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MERCURY CONCENTRATIONS AND LOADS IN A LARGE RIVER SYSTEM TRIBUTARY TO SAN FRANCISCO BAY, CALIFORNIA, USA

Nicole David,*† Lester J. McKee,† Frank J. Black,‡ A. Russell Flegal,‡ Christopher H. Conaway,‡ David H. Schoellhamer,§ and Neil K. Ganju§
†San Francisco Estuary Institute, 7770 Pardee Lane, Oakland, California 94621, USA
‡University of California Santa Cruz, 1156 High Street, Santa Cruz, California 95064, USA
§U.S. Geological Survey, 6000 J Street, Sacramento, California 95819

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Abstract—In order to estimate total mercury (Hg_T) loads entering San Francisco Bay, USA, via the Sacramento–San Joaquin River system, unfiltered water samples were collected between January 2002 and January 2006 during high flow events and analyzed for Hg_T. Unfiltered Hg_T concentrations ranged from 3.2 to 75 ng/L and showed a strong correlation ($r^2 = 0.8$, $p < 0.001$, $n = 78$) to suspended sediment concentrations (SSC). During infrequent large floods, Hg_T concentrations relative to SSC were approximately twice as high as observed during smaller floods. This difference indicates the transport of more Hg-contaminated particles during high discharge events. Daily Hg_T loads in the Sacramento–San Joaquin River at Mallard Island ranged from below the limit of detection to 35 kg. Annual Hg_T loads varied from 61 ± 22 kg ($n = 5$) in water year (WY) 2002 to 470 ± 170 kg ($n = 25$) in WY 2006. The data collected will assist in understanding the long-term recovery of San Francisco Bay from Hg contamination and in implementing the Hg total maximum daily load, the long-term cleanup plan for Hg in the Bay.

Keywords—Loads Sacramento River Mercury San Francisco Bay

INTRODUCTION

Background

Management of mercury (Hg) contamination in large, complex aquatic systems, such as San Francisco Bay, USA, often requires accurate and precise measurements of Hg loads. Because of recent efforts to calculate the maximum amount of total mercury (Hg_T) that can enter San Francisco Bay while still meeting water quality guidelines (http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/TMDLs/sfbaymercurytmdl.shtml), environmental managers have placed a priority on obtaining accurate measurements of Hg loads from the Sacramento–San Joaquin Valley. The Sacramento–San Joaquin River system is impacted by local to regional Hg contamination from historic gold mining and Hg mining [1,2] as well as atmospheric Hg contamination from regional to global sources [3]. The current management approach is based on the premise that Hg_T reductions will result in reduced concentrations of methylmercury entering the food web. While this premise is considered to be generally true, it is also known that the factors controlling Hg methylation, such as the bioavailable fraction of Hg_T and the factors controlling activity of methylating bacteria, can vary substantially [4]. For example, there are large deposits of cinnabar, meta-cinnabar, and elemental Hg in the study area, which could enhance Hg_T loads in rivers, but these forms of Hg are not that bioavailable [5]. Nonetheless, assessment of Hg_T loads is an appropriate starting point in remediation efforts.

Watershed description

San Francisco Bay is a group of interconnected bays located on the Central Coast of California, USA (Fig. 1). Numerous small tributaries drain the Coast Range around the margin of the Bay, representing a watershed area of approximately 6,650 km^2 [6]. However, regarding size and discharge, these tributaries are minor compared to the Sacramento and San Joaquin river watersheds that together drain 154,000 km^2 (~37% of the state of California). Even during storm events, discharge contribution from the San Joaquin River to the Delta represents only approximately 10% of the flow from the Sacramento River, Yolo Bypass, and other associated tributaries (http://wayback.archive-it.org/754/20070615194345/).

The Sacramento River is the 96th largest river system in the world based on average annual discharge [7]. The River is also the largest source of freshwater to San Francisco Bay, the largest estuary on the west coast of North America. With an estimated population of 2,800,000 and a rapid increase in population of over 10% over the past five years (http://quickfacts.census.gov/qfd/states/06/06103.html), the Sacramento Valley is the most populated area within the River watershed. This area also supports an extensive and diverse agriculture, which accounts for the greatest water use in the watershed. The Sacramento River stretches approximately 650 km from its headwaters near Mount Shasta in northern California through the Sacramento–San Joaquin River Delta to San Francisco Bay. With 432 dams that have been built within the watershed over the past 50 years, the Sacramento River's hydrology is extremely modified. It currently has an average annual flow of $25{,}000 \times 10^6$ m^3 and an annual average suspended sediment load of 1×10^6 t [8].

Precipitation in central California is winter dominated, with 94% of the annual precipitation historically occurring in Sacramento between October and April (http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?ca7630). The largest runoff events typically occur in January, February, or March. During these large runoff events, water spills over weirs from the

* To whom correspondence may be addressed (nicoled@sfei.org).
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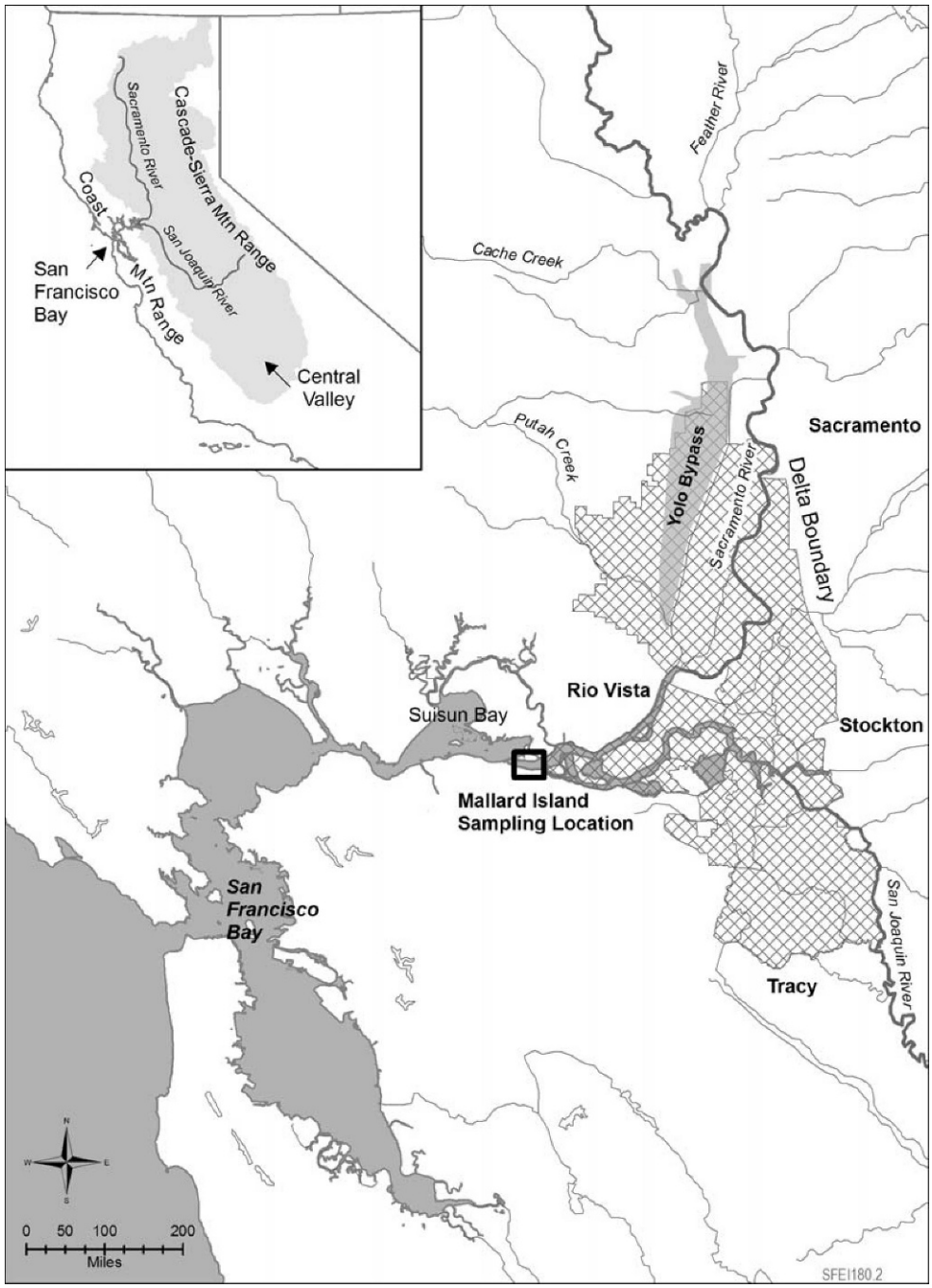

