periods and Clear Lake follows this pattern.

Clear Lake's water column redox values are typically quite positive, generally ranging from ~30 to 300 mV and only rarely ever becoming negative (Supplement), indicating a mostly oxidizing (not reducing) environment. From our knowledge of other lake systems, those conditions would not likely promote high levels of MeHg production.

7. *Source of labile carbon.*—Conversion of inorganic Hg to MeHg is generally higher when sediments contain substantial organic matter (Ullrich et al. 2001). Sediment microbial food chains that are dominated by strong potential methylators such as sulfate- or iron-reducing bacteria are dependent on this organic matter as a source of oxidizable organic substrates and cellular carbon. The abundant cyanobacterial blooms identified above deteriorate at the end of summer, depositing copious amounts of labile carbon onto the sediment–water interface where bioturbation will "till" them into the upper few centimeters of sediment, which promotes high microbial activity and concomitant methylation. Near the mine, binding of Hg and MeHg to carbon-rich particles (Ullrich et al. 2001), which in this case are derived from cyanobacteria, allows for facile transport by wind-driven currents to other regions of the lake (see Rueda et al. 2008, Suchanek et al. 2008d). Methylation by indigenous sediment microbial populations at those remote locations or ingestion and bioaccumulation by local fauna are then postulated to contribute to the disproportionate MeHg accumulation at sites characterized by low TotHg (as discussed in *Results: Sediments*; see also Fig. 4).

Clear Lake is a eutrophic lake and exhibits characteristically high organic carbon in older sediments, with percentage of carbon values ranging from ~10% to 15% in sediment cores from ca. 2000 years before present to ca. 1927, but then decreasing to ~5–10% in surficial sediments (Richerson et al. 2008). Water, however, exhibits considerably lower concentrations, with TOC typically ranging from ~0 to 5.5 mg/L (Supplement), which is in the lower range of most other lake systems (e.g., Jackson 1986, Sorensen et al. 1990). The vast majority of that TOC (~65–75%) is in the dissolved form for both surface and bottom water with DOC concentrations ranging from ~0 to 3 mg/L (Supplement), which is again in the lower range of values reported for most other lake systems (e.g., Jackson 1986, Watras et al. 1995a, b, 1998, Monson and Brezonik 1998).

8. *Concentration of sulfate.*—Sulfate-reducing bacteria require a source of sulfate, and the mine represents that type of source, with up to 4000–5000 mg/L sulfate (Mack 1998, Suchanek et al. 2008a). Sulfate released into Clear Lake seasonally as acid mine drainage is mixed throughout the lake via wind-driven currents (Rueda et al. 2008) and depleted quickly during the spring/summer, when most of the Hg methylation is taking place (Suchanek et al. 2008a). Despite the extremely high sulfate concentrations being discharged from the mine, most sediment porewater sulfate concentrations throughout Clear Lake are typically <20 mg/L (Mack 1998, Shipp and Zierenberg 2008, Suchanek et al. 2008a), and surface and bottom lakewater concentrations typically range from 3 to 8 mg/L (Supplement). These concentrations are in the range that is believed to be optimal for production of MeHg by sulfate-reducing bacteria (Ullrich et al. 2001). Enough sulfate is thereby renewed via molecular diffusion to the upper few centimeters of sediment to fuel the metabolism of these potential methylators.

Sulfate concentrations emanating from the mine are extremely high (Shipp and Zierenberg 2008), but sulfate-reducing bacteria seem not to be active in these sediments below a pH of ~4.5 (D. G. Nelson, *personal communication*). The high net efflux of MeHg from

sediments near the mine that contain floc (Mack 1998) is further evidence for methylation by bacteria other than sulfate reducers and provides an exception to the generalization (Ullrich et al. 2001) that high concentrations of sulfate result in high concentrations of sulfide that in turn inhibit microbial methylation of Hg.

