Sources of mercury to San Francisco Bay surface sediment as revealed by mercury stable isotopes

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ABSTRACT

Mercury (Hg) concentrations and isotopic compositions were examined in shallow-water surface sediment (0-2 cm) from San Francisco (SF) Bay to determine the extent to which historic Hg mining contributes to current Hg contamination in SF Bay, and to assess the use of Hg isotopes to trace sources of contamination in estuaries. Inter-tidal and wetland sediment had total Hg (Hg_T) concentrations ranging from 161 to 1529 ng/g with no simple gradients of spatial variation. In contrast, inter-tidal and wetland sediment displayed a geographic gradient of δ^{202}Hg values, ranging from -0.30‰ in the southern-most part of SF Bay (draining the New Almaden Hg District) to -0.99‰ in the northern-most part of SF Bay near the Sacramento-San Joaquin River Delta. Similar to SF Bay inter-tidal sediment, surface sediment from the Alviso Slough channel draining into South SF Bay had a δ^{202}Hg value of -0.29‰, while surface sediment from the Cosumnes River and Sacramento-San Joaquin River Delta draining into north SF Bay had lower average δ^{202}Hg values of -0.90‰ and -0.75‰, respectively. This isotopic trend suggests that Hg-contaminated sediment from the New Almaden Hg District mixes with Hg-contaminated sediment from a low δ^{202}Hg source north of SF Bay. Tailings and calcines from the New Idria Hg mine in the California Coast Range had average δ^{202}Hg values of -0.37 and +0.03‰, respectively, showing that Hg calcination fractionates Hg isotopes resulting in Hg contamination from Hg(II) mine waste products with higher δ^{202}Hg values than metallic Hg(0) produced from Hg mines. Thus, there is evidence for at least two distinct isotopic signals for Hg contamination in SF Bay: Hg associated with calcine waste materials at Hg mines in the Coast Range, such as New Almaden and New Idria; and Hg(0) produced from these mines and used in placer gold mines and/or in other industrial processes in the Sierra Nevada region and SF Bay area.

1. INTRODUCTION

San Francisco (SF) Bay is one of the largest and most anthropogenically impacted estuaries in North America (NICHOLS et al., 1986), and mercury (Hg) contamination in the SF Bay area has been acknowledged for more than 150 years (CONAWAY et al., 2007). More than 90% of Hg mined in the United States between 1850 and 1980 came from the California Coast Range (CHOE, 2004), much of which is in the extensive SF Bay watershed. Hundreds of Hg mines, including the two most productive in North America (New Almaden and New Idria, which together produced 50% of the Hg mined in the United States) are located within 230 km of SF Bay (CARGILL et al., 1980; RYTUBA, 2000). The New Almaden Mercury District had active operations from 1847 through 1973, and is located within the watershed that contributes to the Guadalupe River, which flows into the southern end of SF Bay. The New Almaden mines and processing plants were located ~30 km south of SF Bay, with at least one off-site Hg processing plant that operated closer to the Bay. Sediment transport from Hg mining areas and leaching of Hg mine waste into waterways have been implicated as an important source of Hg contamination in the history of SF Bay (CONAWAY et al., 2004; GANGULI, 2000; MARVIN-DIPASQUALE, 2007; RYTUBA, 2000; THOMAS et al., 2002). However, the extent to which legacy Hg mining operations continue to be a source of Hg contamination to surface sediment is debated, since significant quantities of Hg also have been introduced to SF Bay from other sources (CONAWAY et al., 2008). Much of the metallic Hg(0) produced at Hg mines was transported and used in placer gold (Au) mining operations in the Sierra Nevada Range, northern Coast Range, and Klamath-Trinity mountains , which are within the northern SF Bay watershed (NRIAGU, 1994). Beginning in the mid-19th century, hydraulic Au mining delivered significant amounts of Hg-contaminated sediment to SF Bay, with an estimated 260 x10^6 m^3 of mining debris deposited between 1856 and 1887 (JAFFE et al., 1998; JAFFE et al., 2007). Natural and anthropogenic modifications of SF Bay and its tributaries has enhanced sediment erosion in parts of SF Bay and exposed previously buried sediment (FREGOSO et al., 2008; JAFFE and FOXGROVER, 2006; JAFFE et al., 2007; Nichols et al., 1986; van Geen and Luoma, 1999), much of has higher Hg concentrations than the sediment that is currently being transported to the bay (Hornberger et al., 1999). More recently, the development of petroleum refineries, chemical manufacturing, and chloralkali production has led to additional environmental Hg contamination in SF Bay. As a highly urbanized estuary, contaminants also enter SF Bay through wastewater effluents, urban runoff, and shipyard pollution (Flegal et al., 1990; Nichols et al., 1986). The relative contribution of these various sources has not been determined.

Total Hg concentrations (Hg_T) are generally elevated in surface sediment throughout San Francisco Bay, often 5 times higher than typical pre-Industrial SF Bay background levels of 60-80 ng/g (Conaway et al., 2007; Conaway et al., 2004; Hornberger et al., 1999). Past studies have indicated that there are a few centers of enhanced Hg contamination, namely in sediment near Alviso Slough and San Pablo Bay (Conaway et al., 2007; Hornberger et al., 1999; Thomas et al., 2002). The spatial distribution of Hg concentrations in SF Bay sediment is not necessarily indicative of the source of that Hg, however (Conaway et al., 2008), because of extensive post-depositional sediment mobility.

Recent studies demonstrate that Hg isotopes can be used to identify different sources of Hg and track them in the environment (Biswas et al., 2008; Carignan et al., 2009; Foucher and Hintelmann, 2006; Foucher et al., 2009; Stetson et al., 2009). Mercury has seven stable isotopes with masses 196, 198, 199, 200, 201, 202 and 204 amu, and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) techniques employed in this study allow for measurement of the Hg isotopic composition with a precision of <±0.1‰ (Bergquist and Blum, 2007; Blum and Bergquist, 2007; Lauretta et al., 2001). Fractionation of Hg isotopes has been observed for multiple biogeochemical processes including volatilization, diffusion, photochemical reduction, microbial reduction, and microbial methylation (Bergquist and Blum, 2007; Estrade et al., 2009; Kritee et al., 2007; Rodriì�guez-Gonzaì�lez et al., 2009; Zheng et al., 2007; Zheng and Hintelmann, 2009), and variations in the isotopic composition of Hg in the environment have been observed in coal, peat, soil, sediment, rock, lichen, moss, fish and snow (Bergquist and Blum, 2007; Biswas et al., 2007; Biswas et al., 2008; Carignan et al., 2009; Foucher et al., 2009; Gehrke et al., 2009; Jackson et al., 2004; Jackson et al., 2008; Sherman et al., 2010; Sherman et al., 2009; Smith et al., 2008; Zambardi et al., 2009). In 2006 a preliminary study of variations in Hg isotopic composition in SF Bay sediment was performed, but the results were inconclusive due to limited sampling and high analytical uncertainty (2SD = ±0.56‰) exceeding variations measured in samples (0.48‰) (Foucher and Hintelmann, 2006). Methods have now advanced to the point that Hg isotope ratios can be measured with high precision (2 SD = ±0.08‰), sufficient to identify variations in the Hg isotopic composition of environmental samples such as SF Bay sediment.

The goal of the current study was to utilize high-precision stable Hg isotope measurements in sediments to ascertain the relative importance of legacy Hg mining sources to SF Bay at the present time. We analyzed mine tailings and calcine (roasted ore) from the non-remediated New Idria Hg Mine to provide an estimate of the Hg isotopic composition of cinnabar (HgS) in the California Coast Range and test whether or not calcined Hg ore and unprocessed ore are isotopically distinct. We then analyzed sediment from Alviso Slough (which connects the Guadalupe R. to South SF Bay and represents the drainage channel from New Almaden Hg mining District to the Bay) to observe a potential Hg mining signal in surface sediment near SF Bay. To evaluate the influence of legacy Hg mining in New Almaden on SF Bay, we analyzed surface (0-2 cm) inter-tidal sediment from twenty coves and embayments along shores throughout SF Bay and wetland sediment from nine seasonal wetlands flanking South SF Bay (Fig. 1). Sampling sites were selected to provide both detailed coverage in the Lower South SF Bay and extensive geographic coverage of the entirety of SF Bay. The sampling locations selected allow for comparison of sediment with different plausible sources of Hg contamination, including legacy mining sites, as well as contemporary urban runoff, municipal waste discharge, and industrial and chemical production.

2. METHODS AND MATERIALS

2.1 Sample collection and storage

Inter-tidal surface (0-2 cm) sediment was collected at twenty locations throughout SF Bay (Tables 1, 2, Fig. 1). Surface coastal wetland sediment was collected at nine locations in South SF Bay (GRENIER et al., 2010), three locations in the Yolo Bypass Water Conservation Area near Sacramento, and two locations in marshes around the Cosumnes River (MARVIN-DIPASQUALE et al., 2007) (Tables 1, 2). Subaqueous surface sediment was collected at two locations in the Cosumnes River channel (MARVIN-DIPASQUALE et al., 2007), and surface sediment (0-2 cm) was also collected along the edge of Almaden Reservoir. All samples were collected using trace-metal clean methods (MARVIN-DIPASQUALE, 2007). At each SF Bay location, four surface samples were collected at 90° intervals around the perimeter of a circle with 2 m radius using acid-cleaned polycarbonate pipe and plastic spatulas. The four samples at each site were combined into a single plastic bag, kept on dry ice in the field, and transferred to freezers (-5°C) within 6 hours of collection. Samples were logged and sub-sampled at the USGS laboratory (Menlo Park, CA) under anaerobic conditions.

Mine debris samples were collected at the New Idria Hg Mine (San Benito Co., CA) in the Diablo Range of the California Coast Ranges, approximately 230 km south of SF Bay. Two representative samples of mine tailings were collected from a tailings debris pile (3641519.°N, 120.67289°W) and one sample was also collected from a calcine debris pile (36.41558°N, 120.67314°W). Polished-section optical analysis verified the occurrence of cinnabar (α-HgS) in tailings and a combination of cinnabar (α-HgS) and metacinnabar (β-HgS) in calcine samples. Samples were stored in opaque low-density polyethylene bottles at ambient temperature until analysis at the University of Michigan.

Fifteen cores were taken in the Alviso Slough, using previously described methods, for a project conducted by the USGS (MARVIN-DIPASQUALE, 2007), and two of these cores were selected for Hg isotope analyses in this study. The cores are from the mainstream channel (0-56 cm [core AS T4 B]) and from the vegetated marsh (right bank) that fringed the channel (0-81 cm [core AS T4 C]); Hg isotopic analyses were performed on three sediment depth intervals in each core. Cores (~100 cm) were collected using a hand-operated piston corer, characterized, and sub-sampled at the USGS (Menlo Park, CA). Sediment was stored in a 3°C refrigerator until receipt at the University of Michigan, where samples were stored in a -20°C freezer.