Fig. 1. Map of San Francisco Bay, California, USA, and the sampling site at Mallard Island, California, USA, where water from the Sacramento–San Joaquin River Delta enters the estuary. The sampling site is approximately 8 km downstream of the confluence of the Sacramento and the San Joaquin Rivers. During floods, water is diverted from the Sacramento River into the Yolo Bypass as part of the Sacramento River flood control system. Large flows bypass the city of Sacramento and flow back into the Sacramento River near Rio Vista, north of the Sacramento–San Joaquin River Delta. The Delta is marked by the cross hatching.

Sacramento River into the Yolo Bypass (Fig. 1) when discharge exceeds 1,980 m^3/s. The Bypass provides flood protection for the city of Sacramento by diverting water through a floodplain. During years of very high river discharge, such as the El Niño event of 1998, as much as 85% of the total flow of the Sacramento River is channeled through the Yolo Bypass. Before it flows back into the Sacramento River near Rio Vista, the Bypass receives additional flow from several tributaries draining the Coast Range Mountains, an area known for historic Hg mining and environmental Hg contamination [9]. One of these tributaries, Cache Creek, has Hg concentrations in water exceeding 250 ng/L and in bed sediment exceeding 500 ng/g dry weight [9].

Rationale for the present study

Particle-bound contaminants that are known to cause toxicological impacts to humans and wildlife in the river delta, the Bay, and the coastal ocean of California include Hg, polychlorinated biphenyls, and others [10,11]. Mercury poses a water quality problem for the Sacramento River, both in terms

of impact on the riparian ecosystem and as a principal source of Hg to the Delta region and San Francisco Bay [9,12,13]. San Francisco Bay has been listed as impaired by the State of California for Hg and a range of other contaminants as defined by section 303(d) of the U.S. Clean Water Act since the early 1990s. The main concern for Hg in the Bay is primarily due to elevated concentrations in fish consumed by humans and wildlife [12]. Accordingly, fish consumption advisories have been issued for San Francisco Bay and the Sacramento–San Joaquin River Delta (http://www.oehha.ca.gov/fish/general/sfbaydelta.html).

Even though a few studies reported Hg concentrations throughout the Sacramento River Basin [9,14], long-term monitoring data from the Sacramento–San Joaquin River system and Hg_T loads were not previously quantified. Consequently, to assess fluvial transport of Hg_T to San Francisco Bay, loads from the Sacramento River watershed, including the contribution of flow from the Yolo Bypass, were studied during high flow events.

METHODS

Parameters measured

Sacramento River discharge has been estimated daily since water year (WY; a water year begins October 1st and ends September 30th of the following year) 1930 by the California Department of Water Resources (DWR). The DWR uses a water balance model, called Dayflow, to calculate a variety of inputs and outputs relevant to the management of the California State Water Project. One of the output parameters is termed ''Delta outflow'' and is the best estimate of discharge from the Sacramento–San Joaquin River system on a daily basis. This measure of discharge was used to calculate the loads presented in the present study. Details of the Dayflow model structure and input and output data have been described by DWR (http://iep.water.ca.gov/dayflow/).

Suspended sediment concentrations (SSC) were measured in the Sacramento River at Mallard Island (38°02′34.06″N, 125°55′12.48″W, WGS 84) near Pittsburg, CA, USA (Fig. 1) since WY 1995. Samples were collected approximately 1 m below the water surface at the end of a pier near a deep water ship channel. Automatic turbidity measurements were taken at 15-min intervals with a self-cleaning optical sensor managed by the U.S. Geological Survey (USGS). All data were retrieved using an automated data processing system and edited utilizing MATLAB® software (The MathWorks) [15]. Turbidity data were converted to SSC using simple linear regression, as described elsewhere [15]. These data form an ideal basis for estimating Hg loads and were previously reported and used to develop new estimates of suspended sediment loads entering San Francisco Bay for WY 1995 to 2003 [8]. Direct determinations of suspended sediment concentrations were made using established methods [16]. Samples were collected in dry, particle-free, leak-proof 500 ml low-density polyethylene bottles. Samples were stored at room temperature for no longer than 10 d prior to analysis. Precision of the SSC measurements, based on field replicates, was less than 5% relative standard deviation.

Because of the high affinity of Hg_T for particles, these SSC data represent an effective means for indirectly estimating Hg_T loads. Partition coefficients (K_d) for Hg have been consistently reported as very high in San Francisco Bay [17,18] and estuarine systems elsewhere [19,20]. This observation was confirmed in the present study, with the log K_ds in six samples collected at Mallard Island in 2002 to 2003 ranging from 5.1 to 5.3. As a result, Hg_T concentrations were only measured in unfiltered water samples.

Sample collection

Water samples for analysis of unfiltered Hg_T in Delta outflow were collected from the pier at Mallard Island and focused on high discharge periods during the five wet seasons of WYs 2002 to 2006, which were typically from December to May. One to three unfiltered water samples were collected per day to characterize Hg_T variation in response to floods. Water samples were collected from approximately 0.25 to 1.0 m below the water surface adjacent to the pier using established trace metal clean techniques [21–24]. Specialized sampling equipment was prepared and trace-metal clean handling techniques were followed. Unfiltered water samples were collected using a peristaltic pump fitted with C-Flex™ tubing (Cole-Parmer Instruments) and a Teflon® (DuPont) sampling tube (Saint-Gobain) facing into the direction of flow and held in the water column with an aluminum pole. Unfiltered water was pumped directly into acid-cleaned glass (2002–2003), Teflon® (2003–2006), or polyethylene terephthalate (2006) bottles [25,26], which were then double bagged in polyethylene zip-top bags. Samples collected from 2002 to 2005 were frozen in the field with dry ice, amended to 1% bromine monochloride (BrCl) during thawing, and allowed to oxidize for at least 4 h prior to analysis (2002–2003), with the majority of samples being analyzed at least 16 h after the addition of BrCl (2003–2005). Samples collected in WY 2006 were kept cold and dark until preservation with BrCl within 12 h of collection, and were analyzed within 16 h of BrCl addition.

Sample analysis

Determination of Hg_T in water samples was performed using standard methods [24,27]. Samples were oxidized by amendment to 1% BrCl and allowed to oxidize as described above, then immediately before analysis the samples were pre-reduced using NH_2OH-HCl. Analyses were then performed using tin chloride reduction, gold trap amalgamation, and quantification by cold vapor atomic fluorescence spectrophotometry.

