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A Mass Balance Mercury Budget for a Mine-Dominated Lake: Clear Lake, California

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Abstract The Sulphur Bank Mercury Mine (SBMM), active intermittently from 1873–1957 and now a USEPA Superfund site, was previously estimated to have contributed at least 100 metric tons (10^5 kg) of mercury (Hg) into the Clear Lake aquatic ecosystem. We have confirmed this minimum estimate. To better quantify the contribution of the mine in relation to other sources of Hg loading into Clear Lake and provide data that might help reduce that loading, we analyzed *Inputs* and *Outputs* of Hg to Clear Lake and *Storage* of Hg in lakebed sediments using a mass balance approach. We evaluated *Inputs* from (1) wet and dry atmospheric deposition from both global/regional and local sources, (2) watershed tributaries, (3) groundwater inflows, (4) lakebed springs and (5) the mine. *Outputs* were quantified from (1) efflux (volatilization) of Hg from the lake surface to the atmosphere, (2) municipal and agricultural water diversions, (3) losses from out-flowing drainage of Cache Creek that feeds into the California Central Valley and (4) biotic Hg removal by humans and wildlife. *Storage* estimates include (1) sediment burial from historic and prehistoric periods (over the past

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150–3,000 years) from sediment cores to ca. 2.5m depth dated using dichloro diphenyl dichloroethane (DDD), ^{210}Pb and ^{14}C and (2) recent Hg deposition in surficial sediments. Surficial sediments collected in October 2003 (11 years after mine site remediation) indicate no reduction (but a possible increase) in sediment Hg concentrations over that time and suggest that remediation has not significantly reduced overall Hg loading to the lake. Currently, the mine is believed to contribute ca. 322–331 kg of Hg annually to Clear Lake, which represents ca. 86–99% of the total Hg loading to the lake. We estimate that natural sedimentation would cover the existing contaminated sediments within ca. 150–300 years.

Keywords Acid mine drainage · Budget · Clear Lake · Mercury · Mass balance · Mercury loading · Mining · Sediments

1 Introduction

Studies on mercury (Hg) contamination in aquatic systems have increased dramatically over the past several decades, especially with the promulgation of human and environmental health criteria that attempt to define safe levels of Hg in the environment with the ultimate goal of reducing methyl Hg (MeHg) concentrations in food resources that are consumed by humans and wildlife (Suchanek et al. in press-b). However, the vast majority of the basic and applied research on this topic has been related to loading and effects from atmospheric sources, with little attention paid to those regions that contain significant Hg sources derived from mining related activities (Wiener and Suchanek 2008). Furthermore, abandoned Hg mines in particular are of major concern because of their potential for long-term human and environmental health impacts (Clarkson 2002; Hylander and Meili 2003; Maramba et al. 2006). Therefore, it is important to document the loading, transport and fate of Hg derived from mining sources, and specifically from Hg mines. The California Coast Range contains nearly 300 abandoned Hg mines and mining prospects (Churchill 2000), of which the Sulphur Bank Mercury Mine (SBMM) at Clear Lake (a shallow, eutrophic, polymictic lake in Lake County) is one of the largest (Suchanek et al. 2003, in press-e; Wiener and Suchanek 2008). As of 1952, cumulative production from the mine was documented at 129,418 flasks[1] of Hg, representing about 10% of the total Hg production for California, which accounted for 89% of the nation's Hg production (Simoons 1952). The total original content of the deposit was estimated at ca. 233,000 flasks, or ca. 7,000 metric tons (White and Roberson 1962).

SBMM was active intermittently from ca. 1873–1957 (Chamberlin et al. 1990; Suchanek et al. in press-e). Operation of the mine along the eastern shoreline of the lake, and subsequent erosion and acid mine drainage, are believed to have contributed at least 100 metric tons (10^5 kg) of total Hg (TotHg) to the lake's aquatic ecosystem (Chamberlin et al. 1990). Clear Lake lies within a region of the California Coast Range known to be rich in naturally occurring Hg ore, cinnabar (Churchill 2000; Shipp and Zierenberg in press). Therefore, annual erosion from Clear Lake's sizeable watershed (ca. 136,380 ha) also contributes a quantifiable Hg load to the lake.

In 1986, the California Department of Health Services issued a fish consumption advisory (based on Hg) for sport fish caught from Clear Lake (Stratton et al. 1987) and in accordance with the Clean Water Act, Clear Lake was placed on California's 303(d) list of impaired water bodies in 1988. In 1990, the U.S. Environmental Protection Agency (USEPA) placed the mine on the National Priority List of Superfund Sites. The USEPA subsequently initiated remediation actions intended to reduce TotHg loading from the mine into Clear Lake. In 1992, actions were taken to reduce annual erosion of soils during heavy precipitation events from a waste rock pile along the shoreline of the lake with extremely high Hg concentrations in soil (up to 1,500 mg/kg dry wt). This process (see Suchanek et al. in press-e) involved (1) reducing the angle of the slope of the wasterock pile along the shoreline from about 45° to 20°, (2) revegetating the wasterock pile slope, and (3) adding rip-rap boulders to the shoreline in front of the mine to reduce erosion from shoreline wave action.

Because Clear Lake has abundant geothermal springs emanating from the lakebed, some have speculated that elevated Hg concentrations in the lake have purely geothermal origin, with an insignificant contribution from anthropogenic mining activities (Varekamp and Waibel 1987). This hypothesis has

[1] A flask=75–76.5 lbs, depending on the mining era.

its origins in deep (20–28m) cores that exhibit some peaks of TotHg during prehistoric times (e.g., at about 3,600, 7,400, 9,500, 18,000 and 34,000 years before present (ybp)) that likely originated from natural processes such as volcanic and/or tectonic events within the Clear Lake Basin (Sims and White 1981). Hg plots from these deep cores and an analysis of historic and prehistoric Hg deposition into the lake are provided in Suchanek et al. (in press-f) and Hg profiles of additional dated cores collected in 1996 and 2000 are given in Richerson et al. (in press). Although evidence supports the mine being a major source of TotHg to Clear Lake (i.e., TotHg in water and sediment decreases exponentially as a function of distance from the mine (Suchanek et al. 1998; in press-c) and the highest Hg peaks in dated cores (calculated from ^{210}Pb dating) are found closest to the mine during time periods associated with extensive Hg mining (Richerson et al. in press; Suchanek et al. in press-f)), it is still important to evaluate whether abundant geothermal springs contribute significantly to Hg loading within the lake.

This Hg budget for Clear Lake is the culmination of a multi-year, interdisciplinary ecosystem-level study (Suchanek et al. in press-e) that traces the origin and pathways of Hg from the ore body at an abandoned Hg mine, through the abiotic (sediment and water) matrices, to lower trophic level species (benthic invertebrates and plankton) and ultimately to higher trophic level species (e.g., fish, birds and mammals). The following hypothesis is posed: the Sulphur Bank Mercury Mine is currently the largest contributor of Hg to Clear Lake. Baseline data represented in several other papers (see Suchanek et al. in press-e for overview) have contributed to a broader understanding of the inputs, outputs and storage of Hg in the abiotic and biotic matrices of this ecosystem. This paper utilizes some of those other data to develop a more comprehensive view of the present status of Hg loading to Clear Lake, the loss of Hg from the lake and storage of Hg in lakebed sediments.

The objectives of this study are to evaluate ongoing Hg loading to Clear Lake, to document the contributions of natural versus anthropogenic contributions to that loading, and to determine whether there has been any significant reduction in loading since the 1992 shoreline remediation. Data are provided on lakebed sediments, stream inputs, regional and local atmospheric deposition and modeled watershed contributions to quantify the known potential sources of Hg loading to and loss from the lake. This budget can provide an initial basis from which to make remedial recommendations for Hg load reduction in Clear Lake. Furthermore, various components in this Hg budget will assist others working at similar sites and allow comparison with other systems more strongly influenced by atmospheric deposition as compared to mining.

2 Methods

The primary components of this Hg budget are inputs, outputs and storage terms. Inputs include: (1) regional and local atmospheric deposition (both wet and dry estimates), (2) lakebed springs, (3) watershed tributaries and (4) the mine. Outputs include: (1) Cache Creek outflow from the lake, (2) water diversions extracted from the lake for agricultural irrigation, (3) efflux to the atmosphere, and (4) biota as fish removed by anglers and wildlife. Storage includes: Hg accumulated in lakebed sediments. In order to document storage, we analyzed (1) surficial sediments (top 1cm) from Ekman dredge samples as representative of modern day Hg deposition in sediments, with assumed eventual storage fate, and (2) deeper sediments from dated cores (to ca. 250 cm depth) as evidence of historic Hg storage in lakebed sediments.

Some of the data used in the development of this Hg budget were collected during a series of studies on the movement, transport and loading of Hg to Clear Lake (39°3′ N; 122°49′ W), detailed in Suchanek et al. (in press-e, in press-c). This contribution utilizes those and other data from the literature to compile a mass balance Hg budget for the lake. All water samples for Hg analysis were collected in acid-washed TeflonT™ bottles and stored on ice. Samples were analyzed for TotHg using bromine monochloride oxidation, stannous chloride reduction, and cold vapor atomic fluorescence analytical methods of Bloom and Crecelius (1983), now EPA Method 1631. All sediment samples were dried at 60°C and crushed by mortar and pestle to pass through a #60 mesh (250 μm) sieve, then analyzed using a standard cold vapor atomic absorption spectrophotometric technique based on EPA standard Method 245.5. For further details, see Suchanek et al. (in press-c).