Sample types and locations are distinguished by prefixes, followed by the approximate distance of each sample from the mouth of Alviso Slough (see below). Inter-tidal sediment sample names have the prefix IT, wetland sediment have the prefix WL, Cosumnes River and Marsh sample names have the prefix CR(R) and CR(M), and Yolo Bypass Wetland Conservation Area sample names have the prefix YB. The Almaden Reservoir sample has the prefix AR. New Idria tailings sample codes have the prefix NI-T, and the calcine sample code is NI-C. Alviso Slough channel and marsh sediment core samples have the prefix AS(R) and AS(M) and a suffix of the sample sediment depth interval (cm). Samples with the same approximate distance from the slough are differentiated with lower-case letters.

To assess the spatial distribution of Hg concentrations and isotopic compositions, the distance of each sample location from the mouth of the Alviso Slough was estimated. The reference location of the mouth of the Alviso Slough is marked as the solid star in Fig. 1. The solid line represents the center line of SF Bay, with perpendicular line segments extending from the center line to sampling locations. The approximate distance of each sample location was estimated from the mouth of the Alviso Slough following the center line to the intersection of the perpendicular line extending to each sample location.

2.2 Hg concentration and isotope analysis

Sediment samples were freeze-dried, and 0.5 to 1.5 g sub-samples were ground in an agate mortar and pestle. New Idria tailings and calcine samples were ground in an alloy tool steel mortar and pestle. Hg was thermally volatilized as Hg(0) at 750°C in a two-stage furnace. Following combustion Hg vapor was carried by a stream of air and O_2 through the second stage of the furnace at 1000°C and into an oxidizing solution of 1% $KMnO_4$ where it was retained in solution as Hg(II). Procedural blanks and the standard reference material SRM 1944 (New York-New Jersey Waterway Sediment) were analyzed for quality control assessment. Prior to isotope analysis, 1% $KMnO_4$ solutions containing the separated Hg were partially neutralized using NH_2OH. The Hg concentrations of 1% $KMnO_4$ solutions were analyzed using a Nippon Instruments MA 2000 atomic absorption spectrometer by methods previously described (GEHRKE et al., 2009). Process replicates of quality control standards agreed with reference Hg concentrations within ±10%, indicating >90% recovery during combustion and trapping. All Hg concentrations are reported in ng/g dry weight. Inter-tidal and wetland sediment sample Hg concentrations were verified by independent acid-digest and atomic fluorescence spectroscopy at the USGS (Menlo Park, CA) and agreed within ±15%.

Hg isotopic compositions were determined using a Nu Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) by methods previously described (BLUM and BERGQUIST, 2007; LAURETTA et al., 2001). Partially neutralized trapping solutions were diluted to a uniform Hg concentration of 5 ng/g for analysis. Using a continuous flow system, Hg(II) was reduced by addition of $SnCl_2$, evolved Hg(0) was separated from solution using a frosted-tip phase separator, a Tl aerosol was produced by a desolvating nebulizer and added to the gas stream, and the sample was introduced to the MC-ICP-MS. Instrumental mass-bias was corrected using the internal Tl standard (NIST 997) and sample-standard bracketing using NIST 3133 at the same concentration and in the same matrix as the samples.

Additionally, on-peak zero corrections were applied. Mass-dependent Hg isotope compositions are reported as δ^{202}Hg in permil (‰), referenced to NIST 3133 (BLUM and BERGQUIST, 2007) and are calculated as:

$$\delta^{202}\text{Hg} = 1000*([(^{202}\text{Hg}/^{198}\text{Hg})_{\text{sample}}]/[(^{202}\text{Hg}/^{198}\text{Hg})_{3133}]-1).$$

Mass independent Hg isotope fractionation is reported as Δ^{199}Hg and Δ^{201}Hg in permil (‰) and following (BLUM and BERGQUIST, 2007) is calculated as:

$$\Delta^{199}\text{Hg} = \delta^{199}\text{Hg}_{\text{measured}} - (\delta^{202}\text{Hg}_{\text{measured}}*0.252)$$

$$\Delta^{201}\text{Hg} = \delta^{201}\text{Hg}_{\text{measured}} - (\delta^{202}\text{Hg}_{\text{measured}}*0.752)$$

The δ^{202}Hg and Δ^{199}Hg values of samples are discussed in the text, used in figures, and listed in tables. Sample Δ^{201}Hg values are listed in tables, and although the total variation is only twice the analytical uncertainty, they are well correlated with Δ^{199}Hg values (Δ^{199}Hg/Δ^{201}Hg = 0.79± 0.13; $r^2 = 0.58$). Analytical uncertainty was evaluated using replicate analyses of the in-house standard UM-Almadén, and replicate analyses of standard reference materials, with average analytical precision of at least ±0.07‰ (2 SD) for δ^{202}Hg, and ±0.04‰ (2 SD) for Δ^{199}Hg and Δ^{201}Hg. The reproducibility of sample Hg isotope compositions was evaluated by replicate combustion of samples and replicates yielded δ^{202}Hg values within analytical uncertainty of ±0.08‰ (2 SD), and Δ^{199}Hg and Δ^{201}Hg values within the analytical uncertainty of ±0.06‰ (2 SD) (Table 1).

3. RESULTS

3.1 Hg isotope composition in New Idria Mine materials

Tailings and calcined ore from the New Idria Hg Mine (New Idria, CA) had distinct Hg isotope compositions. The two samples collected from tailings piles had Hg_T concentrations of 71.26 and 46.47 µg/g, with similar δ^{202}Hg values of -0.43 and -0.33‰, and Δ^{199}Hg values of +0.05 and +0.06‰ (Table 2). Calcined ore had a much higher Hg_T of (976 µg/g). The calcine sample had a much higher δ^{202}Hg value (+0.03‰) but a similar Δ^{199}Hg value (-0.01‰), compared to the tailings (Table 1,2).

3.2 Hg in Alviso Slough sediment

Sediment cores from the Alviso Slough channel and vegetated marsh had Hg_T ranging from 409 to 4011 ng/g (Table 2). Near-surface sediment (AS(Ra[0-7.5]), AS(Ma[0-17])) had Hg_T concentrations of 508 and 409 ng/g, respectively. The maximum Hg_T measured, 4011 ng/g, was in the main channel at depth (AS(Rb[29-42.5])). Analyses of sediment loss on ignition (LOI) and grain size performed at USGS Menlo Park found lower LOI percentage and larger average grain size in most subsurface sediment (MARVIN-DIPASQUALE, 2007), which is consistent with a higher proportion of mining debris (JAMES, 2005; OSLEGER et al., 2008). Additionally, sediment chronology was determined on a core in Triangle Marsh approximately 3 km northeast the Alviso Slough cores that indicated sediment at 35 cm depth was deposited circa 1983 (CONAWAY et al., 2004). The New Almaden Hg mine was operational through the mid 1970s, and it is likely that the deeper sediment depth intervals of the Alviso Slough cores analyzed in this study were deposited prior to mine closure.

The δ^{202}Hg values in the Alviso Slough cores ranged from -0.32 to +0.29‰ and increased with depth (Fig. 5). Near-surface sediment from the channel (AS(Ra[0-7.5]) and the fringing vegetated marsh

(AS(Ma[0-17]) had indistinguishable δ^{202}Hg values of -0.29 and -0.32‰, respectively. Inter-tidal surface sediment collected at two sites upstream in Alviso Slough (IT(-5a), IT(-7)) also had indistinguishable δ^{202}Hg values of -0.32 and -0.30‰.

3.3 Hg in tributaries of the Sacramento and San Joaquin Rivers

Surface (0-2 cm) sediment from the Cosumnes River channel (CR(Ra), CR(Rb)) had Hg_T of 64.9 and 114 ng/g and emergent wetlands in the Cosumnes River delta (CR(Ma), CR(Mb)) had Hg_T of 303 and 419 ng/g (Table 2). Channel samples had δ^{202}Hg values of -0.88 and -0.91‰ and both emergent wetland samples had δ^{202}Hg values of -0.75‰ (Table 2). All Cosumnes River channel and wetland samples had a narrow range of Δ^{199}Hg values from +0.04 to +0.09‰ (mean = 0.07±0.02‰).

Surface (0-2 cm) sediment from permanent wetlands in the Yolo Bypass Water Conservation Area (YB(a), YB(b), YB(c)) had Hg_T ranging from 119 to 147 ng/g (Table 2). Wetland sediment had δ^{202}Hg values ranging from -0.65 to -0.73‰ (-0.70±0.04‰) and Δ^{199}Hg values from +0.08 to +0.16‰ (0.12±0.04‰).

3.4 Hg concentration in San Francisco Bay inter-tidal and wetland sediment

Surface (0-2 cm) inter-tidal sediment had Hg_T ranging from 161 to 846 ng/g (Table 2, Fig. 2). Sites in Alviso Slough surrounding waterways in the Lower South Bay (IT(-7), IT(-5a), IT(-5b), IT(-2), IT(-1)) had elevated Hg_T (320 to 538 ng/g), but the most elevated Hg_T were found along the Martin Luther King Regional Shoreline in Oakland (IT(42a), IT(42b)) (1529, 1265 ng/g) and at embayments near Point Isabel in the Central Bay (IT(62b), IT(62a)) (846, 679 ng/g). Sediment from embayments near the Carquinez Strait in the north Bay (IT(110), IT(115), IT(119), IT(143)) had the lowest Hg_T (161 to 253 ng/g). There was no discernable spatial pattern to the variability in Hg_T of inter-tidal sediment (Fig. 2). Surface (0-2 cm) sediment associated with seasonally flooded wetlands in South SF Bay had Hg_T ranging from 136 to 292 ng/g (Table 2). Like inter-tidal sediment, wetland sediment did not display an obvious spatial pattern of Hg_T concentration.

3.5 Hg isotopic composition in San Francisco Bay inter-tidal and wetland sediment

Inter-tidal sediment had δ^{202}Hg values ranging from -0.99 to -0.30‰ (Table 2). There was a strong correlation of δ^{202}Hg values with distance from the Alviso Slough ($r^2 = 0.83$), with sediment from the Lower South and South Bay ranging from -0.30 to -0.53‰ and sediment from San Pablo Bay and Suisun Bay ranging from -0.59 to -0.99‰ (Fig. 4). Three sites in the Central Bay (IT(42a), IT(42b), IT(52)) had intermediate δ^{202}Hg values (-0.65, -0.66, -0.65‰). Sediment δ^{202}Hg values did not show a significant correlation with Hg_T ($r^2 = 0.06$; Table 2).

Surface inter-tidal sediment Δ^{199}Hg values displayed a very narrow range +0.03 to +0.12‰ (mean Δ^{199}Hg = 0.08 ±0.03‰, 1SD) (Fig. 3), which is only slightly larger than the analytical uncertainty of ±0.04‰, 2SD (Table 2). There was no spatial gradient in sediment Δ^{199}Hg values, and Δ^{199}Hg values did not correlate with sediment δ^{202}Hg or Hg_T.