Quality assurance

Quality assurance samples represented a minimum of 10% of each Hg_T sample batch. The average minimum detection limit for Hg_T over 11 d of analyses, calculated as three times the standard deviation of method blanks, was 0.15 ng/L Hg. Field and bottle blanks were statistically indistinguishable from analytical blanks ($p > 0.05$, t test). Inorganic Hg(II) spike recoveries ranged from 83 to 105%, with a mean of 95% ($n = 24$). The mean of the standard deviation of analytical triplicate and duplicate measurements was 0.34 ng/L Hg ($n = 63$), representing a mean relative standard deviation of 5.7%. Field replicates were collected during each sampling season, with a mean percent difference between replicates of 7.3% ($n = 10$) and with a standard deviation of 7.4%. Blank, spike, and replicate measurements indicated no measurable difference between samples or blanks kept in Teflon versus polyethylene terephthalate containers.

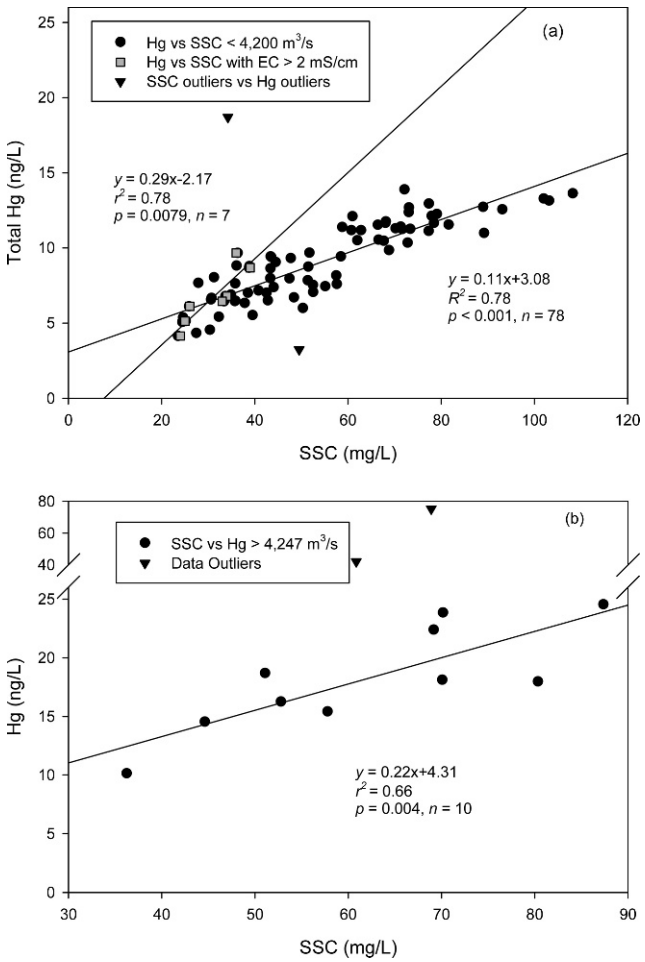

Fig. 2. Correlation between suspended sediment concentration (SSC) and total mercury (Hg_T), generated from all data points collected in the present study. Data outliers (downward triangles) were not included in the equation describing the regression line. (**a**) Mercury concentrations during flows below 4,200 m^3/s. (**b**) Mercury concentrations during flows above 4,200 m^3/s. The two regression lines describing the low salinity flow data were significantly different ($p = 0.0001$).

Calculation of Hg_T loads

The Hg_T loads were calculated using a modification of the methods originally developed for suspended sediment described by McKee et al. [8]. Briefly, Hg_T concentrations were estimated for 15-min intervals using equations derived from simple linear regression for the relationship between SSC and unfiltered Hg_T concentrations. Equations were developed for three different flow and salinity conditions: low flow and low salinity, low flow and high salinity, and high flow (Fig. 2a and b). The regression equation utilized hourly electrical conductivity records available from DWR for Mallard Island (http://cdec.water.ca.gov/cgi-progs/queryFx?s=mal). The relationship between unfiltered Hg_T concentrations and SSC (Fig. 2) was assumed to be constant over time. A similar relationship (0.35 mg/kg) was observed by Schoellhamer et al. [28] for a regression of Hg_T versus SSC in Lower South San Francisco Bay. The higher slope for Lower South Bay is consistent with the history of contamination in this region, which receives runoff from the historic New Almaden Hg mining district.

Missing SSC data were estimated using linear interpolation. Most missing data occurred during low flows when only a very small portion of the annual load (average of 12%) is transported [8]. During WY 2006, SSC data were missing during an extended high flow period (March 20 to May 2, 2006) for which a regression equation ($r^2 = 0.14$, $p < 0.0001$, $n = 3{,}300$) from the previous flood hydrograph was used to estimate sediment concentrations. Estimated 15-min Hg_T concentrations were averaged for each day and combined with daily Delta outflow from the Dayflow model to derive daily advective loads of Hg_T (g). Advective loads represent the contribution of mean flow and SSC, whereas dispersive loads result from the correlation of tidal velocity and SSC fluctuations. In strongly tidal environments, dispersive loads must also be quantified. A correction factor was applied to this daily advective Hg_T load to account for dispersive load using the same method described for suspended sediment [8]. Dispersive load at this location is always landward; neglecting this would cause the load estimates to be biased high (seaward) [8]. The relative contributions of advective and dispersive components to the Hg_T load were estimated using point velocity and concentration data at Mallard Island that were only available for a shorter period of record (WYs 1994 and 1996). The relationship between the ratio of dispersive to advective load and Delta outflow was determined using the point velocity and SSC data over the range of flows encountered during these two WYs. The reasonable assumption was made that this relationship would be valid for other WYs [8]. Although dispersive load is small during high flow periods, it is substantial during the rest of the annual cycle when tidal flushing is dominant. The sum of dispersive and advective loads, therefore, culminated in an improved estimate of Hg_T load. The method of Hg_T loads estimation described above was applied to WYs 2002 to 2006 (the sampling period in which discrete Hg_T measurements were made) and to WYs 1995 to 2001 (for which only discharge, SSC, and salinity data exist). Because no direct measurements of Hg_T concentrations were made prior to October 1, 2001, the estimates of Hg_T loads for this period should be considered tentative.

Estimating material loads in fluvial systems requires a number of assumptions, and each term in the load calculation has an associated error. In general, the errors associated with load calculations are seldom reported in the hydrogeochemical science literature, a fact that allows claims of differences between quantities or suggestions of trends that would not be statistically supported if an analysis of errors was completed. Errors in measuring or estimating loads should not be confused with natural variability associated with climate or some other forcing mechanism. For example, McKee et al. [8] reported that sediment loads in the Sacramento River in the Mallard Island cross section varied from 0.3 to 2.6×10^6 t/year between WY 1995 and 2003. Most of this variation was associated with interannual weather differences. The reported nine-year average in sediment load was 1.2 $\pm$ an error of 0.4×10^6 t/year. This error term represented the sum of the errors associated with both the observations and regression analyses. The error estimation method reported by McKee et al. [8] for suspended sediment was modified to account for additional errors associated with determination of Hg_T loads. The error associated with reducing the 15-min SSC to daily averages (error A in the formula below), errors in flow measurement (error B), laboratory analysis of SSC (error C), SSC-turbidity regression (error D), and heterogeneity in the cross section at Mallard Island (error E) [8] were accounted for. Three additional sources of errors were accounted for to estimate

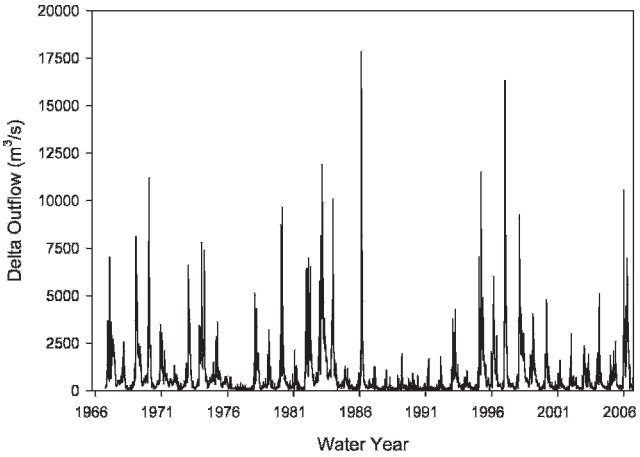

Fig. 3. Daily water discharge (Delta outflow) at Mallard Island, California, USA, measured in cubic meters per second (m^3/s) using output from the Department of Water Resources Dayflow model over a 40-year time period (WYs 1967–2006).