2.1 Inputs

2.1.1 Atmospheric Deposition

Hg deposition (both wet and dry) onto the surface of Clear Lake was estimated using global/regional published data sources as well as local lake-based data sources (evasion from the mine). Hg contributions from deposition onto the terrestrial landscape surrounding the lake are accounted for within the "Watershed" component.

Global/Regional Atmospheric Sources Global/regional atmospheric Hg deposition was estimated using the nearest National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) station at Covelo, California (39°42′25″ N; 123°14′17″ W in Mendocino County) about 75 km north of Clear Lake and about the same distance (ca. 50 km) from the coast (Lindberg and Vermette 1995; Welker and Vermette 1996). Two additional MDN sites are located in the San Francisco Bay region (Steding and Flegal 2002), but those are more influenced by urban processes. Data from the Covelo site yielded a mean concentration of 7.6 ng/L Hg in volume-weighted wet precipitation for 1998–1999 (NADP 2000). Dry deposition data are not collected at Covelo. However, dry deposition reported in several other studies ranged from 31.2% to 66.5% of the total deposition (Shannon and Voldner 1995; Lodenius 1998; Vette et al. 2002; Sakata and Marumoto 2005). Thus, we have employed a range of values for the ratio of dry deposition to wet deposition from 0.45 to 1.99.

The equation below (modified from SFEI 2001) was used to calculate total annual Hg deposition loading from regional/global atmospheric sources that fall directly onto Clear Lake. Note that wet and dry Hg deposition that falls onto the surrounding watershed is already incorporated into the Watershed Input values (below).

$$Dt = Cw * Py * A * (1 + Kd) * 1000$$

where:

Dt average annual Hg deposition to Clear Lake (ng/year)

Cw average concentration of Hg in precipitation (ng/L) = 7.6 (NADP 2000)

Py average annual precipitation (m/year) at Clear Lake = 0.686 (Richerson et al. 1994)

A area of Clear Lake (m^2) = 1.77×10^8 (Richerson et al. 1994)

Kd coefficient used to account for dry deposition (ratio of dry deposition to wet deposition) = range of values from 0.45–1.99 (see references above)

Local Atmospheric Sources There are no significant industrial sources of Hg emissions to the atmosphere in or near the Clear Lake watershed, but some Hg is volatilized and emitted from mine site wastes and native soils in the form of elemental Hg^0 or reactive gaseous Hg (Gustin et al. 2000). Total annual Hg flux from SBMM soils to the atmosphere, measured on several occasions from ca. 25 locations on and off the mine site, was estimated to range from 5.5–34 kg/year (Gustin 2003; Gustin et al. 2003; Nacht et al. 2004). Because the mine is located at the extreme easterly end of Clear Lake and the prevailing winds are from the west–northwest (Suchanek et al. in press-e), it is unlikely that much of this Hg is redeposited onto Clear Lake. Windrose data for Clear Lake (Suchanek et al. in press-e) indicate that winds originate from the east only about 10% of the time. Thus, we have estimated that 10% of the Hg evasion from the SBMM site calculated by other investigators (identified above) would be redeposited onto Clear Lake.

2.1.2 Watershed

Clear Lake drains a watershed area of ca. 1,036 km^2 (Fig. 1). From 1998–2001, TotHg in unfiltered and filtered (0.45 μm pore size) water and total suspended solids (TSS) were analyzed from six streams (Adobe Creek, Cole Creek, Kelsey Creek, Middle Creek, Schindler Creek and Scotts Creek) that drain into Clear Lake and the outlet at Cache Creek that drains Clear Lake on the following dates (with relative flow rate descriptors for the events in parentheses): 2/19/98 (high flow), 5/21/98 (low flow), 11/30/98 (first flush), 5/23/00 (low flow), 1/26/01 (first flush). Three tributaries (Kelsey, Middle and Scott's Creeks) and Cache Creek (at the outflow) also have permanent flow gauges operated by the U.S. Geological Survey (USGS) for which long-term data are available (see http://water.wr.usgs.gov/). At each site, duplicate

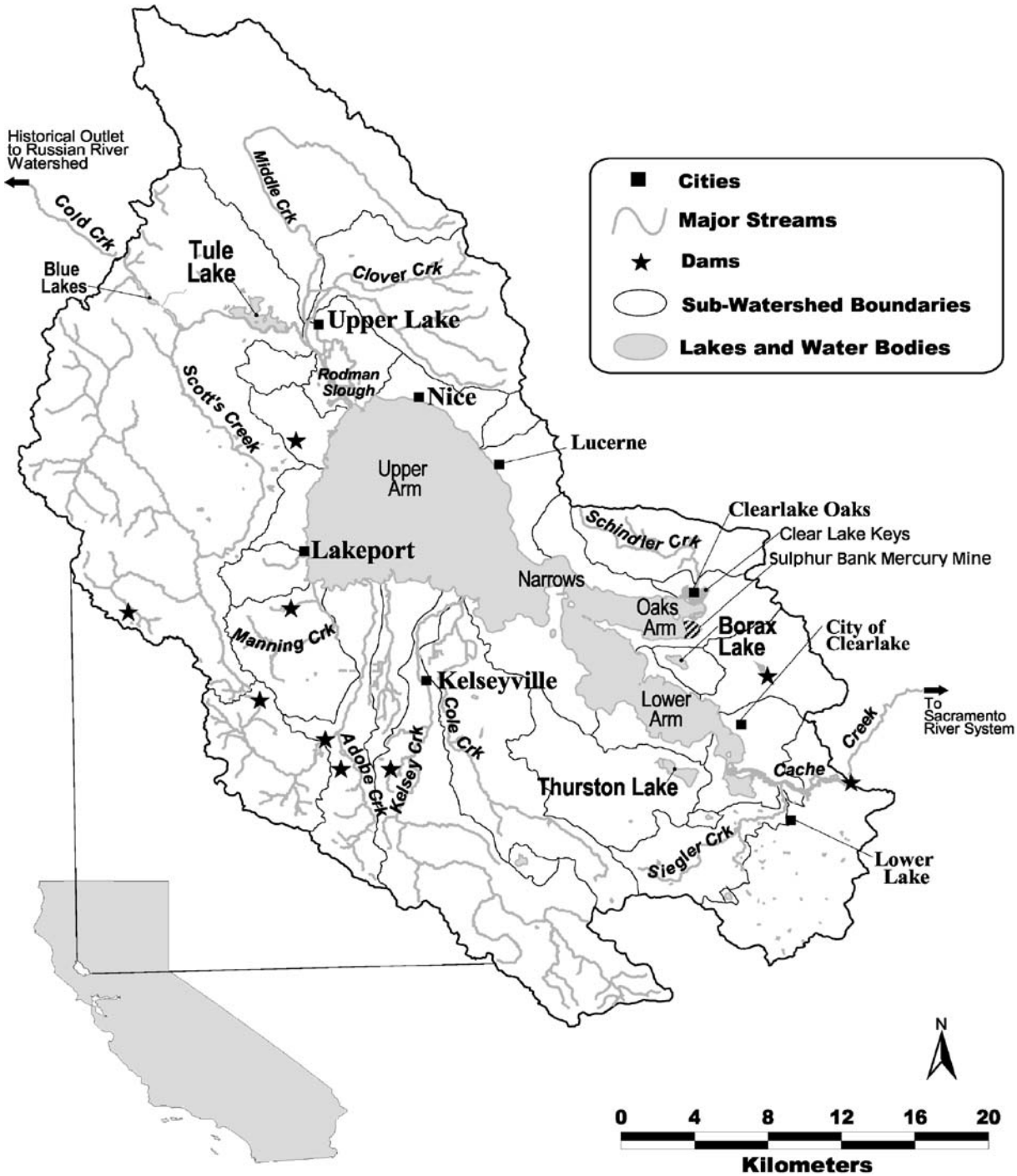

Fig. 1 Clear Lake and surrounding watershed, with sub-watershed boundaries used to calculate Hg loading

water samples were collected into acid-washed 1.0 L TeflonT bottles using ultra-clean protocols (Gill and Bruland 1990; Watras et al. 1992). TSS was analyzed by Century Testing (Bend, OR) using a standard filtration-based multiple weighing technique. Two different approaches (Direct Measurement and GIS Modeling) were used to estimate TotHg loading from the Clear Lake watershed.

