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Mercury Cycling and Bioaccumulation in Clear Lake

## VERTICAL STABILITY OF MERCURY IN HISTORIC AND PREHISTORIC SEDIMENTS FROM CLEAR LAKE, CALIFORNIA

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**Abstract.** Clear Lake, California, USA, is the site of the Sulphur Bank Mercury Mine, now a U.S. Environmental Protection Agency Superfund Site. Intermittent mining from 1873 to 1957 resulted in ~100 Mg of mercury (Hg) being deposited into the lake's ecosystem. Sediment cores to ~2.5 m depth (dated using <sup>210</sup>Pb and <sup>14</sup>C) represent ~3000 years of sedimentation. Clear Lake sediments have experienced Hg deposition from anthropogenic sources (mining) during historic times (to the mid-1900s) and geologic sources during prehistoric times (prior to the mid-1800s). This provides a unique opportunity to evaluate hypotheses relating to (1) the influence of the mine on Hg loading to the lake and (2) the potential upward mobilization of Hg by diagenetic processes proposed by some as an alternative explanation for increased Hg concentrations at the surface of the sediment column believed to be caused by increased global atmospheric deposition.

Although Hg mining began in 1873, no significant evidence of anthropogenic Hg loading was detected in cores prior to open-pit mining ca. 1927, which also involved bulldozing mine waste rock and tailings into the lake. Exponential increases in total Hg (TotHg) and methylmercury (MeHg) were observed above the 1927 horizon, where estimated sedimentation rates were 2.2–20.4 mm/yr and peaks of both forms of Hg maintained vertical stability within the sediment column. Below the 1927 horizon, a slow increase in both TotHg and MeHg with depth was observed from ~1000 to 3000 years before present, where sedimentation rates ranged from ~0.6 to 2.0 mm/yr and elevated Hg profiles appear stable. Vertical stability of Hg in the shallow and deep sediment column suggests that both TotHg and MeHg do not undergo diagenetic upward mobilization within the sediment column under rapid or slow sedimentation rates. Because (1) these data were collected at a site with known anthropogenic and geologic sources and (2) regions of elevated Hg concentrations from both sources remain stable within the sediment column under very different sedimentation regimes, these results also support the hypothesis that elevated Hg at the surface of cores in other worldwide locations likely represents global atmospheric deposition rather than upward diagenetic mobilization.

**Key words:** Clear Lake, California, USA; core; diagenetic mobilization; <sup>14</sup>C; mercury; methylmercury; sediment; Sulphur Bank Mercury Mine; <sup>210</sup>Pb.

### INTRODUCTION

Data presented here from several sediment cores collected in 1996 and 2000 at Clear Lake represent one component of a larger ecosystem-level study that traces the origin and pathways of mercury (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) and ultimately to higher trophic level species (e.g., fish, birds, and mammals). This paper provides both historic (back to the mid-1800s) and prehistoric (to ~3000 years before present) data that address the relative stability of total Hg (TotHg) and methylmercury (MeHg) within the sediment column. These data contribute to a better understanding of Hg deposition in Clear Lake proper and help to elucidate for Clear Lake (and other lakes worldwide) whether Hg exhibits diagenetic upward mobilization within sediments during periods of rapid sedimentation (during historic times as a result of mining) or minimal sedimentation (during prehistoric times during periods of Hg deposition from geologic processes).

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Global deposition of Hg has been linked to anthropogenic emissions to the atmosphere (Engstrom et al. 1994, Rasmussen 1994, Fitzgerald et al. 1998). Recent

estimates suggest that ~70% of atmospheric Hg inputs are of direct or indirect anthropogenic origin and that the annual rate of increase in atmospheric Hg, up to the mid-1980s, was ~0.6–1.0%/yr (Lindqvist 1994, Fitzgerald 1995), with an apparent decline through the 1990s (Kamman and Engstrom 2002, Schuster et al. 2002). The primary sources of this anthropogenically derived Hg are believed to include fossil fuel combustion, chlor-alkali plants, waste incineration, and metal production (Lindqvist 1994, U.S. EPA 1997, Pirrone et al. 1998).

Increased Hg concentrations in the upper sections of sediment cores is prevalent, even in remote regions (Gearing et al. 1991, Benoit et al. 1994, Fitzgerald et al. 1998, Schuster et al. 2002). The most common explanation for this trend is an increase in atmospheric deposition of Hg primarily as a result of increased modern industrial activities (Kemp et al. 1978, Swain et al. 1992, Fitzgerald 1995, Fitzgerald et al. 1998). However, others (Gobeil and Cossa 1993, Rasmussen 1994, Benoit et al. 1998, Gobeil et al. 1999) suggest the possibility of a competing hypothesis to account for elevated Hg in near-surface core sections, i.e., diagenetic upward mobilization of Hg within the sediment column. In this scenario, Hg is hypothesized to migrate as a variety of inorganic and organic species upward to the sediment surface as organo-Hg (II) or Hg (II)-organo-sulfide complexes.

Most previous studies on Hg concentrations in cores have focused on atmospheric sources in systems in which Hg concentrations are <1.0 mg/kg (e.g., Engstrom et al. 1994). In contrast, Clear Lake sediments exhibit Hg concentrations of up to 438 mg/kg in surficial sediments and ~1200 mg/kg in near-surface sediments in the vicinity of an abandoned Hg mine (Suchanek et al. 2008*b, e*). A series of sediment cores to ~250 cm depth, representing an estimated 2500–3000 yr historical record (Richerson et al. 2008), exhibit sharp increases at depth during historic time periods to ~110 mg/kg TotHg and ~3 µg/kg MeHg associated with documented periods of Hg mining. In addition, deeper sections of these cores exhibit elevated concentrations of ~20 mg/kg TotHg and 0.75 µg/kg MeHg from ~1000–3000 years before present likely from geologic sources during prehistoric times when sedimentation rates were extremely low (0.6–1.0 mm/yr). Because of the strong mining Hg signal, a significant geologic Hg signal, and reasonably accurate estimated dates for both, sediment cores from this site represent a unique opportunity to evaluate hypotheses relating to the relative stability of Hg (both TotHg and MeHg) in the depositional history of lake sediments, especially addressing the hypothesis that Hg in buried sediments undergoes diagenetic upward movement that would produce elevated Hg concentrations in the upper sections of lake cores. Lockhart et al. (2000) performed a similar analysis at a variety of sites in Canada, but reported only TotHg and not as strong a Hg deposition signal as is present in Clear Lake. Balogh et al. (1999) and Frazier et al. (2000) also present data on Hg peaks

TABLE 1. History of mining sulfur and mercury at Sulphur Bank Mine, Clear Lake, California, USA.