The South Bay wetland sediment δ^{202}Hg values had a narrow range from -0.50 to -0.68‰ and wetland sediment from Coyote Creek in Lower South Bay (WL(-3)) had a δ^{202}Hg value of -0.44‰ (Table 2, Fig. 4). The δ^{202}Hg values of South Bay surface wetland sediment were similar to δ^{202}Hg values of South Bay surface inter-tidal sediment (δ^{202}Hg = -0.53 and -0.54‰). The Coyote Creek wetland sample (δ^{202}Hg = -0.44‰) was similar to proximal inter-tidal sediment from Alviso Slough (δ^{202}Hg = -0.30 to -0.46‰). Like the inter-tidal sediment, surface sediment associated with seasonal wetlands also displayed a correlation between δ^{202}Hg and distance from the Alviso Slough ($r^2 = 0.67$), with higher values located further to the south (Fig. 4). The wetland sediment had a narrow range of Δ^{199}Hg values from +0.08 to +0.16‰ (mean = 0.13±0.03‰, 1SD), slightly higher than the average inter-tidal sediment Δ^{199}Hg value (Fig. 2).

4. DISCUSSION

4.1 Hg concentration and isotopic composition in mine waste

In order to assess the Hg isotopic composition associated with Hg mine waste from the California Coast Range, we collected calcine and tailings samples from the New Idria Hg Mine in the Diablo Range, 230 km south of SF Bay. The New Almaden Hg Mine, 30 km south of SF Bay, has been extensively remediated since 1998 and surface samples of mine debris are not available for collection. Further south in the Coast Range, the New Idria Hg Mine operated from 1854 to 1972 and, unlike the New Almaden Hg Mine, it has not been remediated since its closure in 1972 (GANGULI, 2000). Both the New Idria and New Almaden Hg deposits are associated with silica-carbonates in Franciscan sandstone and Panoche shale units of the Franciscan complex (BOCTOR et al., 1987; SMITH et al., 2008). Therefore, we anticipate similar Hg isotopic compositions in ore mined in both the New Idria and New Almaden Hg mining districts, and similar relationships between the isotopic composition of Hg in calcine versus tailings.

At approximately 50 Hg mines in the SF Bay watershed, including New Almaden and New Idria, cinnabar (α-HgS) and metacinnabar (β-HgS) ores were mined. Ore was roasted in rotary furnaces at 600-700°C to convert Hg(II) to gaseous Hg(0) (BOCTOR et al., 1987; RYTUBA, 2000), producing roasted ore known as calcine. The volatilized Hg(0) was condensed and the metallic mercury was sold for use in Au placer mines and other industries. Calcination was an incomplete process, often leaving substantial Hg (20-150 μg/g) in the roasted end-product, which can be a considerable source of Hg contamination in Hg mining areas (KIM et al., 2004; RYTUBA, 2000). The incomplete processes employed in the production of metallic Hg are likely to have significantly fractionated the Hg isotopes. Laboratory experiments have demonstrated that thermally volatilizing Hg(0) from a Hg(II) source fractionates Hg isotopes, with lower δ^{202}Hg values in the volatilized Hg(0) and higher δ^{202}Hg values in the residual Hg(II) (KOSTER VAN GROOS et al., 2009). Additionally, evaporation of liquid Hg yields residual liquid Hg with higher δ^{202}Hg values than Hg(0) vapor (ESTRADE et al., 2009). A recent study by Stetson et al. (2009) investigated Hg isotopes in various materials in two Hg mining districts in Texas and Nevada and observed that calcines had higher δ^{202}Hg values than cinnabar collected from the same mines, likely attributable to the volatilization of lighter isotopes of Hg, with residual HgS enriched in heavier isotopes (STETSON et al., 2009).

We found a significant difference in Hg isotopic composition between unroasted and roasted material at the New Idria mine. The two unroasted tailings samples (wall rock containing a small amount of HgS) had variable Hg concentrations (71.3 and 46.5 μg/g) but similar δ^{202}Hg values of -0.43 and -0.33‰. The calcine sample (roasted ore) had a much higher Hg_T (976 μg/g) and a considerably higher δ^{202}Hg value of +0.03‰ (Table 2). Based on these results, we suggest that Hg emanating from tailings and calcines at New Idria mine is likely to have an initial δ^{202}Hg value approximately between -0.4 and 0.0‰. It is notable that surface sediment from the Alviso Slough (AS(Ra[0-7.5])), which receives drainage from the New Almaden Hg mine, has a δ^{202}Hg value of -0.29‰. This is consistent with the Hg contamination in surface sediment of Alviso Slough being derived from legacy Hg mining in the New Almaden District, as has been previously suggested (MARVIN-DIPASQUALE, 2007).

It follows that the metallic Hg(0) produced in the Coast Ranges Hg mines, and subsequently used in the Sierra Nevada placer Au mines, had lower δ^{202}Hg values than residual HgS in the calcines left behind at the Coast Range Hg mine dumps. It is estimated that 10% of the liquid Hg(0) sent to Au mines and other industrial plants was lost during transport and storage (NRIAGU and WONG, 1997). At the placer Au mines, liquid Hg(0) was used in sluice boxes to amalgamate fine Au particles for physical separation from sediment (ALPERS et al., 2005; NRIAGU and WONG, 1997). On average, 10-30% of Hg was not recovered from the sluices (ALPERS et al., 2005), and hydraulic mining debris is a large source of Hg contamination in impacted areas downstream of Au mines (ALPERS et al., 2005; HUNERLACH et al., 2005;

JASINSKI, 1995). Additionally, there has been extensive use of Hg(0) in chemical and material production plants and refineries in the area. We have argued, based on available evidence, that metallic Hg produced and used at Au mines and other industries will have lower δ^{202}Hg values than the Hg emanating from tailings or calcine at legacy Hg mines. To further test this idea, we analyzed Hg isotopes in sediments from Alviso Slough, which drains the New Almaden Hg mining district (see section 4.2) and from the Cosumnes River, which flows through former Au mining districts in the Sierra foothills (see section 4.3).

4.2 Hg concentration and isotopic composition in Alviso Slough sediment core

The New Almaden Mining District has been implicated as the source of Hg contamination to South SF Bay, particularly in sediment deposited during the period of active Hg mining and processing (MARVIN-DIPASQUALE, 2007; THOMAS et al., 2002). The two sediment cores from Alviso Slough, which connects the Guadalupe River to South SF Bay, exhibited elevated Hg_T (409-4011 ng/g) concentrations (Table 2), which is consistent with the previous analyses of these cores and thirteen other cores from the slough (MARVIN-DIPASQUALE, 2007). Of the three depth intervals analyzed, peak concentrations were found at depth in the main channel core (AS(Rb[29-42.5])) (4011 ng/g) and in the vegetated marsh core (AS(Mc[50-81])) (2346 ng/g) (Table 2). As discussed in Section 3.2, it is likely that these deeper sediment layers were deposited while mining operations were active at multiple ore processing facilities in the New Almaden mining District. Near-surface sediment (AS(Ra[0-7.5]), AS(Ma[0-17])) had the lowest Hg_T, with an average Hg_T of 459 ± 70 ng/g. Previous studies of the Guadalupe River and Lower South SF Bay have suggested that surface sediments have lower Hg concentrations due to restoration efforts and gradual environmental recovery after closure of the New Almaden Hg mine in 1973 (CONAWAY et al., 2004; THOMAS et al., 2002).

The Hg isotopic composition variation with depth in the Alviso Slough sediment core suggests a lower contribution of Hg from calcine associated with New Almaden Hg mine waste in recently deposited sediment. The δ^{202}Hg values of the two cores analyzed decreased from +0.29 and +0.20‰ at the base of the cores (43-81 cm) (AS(Rc[43-56]), AS(Mc[50-81])) to -0.29 and -0.32‰ at the surface (AS(Ra[0-7.5]), AS(Ma[0-17])) (Fig. 4). As discussed above, calcines have been observed to have higher δ^{202}Hg values than unroasted ore (STETSON et al., 2009). It is likely that Hg in the deeper sediment in Alviso Slough (AS(Rc[43-56]), AS(Mc[50-81])) result from calcine waste emanating from New Almaden Hg mine. Lower δ^{202}Hg values in more recent sediments are consistent with a lower contribution of Hg from mine calcines to the total Hg in the Alviso Slough surface sediment. Smith et al. (2008) measured the Hg isotopic composition of sedimentary and volcanic rocks in the San Francisco Bay area, which likely represent the background sediment of San Francisco Bay, and reported an average δ^{202}Hg value of -0.63 ± 0.20‰. A mixture of Hg from calcine with high δ^{202}Hg values mixing with ambient Hg from sediments or with unroasted mine tailings could produce the isotopic depth profile observed (Fig. 4).

4.3 Hg concentration and isotopic composition in Cosumnes River and Yolo Bypass

Suspended sediment from hydraulic Au mining has been proposed to have been a dominant source of sediment to the Sacramento-San Joaquin delta and San Francisco Bay during the active mining period (DUNLAP et al., 2008; JAFFE et al., 2007). Studies of Hg concentrations in water and sediment of the Sacramento river system have implicated this historic Au mining as a major source of Hg contamination (DOMAGALSKI, 1998; DOMAGALSKI, 2001; HORNBERGER et al., 1999). Depth profiles of sediment cores analyzed in other studies show that Hg_T peaked in sediment deposited during the height of Au mining operations and has decreased in recent decades to surface sediment concentrations averaging 200-300 ng/g in the Sacramento - San Joaquin Delta (CONAWAY et al., 2003; HORNBERGER et al.,

1999) and lower Hg concentrations (100-180 ng/g) in riverbed sediment within the Sacramento River system (DOMAGALSKI, 2001; HEIM et al., 2007). The Cosumnes River, a tributary to the Sacramento - San Joaquin Delta, flows undammed through former Au mining regions in the western Sierra-Nevada foothills. We analyzed surface sediment from the Cosumnes River main channel and fringing emergent marshes in order to evaluate the Hg isotopic composition of Hg associated with Au mining in this area.

The Hg_T measured in this study was similar to previous studies, with Hg_T concentrations of 65-114 ng/g in the Cosumnes River main channel (CR(Ra), CR(Rb)) and 303-419 ng/g in the fringing marsh (CR(Ma), CR(Mb)) (Table 2). The δ^{202}Hg values of sediments from the Cosumnes River main channel and fringing marshes are significantly lower than those measured in Alviso Slough (AS(Ra[0-7.5]) δ^{202}Hg = -0.29‰, AS(Ma[0-17]) δ^{202}Hg = -0.32‰). Surface sediments from the river channel (CR(Ra), CR(Rb)) have from δ^{202}Hg values of -0.91 and -0.88‰ and the marsh samples (CR(Ma), CR(Mb)) have δ^{202}Hg values of -0.75‰ (n=2). As discussed in section 4.1, it is likely that Hg(0) used in Au mining operations had lower δ^{202}Hg values than HgS ore and calcine. Therefore, lower δ^{202}Hg values in sediment from the Cosumnes River are consistent with a Hg source emanating from Hg used in placer Au mines, and it is likely that the δ^{202}Hg signal of the metallic Hg used is approximately -0.9‰.