Watershed Input (Approach #1—Direct Measurement) TotHg concentrations measured over a range of flow regimes from 1998–2001 (Table 1) were used to develop regression equations between flow rate versus aqueous TotHg concentrations for each of the three USGS-gauged streams using the following equation: $M = C * Q$, where C = concentration (mass/volume), Q = discharge (volume/time), and M = mass loading rate (mass/time). Linear regression equations are given below for each stream:

$$\text{Kelsey Creek} : [\text{Hg}](\text{ng}/L) = 0.0011 * \text{flow rate}(\text{L}/\text{s}) + 2.67\{R^2 = 0.774\}$$
$$\text{Middle Creek} : [\text{Hg}](\text{ng}/\text{L}) = 0.0030 * \text{flow rate}(\text{L}/\text{s}) + 9.50\{R^2 = 0.708\}$$
$$\text{Scotts Creek} : [\text{Hg}](\text{ng}/\text{L}) = 0.0001 * \text{flow rate}(\text{L}/\text{s}) + 9.8\{R^2 = 0.338\}$$

Based on these relationships, two estimates were made for Hg loading from streams into Clear Lake: (1) proportional to the area of the watershed, and (2) proportional to the average annual streamflow of all steams into the lake. Using the Hg concentration values derived from these equations (above), annual Hg loading values from these streams were calculated by multiplying those concentrations by their respective daily flow rates from a 10-year (1990–1999) USGS stream flow dataset that represented a diverse combination of wetter years and drier years. Because some (minimal) data gaps existed in the USGS database for individual days, monthly average loading values were calculated by averaging data for those days with valid flow data and multiplying that value by the number of days in that month. Summing the monthly loads provided a cumulative annual Hg load for gauged streams. For ungauged streams, it was assumed that the flow rate and Hg load from those tributaries was proportional to the area of the drainage basin represented by those tributaries. This is a reasonable assumption since there was shown to be

Table 1 Measured flow rates (Q), aqueous TotHg concentrations (ng/L) and TSS concentrations (mg/L) used to calculate Hg loading from tributaries

	Flow event	Q (L/s)	TotHg (ng/L)	TSS (mg/L)
Kelsey Creek				
2/19/98	High flow	38,515	29.50	383
5/21/98	Low flow	1,105	0.83	1
11/30/98	First flush	35,400	57.40	380
5/23/00	Low flow	906	1.24	5
1/26/01	First flush	3,625	8.20	11
Scotts Creek				
2/19/98	High flow	68,534	17.90	290
5/21/98	Low flow	906	0.96	25
11/30/98	First flush	13,140	16.40	62
5/23/00	Low flow	193	2.83	12
1/26/01	First flush	4,276	13.50	48
Middle Creek				
2/19/98	High flow	42,480	108.00	920
5/21/98	Low flow	1,161	0.65	1
11/30/98	First flush	7,930	82.40	310
5/23/00	Low flow	3,002	1.41	5
1/26/01	First flush	1,614	3.51	2
Cache Creek				
2/19/98	High flow	205,320	7.50	92
5/21/98	Low flow	14,641	7.50	43
11/30/98	First flush	161	5.84	17
5/23/00	Low flow	20,504	5.05	19
1/26/01	First flush	110	30.30	111

a strong correlation between average annual streamflow in the well-gauged Kelsey Creek and five creeks with limited stream gauging (Chamberlin et al. 1990; Richerson et al. 1994). This process resulted in a mean set of Hg loading values from the surrounding watershed for the ten USGS water years. However, annual loading values may overestimate the load coming from Scott's Creek because Hg-laden sediment may become trapped in the Tule Lake Basin before reaching the lake. Alternatively, these calculations may underestimate actual average annual loads because they assume that Hg concentrations in the gauged streams, which all flow into the Upper Arm, are the same for other streams. For example, Schindler Creek, which drains into the Oaks Arm, is not gauged yet has very low flow, but has higher Hg concentrations. Methods for the two estimates are given below.

Proportional to Watershed Area Richerson et al. (1994) calculated the total area of the Clear Lake watershed at 1,036 km^2, with the USGS-gauged streams draining 50.4% of that area, and ungauged streams draining 49.6%. Total Hg loading for the 10year USGS-gauged stream dataset, was then added to the remaining 49.6% of the watershed by multiplying the annual loading estimate for the USGS-gauged streams by 0.984. The sum of these two values represents an estimate of annual TotHg loading based on watershed area.

Proportional to Average Stream Flow Richerson et al. (1994) also calculated the average annual stream flow rate of all streams flowing into Clear Lake at 11,412 L/s, with the USGS-gauged streams representing 63.5% of that flow, and ungauged streams representing 36.5%. Total Hg loading for Clear Lake, calculated from the 10year USGS-gauged stream dataset, was then added to the remaining 36.5% of the flow volume by multiplying the annual loading estimate for the USGS-gauged streams by 0.575. The sum of these two values represents an estimate of annual TotHg loading based on average stream flow.

Watershed Input (Approach #2—GIS Modeling) TotHg and TSS data from the six input streams (above) were combined to yield a regression relationship between TSS and aqueous TotHg concentrations: TotHg (ng/L) = (0.130 × TSS (mg/L)) + 8.456, R^2 = 0.666. This relationship was used in a GIS modeling program (ARC/INFO) that applied land use management factors within the Clear Lake watershed to the Universal Soil Loss Equation (USLE) (Wischmeier and Smith 1960, 1978; Meyer and Wischmeier 1969), yielding a soil (and associated Hg) loading estimate for the watershed based on three different land management scenarios.

The USLE, traditionally applied to calculating soil loss on a field level resolution, was used to calculate the quantity of sediment produced from surface erosion within the Clear Lake watershed on a 30 × 30 m grid cell array, which was then converted to a TSS loading rate. The USLE formula is:

$$A = R * K * LS * C * P$$

where:

A	average annual soil loss (tons/acre)
R	rainfall erosivity index
K	soil erodibility factor
LS	topographical factor—(***L*** = slope length; ***S*** = slope [%])
C	"cropping" or "land management" factor
P	conservation practice factor

Within ARC/INFO's Grid Extension routine, the following data sets were combined. *R* values were selected from a Natural Resource Conservation Service (NRCS) map of *R* values for the Clear Lake Basin (USDA-NRCS 1999). These values were then assigned to isocline polygons representing average precipitation. *K* values were derived from the dominant soil unit in the NRCS SSURGO data set (USDA-NRCS 1998). Slope length, *L*, was calculated using the USGS 30m digital elevation model (DEM) (Teale Data Center 1997) and Hickey's Arc Macro Language slope length algorithms (Hickey et al. 1994). *C*-values were assigned land use types from the USGS National Land Cover Dataset (USGS 1992). The *P* factor was assigned a default value of 1 because detailed field data and support practices were unavailable. The topographic, geologic, and climate variables did not change between the scenarios.

The USLE was applied to the 30 × 30 m cells within a grid of variable land use patterns (normalized by area) for the entire Clear Lake watershed obtained from the U.C. Davis Information Center for the

Environment and mapped by Suchanek et al. (2003). The grids were constructed for three difference scenarios of the "C" (cropping or land management) factor: best, medium and worst, relative to the influence of various land management practices on soil erosion. The definitions of these categories are given in Table 2. The resultant single cell values were then summed and normalized by discreet sub-watershed zones that drain into Clear Lake (Fig. 1). The sub-watershed zones were defined using the point/pour function in ARC/INFO using USGS 30 m DEMs from 1998 provided by the Teale Data Center. A sediment delivery ratio developed by Vanoni (1975) was applied to define the relationship between the area of a watershed (in this case sub-watersheds) and the percentage of suspended sediments that are ultimately delivered as input to the lake.

2.1.3 Lakebed Springs

Water from three high volume lakebed springs (one each in the Oaks Arm, Narrows and Lower Arm) was sampled in 1992 through acid-washed TeflonT tubing using a peristaltic pump lowered from a 22ft (6.7 m) research vessel and analyzed for TotHg.

2.1.4 Groundwater Inflow

Based on data from semiannual monitoring of groundwater reserves (LCFCWCD 1987), and estimates of hydrologic contributions from specific basins surrounding the lake, groundwater inflow rates to Clear Lake have been calculated at approximately 2.2×10^5 to 4.5×10^5 m^3/year (Richerson et al. 1994). However, Hg analyses on unfiltered Clear Lake groundwater found no Hg at a detection level of 0.20 μg/L (unpublished data—Lake County Special Districts).

2.1.5 Sewage/Septic Systems

Zero discharge sewage treatment plants were constructed at Clear Lake in the 1970s using sprayfields for the disposal of secondary-treated waste (Richerson et al. 1994). However, when rare overflow events occur, the volume typically ranges from $4.5–8.8 \times 10^5$ m^3. Assuming a range of Hg concentrations in those sewage waters from 2–25 ng/L (based on the range of Hg concentrations in input streams to Clear Lake) the range of Hg contributed by each event would be on the order of 0.001–0.020 kg. Thus, we have considered the annual Hg contribution from sewage systems to be negligible.

2.2 Outputs

2.2.1 Efflux to the Atmosphere

Volatilization (efflux) of Hg from the air–water interface to the atmosphere (Fitzgerald et al. 1991) represents a potentially significant loss of Hg from lakes. The rate of Hg efflux from the lake to the atmosphere is dependent upon the concentration of Hg in the water and in the atmosphere, temperature and surface wind conditions. Bale (1995, 2000) modified and enhanced an existing finite element model (RMA4q) to estimate Hg transformation, bioavailability and cycling within Clear Lake, including efflux from the air/water interface. Diffusive exchange of Hg from the lake to the atmosphere was modeled as a Fickian diffusion process using a two-layer film model assuming that resistance to transfer is predominantly in the liquid phase. This model assumed an average temperature of 20°C and a background atmospheric Hg concentration of 0.002 ng/L. Hg concentration data collected in Clear Lake sediments and water from 5/15/94 to 3/17/98 (Suchanek et al. 1998, in press-c) were used to calibrate the model at three sites and validate the model at four different sites to calculate diffusive exchange of Hg between the lake surface and the atmosphere. Efflux was modeled using the following equation: $J = K[(Hg^0_{atm}/He) - Hg^0_{water}]$ (Tchobanoglous and Schroeder 1985), where: J = Hg flux from the lake surface to the atmosphere ($\mu g \cdot m^{-2}\ day^{-1}$), K = the Hg mass transfer coefficient (m/day), Hg^0_{atm} = the concentration of Hg^0 in the atmosphere above the lake surface ($\mu g/m^3$), He = Henry's coefficient (dimensionless), and Hg^0_{water} = the concentration of Hg^0 in the water column at the air/water interface ($\mu g/m^3$).