Time period	Mining type	Extracted amount (Mg)
Sulfur mining		
1865–1868	surface pit	$1.0 \times 10^3$
Mercury mining		
1874–1883	surface cuts and one shaft	$3.2 \times 10^3$
1887–1897	surface cuts and two shafts	$4.0 \times 10^2$
1899–1906	two shafts	$2.0 \times 10^1$
1915–1918	reprocessing and surface cuts	$8.0 \times 10^1$
1927–1944	surface pit and two more shafts	$1.2 \times 10^3$
1955–1957	surface pit	$1.2 \times 10^2$
Total Hg		$5.02 \times 10^3$

at depth from anthropogenic sources but do not address the issue of diagenetic mobilization.

Clear Lake is a shallow, polymictic, slightly alkaline, eutrophic lake in the northern California Coast Range, USA. A physical description of Clear Lake as well as recent and historical concentrations of Hg in sediments, water, and biota are provided in papers published elsewhere and in this Special Issue (Suchanek et al. 2003, 2008*a–e*, *in press*). Mining of cinnabar (HgS) from the Sulphur Bank Mercury Mine (a U.S. Environmental Protection Agency [U.S. EPA] Superfund Site since 1990) along the shoreline of the lake, from 1873 to 1957 (Table 1), plus subsequent erosion and acid mine drainage have resulted in the deposition of an estimated 100 Mg of Hg into the Clear Lake aquatic ecosystem. Most of this Hg was deposited in the proximity of the abandoned mine (Chamberlin et al. 1990) but moved throughout the lake by sediment transport processes (Pálmarrsson and Schladow 2008, Rueda et al. 2008). Commercial Hg extraction was accomplished initially by surface scrapes and shaft mining from ca. 1873 to the 1920s. In 1927, shaft mining was replaced by open-pit mining using heavy earthmoving equipment, resulting in a much greater loading of Hg into Clear Lake (Richerson et al. 2008, Suchanek et al. 2008*e*).

Our goal in presenting Hg data here from a series of Clear Lake cores is to evaluate the relative stability of both TotHg and MeHg within lake bed sediments, using the unique attributes of a system highly contaminated with TotHg with a known mining chronology, dated cores, and a steep exponential gradient of sediment Hg concentrations as a function of distance from the mine. The other advantage of Clear Lake sediments in helping to resolve this issue is the fact that, unlike most other systems, Clear Lake has experienced significant Hg inputs from both geologically mediated and anthropogenically derived sources, yet on vastly differing time scales, under vastly different sedimentation regimes, that can be quantified and dated, thus providing an opportunity to discriminate between those types of sources as well as provide data that can evaluate the potential mobility of both prehistoric and historic Hg inputs to the system.

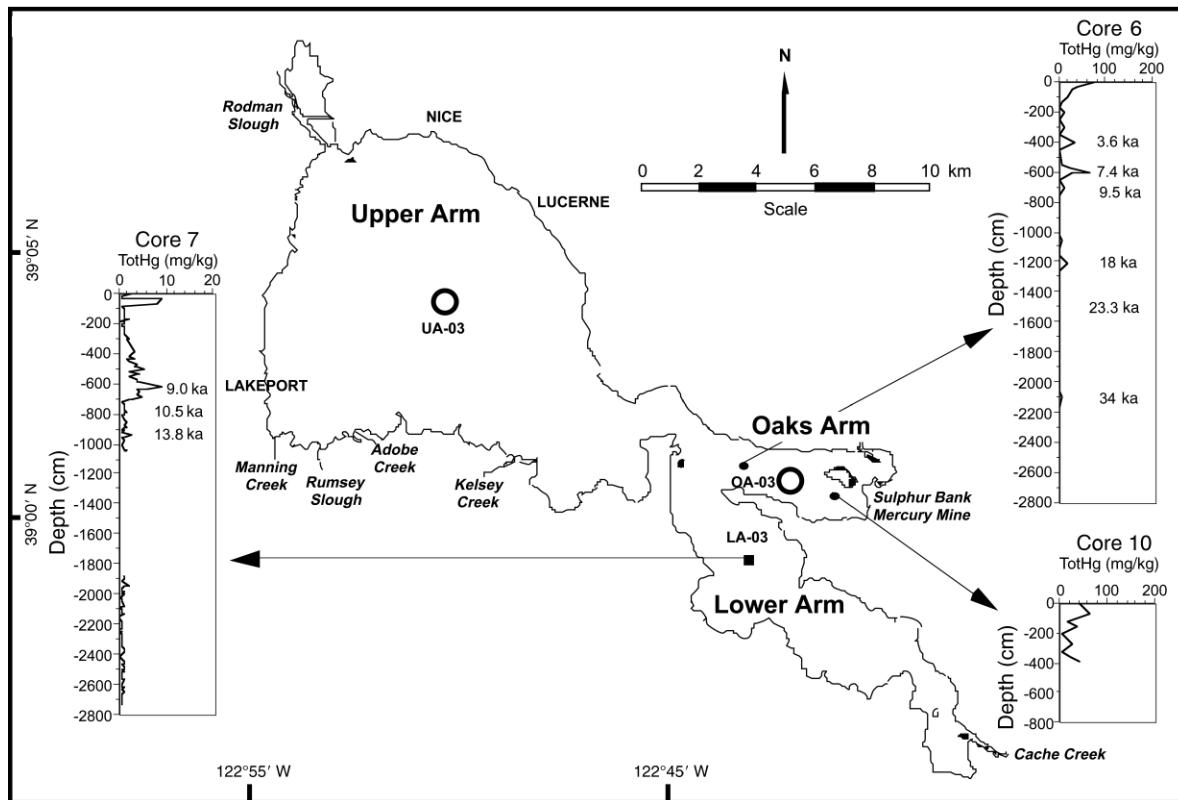


FIG. 1. Total mercury (TotHg, mg/kg = ppm dry mass) in deep prehistoric cores from Clear Lake, California, USA (ka [kiloannum] units indicate thousands of years before present). Note the scale of 0–20 mg/kg TotHg on core 7; the scale on other plots is 0–200 mg/kg. Solid dots mark locations of cores from Sims and White (1981); the solid square marks the location of a core from Varekamp and Waibel (1987). Open circles mark locations of cores collected in 1996 and 2000: Upper Arm (UA-03), Oaks Arm (OA-03 and OA-03A), and Lower Arm (LA-03) (see Richerson et al. 2008).

Using the unique geological (ore body) and anthropogenic (mining) histories of Hg sources found at Clear Lake, we present two sets of hypotheses; one set (A) relates to the specific Clear Lake sediment record, the other (B) is applicable to a wide variety of lake systems worldwide in which Hg has been deposited over varying time scales.