Northwest of the Cosumnes River, the Yolo Bypass Water Conservation Area (YBWCA) is within the Sacramento River watershed, downstream of both Sierra Nevada and Coast Range Au and Hg mine sources. Surface sediment (0-2 cm) from wetlands in YBWCA (YB(a), YB(b), YB(c)) had a mean Hg_T of 135 ± 14 ng/g. The δ^{202}Hg values of YBWCA rice fields are similar but slightly higher than those measured in the Cosumnes River marshes (-0.70 ± 0.04‰, n=3). It is likely that the higher δ^{202}Hg values in YBWCA result from a mixture of metallic Hg with low δ^{202}Hg values used in industry and placer Au mines, and HgS ore and calcine waste with higher δ^{202}Hg values from nearby Hg mines.

4.4 Hg concentration in San Francisco Bay inter-tidal and wetland surface sediment

All intertidal surface sediment samples analyzed in this study had Hg_T elevated above pre-Industrial San Francisco Bay sediment concentrations (60-80 ng/g) (CONAWAY et al., 2004; HORNBERGER et al., 1999), and ranged from 161 to 846 ng/g (Fig. 2, Table 2). Previous studies have suggested that legacy Hg mining in the New Almaden mining District is the dominant source of Hg contamination to South SF Bay, as evidenced by elevated Hg_T in sediment and wildlife in South SF Bay (ACKERMAN et al., 2008; CONAWAY et al., 2004; GREENFIELD et al., 2005; GREENFIELD and JAHN, 2010). However, there are several other locations in SF Bay with equally elevated Hg_T {Marvin-DiPasquale, 2003}. Atmospheric deposition of Hg is relatively uniform throughout SF Bay (TSAI and HOENICKE, 2001) and does not adequately explain spatial variation in sediment HgT concentrations. Moreover, mass-balance calculations suggest that atmospheric deposition is most likely a minor source of Hg to sediments (MACLEOD et al., 2005), with annual atmospheric Hg deposition to SF Bay an order of magnitude less than the Hg load entering SF Bay in suspended sediment alone (ABU-SABA and TANG, 2000; DAVID et al., 2009; TSAI and HOENICKE, 2001). Our analyses do not show a simple spatial pattern in surface inter-tidal sediment Hg_T in SF Bay and the causes of the spatial Hg_T concentration variations observed are not readily identifiable.

Inter-tidal and wetland sediment at the southern extent of SF Bay in Guadalupe Slough (IT(-5b)) and Alviso Slough (IT(-7), IT(-5a), IT(-2), IT(-1)) downstream of the Guadalupe River had elevated Hg_T ranging from 320 to 538 ng/g. Similar sediment Hg_T in Alviso Slough and neighboring areas have been measured in previous studies of subaqueous surface sediment (CONAWAY et al., 2004; MARVIN-DIPASQUALE, 2007; THOMAS et al., 2002; TOPPING et al., 2004). Some researchers have suggested that current industrial activity is the most dominant source of Hg to surface sediment in the South Bay because the volume of freshwater input from urban runoff, municipal waste discharge, and industrial waste discharge are all higher than discharge from the Guadalupe River (FLEGAL et al., 1990). Runoff and discharge from Moffett Federal Airfield and the City of Sunnyvale waste water treatment ponds in Sunnyvale Baylands Park are also potential sources of Hg contamination in Guadalupe and Alviso sloughs. Other researchers have asserted that upstream legacy Hg mining continues to be the primary source of Hg to sediment (MARVIN-DIPASQUALE, 2007; THOMAS et al., 2002). Studies of Hg_T concentration alone are inadequate to settle this debate regarding Hg sources to South Bay sediment.

Interestingly, the highest Hg_T values (679 to 1529 ng/g) were measured in sediment from the Central Bay at sites along the Martin Luther King (MLK) Regional Shoreline (Oakland, CA) (IT(42a), IT(42b)) and along Point Isabel (Richmond, CA) (IT(62a), IT(62b)). Studies of benthic surface sediments in SF Bay had relatively lower Hg_T concentrations in the Central Bay and relatively higher Hg_T in sediments of the South Bay and San Pablo Bay (CONAWAY et al., 2007). It is possible that Hg has been transported south from the Sacramento-San Joaquin Delta and north from the Guadalupe Delta into the Central Bay (JAFFE et al., 2007), but there are also many additional local sources that could have contributed Hg to these sediments. Oakland and Richmond are both highly urbanized centers. The Oakland International Airport is less than 1 km from the two Oakland sites, and a municipal waste incinerator and a chloraklali plant operated in Oakland in previous decades (CONAWAY et al., 2008). Richmond is the site of several oil refineries and Pt. Isabel was previously used as a battery disposal area (LEVINE-FRICKE, 1992). Sediment at the MLK Regional Shoreline is derived from a combination of Oakland watersheds and sediment transported from both the Central and the South Bay during freshwater pulses and flood/ebb tides (RUHL et al., 2001). Sediment at Point Isabel is transported primarily from a combination of the urban watersheds of El Cerrito and Richmond and from San Pablo Bay (RUHL et al., 2001). The Oakland and Richmond sampling site areas are highly influenced by tidal currents, and there is significant sediment re-suspension (RUHL et al., 2001), and post-depositional vertical mixing (FULLER et al., 1999). These and other physical processes may resurface deeper sediment containing more elevated Hg_T concentrations (FULLER et al., 1999).

More than 85 km north from the Guadalupe delta and to the north, San Pablo Bay tidal sediment had Hg_T concentrations ranging from 286 to 314 ng/g near the Petaluma River and San Pedro Peninsula (IT(85), IT(87), IT(90), IT(91)). Other studies have measured similar Hg_T in subaqueous sediment in this area (CONAWAY et al., 2004; HEIM et al., 2007; HORNBERGER et al., 1999; MARVIN-DIPASQUALE et al., 2003a; MARVIN-DIPASQUALE et al., 2003b). Several small historical Au and Hg mines operated in watersheds that contribute to the Petaluma and Napa rivers, which flow into San Pablo Bay, although the majority of sediment load to this region is delivered from the Sacramento and San Joaquin Rivers, which drain the Sierra Nevada (CONAWAY et al., 2007; HORNBERGER et al., 1999; JAFFE et al., 2007; MARVIN-DIPASQUALE et al., 2003a). San Pablo Bay experienced substantial sediment accumulation during the late 19th century due to hydraulic Au-mining discharge (JAFFE et al., 2007) and there is currently a significant input of older sediment eroded from upstream drainage basins (FULLER et al., 1999).

To the east of San Pablo Bay, sediment in Suisun Bay near the Carquinez Strait (IT(110), IT(115), IT(119)) had Hg_T ranging from 161 to 253 ng/g, and sediment at Kirker Creek near the confluence of the San Joaquin and Sacramento River (IT(143)) had 327 ng/g Hg_T (Fig. 1). Au mining was prevalent in watersheds contributing to the San Joaquin and Sacramento Rivers, and has been implicated as a source of Hg and other contaminants to both deep and surface sediment (BOUSE et al., 2010; DUNLAP et al., 2008; HORNBERGER et al., 1999; JAFFE et al., 2007). However, there is also extensive industrial activity in this region, including a large chemical production plant near the site at Kirker Creek, several petroleum refineries, and a water treatment plant near the Carquinez Strait. With this multitude of potential Hg sources, it is interesting that sediment in the Carquinez Strait had the lowest Hg_T measured in this study. It is possible that the relatively lower Hg concentrations in Carquinez Strait derive from differences in sediment deposition dynamics in the narrow passage, but it is also possible that Hg emitted in the area is not locally deposited to sediments. Significant spatial variation in sediment Hg_T has been observed in previous studies and attributed to geochemical and physical sediment characteristics (CONAWAY et al., 2003; HEIM et al., 2007). Complex regions like Suisun Bay and the Carquinez Straight highlight the need for greater understanding of the Hg sources and sediment transport dynamics that contribute to sediment Hg contamination.

Seasonally-flooded wetland surface sediment in the South Bay had slightly lower Hg_T than most inter-tidal sediment, ranging from 188 to 292 ng/g. The one sample collected from the fringing vegetated marsh along Alviso Slough (WL(-3)) had higher Hg_T (292 ng/g) than the other wetland sediment (215 ± 20 ng/g), all of which were collected 7-25 km north of the mouth of Alviso Slough. There is no other apparent pattern of Hg_T, regardless of geographic location or assumed point-sources including urban runoff from Newark, Union City, Redwood City, and several wetlands reconstruction projects. SF Bay wetlands have been suggested as important areas of Hg bioaccumulation in local aquatic food webs (ACKERMAN et al., ; EAGLES-SMITH and ACKERMAN, 2009; HEIM et al., 2007; MARVIN-DIPASQUALE et al., 2003b), and effective ecological protection requires the reliable identification of Hg sources.

In summary, dominant sources of Hg to sediment in San Francisco Bay could not be identified solely by variations in Hg_T. Specifically, the extent to which historic Hg mining in the New Almaden mining District currently influences sediment Hg contamination throughout San Francisco Bay is difficult to determine by the use of Hg_T values alone. Highly elevated Hg_T was measured in South SF Bay, but the highest Hg_T were found in the Oakland and Richmond urban watersheds. The variety of potential sources and lack of spatial patterns of sediment Hg_T demonstrates the need for additional tracers to determine the Hg source(s) in this study area.

4.5 Hg isotopic composition of San Francisco Bay inter-tidal and wetland sediment

There is a systematic spatial gradient in Hg isotopic composition throughout San Francisco Bay. Surface sediments in Lower South and South Bays have higher δ^{202}Hg values than those in Suisun Bay, San Pablo Bay, and Central Bay (Fig. 4). The geographic pattern of Hg isotopic composition in surface sediment suggests that the sources of Hg to the sediment are regional rather than locally controlled, and that Hg delivered from the Guadalupe River system is a likely dominant southern source and Hg delivered from the Sacramento-San Joaquin River system is a likely northern source. The Hg isotopic composition of sediment does not reflect significant contributions from isotopically distinct local point-sources of Hg. While this study did not specifically analyze the Hg isotopic composition of potential Hg point sources, it is likely that Hg pollution from chlor-alkali plants, battery waste, medicinal waste, and shipyard anti-fouling paint have isotopic compositions reflecting the Hg(0) produced from Hg mines and used in industrial applications. If these individual point-sources dominated SF Bay surface sediment Hg contamination, we would expect that the sediments near each source would have Hg isotopic compositions of the metallic Hg endmember within a small geographic area. Our results do not show significant localized variation. Rather, the gradally changing spatial pattern in sediment Hg isotopes is consistent with sediment Hg contamination derived from the mixture of Hg emanating from the Guadalupe and Hg emanating from the northern portion of SF Bay.