A range of gas exchange coefficient (K) values from 0.5–1.0 m/day was obtained from Mason et al. (1993). A realistic set of values for Henry's coefficient (0.29–0.35) was obtained from (Iverfeldt and Persson 1985). A total daily Hg efflux for the lake was calculated using the surface area values of the Oaks Arm, the Upper Arm and the Lower Arm at 1.25×10^7, 1.27×10^8, and 3.72×10^7 m^2, respectively (Richerson et al. 1994), and extrapolating that to an annual value. The

Table 2 Descriptions of Land Use "Cropping" Factors used to model soil erosion rates into Clear Lake assuming three different land management scenarios

	Landuse parameters	"Worst" C-factor		"Medium" C-factor		"Best" C-factor	
		Description	C-factor	Description	C-factor	Description	C-factor
1	Open water	–	0.0000	–	0.0000	–	0.0000
2	Low intensity residential	Highest C-factor with hay mulch on slopes	0.2000	Medium C-factor with crushed stone mulch on slopes	0.0500	Lowest C-factor with wood mulch on slopes	0.0200
3	High intensity residential	Highest C-factor with hay mulch on slopes	0.2000	Medium C-factor with crushed stone mulch on slopes	0.0500	Lowest C-factor with wood mulch on slopes	0.0200
4	Commercial/industrial/transportation	Highest C-factor with hay mulch on slopes	0.2000	Medium C-factor with crushed stone mulch on slopes	0.0500	Lowest C-factor with wood mulch on slopes	0.0200
5	Bare rock/sand/clay	No canopy	0.4500	60% ground cover	0.0910	0% canopy cover, or 95% ground cover	0.0110
6	Quarries/strip mines/gravel pits	No canopy	0.4500	60% ground cover	0.0910	0% canopy cover, or 95% ground cover	0.0110
7	Transistional areas	–	0.0000	–	0.0000	–	0.0000
8	Deciduous forest	Trees, 0% ground cover, 25% canopy cover	0.4200	Trees, 60% grass ground cover, 50% canopy cover	0.0400	Trees, 95% ground cover, 75% canopy cover	0.0030
9	Evergreen forest	20–40% canopy and 70% 1 inch duff	0.0030	70% canopy cover, 85% 2 inch duff	0.0020	Undisturbed forest, 100% canopy cover, 100% 2 inch duff	0.0001
10	Mixed forest	20% canopy, 40% 2 inch duff	0.0090	45% canopy cover, 75% 2 inch duff	0.0040	75% canopy cover, 90% 2 inch duff	0.0010
11	Shrubland	Brush, grass, 0% ground cover, 25% canopy	0.4000	Brush, 60% grass cover, 50% canopy cover	0.0380	Brush, 95+ % grass cover, 75% canopy cover	0.0030
12	Orchards/vineyards/other	Tilled vineyard, 0% ground cover, 15% raised cover	0.9200	Tilled vineyard, 60% ground cover, 15% raised canopy	0.0900	Orchard 95% ground cover, 25–75% raised cover	0.0030
13	Grasslands/herbaceous	Grass, no appreciable canopy cover	0.4500	No appreciable canopy, 60% grass cover	0.0420	Continuous annual grass	0.0100
14	Pasture/hay	Grain–summer fallow, conventional tillage	0.5000	Grain, summer fallow, stubble mulch with residues left	0.3300	Continuous annual grass	0.0100
15	Row crops	3-year row/field crop sequence, no winter cover	0.6800	3-year row/field crop sequence, 2 years of winter cover	0.3600	3 year row/field crop sequence, 3 years of winter cover	0.2100
16	Small grains	Barley/wheat, spring fallow, conventional till	0.3300	Barley/wheat, spring fallow, 2 year cycle, reduced till	0.0800	Barley/wheat, spring fallow, 2 year cycle	0.0400
17	Urban/recreational grasses	Highest values with hay mulch factors	0.2000	Medium C-factor with crushed stone mulch on slopes	0.0500	Lowest C-factor with wood mulch on slopes	0.0200
18	Woody wetlands	Undisturbed wetlands	0.0001	Undisturbed wetlands	0.0001	Undisturbed wetlands	0.0001
19	Emergent herbaceous wetlands	Undisturbed wetlands	0.0001	Undisturbed wetlands	0.0001	Undisturbed wetlands	0.0001

final range of potential annual Hg efflux values (kg/year) was obtained using a combination of the ranges of each of the individual components listed above.

2.2.2 Tributaries—Cache Creek Outflow

TotHg in Cache Creek outflow waters was measured at the Clear Lake outlet to Cache Creek on the same dates and under the same ranges of flow regimes and analyzed the same way as those samples collected for tributary inputs (see above). As with the tributary input data, a regression analysis was used to determine the relationship between flow and Hg concentrations: [Hg] (ng/L) = (0.00001 * flow rate (L/s)) + 5.89 $\{R^2 = 0.335\}$. This relationship was used together with USGS flow data at the permanent gauging station about 3 miles below the Clear Lake Dam to calculate daily Hg loads, and these values were summed to estimate annual Hg outputs for the water years 1990–1999.

2.2.3 Municipal and Agricultural Water Diversions

While water extractions for both municipal and agricultural uses are hard to quantify, Richerson et al. (1994) utilized data on water demand values from the LCFCWCD (1987) to quantify water extractions from Clear Lake at 20.8×10^6 m^3/year, of which roughly half (10.8×10^6 m^3/year) is estimated to derive from municipal/industrial demand and about 10.0×10^6 m^3/year is agricultural usage. We used a long-term range of TotHg concentration in Clear Lake waters (10–20 ng/L from Suchanek et al. in press-c) to calculate both municipal and agricultural extractions.

2.2.4 Removal of Biota

A small, but finite, amount of Hg that is incorporated in fish and other organisms is removed from the lake by commercial and sport fishers as well as by wildlife. A conservative estimate was developed primarily for fish removal by humans. Based on creel survey data from the California Department of Fish and Game, sport anglers remove an estimated 17,300 kg of fish from Clear Lake annually, although this figure likely underestimates catches of catfish, sunfishes and hitch (Macedo, pers. com., Cannata, pers. com.). Commercial harvest data estimates removal of ca. 12,300 kg/year of carp and Sacramento blackfish (Bairrington 2000). These values were used together with average Hg concentrations of fishes (CVRWQCB 1985; Stratton et al. 1987; Suchanek et al. in press-b) to obtain an estimate of Hg removal by humans and wildlife.

2.3 Storage

2.3.1 Sediments

Surficial Sediments Surficial sediments were collected from a 22 ft (6.7 m) research vessel using a 6 in. (15.24 cm) Ekman dredge at 34 sites in October 1992 and again at those same sites in May and October 2003 (Fig. 2). Sediment aliquots (one–two samples per site) were harvested from the top 1cm of sediment. TotHg was analyzed using methods described in Suchanek et al. (in press-c). These data were also used to determine whether mine site remediation efforts by USEPA in the summer of 1992 were effective in reducing Hg erosion and loading into Clear Lake as of 2003.

Sediment Cores Sediment cores (up to ca. 250 cm depth) were collected using 3m long piston cores operated from the research vessel identified above during multiple campaigns in 1996 and 2000. In Richerson et al. (in press) and Osleger et al. (in press) we report on seven of these cores, one in each of the three arms in 1996 and at those same locations again in 2000 but with a duplicate in the Oaks Arm. Core sediments were analyzed for TotHg and dated using a DDD (the pesticide dichloro diphenyl dichloroethane) horizon[2], ^{210}Pb (Richerson et al. in press) and ^{14}C on organic debris within the cores (Osleger et al. in press). Additional details of coring procedures are described in Richerson et al. (in press).

Modeling Hg Storage We based our estimates of modern Hg storage on Hg concentrations in surficial sediments collected by Ekman dredge at the 34 sites mentioned above as well as from the top sections of sediment cores (see Suchanek et al. 1997, in press-c; Richerson et al. 2000, in press). An inverse distance weighted interpolation algorithm (Philip and Watson 1982; Watson and Philip 1985) was utilized within ARC/INFO to extrapolate Hg concentrations from the

[2] The DDD horizon is defined as the vertical position within the sediment core where DDD appeared suddenly and quickly reached a concentration peak, corresponding to the massive application of this pesticide to the lake in 1954. See Richerson et al. (in press) and Osleger et al. (in press) for details of all dating techniques.