*(A) Hypotheses specific to Clear Lake*

*Hypothesis A1.*—Mining at Clear Lake has contributed negligible Hg loading to Clear Lake sediments.

*Hypothesis A2.*—Methylmercury in Clear Lake sediments deposited during or after the onset of Hg mining (1873) has remained stable at depth within the sediment column.

*(B) Hypotheses applicable to other sites worldwide*

*Hypothesis B1.*—Total mercury has remained stable throughout the sediment column during periods of rapid sedimentation (historic times) as well as during periods of low sedimentation rates (prehistoric times).

*Hypothesis B2.*—Methylmercury has remained stable throughout the sediment column during periods of rapid

sedimentation (historic times) as well as during periods of low sedimentation rates (prehistoric times).

#### METHODS

Sediment cores were collected in Clear Lake in 2000 from a 6.7-m research vessel, using a push-rod operated piston corer at three locations in Clear Lake: centrally located in the Oaks Arm, the Upper Arm, and the Lower Arm (Fig. 1). Coring procedures are described in more detail in Richerson et al. (2000, 2008).

For all cores, TotHg was analyzed at the University of California at Davis Environmental Mercury Laboratory on dry, powdered samples using a modified cold-vapor atomic absorption technique (Slotton et al. 1995). Samples were solubilized through digestion in concentrated nitric and sulfuric acids, including a reflux stage with potassium permanganate, under pressure at 90°C. Dissolved Hg in the digests was subsequently volatilized using stannous chloride reductant for detection at 253.7-nm wavelength.

Methylmercury in 1996 cores was analyzed by Battelle Marine Sciences (Sequim, Washington, USA) using a “distillation” method (Bloom 1989, Horvat et al. 1993) that was ultimately determined to create spurious

elevated MeHg concentrations as a result of the analytical procedure (Liang et al. 1996, Bloom et al. 1997). Using the distillation procedure, samples were distilled by reacting an aliquot of sediment in water with sulfuric acid and potassium chloride, then heating the distiller to 125°C (Horvat et al. 1993) and collecting the distillate in a Teflon receiving vial. The distillation method was later replaced by an “extraction” technique to eliminate the artifact. Using this alternate approach, samples were extracted by reacting an aliquot of sediment with acidic potassium bromide solution and copper sulfate and extracting them into methylene chloride. The sample was allowed to react for 1 h and then shaken vigorously for 1 h to move all of the MeHg into a methylene chloride phase. Methylene chloride was then back-extracted into deionized water for analysis. Both preparation techniques put the MeHg into a clean deionized water matrix that is quantified by the same analytical technique, EPA Method 1630:draft. An ethylating agent is added to the distillate/extract to form a volatile methyl-ethylmercury derivative and then purged onto graphitized carbon traps as a means of preconcentration and interference removal. The sample is then isothermally chromatographed, pyrolytically broken down to elemental Hg, and quantified using a cold-vapor atomic fluorescence detector. The quantification method is based upon the emission of 254-nm radiation by excited Hg atoms in an inert gas stream at an intensity that is directly proportional to the amount of Hg in the gas stream. Typical detection limits for the method are 0.005 µg/kg by distillation and 0.02 µg/kg by extraction.

Methylmercury in sediments from year 2000 cores were analyzed using both the distillation and extraction methods. We used a multiple regression model to correct for artifacts in MeHg concentrations from the 1996 cores that were analyzed using only the distillation technique. The correction factor was generated using the 2000 cores for which MeHg was analyzed by both the distillation and extraction methods. We used TotHg and MeHg (distillation) as independent variables for the multiple regression algorithm in JMP version 5.1 (SAS Institute, Cary, North Carolina, USA). The resulting equation,  $\text{MeHg}_{\text{ext}} = 0.0913 + (0.0102 \times \text{TotHg}) + (0.29005 \times \text{MeHg}_{\text{dist}})$ , which explained 92% of the variability in the data ( $P < 0.0001$ ,  $N = 170$ ), was applied to the 1996 MeHg<sub>dist</sub> data to generate the corrected MeHg<sub>ext</sub> values reported here. Plotted core profiles of TotHg, MeHg, and percentage of MeHg are registered on the same vertical scales against one another relative to a time horizon of ca. 1927 (dated using <sup>210</sup>Pb; Richerson et al. 2008), which represents the period when open-pit mining was initiated. However, because of different historical sedimentation rates between different regions of Clear Lake, the vertical alignment of the cores is not perfect. However, we also provide estimated <sup>14</sup>C ages (years before present, relative to the year 2000) for the portions of the cores below the

1927 horizon calculated from organic woody debris extracted from several depths within the cores (methods and original data provided in Osleger et al. 2008).

## RESULTS AND DISCUSSION

Two series of relatively shallow historic cores (to ~1 m depth) were collected from Clear Lake: (1) in 1986 by the California Central Valley Regional Water Quality Control Board (CVRWQCB 1987) and (2) in 1988 by Chamberlin et al. (1990). Those cores were analyzed for TotHg only, and the data are plotted in Fig. 2. In both studies, the highest levels of TotHg were found in cores closest to the mine, with marked peaks sometimes occurring at 30–50 cm depth. Sims and White (1981) and Varekamp and Waibel (1987) also provide TotHg data from three deeper cores (20–28 m sediment depth; age ~40 ka [thousands of years before present]) collected by the U.S. Geological Survey from Clear Lake in 1973, which are plotted in Fig. 1. These deeper cores show trends similar to those observed in the shallow cores, with higher TotHg nearest to the Sulphur Bank cinnabar deposit, even before the mining era. Sims and White (1981) concluded that elevated Hg concentrations in the upper 50 cm of these cores reflect anthropogenic activities associated with mining operations and that deeper anomalies are natural, resulting from volcanic and/or tectonic events. The Clear Lake Volcanic Area underlays the two southeastern arms of the lake, while the larger Upper Arm is mostly underlain by the Franciscan Formation (Sims et al. 1988). Thus, for both near-surface and deep sediments, in both prehistoric and modern times, the Hg deposit at Sulphur Bank has represented a strong point source of Hg loading to Clear Lake. However, Hg concentrations in the geologic past, as far back as ~34,000 years before present, never approached the maximum concentrations (nearly 1200 mg/kg dry mass [DM]; CVRWQCB 1987) observed during the mining era (top 1 m of the sediment column; Fig. 1, core 6). None of the earlier cores were analyzed for MeHg.