9. *Concentration of sulfides.*—The interaction of sulfide and Hg is almost certainly responsible for the low ratios of MeHg:TotHg in Clear Lake biota (Figs. 12 and 13) relative to other Hg-contaminated lakes. Preliminary data indicated that most Clear Lake sediments exhibit SEM:AVS ratios much lower than 1.0, ranging from 0.007 to 0.110 (Suchanek et al. 2000a). Further data collection showed that, with the exception of a flocculent precipitate generated from acid mine drainage immediately adjacent to the mine, AVS (sulfide) concentrations are highest at sites near the mine (e.g., OA-01, OA-04) and generally decline with distance away from the mine ($R^2 = 0.26$, $P < 0.0001$, $N = 44$; Fig. 4A). Ironically, SEM:AVS ratios exhibit an inverse relationship to the AVS concentrations ($R^2 = 0.22$, $P = 0.001$, $N = 44$), with the greatest bioavailability/toxicity (except for the floc samples) expected at sites furthest from the mine in the Upper Arm (e.g., UA-01, UA-04; Fig. 4B). Based on the validity of SEM:AVS ratios accurately predicting bioavailability/toxicity, the floc and sediments at UA-01 would be expected to have the greatest Hg bioavailability and toxicity of any other type or location of sediments in Clear Lake (Fig. 4B). As a corollary to this result, because much of the Hg in the gut of Clear Lake chironomids is almost certainly composed of grains of cinnabar or metacinnabar (HgS, see factor 2 above), with very low SEM:AVS ratios, it would represent a poor substratum for bacterial methylation and a low potential for production of MeHg.

Likewise, colloidal or fine-particulate HgS derived from cinnabar or metacinnabar may represent a significant part of the TotHg in unfiltered water samples throughout the lake (Fig. 8) and may not be readily available for bacterial methylation and subsequent bioaccumulation. Data represented in Figs. 8, 12, and 13 are remarkable when compared with the literature, not so much for the low absolute level of MeHg as for the low ratio due to a high concentration of TotHg yet moderate levels of MeHg.

10. *Complexation with DOM.*—Particularly strong associations have been observed between Hg and DOM. Several investigators have found that, under certain conditions, the bioavailability of Hg (both TotHg and MeHg) may be reduced significantly by complexation with DOM and specifically humic substances, primarily humic and fulvic acids (Grieb et al. 1990, Back and Watras 1995, Driscoll et al 1995, Strumm and Morgan 1996, Sjöblom et al. 2000). In some cases, however, Hg concentrations in invertebrates and fish have been shown to increase with increasing DOM (Driscoll et al. 1995, Watras et al. 1998, Monson

and Brezonik 1999). Because Clear Lake is strongly eutrophic, its DOM is derived primarily from autochthonous sources (disintegration of cyanobacterial blooms) as opposed to allochthonous sources from the watershed as is typical of many other well-studied lake systems. Humic acids in Clear Lake make up ~80% of the total organic carbon in the water column, yet their concentrations are not particularly high, typically ranging from ~1.5 to 3.5 mg/L (Supplement).

11. *Dilution by primary production.*—It is possible that increased primary productivity can dilute the concentration of MeHg within the lake's trophic structure. In some studies, significantly elevated concentrations of Hg have been found in biota from clear, oligotrophic lakes, whereas fish from more eutrophic lakes (like Clear Lake) often contain less Hg (Kidd et al. 1999). Under bloom conditions that are typical of a eutrophic lake, as algal biomass increases, the concentration of Hg per cell decreases, resulting in lowered Hg uptake by consumers and decreased Hg bioaccumulation in the ecosystem (Pickhardt et al. 2002). While this concept has not been tested in Clear Lake, the conditions necessary for this process to operate are present, and the predicted results are consistent with the reduced lakewide production and/or bioaccumulation of MeHg relative to the large bulk Hg loading. Interestingly, largemouth bass from nearby Davis Creek Reservoir, a much deeper oligotrophic water body also contaminated with Hg (and which stratifies seasonally), have up to three times the concentration of Hg as those from Clear Lake (Slotton et al. 1995; D. G. Slotton, *personal communication*).