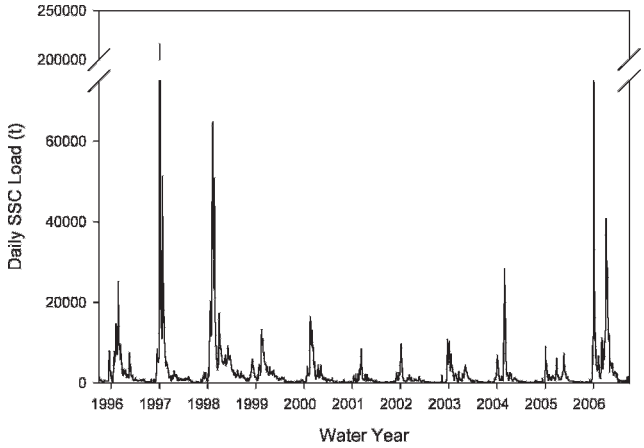

Fig. 4. Daily suspended sediment concentration (SSC) loads at Mallard Island, California, USA, measured in metric tons (t) estimated over a 12-year time period (WYs 1995–2006).

the Hg_T component of the load. The error associated with collection of the sample was set at ±7.3% (error F) based on field replicates, and the error associated with laboratory analysis of Hg_T was estimated to be ±5.7% (error G) based on analytical replicates (see quality assurance section above). The error associated with the Hg-SSC regression was set at ±12% (error H), based on flow-weighting the application of the Hg_T-SSC regression equations (Fig. 2a and b). A total error of ±36% for annual Hg_T loads was calculated as follows:

$$\begin{aligned}\text{Error} &= \left(A^2+B^2+C^2+D^2+E^2+F^2+G^2+H^2\right)^{0.5}\\ &= \left(0.7^2+5^2+5^2+10^2+30^2+7.3^2+5.7^2+12^2\right)\\ &= \pm 36\%\end{aligned}$$

RESULTS

Annual flow

Flow in the Sacramento River at Mallard Island is typified by large intra- and interannual variation (Fig. 3). Greater than 80% of the annual flow occurs between the months of December and May, and the wettest month typically yields 30% of the total annual flow. Annual discharge during the study period of Hg_T observations (WY 2002–2006) varied from 11,000 × 10^6 m^3 to 50,000 × 10^6 m^3 and averaged 23,000 × 10^6 m^3. These discharges were below those observed during WYs 1995 to 2001 (range = 8,600 × 10^6 to 54,000 × 10^6 m^3; average = 34,000 × 10^6 m^3) and less than the 40 year range (3,100 × 10^6 to 79,000 × 10^6 m^3) and average (25,000 × 10^6 m^3).

Sediment concentrations

Suspended sediment concentrations measured at 15-min intervals varied from 12 to 320 mg/L during WYs 2002 to 2006. The highest SSC concentrations occurred during floods when rain-induced runoff supplied sediment from the upper Sacramento–San Joaquin River watershed and high flows supplied the energy to resuspend sediment stored in Delta channels. Continuously measured SSC for WYs 1995 to 2001 varied from 5.0 to 420 mg/L, with the highest concentrations measured during the largest flood in the last 40 years (flood peak January 3, 1997). Daily averaged SSC varied from 8.9 to 140 mg/L during WYs 2002 to 2006 and from 14 to 220 mg/L during WYs 1995 to 2001. The similarity of the sediment loads between these two periods supports the assumption that the relationships between SSC and Hg_T concentrations were applicable for the entire 12-year sediment record.

Sediment loads

Daily suspended sediment loads varied from −4.2 to 110,000 t during WYs 2002 to 2006 and from −7.3 to 210,000 t during WYs 1995 to 2001 (Fig. 4). It was estimated that net upstream transport occurred on just 70 d or 1.6% of the time during the 12-year sediment record. However, given errors associated with the load calculation, the magnitude of upstream transport is not statistically different from zero. During this 12-year period, 5, 10, 20, 50, and 90% of the total suspended sediment load through the Sacramento–San Joaquin River Delta measured at Mallard Island (14 × 10^6 t) occurred in just 0.1, 0.2, 0.7, 5.2, and 37% of the days, respectively. This compares with 5, 10, 20, 50, and 90% of the flow occurring in just 0.4, 1.0, 2.6, 11, and 51% of the days during the entire 12-year record. This difference illustrates the importance of observations made during periods of high flow in climatic regimes with high intra- and inter-annual flow variability, even in large watersheds such as the Sacramento River.

Hg_T concentrations

Unfiltered Hg_T concentrations in the Sacramento–San Joaquin River Delta varied from 4.1 to 25 ng/L during WY 2002 to 2006, with a flow-weighted average particulate concentration of 0.2 mg/kg. The only exceptions were four samples with unfiltered Hg_T concentrations of 3.2, 19, 42, and 75 ng/L, which were determined to be outliers of the linear regression between SSC and Hg_T. These outliers occurred during three different floods, and there was no reason to reject the data based on quality assurance. The working hypothesis was that the cause of the outliers could have been erosion or resuspension of exceptionally high levels of Hg-contaminated sediments stored near-field in bed, bank, or wetlands deposits. However, other observations (N.K. Ganju, unpublished data) support the conclusion that the water column at the sampling location is well mixed. Alternatively, the anomalously high Hg_T concentrations could have been introduced into the sample with plant or invertebrate detritus. While there was no

Table 1. Annual sediment and Hg loads at Mallard Island, California, USA, from 1995 to 2006. Mercury load estimates were revised after different concentrations were found during different flow scenarios

Water year	Flow (Mm^3)	Sediment ± error (t)	Hg ± error (kg)
1995	52,000	2.6 ± 0.8	600 ± 220
1996	31,000	1.0 ± 0.3	210 ± 76
1997	42,000	2.2 ± 0.7	580 ± 210
1998	54,000	2.4 ± 0.8	540 ± 190
1999	28,000	0.8 ± 0.3	160 ± 59
2000	22,000	0.7 ± 0.2	140 ± 51
2001	8,600	0.3 ± 0.1	53 ± 19
2002	11,000	0.3 ± 0.1	61 ± 22
2003	17,000	0.5 ± 0.2	100 ± 36
2004	19,000	0.6 ± 0.2	130 ± 47
2005	19,000	0.4 ± 0.1	86 ± 31
2006	50,000	2.0 ± 0.6	470 ± 170
Average	29,000	1.2 ± 0.4	260 ± 94

reason to reject these outlier data, there was a possibility that their use would bias the Hg_T load calculation unduly. Therefore, the outliers were not used to develop the regression equations (Fig. 2), to interpolate the data between observations, or to estimate Hg_T concentrations and loads for the extended sediment record because they do not represent commonly occurring conditions in the system.