Most of the shorter cores collected in the 1980s from the Oaks Arm (Fig. 2) also exhibit peaks of TotHg at depth and at the same peak concentrations as those collected in 2000 that are presented here and in Richerson et al. (2008), with the exception of those cores collected closest to the mine in which concentrations reached nearly 1200 mg/kg. Some of those cores (e.g., core OA-01 from June 1986 and possibly core OA-02 from June 1986 and core 3 from July 1986) appear not to have penetrated deep enough to reach the exponential increase at the 1927 horizon. In addition, the two cores from the Upper Arm in 1986 (UA-01 and UA-02) have TotHg profiles consistent with most of the cores collected in 1996 and 2000, i.e., increasing with depth toward a peak associated with the advent of open-pit mining. In general, the cores from the 1980s (Fig. 2) and from our study (Fig. 3) do not exhibit a gradual increase toward the surface (which could suggest

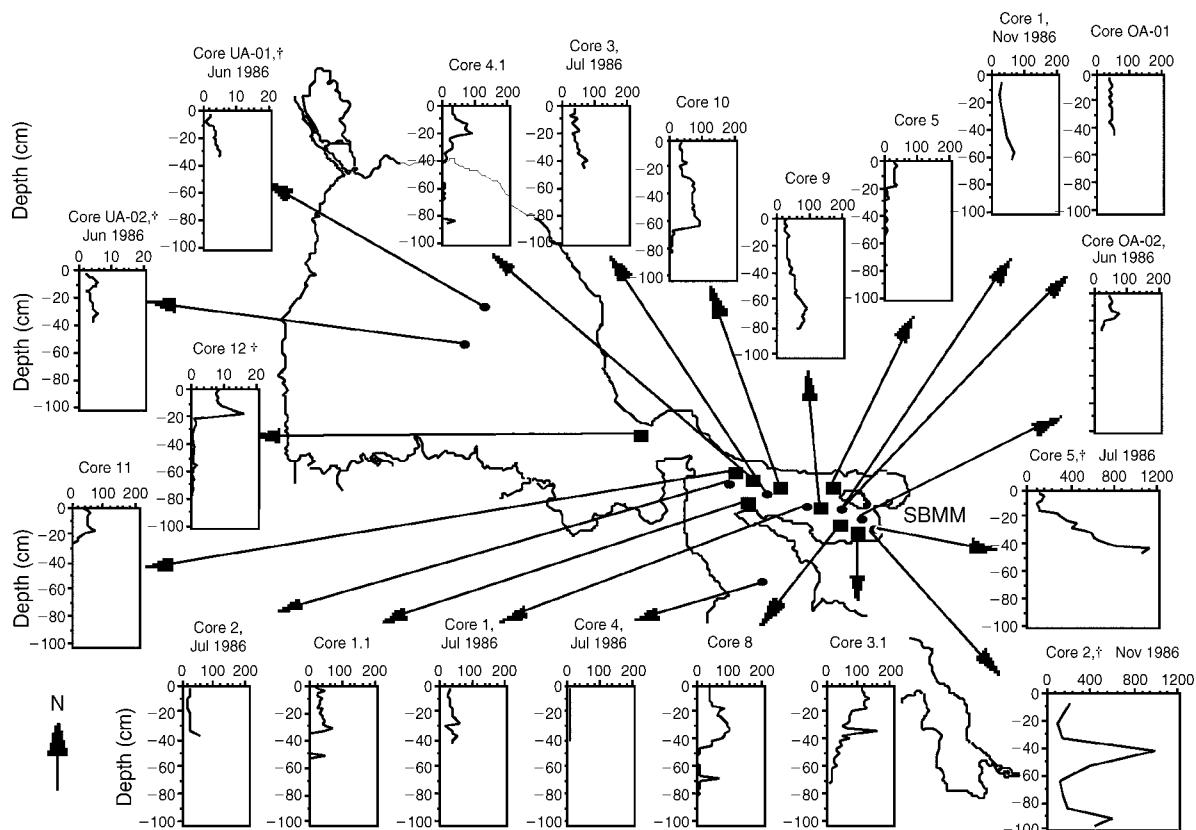


FIG. 2. Total mercury (TotHg, mg/kg = ppm dry mass) in shallow historic sediment cores from Clear Lake. Solid dots mark locations of cores from 1986 (CVRWQCB 1987); solid squares mark locations of cores from 1988 (Chamberlin et al. 1990). Cores with daggers denote differences in scales: the scale of three cores in Upper Arm is 0–20 mg/kg, the scale of two lower right cores is 0–1200 mg/kg, and all other plots have a scale of 0–200 mg/kg. The abbreviation “SBMM” marks the location of the Sulphur Bank Mercury Mine.

diagenetic upward movement of Hg). Instead, these peaks are fixed at depth, and although no dating was performed on the cores from the 1980s, their profiles are consistent with those collected in 2000.

Cores to 28-m depth collected in the 1970s (Fig. 1) also indicate that for both shallow and deep depths within the Clear Lake sediment column, peaks of TotHg existed long before any anthropogenic influence of mining and have remained fixed for 9000–34000 yr. Although Clear Lake is located in an active volcanic region, volcanic ash is usually devoid of adsorbed Hg (Varekamp and Buseck 1981), so this is an unlikely source of these deep Hg peaks. However, these peaks are believed to represent Hg from subaqueous hot springs and gas vents, located largely along faults (Sims and Rymer 1975, Varekamp and Waibel 1987). Over time, the fluid pathways may have become sealed as a result of hydrothermal mineral precipitation, resulting in decreased fluid discharge into the lake and therefore lowered Hg deposition in the sediments in more modern times (Varekamp and Waibel 1987). Additional evidence that this profile is unique to the Hg source in the Clear Lake area derive from other cores collected in Lake

Tahoe (also in northern California), showing no elevated background Hg to ~1450 years before present (Heyvaert et al. 2000).

Total mercury profiles in six representative cores collected from Clear Lake, three each from 1996 and 2000 (from Richerson et al. 2008), are shown in Fig. 3. The top portions of some cores (i.e., cores UA-03 and OA-03 from 1996 and LA-03 from 2000) were not fully retrieved; thus, the tops of those profiles do not represent the sediment–water interface. The vertical alignment of the cores relative to one another was adjusted to an approximate date of 1927 using  $^{210}\text{Pb}$  dating (see Richerson et al. 2008). The profiles and locations of TotHg peaks are virtually identical in all cores with an exponential increase in TotHg at the estimated 1927 horizon (H-1927), reaching a peak of ~110 mg/kg TotHg at the height of the mining era. The H-1927 horizon represents the start of extensive open-pit Hg mining operations when  $1 \times 10^6 \text{ m}^3$  of tailings, waste rock, and ore were physically bulldozed from the mine site into the lake (Chamberlin et al. 1990) during the second most productive mining period (see Table 1 and Suchanek et al. 2008e). Subsequent minor peaks toward

the surface from H-1927 likely correspond to additional periods of Hg mining until 1957 when mining ceased. Subsequently, continued erosion of the steeply sloped waste rock piles along the shoreline of Clear Lake yielded substantial inputs of Hg-laden sediments until 1992, when the waste rock piles were remediated (see Suchanek et al. 2008e). The upper section of the 2000 Lower Arm core (LA-03) was not recovered during collection, so no comparisons could be made during the period of most active mining. However, the single sample collected immediately above H-1927 in that LA-03 core exhibited a comparable exponential increase in Hg as do the other five cores.