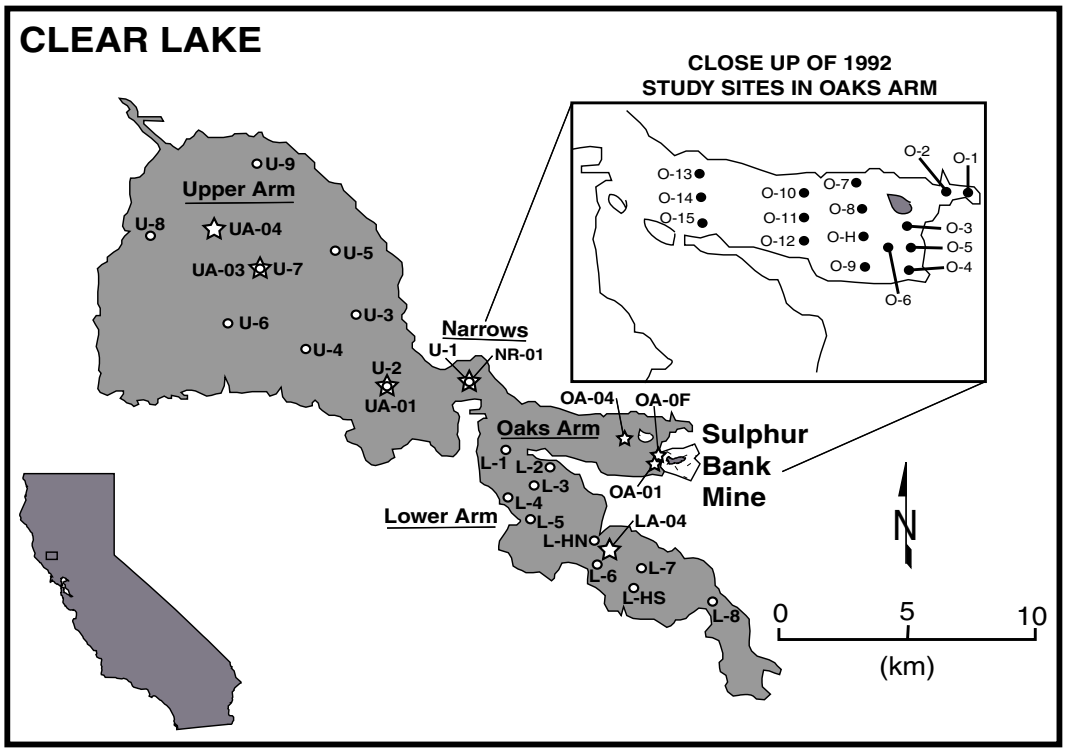

Fig. 2 Clear Lake site map for sediment sampling locations in 1992 and 2003

34 sites to the entire lake surface. Over the range of depths from our 2.5 m long cores, sedimentation rates in Clear Lake have been estimated at 0.6–20.4 mm/year, with different sedimentation rates at three distinct depth regimes (Richerson et al. in press; Osleger et al. in press).

To estimate the time needed for natural sedimentation to cover Hg-contaminated sediments, we used the following algorithm from Reible et al. (1991): $T_{1/2} = [(\ln 2)\ Z_m]/S$, where $T_{1/2}$ = the half-life of sediment burial (years), Z_m = depth of the mixed layer (cm)—in our case from bioturbation (Suchanek et al. in press-d), and S = sedimentation rate (cm/year).

3 Results and Discussion

3.1 Inputs

3.1.1 Global/Regional Atmospheric Sources

Long-term average Hg concentration in rainwater at the Covelo NADP site is 5.6 ng/L, but the average for 1998–1999 was 7.6 ng/L. Using the formula given in Section 2 and applying both values (5.6 and 7.6 ng/L), this translates into a range for wet deposition Hg loading for the surface area and precipitation regime at Clear Lake of 0.680–0.923 kg/year. Based on the range of values for dry deposition reported in the literature (31.2% to 66.5% of total deposition, see Section 2), this yields a range of dry to wet deposition ratios (Kd values) of 0.45 to 1.99. Applying these to the equation for Hg loading yields a range of 0.99–2.76 kg/year of Hg from atmospheric deposition (wet + dry), with the range of dry deposition from 0.31–1.84 kg/year and wet deposition from 0.68–0.92 kg/year. These values are more than two orders of magnitude smaller than the estimated amount of Hg loading (319.9–378.7 kg) to lakebed sediments annually (see Section 3.3).

These estimates are similar to nation-wide estimates of atmospheric Hg deposition prepared for the Mercury Study Report to Congress (MSRC) (USEPA 1997). Authors of the MSRC used the RELMAP (Regional Lagrangian Model of Air Pollution) model to predict the average annual atmospheric Hg concentration and the wet and dry deposition flux for each cell in a 40 km square grid over the continental

United States (US). Emission, fate and transport of airborne Hg over the continental US were modeled using meteorological field data from 1989. Although the model incorporated over 10,000 Hg-emitting units such as municipal waste combustors and chloralkali plants, no data specific to Hg in air-borne dust or vapor from inactive Hg mine sites were used. Results of modeling with RELMAP were compared with measurements of Hg deposited in air, available mainly for points in the upper Midwest, Florida and the Northeast (USEPA 1997). Hg deposition rates for western states developed using RELMAP were 0.86, 2.32 and 8.00 μg • $m^{-2}year^{-1}$ for the 10th, 50th and 90th percentiles of deposition, respectively. Using the 90th percentile estimate of 8.00 μg • $m^{-2}year^{-1}$ applied to the surface area of Clear Lake results in an estimated total annual deposition of 1.4 kg/year, which is in the mid range of our calculated values.

3.1.2 Local Atmospheric Sources

Based on several sampling campaigns, reactive gaseous Hg fluxes from the SBMM site to the atmosphere have been estimated at 5.5–34 kg/year (Gustin 2003; Gustin et al. 2003; Nacht et al. 2004). Assuming that easterly winds blow from the mine site back onto the lake about 10% of the time (see Section 2), we estimate that Hg redeposition from the mine site onto the lake ranges from 0.55–3.40 kg/year. This assumes that all of the volatilized Hg from the mine site enters Clear Lake when winds blow from the east.

3.1.3 Lakebed Springs

Data from Suchanek et al. (1998, 2000a, in press-c) indicate that no additional Hg sources derive from lakebed springs. These data support those of previous investigators who reported that lakebed springs distant from the mine site show no evidence of high temperature interaction with volcanic rocks (Donnelly-Nolan et al. 1993; Goff and Janik 1993) and are not likely to contribute significant Hg to Clear Lake. Thus, the contribution from lakebed springs is zero.

3.1.4 Watershed Input

Approach #1—Direct Measurement Two different scenarios based on direct measurements of aqueous Hg in Clear Lake tributaries were used to estimate Hg loading from the watershed: (1) proportional to watershed area, and (2) proportional to average stream flow. Based on the relationship between flow

Table 3 Annual and mean (plus standard error—S.E.) TotHg loading (kg/year) into Clear Lake for the water years 1990–1999 from USGS-gauged streams and extrapolated annual TotHg loading from un-gauged streams based on two scenarios: (1) watershed area, (2) stream volume

	Water year										Mean	S.E.
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999		
Gauged streams												
Kelsey Creek	0.23	0.73	0.42	1.97	0.18	5.31	1.48	2.34	3.59	1.60	1.78	0.47
Scotts Creek	0.13	0.33	0.34	1.45	0.19	2.83	1.41	1.63	3.04	1.11	1.25	0.30
Middle Creek	0.23	0.75	1.21	5.75	0.21	9.82	5.02	2.84	17.75	4.96	4.85	1.58
Annual loading from gauged streams	0.59	1.80	1.96	9.17	0.58	17.96	7.91	6.80	24.38	7.66	7.88	2.27
Annual loading from un-gauged streams												
Watershed area scenario (49.6%)	0.58	1.78	1.93	9.02	0.57	17.67	7.78	6.69	23.99	7.54	7.75	2.23
Stream volume scenario (36.5%)	0.34	1.04	1.13	5.27	0.33	10.33	4.55	3.91	14.02	4.40	4.53	1.30
Total annual loading												
Watershed area scenario	1.17	3.58	3.89	18.19	1.15	35.63	15.69	13.49	48.37	15.20	15.63	4.50
Stream volume scenario	0.93	2.84	3.09	14.44	0.91	28.29	12.46	10.71	38.40	12.06	12.41	3.57
Total annual output												
Cache Creek outflow	0.00	0.02	0.31	1.31	0.32	6.45	4.32	4.39	7.57	3.21	2.79	0.81

Output down Cache Creek represents the sole tributary outflow from Clear Lake. Note: 1990 was a drought year

rate and aqueous Hg concentrations, the 10 year USGS flow rate data for gauged streams and extrapolation to ungauged streams, average annual loading estimates for TotHg for the water years 1990–1999 are provided in Table 3. Using the first scenario (proportional to watershed area), total annual tributary Hg loading estimates range from ca. 1.2–48.4 kg/year, with a 10 year average of 15.6 kg/year. The second scenario, based on annual average stream flow, yields Hg loading estimates ranging from ca. 0.9–38.4 kg/year, with a 10 year average of 12.4 kg/year. Therefore, we have considered a range of Hg contributions from streams at 0.9–48.4 kg/year. These values compare reasonably well with tributary Hg loading estimates from other streams in this region of California with comparable sediment sources but outside of the Clear Lake watershed from 2000–2001 yielding estimates of 0.5–12 kg/year (Domagalski et al. 2004).