Inter-tidal sediments south of SF Bay in Alviso Slough (IT(-7), IT(-5a), IT(-2)) had similar Hg isotopic composition, with δ^{202}Hg values ranging from -0.36 to -0.30‰, identical to subaqueous surface sediment in the Alviso Slough channel (AS(Ra[0-7.5])) with a δ^{202}Hg value of -0.29‰ (Table 2, Fig. 3). Sediment from neighboring Guadalupe Slough (IT(-5b)) and the confluence of Coyote Creek with the Alviso Slough (IT(-1)) had slightly lower δ^{202}Hg values, ranging from -0.46 to -0.43‰, and wetland sediment flanking Coyote Creek has a δ^{202}Hg value of -0.44‰. It is likely that sediment in these sloughs that neighbor Alviso Slough primarily contain Hg-contaminated sediment transported down the Guadalupe River, but they also contain some Hg from surrounding watersheds. The Great Valley sedimentary rock sequence and Clear Lake volcanic rock sequence from the northern and central California coastline have a mean δ^{202}Hg value of -0.63 ±20‰ (SMITH et al., 2008), which is likely to be a good estimate of the value for uncontaminated sediment in the San Francisco Bay area. The slightly lower δ^{202}Hg values observed in Guadalupe Slough and Coyote Creek could result from a mixture of Hg transported down the Guadalupe River and Hg from background sediment or industrial operations. Moving north, sediment in South Bay (IT(14) to IT(42b)) have lower δ^{202}Hg values ranging from -0.53 to -0.59‰ (Table 2, Fig. 1,3). Wetland sediments from South Bay have similar Hg isotopic composition to neighboring inter-tidal sediment, with δ^{202}Hg values ranging from -0.50 to -0.68‰, and display the same geographic gradient in Hg isotopic composition (Fig. 1,3).

Sediments in the northern parts of San Francisco Bay have lower δ^{202}Hg values than those in the South Bay. Surface sediments in the Central Bay (IT(52), IT(62a), IT(62b)) and San Pablo Bay (IT(85) to IT(91)) have δ^{202}Hg values ranging from -0.59to -0.73‰ (Table 2, Fig. 1,3). To the northeast, surface sediments in the Carquinez Strait (IT(110), IT(115), IT(119)) and Suisun Bay (IT(143)) have the lowest δ^{202}Hg values, ranging from -0.74 to -0.99‰. In general, sediments further north and nearer the Sacramento-San Joaquin Delta have lower δ^{202}Hg values (Fig. 3), and their δ^{202}Hg values are lower than are expected for uncontaminated sediment, assumed to be ~-0.6‰ (SMITH et al., 2008). The δ^{202}Hg values in Sacramento Delta sediments are similar those measured in the Cosumnes River channel (CR(Ra,Rb) δ^{202}Hg = -0.91‰, -0.88‰; CR(Ma,Mb) δ^{202}Hg = -0.75‰) and suggest that the source of Hg in the Cosumnes River is also the source of Hg in the Delta. Therefore, it is likely that metallic Hg is the low δ^{202}Hg (-0.9‰) source of Hg entering SF Bay via the Sacramento Delta.

The geographic pattern of Hg isotopic composition in surface sediment is moderated by sediment transport and mixing in San Francisco Bay. The Sacramento River is the primary source of sediment to Suisun and San Pablo Bay, and may supply up to 90% of the sediment entering the greater San Francisco Bay (JAFFE et al., 2007). Fifty-year reconstructions of bathymetry in South San Francisco Bay suggest a net transport of sediment from the Central Bay southward (JAFFE and FOXGROVER, 2006). We suggest that contaminated sediment transported southward from the Sacramento River system, with δ^{202}Hg values of -0.9‰, gradually mixes with sediment from the Guadalupe River system, with δ^{202}Hg values of ~-0.3‰, producing the observed spatial δ^{202}Hg gradient through San Francisco Bay. It is also possible that a third source of Hg with intermediate δ^{202}Hg value (between -0.3‰ and-0.9‰) emanates from the Central Bay and mixes with the northern and southern Hg sources. Our results are consistent with the mixing of two, or possibly three, dominant regional Hg sources to SF Bay.

The spatial gradient of sediment δ^{202}Hg values suggests that locations with highly elevated Hg_T (e.g. IT(42a,b), IT(42a,b), IT(-7)) are not due to the influence of contemporary local point sources. Rather, elevated Hg_T in San Francisco Bay sediment likely arises from re-suspension or exposure of buried sediment that were deposited with higher Hg_T. Numerous studies have shown that Hg_T in sediment were generally higher in past decades (CONAWAY et al., 2007) and natural erosion and dredging operations in the Bay routinely expose older sediment, including those initially deposited during the peak Hg mining and hydraulic Au mining era (FREGOSO et al., 2008; VAN GEEN and LUOMA, 1999). Studies have suggested that exposure of this older sediment is a significant source of Hg to the surface environment (CONAWAY et al., 2007; VAN GEEN and LUOMA, 1999), and the Hg isotopic data are consistent with this hypothesis.

Within the sediment, it may be possible for Hg isotopes to be fractionated by biotic or abiotic reduction of Hg(II) to volatile Hg(0). If Hg volatilization were due to photoreduction, laboratory studies indicate that the observed 0.6‰ range of δ^{202}Hg values would be accompanied by a concurrent shift of ~0.7‰ in Δ^{199}Hg values (BERGQUIST and BLUM, 2007). There is only a 0.09‰ total range in Δ^{199}Hg values (see section 4.5) in SF Bay sediments, therefore differing degrees of Hg photoreduction cannot explain the observed Hg isotope variation in SF Bay sediments.

To assess the potential magnitude of in-situ biotic Hg isotope fractionation which does not have accompanying shifts in Δ^{199}Hg, on the observed sediment isotope composition, we calculated the fraction of Hg(0) production and subsequent volatilization that would be required to produce a 0.1‰ shift in sediment δ^{202}Hg values. We used the Raleigh distillation equation:

$$\ln(R_{sed\text{-}R}/R_{sed\text{-}0}) = [(1/\alpha) - 1]*\ln(f)$$

where $R_{sed\text{-}R}$ is the ratio of ^{202}Hg/^{198}Hg in the remaining sediment, $R_{sed\text{-}0}$ is the ratio of ^{202}Hg/^{198}Hg in the sediment prior to any in-situ reduction and volatilization, α is the fractionation factor between volatilized Hg and initial Hg, and f is the fraction of Hg remaining in the sediment. Using the range of published fractionation factors for Hg(II) reduction (α = 1.0004 -1.0020) (BERGQUIST and BLUM, 2007; KRITEE et al., 2008; KRITEE et al., 2007), we estimate between 5 and 22% of the total Hg in sediment would need to be removed via volatilization to produce a 0.1‰ shift in the residual sediment δ^{202}Hg value. Overall, San Francisco Bay sediment had a 0.6‰ range of δ^{202}Hg values. We calculate that removal of 26-74% of sediment Hg would be required to produce the total observed range of δ^{202}Hg values. It is extremely unlikely that in-situ reduction and volatilization processes could liberate such a large proportion of Hg(0), and this process does not provide an explanation for the observed spatial trend in sediment δ^{202}Hg values. Furthermore, mass-balance estimates suggest that there is a net flux of Hg into the sediment from the water column (MACLEOD et al., 2005). Therefore, we suggest that the range of SF Bay sediment δ^{202}Hg values reflect the δ^{202}Hg values of Hg inputs to the Bay.

4.6 Mass-Independent Fractionation of Hg in sediment

In addition to mass-dependent fractionation (MDF) of Hg isotopes, Hg isotopes undergo mass-independent fractionation (MIF), reported as Δ^{199}Hg values. While many processes are known to cause MDF of Hg isotopes, only a few processes are known to cause MIF (BERGQUIST and BLUM, 2007; ESTRADE et al., 2009). MIF is thought to result from either differences in reaction probabilities due to different magnetic spins in even and odd isotopes (magnetic isotope effect) (BUCHACHENKO et al., 2008) or differences in the relationship between nuclear volume and nuclear charge radii between isotopes (nuclear field shift effect) (SCHAUBLE, 2007). In the environment, MIF is believed to principally result from photochemical reduction of Hg(II) and MeHg species (BERGQUIST and BLUM, 2007; ZHENG and HINTELMANN, 2009). In San Francisco Bay sediment, it is likely that the Δ^{199}Hg values reflect a combination of the Δ^{199}Hg value of the source Hg, modified somewhat by photo-reduction of dissolved Hg(II) prior to initial incorporation into sediment. The inter-tidal surface sediment had a narrow range of Δ^{199}Hg values from +0.04 to +0.14‰ (mean = 0.08±0.03‰), with no geographic pattern or correlation to point sources. The small range of Δ^{199}Hg values in the sediment sampled suggests that a only a small degree (< 10%) (BERGQUIST and BLUM, 2007) of photochemical Hg-reduction has occurred in each location.

Wetland sediment had slightly elevated Δ^{199}Hg values compared to intertidal sediment, ranging from +0.08 to +0.16‰ (wetlands mean = 0.13±0.03‰), which suggests that a slightly greater proportion (< 15%) of the Hg(II) pool had been photochemically reduced and evaded from wetland sediment, compared to inter-tidal sediment. MIF signatures can be preserved through multiple photo-reduction cycles, producing a summed effect on the MIF measured. The wetlands seasonally flood and dry, which could promote seasonal exposure to direct sunlight. Additionally, wetlands are higher on the landscape than inter-tidal sediment and receive more prolonged daily exposure to sunlight. Enhanced seasonal and daily exposure of wetlands to sunlight could result in higher Δ^{199}Hg values. Interestingly, deep marine sediment from the mid-Pleistocene Mediterranean Sea have an average Δ^{199}Hg value of 0.09±0.5‰ (GEHRKE et al., 2009), which is similar to both wetland and inter-tidal sediment in San Francisco Bay.

5. CONCLUSIONS

Mercury concentrations (Hg_T) of surface inter-tidal and wetland sediments in San Francisco Bay were elevated above background levels, ranging from 161 to 1529 ng/g. Although sediment Hg_T concentrations were elevated, there was no consistent spatial pattern of Hg_T. The New Almaden Hg mining District historically contributed Hg contamination to SF Bay via the Guadalupe River and we measured significantly elevated Hg_T in Guadalupe Delta sediments. The highest Hg_T measured were in Oakland and Richmond in the Central Bay and the lowest Hg_T measured were in sediments along the Carquinez Strait. The spatial distribution of Hg concentration does not distinguish the primary sources of Hg to current surface sediments. To improve our ability to infer contributing Hg sources, Hg stable isotopes were employed as a method for Hg source identification and to determine the relative influence of Hg from legacy mining in the New Almaden mining District versus other Hg sources on Hg contamination in SF Bay.

The Hg isotopic composition of tailings and calcine waste from New Idria Hg Mine suggests that Hg contamination emanating from Hg mine waste is isotopically distinct from the metallic Hg produced and used in industrial and Au mining practices. Tailings had an average δ^{202}Hg value of -0.38 ± 0.07‰, and calcine had a δ^{202}Hg value of +0.03 ± 0.03‰, indicating that Hg mine waste will have higher δ^{202}Hg values than Hg(0) products. Sediment cores from Alviso Slough have δ^{202}Hg values ranging from +0.29 to -0.32, decreasing from the deepest samples to the surface sediment. This suggests that the Hg isotopic composition of Hg contamination entering Alviso Slough from the New Almaden Hg mining District has changed over time, but currently has a δ^{202}Hg value of ~-0.3‰. In northern watersheds of SF Bay, wetland and riverbed surface sediment from the Cosumnes River and Yolo Bypass have δ^{202}Hg values ranging from -0.91 to -0.72‰, and it is likely that a δ^{202}Hg of ~-0.9‰ is representative of Hg contamination emanating from Au mining and industrial districts in the Sierra-Nevada foothills.