Based on the regression equations (Fig. 2) and the assumption that there are no long-term temporal trends, it was estimated that unfiltered Hg_T concentrations in the Sacramento–San Joaquin River Delta at Mallard Island during WY 1995 to 2006 would have varied from 1.8 to 54 ng/L. The U.S. Environmental Protection Agency recommends three water quality criteria for mercury: the 1-h episodic Hg_T concentration is not to exceed 2,400 ng/L (http://www.waterboards.ca.gov/sanfranciscobay/basin_planning.shtml); the 4-d average Hg_T concentration is not to exceed 25 ng/L; and the 30-d average Hg_T concentration is not to exceed 50 ng/L [29]. The results of the present study suggest that the 1-h and 30-d water quality criteria were not exceeded in the sampling cross section at Mallard Island. However, the 4-d average Hg_T concentration was exceeded during six time periods for WYs 1995 to 2006. The periods of exceedance were 4 to 10 d long, and the highest 4-d average Hg_T concentration was estimated to be 49 ng/L from January 13 to 16, 1995.

Hg_T loads

Daily Hg_T loads varied from below the limit of detection to 35 kg during WYs 2002 to 2006 and from −0.1 to 57 kg during WYs 1995 to 2001. Again, although upstream Hg_T transport was calculated for some days in the dry season, the upstream Hg_T transport is not statistically different from zero for the same reasons as stated above for suspended sediment loads. During high flows, Hg_T loads were greatest, and during the 12-year record, 5, 10, 20, 50, and 90% of the Hg_T load occurred in just 0.1, 0.2, 0.6, 4.3, and 42% of the days, respectively. Thus, to observe most of the load in climatic regimes with high intra-annual flow variability, sampling strategies must focus on high flows, even in large watersheds such as the Sacramento River. Flood-induced increases in particulate Hg concentrations were slightly more persistent in the system, potentially because a small component (11 to 24%) of Hg_T is transported in the dissolved phase (based on six samples collected during low to moderate flows). Estimated annual Hg_T loads ranged from 61 ± 21 kg in WY 2002 to 470 ± 170 kg in WY 2006 during the period of Hg_T observations (Table 1). For the period with no Hg_T measurements (WY 1995–2001), Hg_T loads were calculated that would have varied from 53 ± 19 kg in WY 2001 to 600 ± 220 kg in WY 1995. Based on these calculations, the average annual Hg_T load passing into San Francisco Bay through the cross section at Mallard Island for WY 1995 to 2006 was 260 ± 94 kg (Table 1).

DISCUSSION

The more accurate estimates in the present study of long-term Hg_T loads to San Francisco Bay via the Sacramento–San Joaquin River system will help to better inform efforts to mitigate and reduce Hg contamination. The improvements made were achieved by applying a better sediment-loading methodology, a new estimate of suspended sediment load, improved Hg_T concentration data collected during large storms, and continuous SSC data as a surrogate for Hg_T concentration based on different Hg_T-SSC relationships.

The use of the high affinity of Hg_T for particles and the measured relationship between Hg_T and SSC concentrations allowed for Hg_T loads to be estimated using sediment transport, rather than the more commonly used method of approximating pollutant loads by measuring discharge (an easily measured parameter) and multiplying by a pathway-specific Hg concentration factor. The use of suspended sediment loads that have been directly or indirectly measured to estimate Hg_T loads obviates errors associated with the attenuation of eroded sediments (or buffering capacity), which increases with increasing watershed size [30,31]. The storage of some metals, for example, in the sediments of the fluvial reaches of channels and floodplains is typically 10 to 50%, and as high as 95%, of the magnitude of channel loads [32]. As a result, relying simply upon discharge to estimate Hg loads will result in inaccurate results due to the inability to account for the transport, deposition, and remobilization of Hg contaminated sediments within a watershed under different flow regimes. Even when sediment loads are used to estimate pollutant loads, concentration data are often collected during low-flow periods, in tidal reaches, or in reaches further upstream from the margin of the coastal ecosystem of interest and may not be applicable for load calculations. These uncertainties will be reflected in load estimates and lower confidence in subsequent management initiatives.

Although storage of sediments within large watersheds and associated buffering capacity can be viewed as ecologically beneficial aspects of large river systems, in the case of mercury this may not be accurate. The transformation of labile Hg into methylated forms is a potential consequence of long residence times and storage that might lead to greater bioaccumulation in ecosystems downstream.

Processes of Hg transport

Rainfall-induced river flow causes an increase in both suspended sediment and Hg_T concentrations in small and moderate-sized river systems with watershed areas of $<$100,000 km^2 [e.g., 33–38]. These increases occur because of the combined effects of erosion and resuspension of sediment and Hg within the channel [9] and an increased supply of sediment and Hg from outside the channel systems. This additional sediment originating outside the channel can be due to landslide, debris flow, gully, or sheetwash sediment supply [35], while the Hg can also be derived from contaminated tailings or other mining material [39], or urban and agricul-

tural sources [34,36]. The spatial and temporal coupling of these processes increases in complexity as watershed size increases. For example, as watershed size increases, so too does the heterogeneity of rainfall, runoff, and snowmelt. In addition, large river systems typically have heterogeneous land uses that include large areas of agriculture and patches of urban, industrial, and mining areas. These systems also usually have floodplains or deltas and are often managed to provide flood protection and water for irrigation and municipal water supplies. These factors combine to confound typical rainfall–runoff relationships found in smaller river watersheds, as well as the quantification of processes related to water flow, sediment transport, and contaminant cycling.

Despite these confounding factors in larger watersheds, a strong relationship exists between SSC and unfiltered Hg_T in the Sacramento–San Joaquin River system, as has previously been described in many of the smaller watersheds [35]. However, unlike many of the studies of small river watersheds, the relationship changed depending on the flow regime. As shown in Figure 2, particles mobilized during the larger discharge events (above 4,200 m^3/s) had 1.9 times higher ($p < 0.001$, t test) Hg_T concentrations normalized to SSC than those transported at lower flows (below 4,200 m^3/s). During storms that induce moderate flows, the data suggest that the Hg_T load in the system is dominated by urban and agricultural sources. At increased flows above a threshold, which appears to be roughly 4,200 m^3/s, proportionally greater levels of Hg-contaminated particles derived from historic mining sources in the watershed [9] are transported through the system mixing with the less contaminated urban- and agricultural-derived particles [40].

Another relationship between SSC and unfiltered Hg_T was found to exist for tidally derived high salinity water masses flowing inland from Suisun Bay. These waters had moderate levels of Hg-contaminated particles with an average Hg_T/SSC ratio of 0.29 mg/kg that were mobilized landward by tidal currents during low flows. This observation appears consistent with previous discussions of the distribution of contaminated sediments in the Bay–Delta system and the notion that the largest and most contaminated mass of sediment passed into San Francisco Bay many decades ago [41].

Magnitude of annual loads

Management of sensitive coastal systems requires the determination of river contaminant loads with an accuracy that enables comparisons to other mass inputs, a situation that is confounded by limited data and methodologies for data collection and interpretation. The present study estimates that the average annual Hg_T load entering San Francisco Bay via the Sacramento–San Joaquin River (260 ± 94 kg) is less than half of the previous estimates. The variation in Hg_T loads reported does not reflect changes in the Sacramento–San Joaquin River or Delta, but rather improvements in sediment load data and Hg_T concentrations that have lead to an improved understanding of Hg_T transport.

In 1979, Krone estimated a sediment load of 3×10^6 t for the Sacramento–San Joaquin River (http://www.estuaryarchive.org/archive/conomos_1979). This calculated load is substantially higher than actual contemporary sediment loads for two reasons. First, suspended sediment loads in the Sacramento River decreased by one half from 1957 to 2001 (http://repositories.cdlib.org/jmie/sfews/vol2/iss2/art2), and second, Krone's original estimate relied upon the incorrect assumption that no sediment was stored within the Delta [42]. Using improved methods for measuring and calculating suspended sediment loads, McKee et al. [8] recently reported a 9-year average suspended sediment load for the Sacramento–San Joaquin River of $1.2 \times 10^6 \pm 0.4 \times 10^6$ t.