Approach #2—Modeling Using a modeling approach that incorporates the relationship between TSS and aqueous Hg concentrations, as well as soil mobilization projections under varying "cover" or "land use management" scenarios, Hg loading from the Clear Lake watershed is similar to that obtained using Approach #1 (Direct Measurement). Under the three land use management scenarios (best, medium, worst), the range of TotHg delivered to Clear Lake was estimated at 2.1, 2.9 and 25.2 kg/year, respectively. Given that crop cover may be hard to estimate, and changes frequently, Hg loading under different land management strategies may be altered by an order of magnitude as a result of variable erosion patterns. Thus, as monitoring data on land use practices are refined, this modeling approach may become increasingly more useful in estimating Hg mass loading to Clear Lake. Because the calculated range of Hg loading from the watershed using the direct measurement approach is larger than the range using the modeling approach, we have used the values produced from direct measurement to bound the uncertainties.

3.1.5 Groundwater Input

Groundwater inflow rates of 2.2×10^5 to 4.5×10^5 m^3/year, represent only ca. 0.04–0.09% of the surface water inflow to Clear Lake (Richerson et al. 1994), and no Hg has been detected in groundwater wells at Clear Lake (unpublished data—Lake County Special Districts). The detection level for Hg analyses performed on Clear Lake groundwater samples was 0.2 μg/L. Even if all the groundwater inflow at the highest flow rate had concentrations of 0.2 μg/L, the annual Hg contribution to Clear Lake from this source would be 0.09 kg/year. Thus, we have estimated a range of 0–0.09 kg/year for this component.

3.2 Outputs

3.2.1 Efflux to the Atmosphere

The efflux component of the modified RMA4q model (Bale 1995, 2000), combined with the aqueous TotHg concentration data for Hg from the 1994–1998 Long-term Lake Study (Suchanek et al. in press-c), and the range in potential gas exchange coefficients (K) and Henry's coefficient (He) provided in Section 2, yielded a range of daily Hg efflux values (μg • m^{-2} day^{-1}) for the three arms of Clear Lake: Oaks Arm (0.100–0.201), Upper Arm (0.020–0.041) and Lower Arm (0.020–−0.041). Loux (2000) reported hourly rates of Hg evasion (efflux) from several lakes in the United States, Canada and Sweden that ranged from 0.08–20.00 ng • m^{-2} h^{-1}. When scaled up to daily rates, these values ranged from 0.0019–0.4800 μg • m^{-2} day^{-1}, which encompass the range of values we obtained for Clear Lake. Applying the individual surface areas for each arm yielded cumulative annual Hg efflux values (kg/year) for the three separate arms: Oaks Arm (0.455–0.915), Upper Arm (0.912–1.879) and Lower Arm (0.267–0.550); total lake = 1.634–3.344 kg/year.

3.2.2 Cache Creek Outflow

Three independent estimates of TotHg output via Cache Creek are reported here. Using direct measurements of aqueous Hg concentrations in the Cache Creek outflow from 1998 and 2000, multiplied by daily flow rate data from the USGS gauging station in Cache Creek yielded a range of annual Hg export of «1.0 to 7.57 kg/year for the 10 years of available flow data from 1990–1999, with a 10 year average of 2.79 kg/year (see Table 3). In addition, two other studies have produced datasets that estimate Hg outflow from Clear Lake and were used for compar-

ison to quantify uncertainty in our estimate of this parameter. Foe and Croyle (1998) provide Hg loading estimates at the Clear Lake dam feeding into Cache Creek during the relatively wet period from February 1996 to June 1997 of 11 kg/year. Domagalski et al. (2004) collected comparable data just below the dam from January 2000 to May 2001, representing relatively low water years, reporting Hg export into Cache Creek at 1.7 kg/year. However, given the large range of values for wet and dry years, we believe the average of 2.8 kg/year (representing a mixture of wetter and drier years calculated from the 10 year USGS flow database) represents the most reasonable estimate for the long-term average Hg output from Clear Lake to Cache Creek.

3.2.3 Municipal and Agricultural Water Diversions

Using the values for Clear Lake water extractions for municipal/industrial uses of 10.8×10^6 m^3/year and for agricultural purposes of 9.95×10^6 m^3/year (Richerson et al. 1994) together with a range of average aqueous TotHg concentrations of 10–20 ng/L in Clear Lake (Suchanek et al. in press-c) yields a range of 0.21–0.42 kg/year of Hg removed from Clear Lake from these diversions. This may represent an over-estimate because some of the extracted water will make its way back to the lake via drainage over agricultural fields and storm drains, however this component has not been quantified.

3.2.4 Biotic Hg Removed by Humans and Wildlife

Using the annual Clear Lake estimates of 17,300 kg of fish removed by sport anglers (Macedo 1991; Cannata 2000), and the additional 12,300 kg of carp and Sacramento blackfish removed commercially, and applying average concentrations of Hg in the various fish species (from CVRWQCB 1985, 2002; Stratton et al. 1987; Suchanek et al. in press-b) yields an average of 0.007 kg/year removed from Clear Lake by humans. Underestimates of catch and wildlife removal values are unknown, but it is possible that they may be as much as the angler and commercial fish removal combined. To be conservative, we doubled this value to 0.014 kg/year, which is still an extremely small portion of the total Hg removal. Thus, a reasonably conservative range for biotic Hg removal is 0.007–0.014 kg/year.

3.3 Storage

3.3.1 Modern Distribution of Hg In Surficial Sediments

The May 2003 Ekman dredge sampling yielded the highest lakebed surficial sediment TotHg concentration during our study (438 mg/kg dw at site O-5), although the CVRWQCB (1987) reported 1,000–1,180 mg/kg dw in near-surface sediments close to the mine. Hg concentrations at each site for October 1992 and October 2003 demonstrate that TotHg had not declined significantly 11 years after the 1992 mine remediation (Fig. 3). In fact, for both the May and October 2003 samplings, a two-tailed Paired *t*-test indicates that on a lake-wide basis, TotHg concentrations have increased significantly over the 11year period ($P = 0.042$). Using the Hg concentrations at the 34 sites, we applied the same ARC/INFO inverse distance weighted interpolation as that used to estimate Hg storage, to calculate the percentage of the Clear Lake sediment area that contained sediment Hg in a range of concentration categories (Table 4). From this calculation, over 85% of the sediment surface area is ≤5 mg/kg dw and ca. 0.1% is greater than 160 mg/kg dw.

3.3.2 Modern/Ongoing Hg Storage

Using extrapolations from ^{210}Pb dating and the DDD horizons for sediment cores from the years 1996 and 2000, we estimate that the average sedimentation rate at the sediment/water interface (as of the year 2000) was 3–4 mm/year (see Osleger et al. in press; Richerson et al. in press); thus, we used an estimated average sedimentation rate of 3.5mm/year for surficial sediments. To obtain a lake-wide estimate of modern annual Hg loading to Clear Lake, we applied the Hg concentration data from surficial sediments collected in 1992 and 2003 at the 34 collection sites (see above) to the inverse distance weighted interpolation GIS modeling approach. Using the modern sedimentation rate of 3.5 mm/year, we calculated annual Hg loading in October 1992/2003 for each arm as follows: Lower Arm = 63.7/70.4 kg; Upper Arm = 158.9/178.2 kg; Oaks Arm = 257.3/319.6 kg; total for Clear Lake = 479.9/568.2 kg. However, these values need to be adjusted. The modeling approach we used assumed a constant sedimentation rate over the entire surface area of the lake. This is almost certainly unrealistic

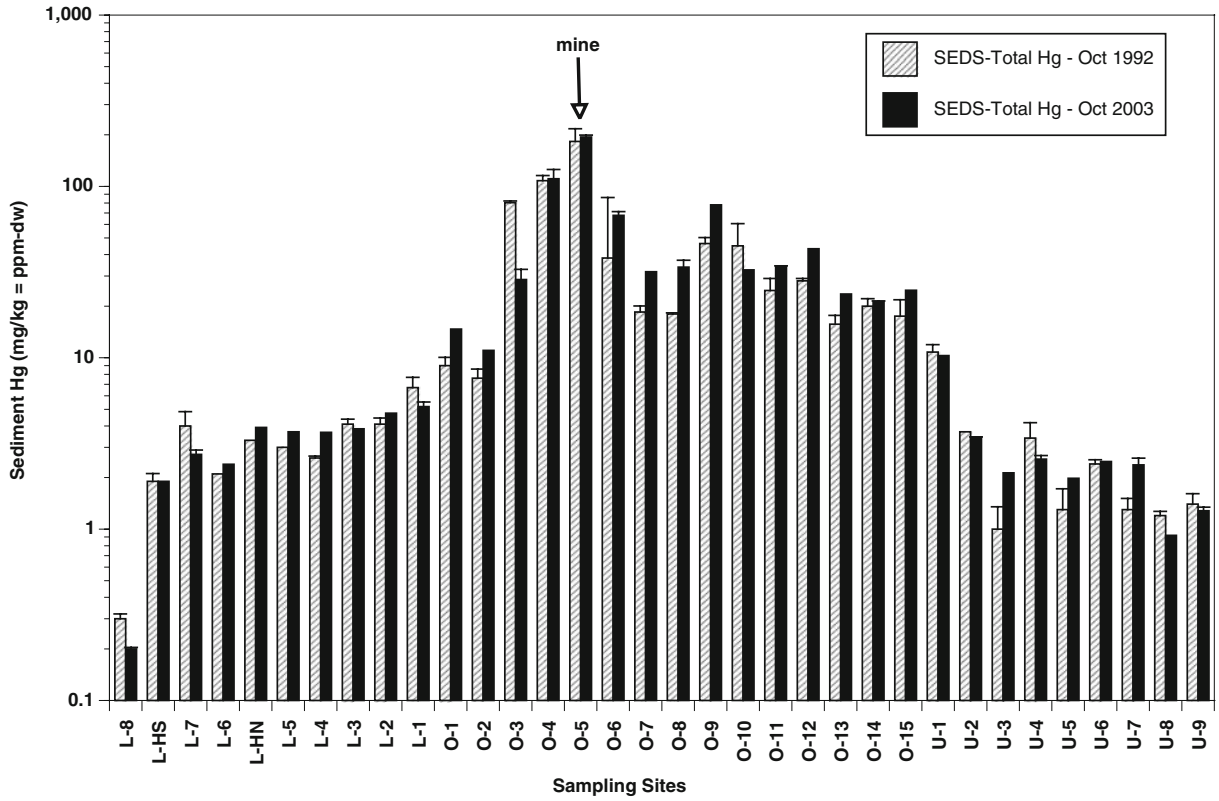

Fig. 3 Mean sediment TotHg concentrations from October 1992 and October 2003 at 34 sites throughout Clear Lake. Site codes starting with *L* lower arm, *O* oaks arm and *U* upper arm. See Suchanek et al. (in press-c) for more specific site locations. *Arrow* indicates location of the mine. *Error bars* represent one standard deviation where replicates were taken