There is a clear spatial pattern in the Hg isotopic composition of surface sediment in SF Bay that suggests the gradual mixing of two dominant regional Hg sources that are isotopically distinct from each other. Inter-tidal sediment has δ^{202}Hg values ranging from -0.30 to -0.99‰ with a systematic transition from higher δ^{202}Hg values in the Alviso Slough and South Bay to lower δ^{202}Hg values in San Pablo Bay and Suisun Bay in northern SF Bay. Wetland surface sediments in the South Bay have a narrow range of δ^{202}Hg values (-0.67 to -0.50‰) that are consistent with inter-tidal surface sediment from the same geographic area. The observed Hg isotopic pattern leads us to the interpretation that Hg mine waste with δ^{202}Hg ~-0.3‰ emanates from the New Almaden Hg mining District and enters the southern portions of SF Bay, and that a second Hg source, such as Hg(0) used in Au mining and industrial activities with δ^{202}Hg ~-0.9‰, emanates from the Sacramento and San Joaquin watersheds and extends into the northern SF Bay. These two sources gradually mix throughout the SF Bay system, driven by the significant currents and tidal action. The spatial pattern of Hg isotopic composition also suggests that these two major sources, rather than multiple localized sources, dominate Hg contamination in SF Bay. This study demonstrates that Hg isotope ratios in environmental samples can be used effectively to distinguish and trace different sources of Hg contamination in coastal areas.

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TABLES

Table 1: Hg Isotopes of sample replicates

Sample Code	Latitude (N)	Longitude (W)	Hg_T (ng/g)	δ^{202}Hg (‰)	Δ^{201}Hg (‰)	Δ^{199}Hg (‰)
NI(C)	36.41558	120.67314	1,013,400	0.05	0.01	0.00
NI(C)	36.41558	120.67314	939,060	0.00	-0.02	-0.02
NI(C) average	36.41558	120.67314	976,230	0.03	0.00	-0.01
1 SD			52,560	0.03	0.02	0.02
CR(Ma)	38.25867	121.42783	297	-0.78	0.00	0.08
CR(Ma)	38.25867	121.42783	310	-0.73	-0.04	0.07
CR(Ma) average	38.25867	121.42783	303	-0.75	-0.02	0.07
1 SD			9	0.03	0.01	0.01
IT(90)	38.18214	122.56315	248	-0.71	0.06	0.09
IT(90)	38.18214	122.56315	324	-0.59	0.06	0.06
IT(90) average	38.18214	122.56315	286	-0.65	0.06	0.08
1 SD			53	0.08	0.00	0.02
IT(-2)	37.44747	121.01978	431	-0.45	0.01	0.04
IT(-2)	37.44747	121.01978	361	-0.35	0.03	0.05
IT(-2) average	37.44747	121.01978	396	-0.36	0.03	0.07
1 SD			49	0.07	0.02	0.01
IT(-5b)	37.42397	122.01451	335	-0.42	0.05	0.12
IT(-5b)	37.42397	122.01451	306	-0.44	0.03	0.05
IT(-5b) average	37.42397	122.01451	320	-0.43	0.04	0.09
1 SD			20	0.02	0.01	0.04
IT(-7)	37.42284	121.97562	538	-0.31	0.06	0.11
IT(-7)	37.42284	121.97562	531	-0.30	0.05	0.03
IT(-7) average	37.42284	121.97562	534	-0.30	0.05	0.07
1 SD			5	0.01	0.01	0.05

Table 2: Hg concentration and isotopic composition in sediments

Site Code	Latitude (N)	Longitude (W)	Hg_T (ng/g)	δ^{202}Hg (‰)	Δ^{201}Hg (‰)	Δ^{199}Hg (‰)
New Idria Hg Mine Materials						
NI(Ta)	36.41519	120.67289	46,470	-0.33	0.03	0.06
NI(Tb)	36.41506	120.67244	71,260	-0.43	0.04	0.05
NI(C)	36.41558	120.67314	976,230	0.03	0.00	-0.01
Alviso Slough Sediment Core						
AS(-4a[0-7.5])	37.44381	122.00564	508	-0.29	0.08	0.07
AS(-4b[29-42.5])	37.44381	122.00564	4011	-0.06	0.03	0.03
AS(-4c[43-56])	37.44381	122.00564	832	0.29	0.01	0.03
AS(-4d[0-17])	37.44347	122.00639	409	-0.32	0.01	0.01
AS(-4e[44-68.5])	37.44347	122.00639	1144	-0.15	0.02	0.03
AS(-4f[50-81])	37.44347	122.00639	2346	0.20	-0.03	0.00
Cosumnes River and Yolo Bypass Sediment						
CR(Rb)	38.25750	121.43338	114	-0.91	0.00	0.09
CR(Ra)	38.25447	121.42277	65	-0.88	-0.01	0.06
CR(Ma)	38.25867	121.42783	303	-0.75	-0.02	0.07
CR(Mb)	38.25815	121.43704	419	-0.75	0.02	0.04
YB(a)	38.55204	121.59633	147	-0.72	0.03	0.12
YB(c)	38.52253	121.60132	119	-0.65	0.02	0.08
YB(b)	38.54918	121.59082	139	-0.73	0.10	0.16
Inter-tidal Sediment						
IT(-7)	37.42284	121.97562	534	-0.30	0.05	0.07
IT(-5b)	37.42397	122.01451	320	-0.43	0.04	0.09
IT(-5a)	37.43853	121.99225	473	-0.32	0.02	0.07
IT(-2)	37.44747	121.01978	396	-0.36	0.03	0.07
IT(-1)	37.45940	122.02139	343	-0.46	0.08	0.12
IT(14)	37.50275	122.16677	400	-0.53	0.08	0.09
IT(21)	37.53339	122.23190	379	-0.54	0.04	0.06
IT(42b)	37.74245	122.20955	1265	-0.59	0.10	0.14
IT(42a)	37.74244	122.20967	1529	-0.53	0.04	0.06
IT(52)	37.77322	122.39388	231	-0.65	0.07	0.10
IT(62a)	37.90430	122.31963	679	-0.65	0.11	0.12
IT(62b)	37.90330	122.32509	846	-0.66	0.05	0.06
IT(91)	38.20895	122.57868	295	-0.73	0.02	0.05
IT(90)	38.18214	122.56315	286	-0.65	0.06	0.08
IT(85)	38.01280	122.49023	314	-0.62	0.04	0.08
IT(87)	38.04815	122.49757	311	-0.59	0.05	0.07
IT(110)	38.06389	122.19289	253	-0.90	0.03	0.10
IT(115)	38.02093	122.14083	161	-0.74	0.06	0.11
IT(119)	38.01966	122.09418	192	-0.99	-0.01	0.07
IT(143)	38.02472	121.84380	327	-0.85	0.02	0.09

Wetland Sediment						
WL(-3)	37.46171	121.98881	292	-0.44	0.06	0.08
WL(9c)	37.51592	122.08149	238	-0.50	0.07	0.12
WL(9a)	37.50623	122.09018	204	-0.61	0.06	0.11
WL(9b)	37.50835	122.09745	232	-0.56	0.03	0.08
WL(16)	37.51171	122.18037	208	-0.60	0.12	0.16
WL(18)	37.52216	122.19995	208	-0.68	0.10	0.14
WL(21)	37.53107	122.23251	244	-0.66	0.11	0.16
WL(22)	37.59131	122.14605	201	-0.57	0.04	0.14
WL(24)	37.55169	122.24841	188	-0.67	0.11	0.14
Almaden Reservoir Sediment						
AR(a)	37.16272	121.83618	2866	-0.44	-0.01	0.03

FIGURE CAPTIONS

Figure 1: (a) Location of sampled inter-tidal and wetland surface sediments with (b) detailed map of Lower South Bay sampling locations, (c) map showing New Almaden Hg Mine, New Idria Hg Mine, San Francisco Bay, Cosumnes River, and Yolo Bypass. The star marks the mouth of the Alviso Slough; the black line depicts the approximate center-line of San Francisco Bay. Open triangles indicate inter-tidal sediment sampling locations, open squares indicate wetland locations, and the open circles indicate the location of Alviso Slough cores. Perpendicular lines were drawn between sample locations and the SF Bay center-line to approximate the distance of the sampling location from the Alviso Slough.

Figure 2: The Hg_T concentration versus the approximate distance of each sample site from the mouth of the Alviso Slough. Distances were estimated using the procedure described in Section 2.1. Grey diamonds represent tidal surface (0-2 cm) sediments and white squares represent wetland surface (0-2 cm) sediments. Error bars are within symbols.

Figure 3: The Hg isotopic composition of inter-tidal and wetland sediments. Grey diamonds represent inter-tidal surface (0-2 cm) sediments and white squares represent wetland surface (0-2 cm) sediments.

Figure 4: The δ^{202}Hg of sediments versus the approximate distance of each sample site from the mouth of the Alviso Slough. Bays corresponding to approximate distances are listed. Grey diamonds represent inter-tidal surface (0-2 cm) sediments; white squares represent wetland surface (0-2 cm) sediments; the triangle represents near-surface sediment (0-7.5 cm) from the Alviso Slough channel. Stars at -0.90‰, -0.70‰, -0.44‰, and -0.30‰ represent the δ^{202}Hg of surface sediments from the Cosumnes River channel (n=2), Cosumnes River wetlands (n=5), Almaden Reservoir (n=1), and Alviso Slough channel (n=2). Cosumnes River sediments are located further northeast of SF Bay and the Almaden Reservoir is located further south of SF Bay than is represented on the figure.

Figure 5: Depth profile of δ^{202}Hg in the Alviso Slough channel center and vegetated marsh along the west bank. New Almaden Hg Mine is 30 km upstream of the sampling location. The depth of each symbol is the average depth of each sediment sample analyzed and grey vertical bars indicate the sample depth interval. Sample Hg_T concentrations (ng/g) are labeled next to each symbol. The δ^{202}Hg in each core increases with depth, indicating a higher δ^{202}Hg in older sediment, likely associated with greater influence from mining activity.