While the TotHg profiles in cores from the Upper Arm (~14 km from the mine) and Lower Arm (~6 km from the mine, via a water route) are comparable to the two Oaks Arm cores, they are about 20 times lower in concentration (note the different abscissa scales). There is also a gradual increase in TotHg with increasing depth beginning at ~1000 years before present (especially in the Oaks Arm and Lower Arm cores), which suggests a gradual increase in a natural geological source that has contributed to Clear Lake's Hg loading in prehistoric times (also see deep profiles for the Oaks Arm and Lower Arm in Fig. 1). Two observations seem clear. The upper (more shallow) profiles do not exhibit a gradual increase in TotHg toward the surface, but rather show peaks that appear stable relative to the dates they were deposited, which correspond to specific horizons of Hg mining. The deeper TotHg profiles from the Oaks Arm and Lower Arm exhibit a gradual increasing trend with depth that most likely reflects input of Hg from geological processes from the Hg ore body.

Methylmercury profiles for the same cores are also provided in Fig. 3. In the upper regions of these cores, exponential increases and peaks of MeHg also correspond to the onset of open-pit mining ca. 1927, reaching a maximum in the two Oaks Arm cores (OA-03 in 1996 and OA-03A in 2000) of ~2.5–3.5  $\mu\text{g}/\text{kg}$  at the peak of the mining era, with similar (but not identical) profiles to that of TotHg. Methylmercury from Upper Arm and Lower Arm cores is only 5–10 times lower in magnitude rather than the factor of 20 differential exhibited by the same cores for TotHg. In the deeper core regions of most cores, especially evident in the 2000 cores and the Oaks Arm cores, a gradual increase in MeHg with depth from a background concentration of ~0.1–0.2  $\mu\text{g}/\text{kg}$  is evident, reflecting a pattern similar to that observed in the TotHg profiles with the initiation of that increase occurring at ~650–1000 years before present, although it is unclear when this increase begins in the Lower Arm core (LA-03 in 2000). It is also possible that the existing peaks of MeHg may be the result of methylation/demethylation processes and only represent remnants of a much greater concentration of MeHg that has been mostly demethylated upon burial in the sediment column.

Although subsurface MeHg peaks are pronounced, these core profiles also show a pronounced increase of

MeHg near the sediment surface (e.g., LA-03 in 1996 and UA-03 and OA-03A in 2000). Two possible scenarios may explain this trend: (1) MeHg is produced at or near the sediment–water interface at all locations in Clear Lake, nonlinearly related to the concentration of TotHg and/or (2) the most significant production of MeHg occurs nearest the mine, with subsequent transport to other regions of Clear Lake via wind-driven currents. The greatest activity of sulfate-reducing bacteria, believed to be significant methylators of inorganic Hg in all freshwater and estuarine sediments examined to date (Compeau and Bartha 1985, Kerry et al. 1991, Gilmour et al. 1992), is confined to the upper few centimeters of Clear Lake sediments (Mack 1998). Interestingly, Hg methylation in Clear Lake surficial sediments is dominated by both sulfate-reducing bacteria (Mack 1998) and a recently reported iron-reducing bacteria (Fleming et al. 2006). Each group contributes ~40–50% of the active Hg methylation potential in Clear Lake sediments. Once generated at or near the sediment–water interface, MeHg is then likely redistributed by bioturbation to a maximum depth of ~10–15 cm (Kikuchi and Kurihara 1977, Krezoski et al. 1978, Robbins 1982, Karickhoff and Morris 1985, Mack et al. 1997, Suchanek et al. 2008c). In Clear Lake, the invertebrates likely responsible for this bioturbation are predominantly chironomid insect larvae and oligochaetes (see Suchanek et al. 2000a, 2008c). Carp also contribute to bioturbation by rooting through lake bed sediments, although their effect has not been quantified. Preliminary results from laboratory tank experiments indicate that bioturbation in Clear Lake sediments is limited to ~10–15 cm, with evidence of surface-generated MeHg being mixed to that depth as exhibited in Fig. 3 (also see Richerson et al. 2008, Suchanek et al. 2008c).

Methylmercury concentrations in Clear Lake sediment cores (at ~0.1–3.5  $\mu\text{g}/\text{kg}$ ) are at the low range compared with contaminated and noncontaminated sites worldwide. Cores from a small seepage lake in northern Minnesota, USA, yielded MeHg concentrations near zero in the deepest regions of five 55–60 cm deep cores, but typically increasing to ~3–5  $\mu\text{g}/\text{kg}$  at the surface (Hines et al. 2004). Cores to ~55–75 cm depth from a Superfund site in Massachusetts yielded maximum MeHg concentrations from 1.3 to 30  $\mu\text{g}/\text{kg}$  (Norton et al. 2004). Several cores of relatively comparable depths from shallow contaminated freshwater depressions in the United Kingdom yielded maximum MeHg concentrations of 5.9–33.4  $\mu\text{g}/\text{kg}$  throughout their depth range (Croston et al. 1996).

The percentage of TotHg that is MeHg (Fig. 3) is variable among the cores, ranging from ~0.001 to 0.01% in the most contaminated sites near the mine (Oaks Arm, OA-03) and up to about an order of magnitude higher (~0.005–0.1%) at Upper Arm and Lower Arm sites further from the point source of Hg loading (the mine). The vertical profiles of percentage of MeHg,