because some of the shoreline areas are rocky and have lower sedimentation rates compared with those sites in the central regions of the lake. 'Sediment focusing,' the process whereby lacustrine sediments are differentially deposited in the deeper regions of lakes (Likens and Davis 1975; Hilton 1985; Blais and Kalff 1995), would likely concentrate sediments in the central regions of each arm of Clear Lake where we collected our cores. Because of the complexities in bathymetry, current regimes, wave action and remobilization of sediment particles by gaseous springs, it would be virtually impossible to calculate an accurate "average" sedimentation rate for the entire area of Clear Lake. However, during the development of a mass balance phosphorus budget for Clear Lake, Richerson et al. (1994) developed a correction factor

Table 4 Area and percent of Clear Lake sediments containing ranges of TotHg (dry wt) concentrations calculated using ArcInfo's inverse distance weighted interpolation routine

Sediment total Hg concentration (mg/kg)	Area in Clear Lake (m^2)	Percent of Clear Lake area
0–5	136,810,000	85.3
5–10	5,380,000	3.4
10–20	5,500,000	3.4
20–40	6,490,000	4.0
40–80	4,710,000	2.9
80–160	1,350,000	0.8
160–438	110,000	0.1
Total area	160,350,000	

for sedimentation rate and sediment focusing of 66%, which provided a reasonably balanced budget based on known inputs and outputs to and from the sediments. Assuming those sedimentation rate processes would be similar, we applied the same sediment focusing correction factor of 66% to our initial Hg loading estimates (above) to yield an estimate for annual Hg loading into Clear Lake for the years 1992/2003: Lower Arm = 42.5/46.9 kg; Upper Arm = 105.8 /118.6 kg; Oaks Arm = 171.6/213.1 kg; total for Clear Lake = 319.9/378.7 kg. Thus, the range of Hg loading for the years in which we have storage estimates is 319.9–378.7 kg/year.

3.3.3 Historic Hg Loading

Hg loading in modern times is markedly different than during the mining era. The magnitude of Hg loading and storage in Clear Lake sediments has varied substantially over the past century and is a reflection of varying mining practices (Richerson et al. 2000, in press; Suchanek et al. in press-e). The average concentration of Hg in Oaks Arm sediments prior to the onset of Hg mining in the 1800s was about 7 mg/kg dw (Sims and White 1981). Hg mining at the SBMM began in 1873, replacing sulfur mining at the site (Suchanek et al. 2003, in press-e). Shaft mining and surface cuts were the predominant methods used until open pit mining became prevalent after the advent of mechanized earth moving equipment in the 1920s (Richerson et al. 2000, in press).

Sediment cores collected in 1996 and 2000, and dated using ^{210}Pb and ^{14}C, provide an excellent record of Hg accumulation in Clear Lake sediments over the past 3,000 years, especially during the most intense mining era after 1900 (Richerson et al. 2000, in press; Osleger et al. in press). During the peak of open pit mining, from 1927 to 1945, ca. 5,000 tons (4.54×10^6 kg) of Hg were extracted from the mine (Suchanek et al. in press-f), with significant increases in the deposition of Hg into Clear Lake sediments during that period (Richerson et al. in press). Sediment Hg concentrations in the middle of the Oaks Arm increased more than ten fold, to about 80–110 mg/kg at some of our coring sites; other locations in the Oaks Arm still had concentrations over 400 mg/kg in the year 2003 (see above).

In order to estimate Hg loading during the height of the mining era (ca. 1935), Hg data from the deep sections of several cores (OA-03, UA-03 and LA-03, collected in 2000) that exhibited Hg peaks from mining (Richerson et al. in press) were compared with Hg data from surficial sediments (Fig. 3) yielding a multiplier factor range of 1.63–2.37 for Hg concentrations between surface and deep sections. This multiplier factor was then applied to the Hg concentrations in surficial sediments collected in the Ekman grab samples (Fig. 3) to estimate what the distribution of Hg concentrations and the lake-wide loading would have been around 1935 based on the peak Hg concentrations documented in the cores. Sedimentation rates during this era have been estimated (using ^{210}Pb dating—Richerson et al. in press; Osleger et al. in press) at ca. 20.4 mm/year at the height of the mining period. Using (1) the inverse distance weighted interpolation GIS modeling approach described above, (2) the sediment focusing factor of 66%, (3) the estimated sedimentation rate of 20.4 mm/year, and (4) the known Hg concentrations from cores for each arm at the height of open pit mining, we estimate that the range of TotHg loading into each arm of Clear Lake during the height of open pit mining would have been: Lower Arm (524 to 726 kg/year), Upper Arm (1,326 to 1,927 kg/year), Oaks Arm (2,381 to 3,463 kg/year); TOTAL = (4,232 to 6,117 kg/year). Further extrapolation of the annual Hg loading for each year during the open-pit mining era and beyond (1927–2000) yielded a cumulative Hg loading of 109,972 kg (ca. 110 metric tons), consistent with the 100 metric tons of Hg estimated by Chamberlin et al. (1990) that were released into the Clear Lake aquatic ecosystem and stored in lakebed sediments.

3.4 Calculation of Hg Input from the Sulphur Bank Mercury Mine

Currently, no direct measurements of Hg loading to Clear Lake from the Sulphur Bank Mercury Mine exist. Our estimates of Hg loading to the lake that are attributed to the mine depend upon several forms of direct measurements, and other calculations that have some degree of uncertainty. Ultimately, the contribution from the mine is a difference calculation between Inputs, Outputs and Storage terms. Because the majority of data collected to date suggest that Hg Input contributions from atmospheric deposition, watershed tributaries, lakebed springs and groundwater, as well as Hg Outputs to the atmosphere, water diversions, biotic

removal and stream outflow from the lake are relatively negligible, the greatest uncertainty lies in the calculation of total ongoing Hg storage in sediments. The uncertainties derive, to a certain degree, from (1) the two sets of direct measurements of Hg in surficial sediments at 34 sites throughout the lake in 1992 and 2003, (2) calculations of modern sedimentation rates from dated cores (Osleger et al. in press; Richerson et al. in press) at 3–4 mm/year (we used an average value of 3.5mm/year) and (3) our estimate of the sediment focusing correction factor (66%). We are very confident in our direct measurement of Hg concentrations in surficial sediments in 1992 and 2003. We are also confident that our estimate of modern sedimentation rates is well bounded and justified. The sediment focusing factor of 66% was derived from a previous study that provided a balanced sediment budget in 1994, and we have no reason to believe that sedimentation patterns have changed since then.

Based on dated cores, Hg loading increased exponentially during the onset of Hg mining from the SBMM (Richerson et al. in press). Ongoing Hg loading to the lake is also related strongly to continuing acid mine drainage input from the mine (Suchanek et al. 2000a, b, in press-e; Shipp and Zierenberg in press). To date, no direct field measurements of Hg loading into Clear Lake contributed by acid mine drainage or groundwater input at the mine site have been performed, although the USEPA has produced some preliminary estimates of Hg contributions from the mine by modeling mine site groundwater flow using data from monitoring wells. Their estimates of Hg loading from the mine site to Clear Lake range from 1.10 to 1.47 kg/year (Jewett et al. 2000).

However, we have taken a different approach. We estimated the current Hg loading contribution of the SBMM by difference calculations using the equation INPUTS − OUTPUTS = STORAGE, where Hg mass terms are defined by:

INPUTS = (atmospheric deposition + tributaries + lakebed springs + groundwater + mine)
OUTPUTS = (efflux to atmosphere + water diversions + biota removal + Cache Creek outflow)
STORAGE = (burial into sediments).

Because we have quantified estimates for the other terms in this equation, including estimates of uncertainty for the component values, solving for the input contribution from the unknown mine term yields a range of annual Hg loading values from the mine of 322.1–330.6 kg/year. We are aware of no other significant sources of Hg input to Clear Lake.

While we are confident in our estimate of the range of Hg contribution from the mine, we do not know the origin of that contribution. Because of the effectiveness of the 1992 remediation, the most likely input source points to ongoing acid mine drainage from the mine into the lake.