Similarly, the Hg_T concentration data for water and suspended sediment of the Sacramento–San Joaquin River required to accurately estimate Hg_T loads have only recently been collected. Prior to 2000, the only measurements of Hg_T in this river system were collected either upstream of the Delta during floods [13,14] or during low river flow at the head of the estuary [17,43]. Although previous studies [9,14] have documented the amount of Hg_T transported down Cache Creek and the Sacramento River, the present study is the first to provide estimates of Hg_T loads entering San Francisco Bay via the Sacramento–San Joaquin River over multiple years and under a range of climatic extremes and different flow regimes.

The factors that underpin the improved Hg_T loads calculated in the present study were as follows: the collection of unfiltered Hg_T during storms when the majority of Hg is transported in the particulate phase; improved estimates of suspended sediment load [8]; and the use of continuous SSC data as a surrogate for Hg_T based on the sediment and Hg_T relations. The methods presented here are applicable to other large watersheds, and if applied elsewhere would likely facilitate more effective management of Hg in sensitive coastal ecosystems.

Comparison to other studies

Unfiltered Hg_T concentrations measured in the Sacramento–San Joaquin River at Mallard Island during this five-year study (3.2 to 75 ng/L) were similar in magnitude to those reported previously for rivers in the Central Valley of California [13,40], although method and site-specific differences contribute to some variation. Gill and Bruland [44] reported a Hg_T concentration of 4.6 ng/L for the Sacramento River at Freeport. Roth et al. [45] found Hg_T concentrations ranging from the detection limit to 81 ng/L between Shasta Dam and Freeport. Foe and Croyle [13] described unfiltered Hg_T concentrations in the Sacramento River between 2.4 and 87 ng/L and in the Yolo Bypass between 7.2 and 700 ng/L. Domagalski [40] reported concentrations of 2.0 to 18 ng/L throughout the Sacramento River Basin and a mean of 30 ng/L for the Yolo Bypass. In a later study by Domagalski [14], concentrations of 2.6 to 11 ng/L and 17 to 20 ng/L were measured throughout the Sacramento River Basin and Yolo Bypass, respectively, with the highest concentrations at a site downstream of a historic mining area. Conaway et al. [17] reported Hg_T concentrations of 1.2 to 46 ng/L in the North Bay and the lower end of the Sacramento and the San Joaquin Rivers, and Choe et al. [18] found Hg_T concentrations ranging from 4.0 to 20 ng/L also in the northern part of San Francisco Bay.

A comparison of yield estimates (annual amount of Hg load normalized to watershed area) from the Sacramento–San Joaquin Delta with other large river systems in the world suggests that Hg contamination averaged across the entire Sacramento watershed (154,000 km^2) is relatively low (1.7 g/km^2/year). However, this could be attributed to the hydrological modifications that were made to the rivers over the past 50 years. The size of the watershed actively contributing to the loads measured at Mallard Island would be much smaller than 154,000 km^2, since approximately 432

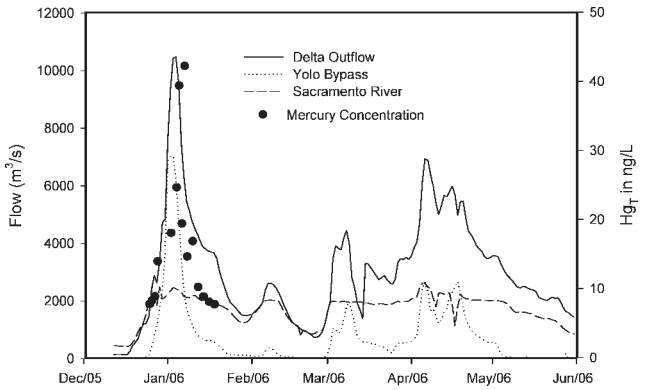

Fig. 5. Flows at Mallard Island, California, USA (Delta outflow) measured in cubic meters per second (m^3/s) and input from the Sacramento River and Yolo Bypass during the wet season of WY 2006. Additionally, total mercury (Hg_T) concentrations, measured in nanograms per liter (ng/L) sampled during the same time period, are displayed in the graph.

reservoirs retain water from the river and also trap sediment and particle-bound contaminants behind the dams. Currently no estimate is available that quantifies the watershed area upstream of these reservoirs. If only the area below all reservoirs is considered, as this is the effective area contributing to Hg loads in Delta outflow, Hg contamination in this watershed becomes more severe relative to other systems of similar size but with fewer reservoirs.

Sources of Hg in the watershed

The sources of Hg in the watershed of large rivers, such as the Sacramento River, can include the natural or anthropogenically enhanced erosion of Hg-bearing soils and rocks, mining, long-range atmospheric deposition, local atmospheric deposition from fossil fuel combustion, or chemicals from agricultural, urban, and industrial runoff [46]. Whether the sources are anthropogenic or naturally occurring is an important consideration with respect to remediation. As mentioned earlier, historic Hg and gold mining districts are an important source of the particle-bound Hg that has been stored in the watershed for decades [9]. On the west side of the Sacramento Valley, where historic Hg mines are abundant, Foe and Croyle [13] showed that the Cache Creek watershed, although covering only 4% of the Sacramento River watershed, can contribute as much as 50% of the annual Hg_T load that is transported downstream into the Sacramento River via the Yolo Bypass. Flows in the Yolo Bypass are therefore heavily influenced by runoff from historic Hg mining areas. The hydrographs for the Sacramento River, the Yolo Bypass, and the calculated total Delta outflow (Fig. 5) indicate that at a total Delta outflow of 4,200 m^3/s, the Yolo Bypass contributes approximately 50% of the total flow passing through the Mallard Island cross section. When flows from the Yolo Bypass exceeded flows in the Sacramento River, the signal of more contaminated particles from the Hg mining region became apparent. This suggests that contaminated sediments, transported from the Coast Range mercury mines into the Yolo Bypass, contribute to increased Hg_T loads to the Bay during large storms with higher flows.

Atmospheric deposition can be an important source of the mercury that is transported by rivers to coastal aquatic ecosystems. For example, direct wet deposition to tributaries was estimated to contribute more than half of the Hg entering Chesapeake Bay [47]. Previous studies measured wet and dry deposition in the San Francisco Bay area and estimated an average wet deposition of approximately 4.4 $g/km^2/year$ [48]. If this rate would apply to the entire Sacramento–San Joaquin watershed, a maximum of 650 kg of Hg would be deposited through rainfall during a year. If an estimate of dry deposition is included as well (e.g., 19 $g/km^2/year$) [49], the estimate of total atmospheric Hg input could theoretically be as high as 3,600 kg, although the losses via evasion and retention during transport from upland systems to riparian systems are not known. Thus, it appears that measured riverine loads may be as little as 7% of total atmospheric deposition, a finding that is consistent with previous studies [50]. Evidence from other studies [3] also indicates that Hg from atmospheric deposition is a significant source in relatively pristine, nonindustrialized basins in the Sierra Nevada Mountain Range, on the east side of the Sacramento River Basin. Thus, despite a history of Hg mining and use of Hg in gold extraction, it is possible that atmospheric deposition is a large source of Hg transported by the Sacramento River past Mallard Island.

Mercury exports from small to moderate-sized agricultural watersheds, where sources include natural soil Hg, atmospheric deposition, application of agricultural chemicals, and minor or moderate urban sources (and not extensive mining activity), appear to vary from 0.3 to 6.4 $g/km^2/year$ (average of 2 $g/km^2/year$). Applying the average of this range to the Sacramento River system yields an annual average load of 310 kg (range 46 to 990 kg) compared to the 260 kg measured in the present study. It may be appropriate to apply the lower end of the range given the argument above that large river systems would likely store a greater mass of sediment and Hg in channels and floodplains. In any case, it appears a large component of the total annual average load may be accounted for by urban and nonurban runoff, municipal and industrial wastewater, and farming sources that are typical of other mixed land use watersheds [51,52]. If this is true, then cleanup of sites contaminated by mining activities, despite being a potentially controllable source, may have little impact on Hg_T loads at the bottom of the watershed.