In summary, although Clear Lake experiences an extremely large amount of inorganic Hg loading from the Sulphur Bank Mercury Mine, net MeHg production and bioaccumulation appear to be significantly less than what might be expected based on the TotHg loading to the lake. This is likely due to several primary factors: reduced bioavailability of the chemical form of Hg derived from the mine (i.e., cinnabar and metacinnabar); the alkaline nature of the lake water; the shallow depth of the lake, which prevents stratification and thus reduces anoxic conditions that might otherwise develop in a stratified hypolimnion; and possible dilution of MeHg by a highly productive aquatic ecosystem.

### Implications for TMDL implementation for mercury-contaminated sites

In 1988 the California Regional Water Quality Control Board placed Clear Lake on the federal Clean Water Act (CWA) 303(d) List of Impaired Waterbodies based on high concentrations of Hg in fish and waterfowl and the existence of a fish consumption advisory (CVRWQCB 2001, Suchanek et al. 2008d). By definition, an Impaired Waterbody does not support all of its designated beneficial uses, and these uses vary from water body to water body. Beneficial Uses for Clear Lake are identified in Table 1. Because of the

"Impaired Waterbody" designation, under the CWA, the state of California is required to formulate a TMDL for Hg entering the lake and develop a "Numeric Target" for reducing that loading. The Numeric Target approach to load reduction focuses primarily on reductions in TotHg loading (regardless of the chemical form of the Hg source), which, through a series of assumptions and conversions in a "Linkage Analysis," is projected to equivalent MeHg concentrations in various trophic-level species. As such, this analysis assumes a direct proportional relationship between TotHg inorganic Hg loading into Clear Lake and concentrations of MeHg in biota, especially larger biota such as fish that are consumed by higher trophic level wildlife species and humans (CVRWQCB 2001). In the case of Clear Lake, the concentration of Hg in water is assumed proportional (through the application of a bioaccumulation factor) to the concentration of MeHg in fish (the primary target in which Hg is to be reduced). The question asked in the Clear Lake TMDL analysis was "How much should mercury loads be reduced in order to meet the target concentrations of mercury in fish tissue?" And the stated focus of the TMDL was "... to control loads of inorganic mercury in the active sediment layer" (CVRWQCB 2002a:48).

Because (1) there is a weak relationship between TotHg loading into Clear Lake and MeHg concentrations in Clear Lake biota, (2) that relationship varies throughout different regions within the lake, and (3) various species of fishes in Clear Lake cannot be assigned accurately to specific trophic levels, the basis for the development of the TMDL Numeric Target approach needs reevaluation. A more thorough attempt to define more accurately the trophic levels of common fish species in Clear Lake has been accomplished using $\delta^{13}C$ and $\delta^{15}N$ stable isotopes (see Eagles-Smith et al. 2008).

Our studies suggest that evaluating the factors that increase the potential for Hg methylation, including varying chemical forms of Hg that may have differential methylation potential, rather than evaluating absolute TotHg loading, would be the most effective approach. Reductions in those factors or sources that promote methylation may better help to reduce elevated concentrations in Clear Lake fish species, which would then reduce risk to wildlife and humans. Examples of Hg sources entering Clear Lake that could have dramatically different methylation potential are: (1) native soils eroded from the surrounding watershed, (2) sediments and/or water from rice fields immediately upstream from Clear Lake, (3) mine tailings and waste rock that erode from the mine site, and (4) acid mine drainage carrying Hg in dissolved form via surface and subsurface conduits. Because mine tailings and waste rock are composed primarily of cinnabar, metacinnabar, and corderoite (Kim et al. 2000), which have low methylation potential (Bloom et al. 2003), these sources would not likely contribute significantly to MeHg production

TABLE 1. Existing and potential beneficial uses of Clear Lake in California, USA (CVRWQCB 2001).

| Beneficial use | Status |
| --- | --- |
| Municipal and domestic water supply | existing |
| Agriculture | |
|   Irrigation | existing |
|   Stock watering | existing |
| Contact recreation (e.g., swimming, water skiing) | existing |
| Canoeing and rafting | existing |
| Other non-contact recreation (e.g., boating, picnicking) | existing |
| Warm-water fish habitat | existing |
| Spawning area for warm-water fish | existing |
| Wildlife habitat | existing† |
| Sport/recreational fishery | existing† |
| Cold-water fish habitat | potential |