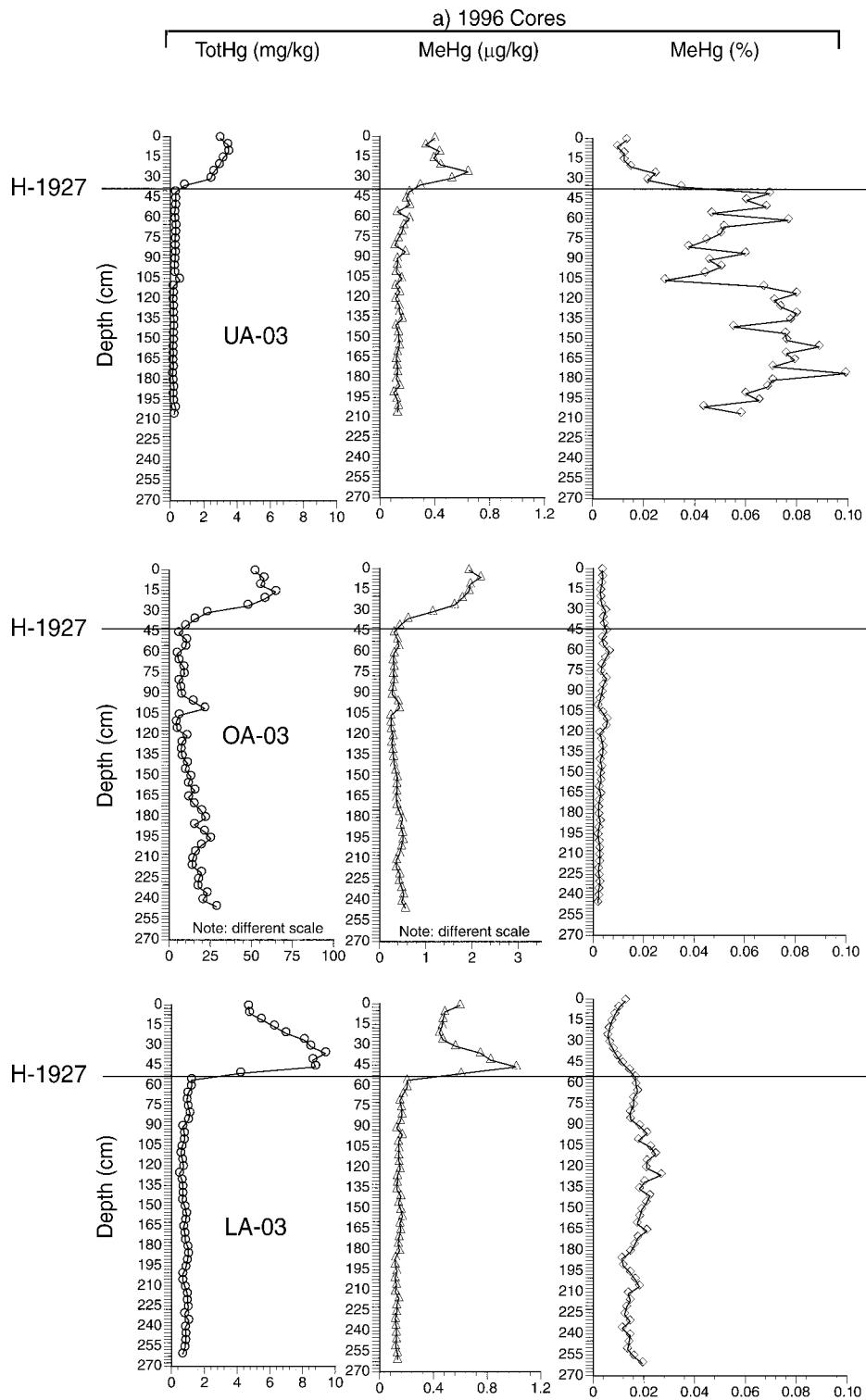


FIG. 3. Total mercury (TotHg; mg/kg dry mass), methylmercury (MeHg,  $\mu\text{g}/\text{kg}$  dry mass), and percentage of MeHg in six cores from Clear Lake, three each in (a) 1996 and (b) 2000 from the Upper Arm (UA), Oaks Arm (OA), and Lower Arm (LA). Note different scales on abscissa for TotHg and MeHg in OA cores. Cores are aligned relative to one another based on an estimated date of 1927 (H-1927 from Richerson et al. [2008]). Horizons H-1954 and H-1927 represent date horizons estimated from dichlorodiphenyldichloroethane (DDD) concentrations and  $^{210}\text{Pb}$ , respectively. Arrows designating sediment ages (years before present, relative to the year 2000) were estimated from  $^{14}\text{C}$  dating and apply to year 2000 cores only (Richerson et al. 2008).

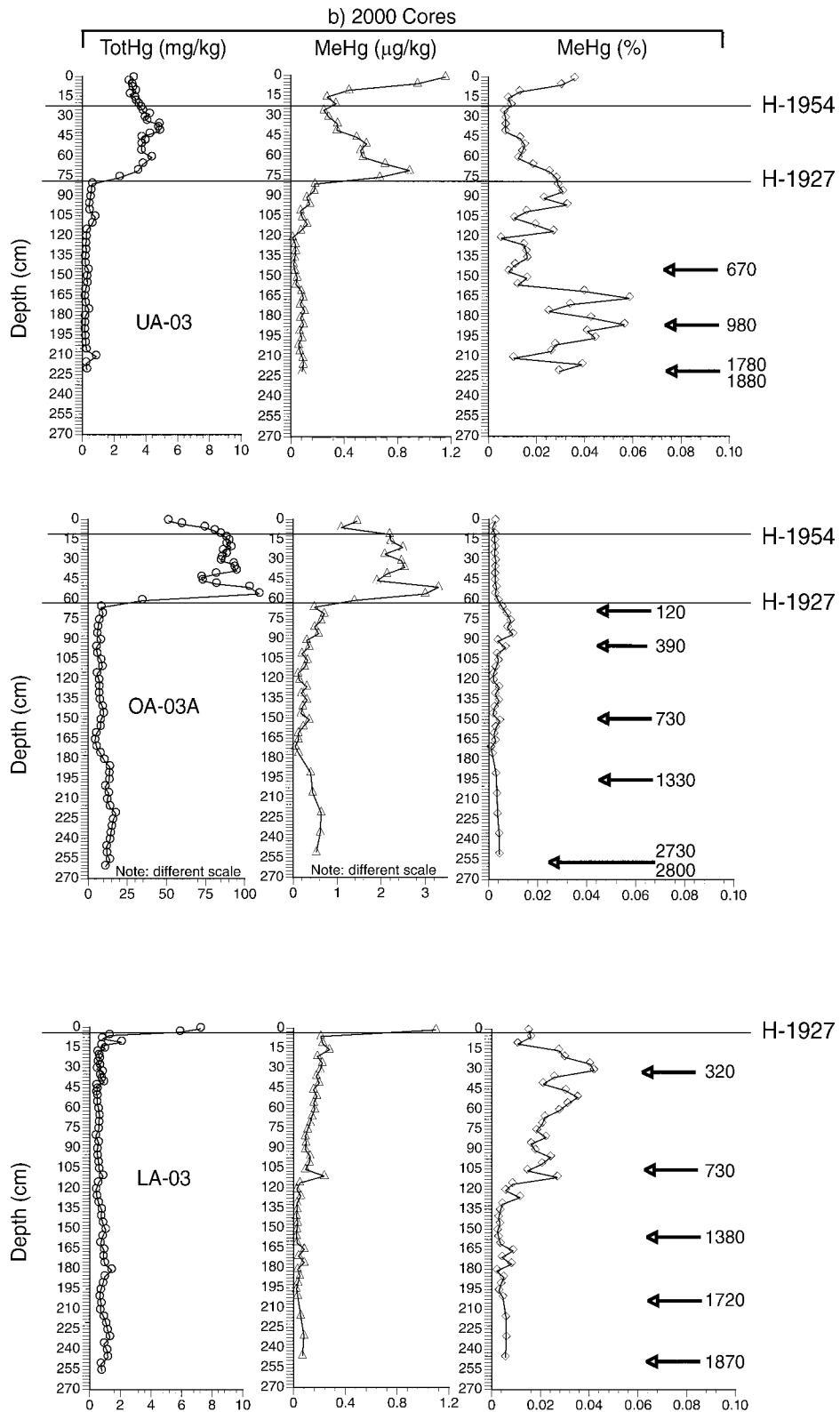


FIG. 3. Continued.