At the watershed scale, sources conceptually thought of as separate likely intermingle to form the downstream loads that occur during floods. De Oliveira et al. [53] discussed the role of biogeochemical cycles in retaining and releasing Hg in soils, and the role of deforestation, forest fires, and other human perturbations in land use on the mobilization or remobilization of Hg for the Amazon River basin in northern Brazil. Similar processes probably occur in California, where extensive Hg and gold mining occurred throughout much of the watershed. A great amount of this Hg was likely released to the atmosphere, deposited widely across the region, retained by soils, and eventually released to air and surface waters again through forest fires, deforestation, and other natural processes and anthropogenic activities.

Future trends

Predicting future trends in Hg_T loads for the Sacramento–San Joaquin River and other large river systems will require predicting changes in Hg sources and transport pathways. Global climate change must also be considered when predicting future Hg_T loads due to its potential to influence factors ranging from precipitation to atmospheric transport of Hg. Predictions for the effect of global climate change on precipitation and other factors in California are currently

highly variable and controversial [54,55]. Many predictions suggest that warming will result in increased runoff in the winter and decreased spring and summer runoff. This is expected to be accompanied by greater snow pack accumulation at higher elevations in the Cascade and Sierra Nevada Mountain Range in California but earlier snowmelt [56]. In addition, the state will possibly see an increase in overall precipitation [57,58], and a larger fraction of precipitation is expected to occur as rain at the expense of snow. The combined effect of these would likely be larger and more frequent floods during the winter rainy season. Warmer, high-intensity storms, like the one observed in January 2006, will cause high flows in the Sacramento watershed, resulting in increased erosion of contaminated sediment and Hg loads to San Francisco Bay.

Additionally, tide gauges in San Francisco Bay have indicated rising sea levels since 1950 which has been attributed to the thermal expansion of the oceans in combination with the melting of the ice caps [59]. Flick et al. [60] estimated a sea level rise of 2.4 mm/year for the 20th century while Ryan and Noble [61] estimated it to be 1.9 mm/year. Continuing rising sea levels associated with winter storms would likely result in a drastic increase in the hydrostatic pressures exerted on the levees and consequent levee failures (http://repositories.cdlib.org/jmie/sfews/vol3/iss1/art5), and also floods that fill floodplains and create more temporary wetlands. A steady supply of Hg from the Sacramento River to these seasonal wetlands could combine with increased rates of microbial activity to cause increased methylmercury production and accumulation in the food web [62].

Implications for management

The results from the present study can be combined with information on other important Hg sources to provide improved estimates of Hg_T loads to San Francisco Bay. This, in turn, will provide a better foundation for the management of Hg contamination in the Bay. In 2000, the Hg load from the Sacramento River watershed was estimated to contribute 73% of the allochthonous load to the Bay annually. The Hg_T loads from the Sacramento–San Joaquin River presented here are substantially lower (20% of the allochthonous load to the Bay) than those previously estimated. These improved Hg_T loads suggest that the Sacramento–San Joaquin River is not the overwhelmingly dominant source of Hg_T to the Bay as was once believed [17]. The anticipated paradigm shift these improved Hg_T load measurements will precipitate will undoubtedly have a major influence on efforts to reduce Hg_T loads and mitigate Hg toxicity in the Bay Area. With an increased focus on smaller watersheds, similar levels of analysis may be necessary for other large river systems of the world that could have similar impacts to management elsewhere.

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REFERENCES

1. James LA. 2005. Sediment from hydraulic mining detained by Englebright and small dams in the Yuba basin. *Geomorphology* 71: 202–226.
2. Ganguli PM, Mason RP, Abu-Saba KE, Anderson RS, Flegal AR. 2000. Mercury speciation in drainage from the New Idria mercury mine, California. *Environ Sci Technol* 34:4773–4779.
3. Sanders RD, Coale KH, Gill GA, Andrews AH, Stephenson M. 2008. Recent increase in atmospheric deposition of mercury to California aquatic systems inferred from a 300-year geochronological assessment of lake sediments. *Appl Geochem* 23:399–407.
4. Heyes A, Mason RP, Kim E-H, Sunderland E. 2006. Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes. *Mar Chem* 102:134–147.
5. Kim CS, Rytuba JJ, Brown GE. 2004. Geological and anthropogenic factors influencing mercury speciation in mine wastes: An EXAFS spectroscopy study. *Appl Geochem* 19:379–393.
6. McKee LJ, Leatherbarrow JE, Pearce S, Davis JA. 2003. A review of urban runoff processes in the Bay Area: Existing knowledge, conceptual models, and monitoring recommendations. San Francisco Estuary Institute Contribution 66. Final Report. San Francisco Estuary Institute, Oakland, CA, USA.
7. Leopold LB. 1996. *A View of the River*. Harvard University Press, Cambridge, MA, USA.
8. McKee LJ, Ganju NK, Schoellhamer DH. 2006. Estimates of suspended sediment entering San Francisco Bay from the Sacramento and San Joaquin Delta, San Francisco Bay, California. *J Hydrol* 323:335–352.
9. Domagalski JL, Alpers CN, Slotton DG, Suchanek TH, Ayers SM. 2004. Mercury and methylmercury concentrations and loads in Cache Creek watershed, California. *Sci Total Environ* 327:215–237.
10. Wiener JG, Suchanek TH. 2008. The basis for ecotoxicological concern in aquatic ecosystems contaminated by historical mercury mining. *Ecol Appl* 18:A3–A11.
11. Mergler D, Anderson HA, Chan LHM, Mahaffey KR, Murray M, Sakamoto M, Stern AH. 2007. Methylmercury exposure and health effects in humans: A worldwide concern. *Ambio* 36:3–11.
12. Conaway CH, Black FJ, Grieb TM, Roy S, Flegal AR. 2008. Mercury in the San Francisco Estuary. *Rev Environ Contam Toxicol* 194:29–54.
13. Foe C, Croyle W. 1998. Mercury concentrations and loads from the Sacramento River and from Cache Creek to the Sacramento-San Joaquin Delta Estuary. California State Water Resources Control Board, Sacramento, CA.
14. Domagalski J. 2001. Mercury and methylmercury in water and sediment of the Sacramento River Basin, California. *Appl Geochem* 16:1677–1691.
15. Buchanan PA, Ganju NK. 2005. Summary of suspended sediment concentration data, San Francisco Bay, California, Water Year 2003. Data Series Report 113. U.S. Geological Survey, Sacramento, CA.
16. American Society for Testing Materials. 1999. Standard test method for determining sediment concentration in water samples: D 3977–97. In *Annual Book of ASTM Standards*, Vol. 11. West Conshohocken, PA, pp 389–394.
17. Conaway CH, Squire S, Mason RP, Flegal AR. 2003. Mercury speciation in the San Francisco estuary. *Mar Chem* 80:199–225.
18. Choe KY, Gill GA, Lehman R. 2003. Distribution of particulate, colloidal, and dissolved mercury in San Francisco Bay Estuary. 1. Total mercury. *Limnol Oceanogr* 48:1535–1546.
19. Turner A, Millward GE, Le Roux SM. 2001. Sediment–water partitioning of inorganic mercury in estuaries. *Environ Sci Technol* 35:4648–4654.
20. Horowitz AJ. 1995. *The Use of Suspended Sediment and Associated Trace Elements in Water Quality Studies*. International Association of Hydrological Sciences, Special Publication 4. IAHS Press, Wallingford, UK.
21. Flegal AR, Smith GJ, Gill GA, Sanudo-Wilhelmy S, Anderson LCD. 1991. Dissolved trace element cycles in the San Francisco Bay estuary. *Mar Chem* 36:329–363.