3.5 Mass Balance

Using all known inputs, outputs and storage terms, we provide a current best estimate of the range of values for Hg loading into Clear Lake (Fig. 4). To estimate the Hg loading contribution from the mine (the only value for which there exist no direct

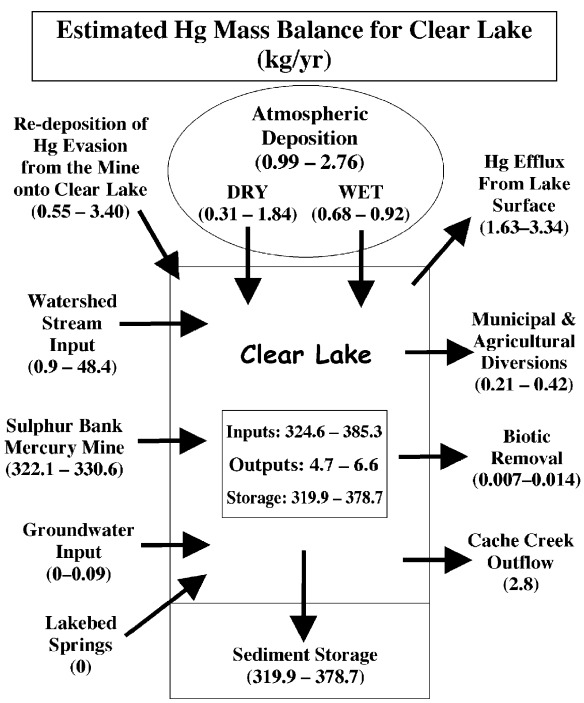

Fig. 4 Estimated TotHg mass balance for Clear Lake (kg/year)

measurements), we have used the minimum and maximum values for the known component inputs, outputs and storage terms to bound the range of estimated values. Solving for the contribution from the SBMM yields a range of estimated annual Hg loading of 322.11–330.63 kg/year, which represents 86–99% of the total Hg loading. Thus, the range of values for TotHg Inputs = 324.6–385.3 kg/year, Outputs = 4.7–6.6 kg/year and Storage = 319.9–378.7 kg/year.

3.6 Reducing Hg Contamination in Clear Lake by Natural Sedimentation

If (1) the primary source of Hg-laden mine rubble (from the tailings and waste rock piles along the mine shoreline) has been mostly stabilized by the 1992 remediation efforts of the USEPA, (2) modern sedimentation rates have been accurately estimated at ca. 3.5 mm/year, (3) no other significant sources of Hg are being introduced into Clear Lake, and (4) maximum bioturbation depth is assumed to be ca. 15 cm (Suchanek et al. in press-d), natural sedimentation would be expected to cover the near-surface sediments. Using the previously defined equation (Reible et al. 1991) and the aforementioned parameters, the half-life of Hg-contaminated sediment burial would be approx. 29.7 years. Bioturbation would continually mix surface Hg to depth, and likely bring some deeper sediments to the surface, thereby increasing the actual time of burial until the majority of these sediments were buried. It would take about five to ten half-lives (ca. 150–300 years) for contaminated material to reach background concentrations. After five half-lives, ca. 3% of the original concentration would remain at the surface and after ten half-lives ca. 0.1% of the original concentration would remain at the surface.

There have, however, been anecdotal observations of scouring and low sedimentation rates in the Oaks Arm near the mine (authors' observations). Thus, if sedimentation is lower near the mine (where the greatest contamination resides) than the average lake-wide sedimentation rate calculated from the dated cores collected at Clear Lake (see Richerson et al. in press), then the estimated time for Hg-contaminated sediments to be buried may be significantly longer than those calculated above.

4 Conclusions

Although Clear Lake is one of the most Hg-contaminated lakes in the world (Suchanek et al. 2000a, in press-e, in press-c), with a well defined point source of Hg emanating from the region of the mine (derived from the ore body in prehistoric times and from Hg mining in historic times), there has been considerable divergence of opinion over the present day source and quantity of Hg loading from the mine to Clear Lake. Clearly, uncertainties exist in the precise quantification of Hg loading from the mine. Based on an approach using a model of groundwater flow through test wells at the mine site and using no other data and assuming no other input from the mine, Jewett et al. (2000) hypothesized that the mine contributes negligible Hg loading (i.e., 1.10–1.47 kg/year) to the lake. However, based on a mass balance approach, incorporating all known inputs, outputs and storage terms, our calculations suggest strongly that Clear Lake receives an estimated 325–385 kg/year of Hg from all sources, with ca. 322–331 kg/year derived from the mine, ca. 86–99% of the total Hg loading to the lake. Thus, using our calculations, the original hypothesis posed is accepted; the Sulphur Bank Mercury Mine currently contributes the vast majority of Hg contamination to Clear Lake.

The resampling of surficial sediments in 2003, at 34 sites originally sampled in 1992, suggests that sediment TotHg has not decreased, but has exhibited a statistically significant increase during the period from 1992–2003. At a minimum, this implies that the 1992 remediation at the mine site has not reduced Hg loading to Clear Lake as of 2003. While it may have reduced erosion from the waste rock piles into the lake, either the remediation may not have been successful in significantly reducing overall Hg loading to the lake, or insufficient time has passed for such a change to be detected.

A likely source of ongoing Hg input to Clear Lake is dissolved Hg originating from the mine. These mine sources could be derived from particulate or dissolved Hg. Annual production of a white flocculent precipitate high in Hg has been observed along the shoreline immediately in front of the mine every year since it was first observed and quantified in 1995 (Suchanek et al. 1997, 2000a) and continues to the present day. These observations indicate that the mine is still actively leaching acidic fluids (pH 2.8–3.0)

into Clear Lake that mix with Clear Lake waters (ca. pH 8) (see Shipp and Zierenberg in press). In addition, acid mine drainage in porewater fluids emanating from the mine in surface releases near the mine and sub-sediment conduits away from the mine are a likely source of dissolved Hg loading to Clear Lake (Shipp and Zierenberg in press) especially during the winter/spring rainy season. It is important to note that the proportion of dissolved TotHg in Clear Lake waters is highest at nearly all sites sampled during winter/spring periods and lowest during summer/fall (Suchanek et al. in press-c), consistent with the hypothesis that the flow of acid mine drainage from the mine site to the lake during higher precipitation periods is responsible for the ongoing input of large volumes of dissolved Hg into Clear Lake (see Shipp and Zierenberg in press). This ongoing flow into the lake is almost certainly driven by the pressure differential created by a 4 m head of water in the Herman Pit (containing ca. pH 3 water) on the mine site relative to the lake surface (Shipp and Zierenberg in press; Schladow and Clark in press).

These results have implications for potential remediation options for elevated Hg concentrations in Clear Lake sediments. First, however, it must be noted that between the termination of mining operations in 1957 and the mine site remediation in 1992 there had been continual input of Hg to the sediments of the Oaks Arm of Clear Lake from erosion of steeply sloped tailings and waste rock piles along the eastern shoreline of the lake (see Suchanek et al. in press-e). The significant remediation effort in 1992, reducing the waste rock slope and adding large protective rip-rap boulders at the shoreline, appears to have been extremely effective in reducing or nearly completely eliminating further erosion. Hg concentrations in surficial sediments collected 11years after the remediation in 2003 should have reflected a significant source reduction from that earlier loading from erosion, but didn't (Fig. 3). This lack of a significant decrease may be unrelated to erosion. Rather, it is more likely related to ongoing acid mine drainage derived from fluid sources that emanate from the mine via surface flow and sub-sediment conduits that introduce Hg dissolved in acid mine drainage into Clear Lake (see Shipp and Zierenberg in press). Any remediation options must consider both solid phase Hg bound to sediments and particles as well as dissolved Hg derived from acid mine drainage.

Based on the evident point source distribution of Hg in the sediments, water and biota of Clear Lake (Suchanek et al. 1998, 2000a, b, in press-c) as well as the mass balance data in this paper, the SBMM appears to be the overwhelming primary source of Hg loading to Clear Lake. However, now it is important to define more precisely the chemical forms of Hg, the origin of that Hg from within the mine site and the quantities of Hg from each of those sources. While cinnabar ore appears to be rather refractory and may not represent as great a risk to biota in Clear Lake (Bloom et al. 2003; Suchanek et al. in press-a), Hg in dissolved form is much more likely to be methylated and therefore become bioaccumulated and toxic. Based on the cumulative data presented to date (summarized in Suchanek et al. in press-e), the most important sources and pathways for ongoing Hg transport from the mine to Clear Lake appear to be: (1) further erosion of Hg-contaminated soils from tailings piles or waste rock piles along the shoreline of the lake, although this is an unlikely significant source because of the effectiveness of the 1992 remediation, (2) transport of dissolved and/or particulate Hg through conduits in the unconsolidated rubble in those tailings or waste rock piles, (3) leaching of Hg in dissolved form from those same tailings or waste rock piles flowing into the shallow near-shore lake environment, and (4) transport of dissolved Hg in acid mine drainage that follows sub-sediment pathways out into Clear Lake.

Because of the complexity of the mine site, we recommend further investigations that involve direct measurements of Hg loading from the mine site. This approach should focus on the importance of accurately quantifying the different forms and sources of Hg loading from the mine site into Clear Lake before remediation efforts are begun. This approach should also include quantification of Hg loading from both particulate and dissolved forms, and should quantify the amount of loading being transported over the surface of the mine soils and within the tailings and waste rock piles, as well as along potential conduits and through sub-sediment pathways out into the lake.

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