while somewhat variable, remain within a fairly defined range above and below the 1927 horizon of open-pit mining, with some temporal trends. In most cases, there is a slight increase in the percentage of MeHg upward toward the 1927 horizon, with a noticeable decline above that period and a return to increased percentage of MeHg observed in those sediments nearest the sediment–water interface.

The elevated percentage of MeHg at depth in the Upper Arm core may reflect relatively greater bioavailability of Hg during the time of deposition when these sediments were at the surface. This relative increase in percentage of MeHg for sites distant from the mine has already been shown for surficial sediments in Clear Lake (Suchanek et al. 2008a, b), and these data support this trend for deeper sediments as well. This increased proportion of MeHg as a function of distance from the mine likely reflects increased bioavailability for methylation (saturation) of the existing inorganic cinnabar-based Hg near the mine (Suchanek et al. 2008a, b) although differential down-core transport of MeHg is consistent with this pattern as well. However, MeHg is less particle reactive (i.e., it has a smaller  $K_d$  [partition coefficient]) in pore waters than inorganic Hg, but the profiles for TotHg and MeHg in the deeper portions of Oaks Arm cores are very similar. If there were significantly greater diagenetic upward mobilization of MeHg (due to greater particle reactivity) as compared with TotHg, one would expect to see somewhat different profiles for TotHg vs. MeHg.

The slight increase in MeHg with depth (more than or equal to ~1000 years before present) suggests that the Hg that entered the lake naturally from geologic processes was also readily methylated in situ and preserved. The deep-core increase and maxima in MeHg (beginning below the 1927 horizon) are not likely a reflection of recent activities of deep sulfate-reducing or iron-reducing bacteria for two reasons. First, overall microbial activity is known to decline with increasing sediment depth due to the refractory nature of residual organic carbon. Second, methanogens, which are a group of anaerobes that dominate sediment processes below the depth at which sulfate and  $\text{Fe}^{3+}$  are depleted, have been shown in several studies not to contribute to methylation (Compeau and Bartha 1985, Kerry et al. 1991, Gilmour et al. 1998, Pak and Bartha 1998). In the few studies in which aggregate rates of microbial methylation vs. sediment depth have been measured, rates decreased monotonically (and in some cases exponentially) with increasing depth (Korthals and Winfrey 1987, Gilmour et al. 1998, Hammerschmidt and Fitzgerald 2004), and this also supports the view that subsurface peaks are due to sequestration.

#### *Deposition and possible diagenetic movement of mercury in Clear Lake sediments*

The preponderance of core data from this project and historical sources support the hypothesis that variations

in TotHg and MeHg in the recent sediment column can be traced to modern open-pit mining activity (with subsequent dumping or erosion) from the mine beginning about 1927. These conclusions are in contrast to the hypothesis that TotHg or MeHg undergoes diagenetic upward mobilization in the sediment column, which would result in an accumulation of Hg at the sediment surface. If diagenetic upward mobilization of Hg were a more significant process here, we would expect to observe more of the deeper deposited Hg to have migrated upward and occur nearer to the surface of the cores, at least over the timescale of several millennia in the deeper regions of the cores where sedimentation is extremely slow and diffusion would be more likely.

It is also useful to note that flooding events during winter and spring of 1995 caused overflow of water from the Herman Pit (a contained water body on the mine site) and the discharge of acid water into Clear Lake (Suchanek et al. 2000b, c). A resulting white flocculent material, identified as  $\text{AlSi}_2$ , exhibited relatively low TotHg concentrations but much higher MeHg concentrations later in the summer than any other sites sampled at Clear Lake. If this precipitate is produced during heavy flooding years and/or rainy seasons each year and deposited onto the sediments of Clear Lake, this may also represent a significant historic and ongoing source term contributing to the MeHg pool within the sediment column as well as the biotic components of the ecosystem. The 1995 spike in Hg loading from the mine was also reflected as an increase in tissue Hg of young-of-the-year largemouth bass (*Micropterus salmoides*) later that year (Suchanek et al. 2008d).

Proponents of the diagenetic movement hypothesis might argue that the mass of Hg present in Clear Lake is simply so large that it masks the evidence of upward migration of Hg in the sediments. But the advantage of the Clear Lake system in testing this hypothesis is that there is an enormous gradient of Hg concentrations in surficial sediments and cores. Sites distant from the mine (e.g., in the Upper Arm) are not nearly so heavily contaminated as sites near the mine. At a minimum, even in the least contaminated sites in Clear Lake, upward diagenetic movement of Hg does not appear to be a dominant process. Of course, we cannot rule out some difference between Clear Lake and other Hg-contaminated lakes that explains the lack of diagenetic movement in our system. The relatively low rate of Hg methylation in Clear Lake (Suchanek et al. 2008a) suggests that Hg-related chemistry is unusual in this system and is likely related to the chemical form of Hg. That is, when Hg is bound as cinnabar or metacinnabar (HgS), methylation potential is significantly reduced.