22. Gill GA, Fitzgerald WF. 1985. Picomolar mercury measurements in seawater and other materials using stannous chloride reduction and two-stage gold amalgamation with gas phase detection. *Mar Chem* 20:227–243.
23. U.S. Environmental Protection Agency. 1995. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. EPA 821-R-95-034. Office of Water, Washington, DC.
24. U.S. Environmental Protection Agency. 2002. Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. EPA-821-R-02-019. Office of Water, Washington, DC.
25. Fadini PS, Jardim WF. 2000. Storage of natural water samples for total and reactive mercury analysis in PET bottles. *Analyst* 125: 549–551.
26. Parker JL, Bloom NS. 2005. Preservation and storage techniques for low-level aqueous mercury speciation. *Sci Total Environ* 337: 253–263.
27. Bloom NS, Fitzgerald WF. 1988. Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Anal Chim Acta* 208:151–161.
28. Schoellhamer DH, Mumley TE, Leatherbarrow JE. 2007. Suspended sediment and sediment-associated contaminants in San Francisco Bay. *Environ Res* 105:119–131.
29. U.S. Environmental Protection Agency. 2000. *California Toxics Rule*. 40 CFR, Part 131.38 Region 9 Office of Water, San Francisco, CA.
30. Novotny G, Chesters V. 1989. Delivery of sediments and pollutants from nonpoint sources: A water quality perspective. *J Soil Water Conserv* 44:568–576.
31. Walling DE. 2006. Human impact on land-ocean sediment transfer by the world's rivers. *Geomorphology* 79:192–216.
32. Walling DE, Owens PN, Carter J, Leeks GJL, Lewis S, Meharg AA, Wright J. 2003. Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. *Appl Geochem* 18:195–220.
33. Paraquetti HHM, Ayres GA, de Almeida MD, Molisani MM, de Lacerda LD. 2004. Mercury distribution, speciation and flux in the Sepetiba Bay tributaries, SE Brazil. *Water Res* 38:1439–1448.
34. Hurley JP, Cowell SE, Shafer MM, Hughes PE. 1998. Tributary loading of mercury to Lake Michigan: Importance of seasonal events and phase partitioning. *Sci Total Environ* 213:129–137.
35. Whyte DC, Kirchner JW. 2000. Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges. *Sci Total Environ* 260:1–9.
36. Lawson NM, Mason RP. 2001. Concentration of mercury, methylmercury, cadmium, lead, arsenic, and selenium in the rain and stream water of two contrasting watersheds in western Maryland. *Water Res* 35:4039–4052.
37. Yin X, Balogh S. 2002. Mercury concentrations in streams and river water: An analytical framework applied to Minnesota and Wisconsin (USA). *Water Air Soil Pollut* 138:79–100.
38. Wall GR, Ingleston HH, Litten S. 2005. Calculating mercury loading to the Tidal Hudson River, New York, using rating curve and surrogate methodologies. *Water Air Soil Pollut* 165:233–248.
39. Wayne DM, Warwick JJ, Lechler PL, Gill JA, Lyons WB. 1996. Mercury contamination in the Carson River, Nevada: A preliminary study of the impact of mining wastes. *Water Air Soil Pollut* 92:391–408.
40. Domagalski J. 1998. Occurrence and transport of total mercury and methyl mercury in the Sacramento River basin, California. *J Geochem Explor* 64:277–291.
41. Hornberger MI, Luoma SN, van Geen A, Fuller C, Anima R. 1999. Historical trends of metals in the sediments of San Francisco Bay, California. *Mar Chem* 64:39–55.
42. Wright SA, Schoellhamer DH. 2005. Estimating sediment budgets at the interface between rivers and estuaries with application to the Sacramento-San Joaquin River Delta. *Water Resour Res* 41:1–17.
43. Conaway CH, Ross JRM, Looker R, Mason RP, Flegal AR. 2007. Decadal mercury trends in San Francisco Estuary sediments. *Environ Res* 105:53–66.
44. Gill GA, Bruland KW. 1990. Mercury speciation in surface freshwater systems in California and other areas. *Environ Sci Technol* 24:1392–1400.
45. Roth DA, Taylor HE, Domagalski J, Dileanis P, Peart DB, Antweiler RC, Alpers CN. 2001. Distribution of inorganic mercury in Sacramento River water and suspended colloidal sediment material. *Arch Environ Contam Toxicol* 40:161–172.
46. Nriagu JO. 1990. Global metal pollution: Poisoning the biosphere. *Environment* 32:7–11.
47. Mason RP, Lawson NM, Sullivan KA. 1997. Atmospheric deposition to the Chesapeake Bay Watershed—Regional and local sources. *Atmos Environ* 31:3531–3540.
48. Steding DJ, Flegal AR. 2002. Mercury concentrations in coastal California precipitation: Evidence of local and trans-Pacific fluxes of mercury to North America. *J Geophys Res* 107:4764.
49. Tsai P, Hoenicke R. 2001. San Francisco Bay atmospheric deposition pilot study. Part 1: Mercury. San Francisco Estuary Institute, Oakland, CA, USA.
50. Sorensen JA, Glass GE, Schmidt KW, Huber JK, Rapp GR. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty Northern Minnesota Lakes. *Environ Sci Technol* 24:1716–1727.
51. Balogh SJ, Meyer ML, Johnson DK. 1998. Transport of mercury in three contrasting river basins. *Environ Sci Technol* 32:456–462.
52. Lawson N, Mason R, Laporte JM. 2001. The fate and transport of mercury, methylmercury, and other trace metals in Chesapeake Bay tributaries. *Water Res* 35:501–515.
53. De Oliveira SMB, Melfi AJ, Fostier AH, Forti MC, Fávaro DIT, Boulet R. 2001. Soil as an important sink for mercury in the Amazon. *Air Water Soil Pollut* 126:321–337.
54. Roos M. 2002. The effects of global climate change on California water resources. Publication 500-03-025FS. The California Energy Commission, Sacramento, CA, USA.
55. Dettinger MD. 2005. From climate-change spaghetti to climate-change distributions for 21st century California. *San Francisco Estuary Watershed Sci* 3:1–14.
56. California Energy Commission. 2005. Climate change impacts and adaptations in California. CEC-5002005-103-SD. Staff paper. Sacramento, CA, USA.
57. Regonda SK, Rajagopalan B, Clark M, Pitlick J. 2004. Seasonal cycle shifts in hydroclimatology over the Western United States. *Journal of Climate* 18:372–384.
58. Groisman PY, Knight RW, Karl TR. 2001. Heavy precipitation and high streamflow in the contiguous United States: Trends in the twentieth century. *Bull Am Meteorol Soc* 82:219–246.
59. Bromirski PD, Flick RE, Cayan DR. 2003. Storminess variability along the California coast: 1858–2000. *Journal of Climate* 16:982–993.
60. Flick RE, Murray JF, Ewing LC. 2003. Trends in United States tidal datum statistics and tide range. *Journal of Waterway, Port, Coastal and Ocean Engineering* 129:155–164.
61. Ryan HF, Noble MA. 2007. Sea level fluctuations in central California at subtidal to decadal and longer time scales with implications for San Francisco Bay, California. *Estuar Coast Shelf Sci* 73:358–550.
62. Heim WA, Coale KH, Stephenson M, Choe KY, Gill GA, Foe C. 2007. Spatial and habitat-based variations in total and methyl mercury concentrations in surficial sediments in the San Francisco Bay-Delta. *Environ Sci Technol* 41:3501–3507.