† Beneficial uses determined by the Regional Water Quality Control Board and U.S. EPA to be impaired by Hg in Clear Lake.

and subsequent bioaccumulation. However, Hg in dissolved form may yield much higher production of MeHg and, therefore, may be a much more effective source to influence a significant reduction of Hg in fish tissues. Since MeHg, not TotHg, should be the chemical form of concern with respect to impaired use by wildlife and humans, the sources to be reduced should have a more direct linkage to the ultimate production of MeHg in biota, whatever their trophic position may be. To accomplish this, a more thorough understanding of the processes that control the production of MeHg in Clear Lake is needed before an optimum load reduction plan is enacted. Simply reducing bulk inorganic Hg loading, especially if the source material being loaded is largely refractory Hg (as is the waste rock and tailings from the mine), with little potential to methylate, may do little to reduce the ultimate target of the TMDL, Hg in fish tissues.

CONCLUSIONS AND RECOMMENDATIONS

Data presented here suggest that the production of MeHg is highly dependent upon the nature of the Hg sources and the conditions of the environment into which those sources are deposited. By comparing literature on MeHg from a wide variety of lakes, both natural and altered, we have found that sites influenced by chloralkali plants appear to exhibit the highest potential to yield significantly elevated MeHg in water and lower trophic level biota. This is consistent with observations on Hg in fishes (Wiener et al. 2003). These observations are of particular concern because the chloralkali industry is the largest consumer of Hg in the world (Hylander and Meili 2005). Sites influenced by gold and silver mines, while often having extremely high inorganic Hg concentrations, exhibit higher MeHg values than sites influenced by cinnabar Hg mines, but lower than those near chloralkali plants. Cinnabar Hg mines seem to have the lowest potential to produce

MeHg, even from large quantities of inorganic Hg. Remote and non-contaminated sites appear to have the highest relative potential to yield MeHg from relatively small amounts of inorganic Hg.

### Clear Lake management issues

Based on available data, we predict that if environmental conditions at Clear Lake were different, there could be much higher concentrations of MeHg in its biota. For example, if the lake were deeper (either naturally or as a result of dredging), then it would be more likely to stratify during the summer months and develop a significant thermocline and associated hypolimnion in which more anoxic conditions would prevail and Hg methylation would be enhanced. Stratification would be expected to break down during winter months, causing this hypolimnetic water, including the MeHg pool, to "turn over" and mix with the rest of the Clear Lake system and likely increase MeHg concentrations in biota. Over the past several decades, there have been strong recommendations by some citizen groups to dredge Clear Lake with the belief that this would create much deeper and cooler habitats to support additional fish populations and resolve other environmental issues. However, from a MeHg contamination perspective, it is quite likely that this action would increase significantly the Hg concentrations in the lake's biota, including the edible fish populations. Thus, from this perspective, dredging should not be a recommended action. In general, in a national context, shallow lakes have many potential problems, including internal nutrient cycling and eutrophication, but the presence of Hg contamination in lakes has not been discussed as a general management concern of great importance (Cooke et al. 2001). As implied by the consequences of increasing MeHg production discussed above, a better understanding of various management options, especially in the presence of a potential Hg source, is necessary to avoid placing natural resources at greater risk of contamination.

There appear to be two primary sources of Hg loading to Clear Lake: (1) bulk loading of material derived of cinnabar ore, mostly as erosional products from the terrestrial part of the mine and remobilized lake bed sediments (Suchanek et al. 2008d), and (2) $Hg^{+2}$ entering the lake along sub-sediment conduits in dissolved form with acid mine drainage from the mine site (Shipp and Zierenberg 2008, Suchanek et al. 2008d). If the pH of Clear Lake (presently ~8.0) or areas within Clear Lake were more acidic, this would likely result in enhanced production of MeHg. Therefore, acid mine drainage from the mine should be reduced as much as possible.

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## SUPPLEMENT

Limnological and chemical data for surface water and bottom water from seven stations at Clear Lake over 22 potential sampling dates from May 1994 through May 1997 (*Ecological Archives* A018-075-S1).