#### *Source of Clear Lake's mercury contamination*

Because there exist significant peaks of TotHg in deeper sediments of Clear Lake (see results from 28 m deep cores in Fig. 1), speculation has arisen (Varekamp and Waibel 1987) that virtually all of the Hg in Clear

Lake sediments is naturally derived and that the influence of mining operations on Hg deposition to Clear Lake has been negligible. Other than the mining era peak of TotHg, ~10 mg/kg in the Oaks Arm 2000 core and the nearly 1200 mg/kg peak in the 1986 cores, both of which must represent anthropogenic inputs, the next highest peak (~65 mg/kg) was found at a depth corresponding to ~7400 years before present, with another peak (~30 mg/kg) at ~3600 years before present and other minor peaks (<20 mg/kg) at ~1500, 2500, 9500, 18 000, 23 300, 25 000, and 34 000 years before present. The most recent volcanic activity at Clear Lake was ~10 000 years before present (Sims and Rymer 1975, Donnelly-Nolan et al. 1981), which could correspond to the 9500 years before present peak of Hg deposition. The other peaks, however, are likely the result of tectonic activities and associated hydrothermal activity. Sims and White (1981) note that the first notable increase of Hg in their cores was ~34 000 years before present, which they interpret as input from an andesite flow being cut by a fault, thereby providing permeable channels for the discharge of Hg-bearing ore fluids to this section of Clear Lake. Varekamp and Waibel (1987) similarly speculate on the movement of Hg-laden geothermal fluids along activated fractures and faults, providing elevated levels of TotHg in deeper core sections. However, we have analyzed water emanating from springs in many locations around Clear Lake (see Suchanek et al. 1998, 2008b) and have not found elevated levels of Hg in the vicinity of present-day springs, indicating that the primary overwhelming source for Hg in surficial sediments of Clear Lake still remains the Sulphur Bank Mercury Mine (Suchanek et al., *in press*). Therefore, we concur with the hypothesis of Sims and White (1981) that variations in the Hg content of the deeper sections of their core 6 reflect variations in the amount of Hg escaping into Clear Lake while the Sulphur Bank Hg deposit was being formed, but Hg in the near-surface sections of the core is most likely due to mining activities and erosion of waste rock piles that accumulated on and near the lake shoreline. Indeed, as evidenced from historical reconstructions of shorelines (Chamberlin et al. 1990) and photographs of the mining operations, it is clear that substantial waste rock piles associated with the mining operation were actively bulldozed out from the mine site into the nearshore regions of the Oaks Arm, extending the shoreline in some places by an additional 100 m.

Sims and White (1981) further speculate that although the Hg mineral deposited in the Sulphur Bank deposit was cinnabar (HgS), the Hg contained below the upper meter of their core 6 was probably not detrital cinnabar because the cinnabar of the ore deposit was precipitated near and below the local water table and not directly exposed to erosion before mining began in the 1800s. Hence, another possible test of the anthropogenic origin of the Hg deposited into Clear Lake could be obtained by analyzing the chemical form of Hg before and after

mining operations using sediments obtained from cores deeper than ~70–80 cm (corresponding to the approximate horizon of anthropogenic mining operations [see Richerson et al. 2008 and Osleger et al. 2008]).

Data from our cores, including historic (70–100 years before present) Hg deposition with known Hg inputs of anthropogenic origin and prehistoric (1000–3000 years before present) time periods with Hg deposition of geologic origin, are consistent with the interpretation that Hg (both TotHg and MeHg) does not undergo upward diagenetic mobilization in the sediment column. Thus, we believe that the prominent vertical stability of both TotHg and MeHg peaks at depth support the case forwarded by Fitzgerald et al. (1998) that increases in Hg concentrations in the upper regions of sediment cores at sites that are not influenced by local anthropogenic sources are evidence of increased atmospheric deposition. In our case, this conclusion is based not on the absence of Hg peaks at the surface, but on the presence of (1) well-defined Hg peaks at depth during periods of elevated sedimentation rates (derived from mining) that have remained stable over a century and (2) zones of elevated Hg (of geologic origin) in the deepest regions of our cores (from 1000 to 3000 years before present) during periods of very low sedimentation rates. Thus the advantage of using Hg data from Clear Lake sediment cores is that we can use Hg peaks with a known and dated depositional history to evaluate the potential for these peaks to migrate beyond the dates in which they were deposited. At least in Clear Lake, TotHg and MeHg remain stable in the sediment column for very long periods of time.

#### CONCLUSIONS

This study proposed two sets of hypotheses, one set for Clear Lake proper, the second set for processes that relate to other lake systems.

##### (A) Hypotheses applicable to Clear Lake

*Hypothesis A1: Mining at Clear Lake has contributed negligible Hg loading to Clear Lake sediments.*—Data presented here, along with the  $^{210}\text{Pb}$  and  $^{14}\text{C}$  sediment dates provided by Richerson et al. (2008) and Osleger et al. (2008), suggest strongly that Hg loading from the Sulphur Bank Mercury Mine contributed significant Hg loading to Clear Lake sediments starting in ca. 1927 when the use of heavy earthmoving equipment became prevalent and mine tailings and waste rock were bulldozed into the shallow regions of Clear Lake. These Hg-laden sediments were then redistributed throughout the lake by wind-driven currents and appear in all cores collected throughout Clear Lake. Our data indicate that the mine has contributed (and still contributes) the majority of Hg loading to Clear Lake (Suchanek et al., *in press*). Therefore, this hypothesis is rejected.

*Hypothesis A2: Methylmercury in Clear Lake sediments during or after the onset of Hg mining (1873) has maintained vertical stability at depth within the sediment*

column.—Although the onset of sulfur mining at the Sulphur Bank Mine occurred in 1865 and Hg mining began in 1873, there does not appear to be an increase in Hg deposition toward the surface of these cores until the 1927 horizon (H-1927). At this point both TotHg and MeHg increase exponentially to well-defined peaks associated with the period of most active Hg mining (Fig. 3). These peaks appear to remain sequestered and maintain vertical stability within the sediment column at the same depth intervals in which they were deposited. The peaks may be significantly smaller than they were during their formation, but they do not appear to have migrated upward. Thus, this hypothesis is accepted.

(B) *Hypotheses applicable to other lake systems worldwide*

*Hypothesis B1: Total mercury has remained stable within the sediment column during periods of rapid sedimentation (historic times) as well as during periods of low sedimentation rates (prehistoric times).*—Sedimentation rates during historic times (above the 1927 horizon) reached ~2.2–20.4 mm/yr during and after the initiation of open-pit mining. Total mercury profiles within this interval of the sediment column remain distinct and show no evidence of migrating upward through the sediment. During prehistoric times, when sedimentation rates were ~0.6–2.0 mm/yr, increases in TotHg with increasing depth are evident in most of our cores, suggesting geologic processes as the source of the Hg increase. These intervals of increased Hg concentrations at depth are consistent among most cores and have maintained their vertical stability for ~1000–3000 yr. Thus, within both historic and prehistoric time periods, TotHg has remained stable within the sediment column, and this hypothesis is accepted.

*Hypothesis B2: Methylmercury has remained stable throughout the sediment column during periods of rapid sedimentation (historic times), as well as during periods of low sedimentation rates (prehistoric times).*—Methylmercury profiles are similar (but not identical) to TotHg profiles for historic time periods (above the 1927 horizon) under conditions of rapid sedimentation rates and for prehistoric time periods (below the 1927 horizon) under conditions of low sedimentation rates. Thus under both conditions, MeHg has maintained its vertical stability within the sediment column, and this hypothesis is accepted.

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