FIGURES

Figure 1a

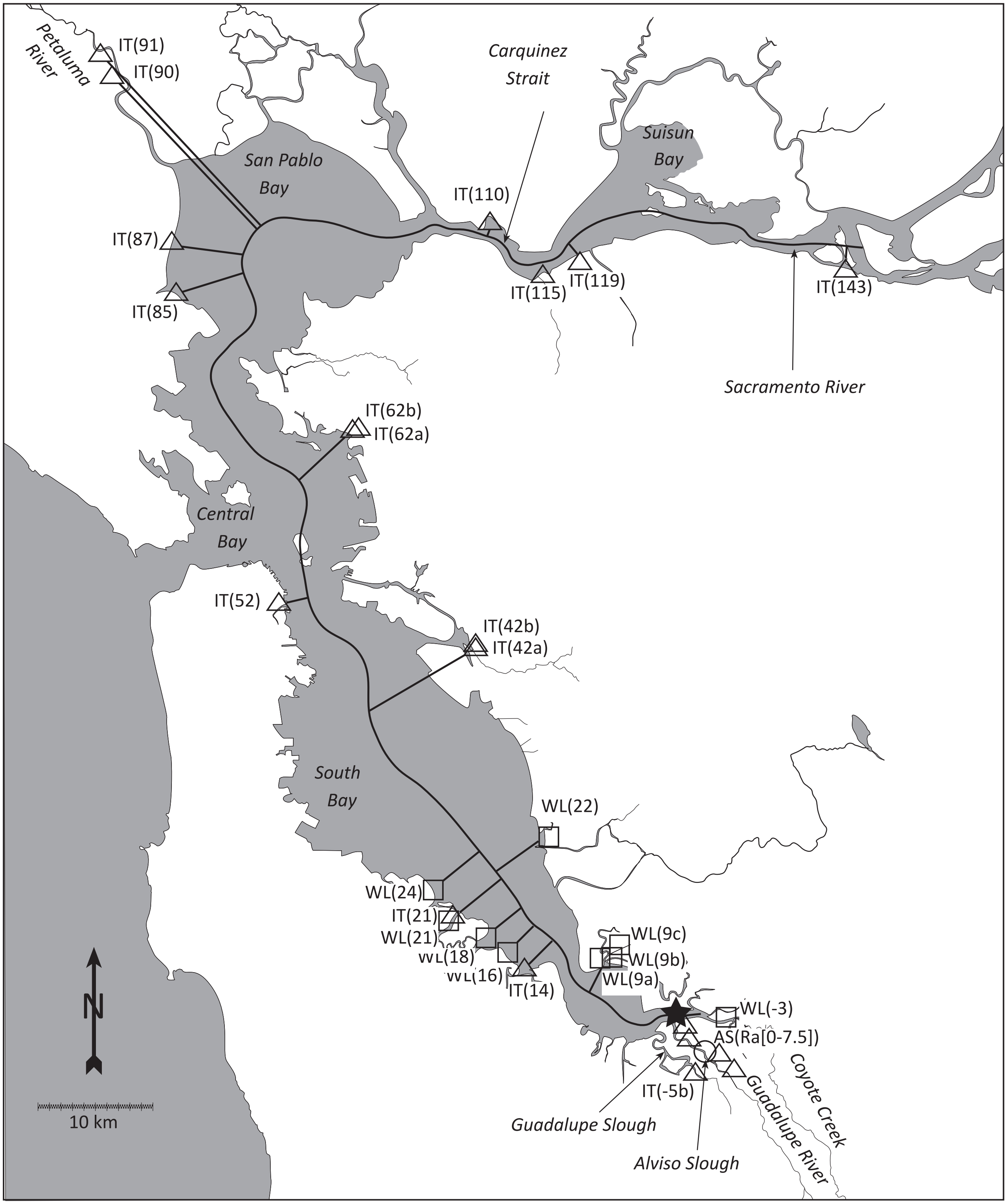


Figure 1b

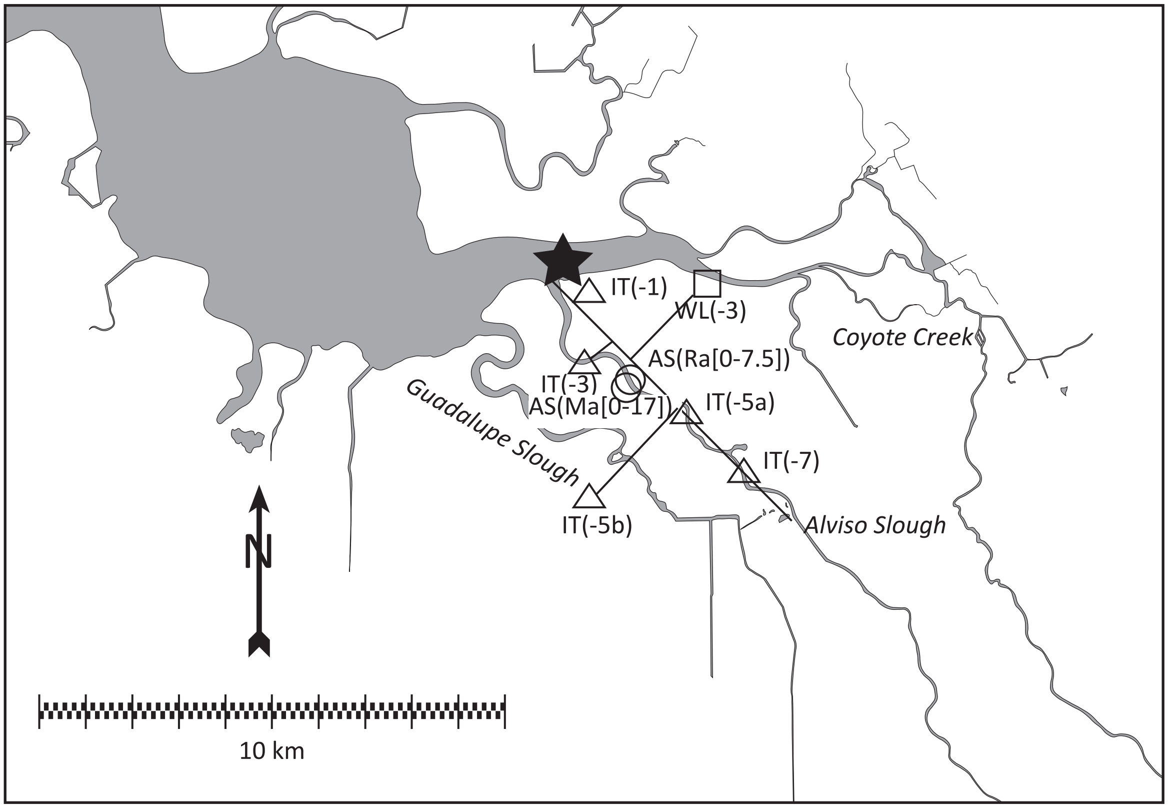

IT(-1)
WL(-3)
Coyote Creek
AS(Ra[0-7.5])
IT(-3)
AS(Ma[0-17])
IT(-5a)
Guadalupe Slough
IT(-7)
IT(-5b)
Alviso Slough
N
10 km

Figure 1c

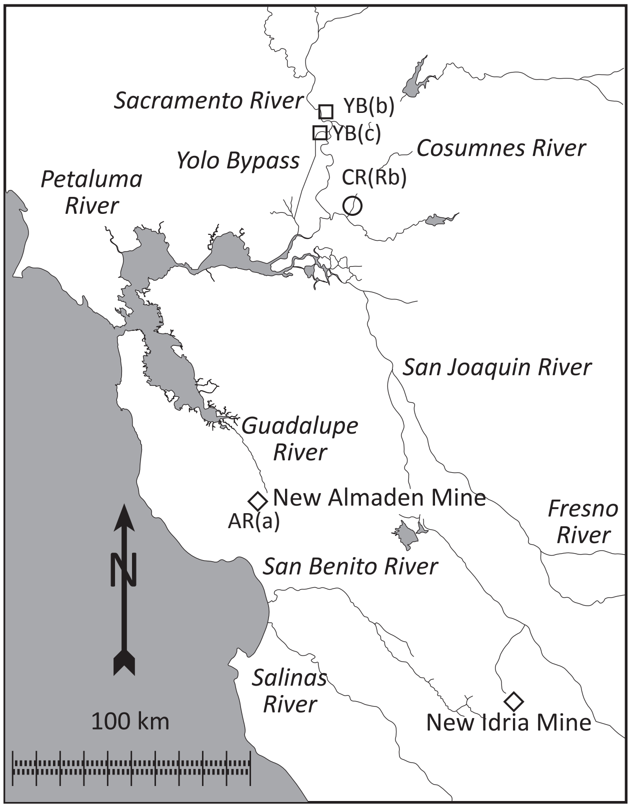
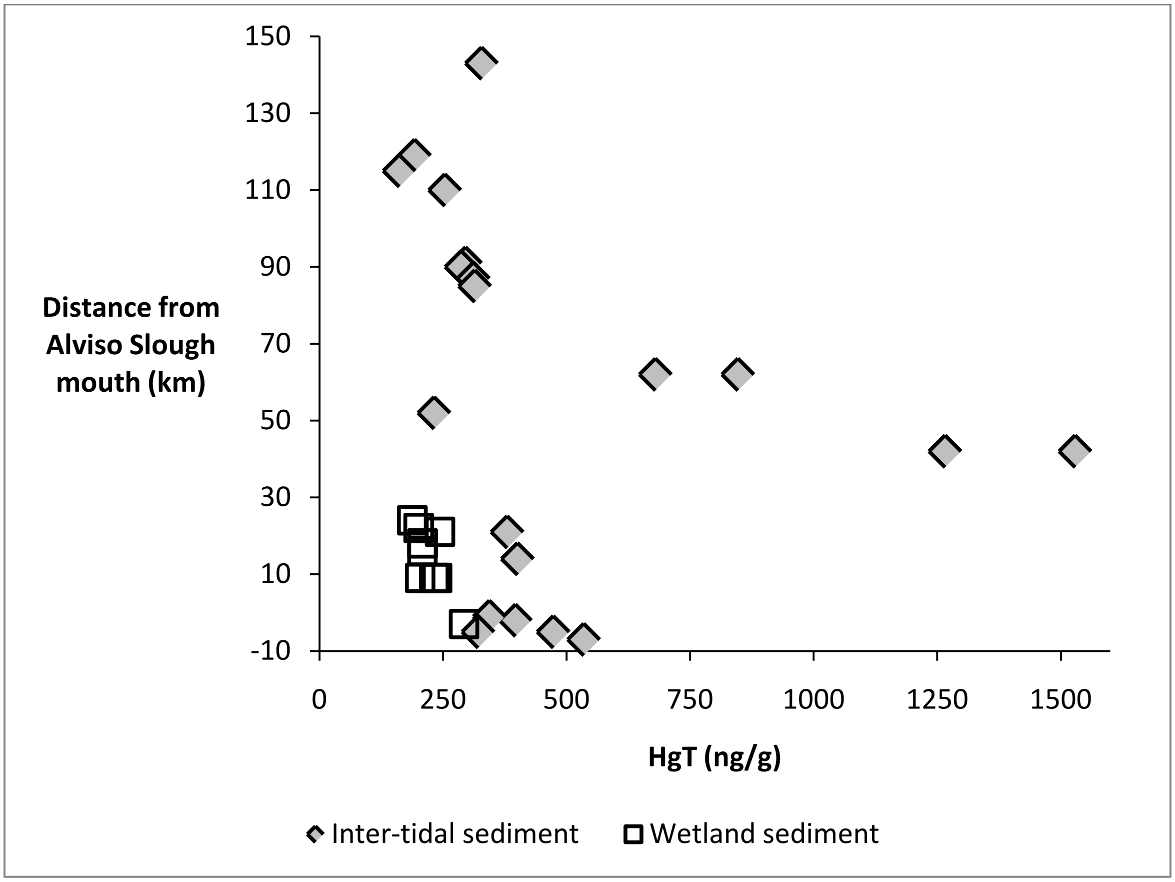
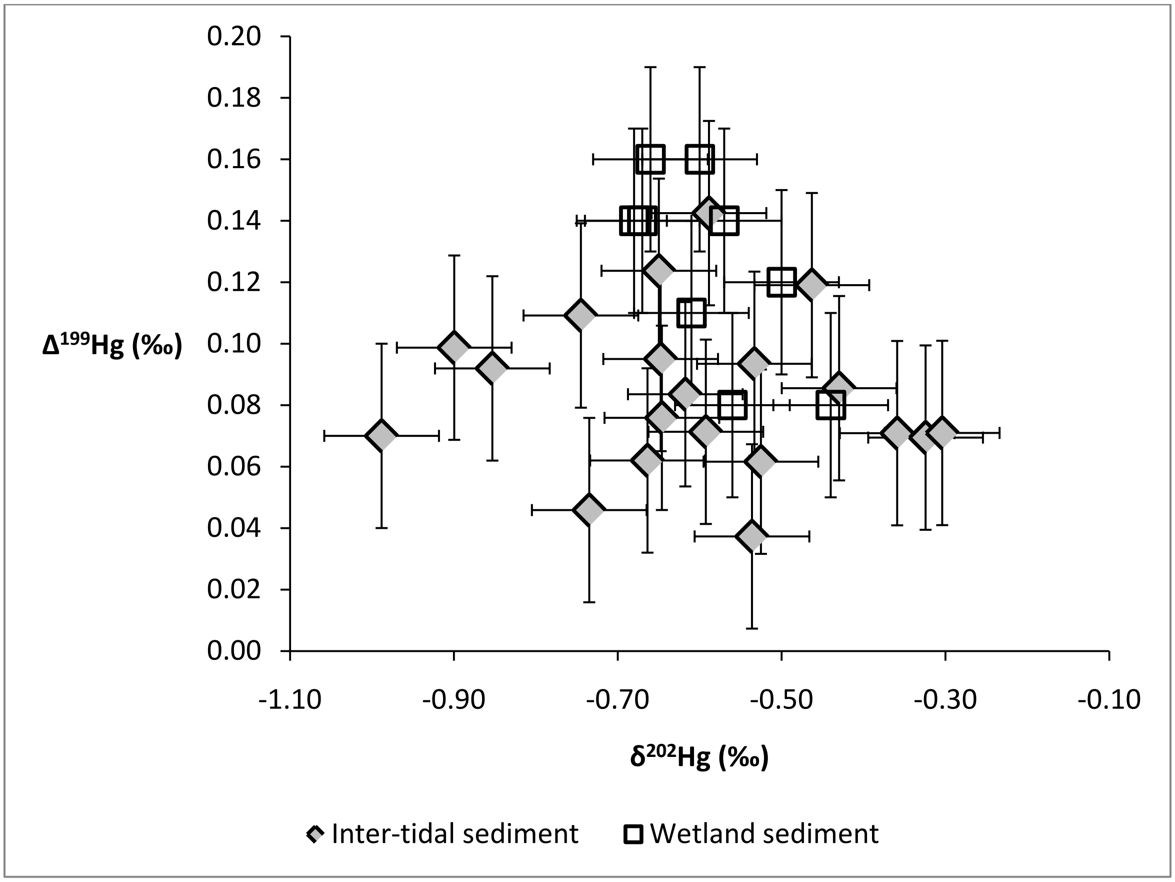

Sacramento River
YB(b)
YB(c)
Cosumnes River
Yolo Bypass
CR(Rb)
Petaluma
River
San Joaquin River
Guadalupe
River
New Almaden Mine
AR(a)
Fresno
River
N
San Benito River
Salinas
River
New Idria Mine
100 km

Figure 2:



Distance from Alviso Slough mouth (km)
150
130
110
90
70
50
30
10
-10
0
250
500
750
1000
1250
1500
HgT (ng/g)
Inter-tidal sediment
Wetland sediment

Figure 3:



0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Δ^{199}Hg (‰)
-1.10
-0.90
-0.70
-0.50
-0.30
-0.10
δ^{202}Hg (‰)
Inter-tidal sediment
Wetland sediment

Figure 4:

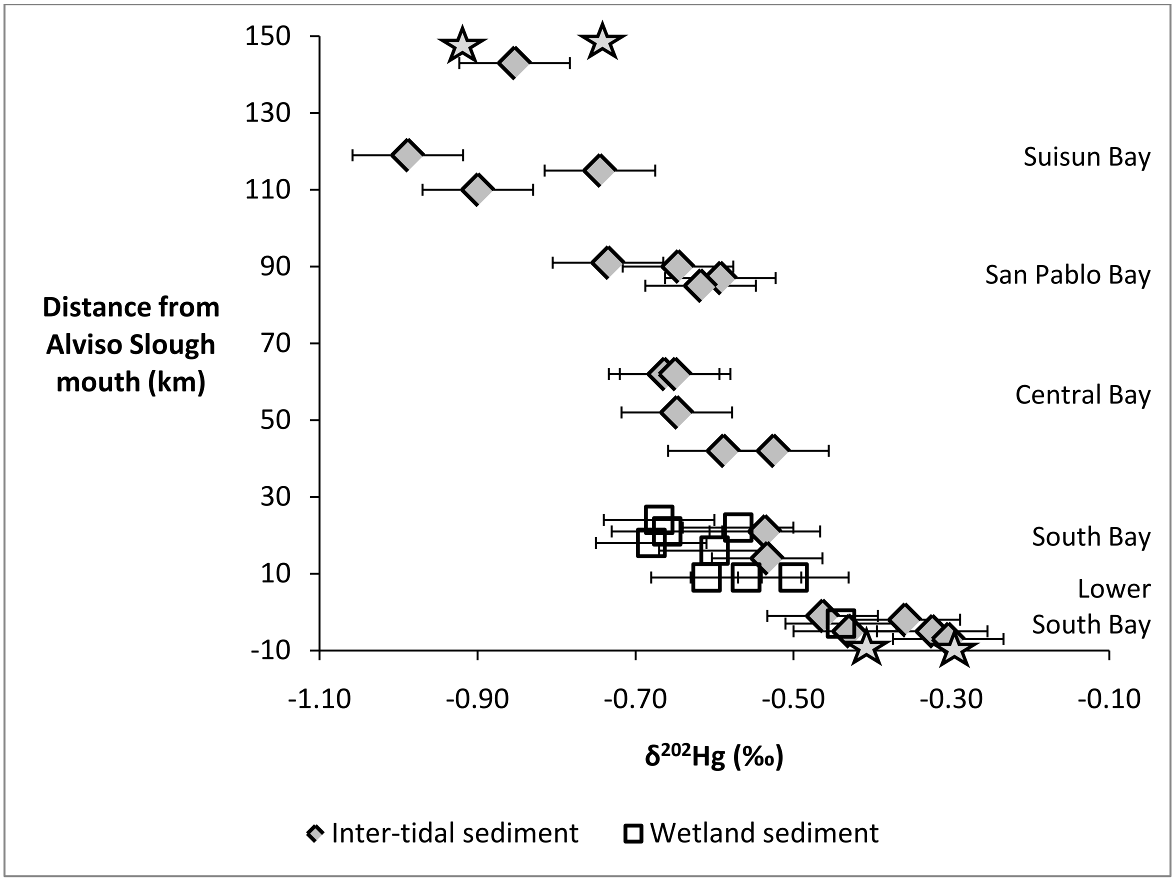
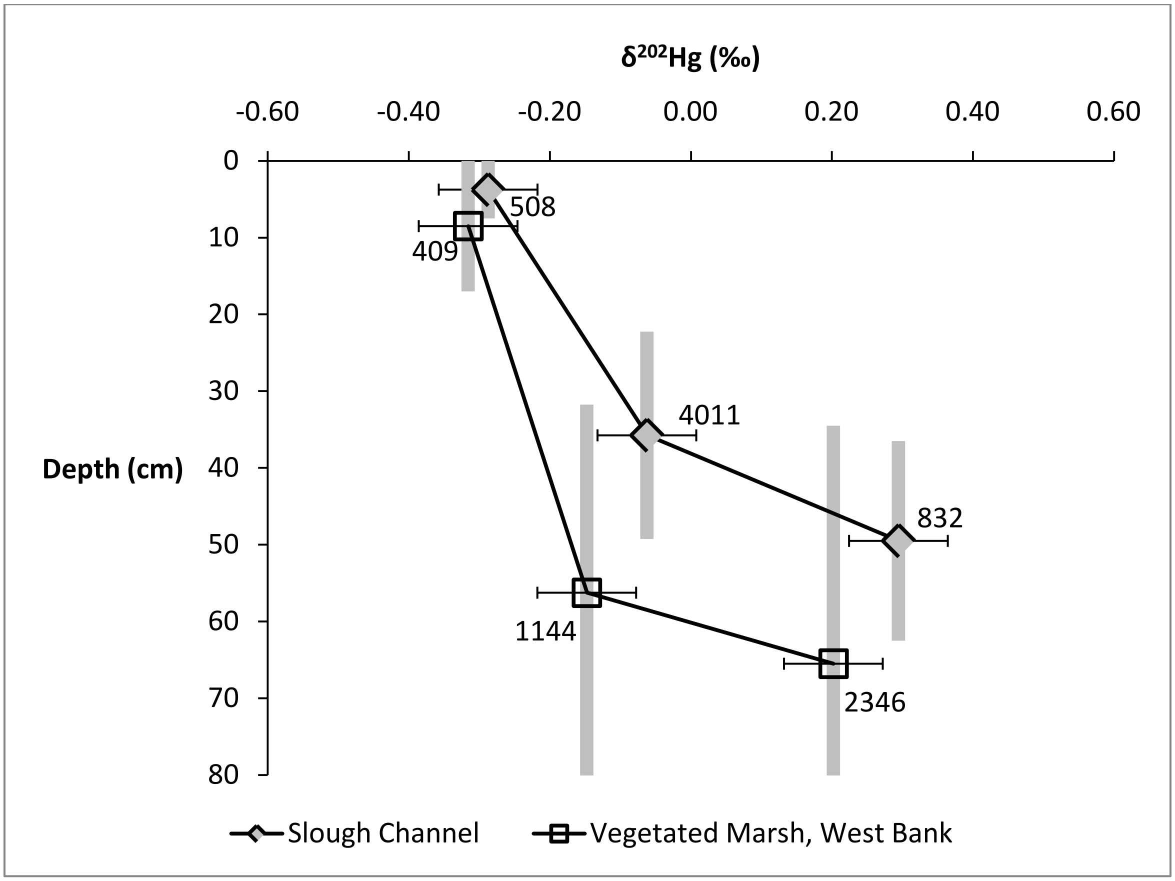

150
130
110
90
70
50
30
10
-10
Distance from Alviso Slough mouth (km)
-1.10
-0.90
-0.70
-0.50
-0.30
-0.10
δ^{202}Hg (‰)
Suisun Bay
San Pablo Bay
Central Bay
South Bay
Lower South Bay
Inter-tidal sediment
Wetland sediment

Figure 5:


δ202Hg (‰)
-0.60
-0.40
-0.20
0.00
0.20
0.40
0.60
Depth (cm)
0
10
20
30
40
50
60
70
80
508
409
4011
832
1144
2346
Slough Channel
Vegetated Marsh, West Bank