



# An isotopic record of mercury in San Francisco Bay sediment



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## ABSTRACT

We analyzed eight sediment cores from wetland and subtidal locations around San Francisco (SF) Bay, terrace sediment from the Yuba River, CA and precipitation from the SF Bay region. We defined the Hg isotopic composition of uncontaminated SF Bay sediment, two contributing endmember sediments contaminated by distinct Hg sources, and regional precipitation. Deep subtidal sediments with pre-mining THg concentrations (less than 60 ng/g) have  $\delta^{202}\text{Hg}$  of  $-0.98 \pm 0.06\text{‰}$  and  $\Delta^{199}\text{Hg}$  of  $0.17 \pm 0.03\text{‰}$  (1 s.d.;  $n = 5$ ). The  $\delta^{202}\text{Hg}$  of subtidal sediment in SF Bay systematically changed between pre-mining, circa 1960, and surface sediment. In circa 1960 sediment  $\delta^{202}\text{Hg}$  ranges from  $-0.63$  to  $-0.32\text{‰}$  ( $\pm 0.10\text{‰}$ ) with higher  $\delta^{202}\text{Hg}$  in the south and lower  $\delta^{202}\text{Hg}$  in the north; however in surface sediment  $\delta^{202}\text{Hg}$  is nearly constant and averages  $-0.52 \pm 0.04\text{‰}$  (1 s.d.;  $n = 6$ ). These latter values for SF Bay surface sediment are similar to those for terrace sediment along the Yuba River that have  $\delta^{202}\text{Hg}$  of  $-0.57 \pm 0.10\text{‰}$  and  $\Delta^{199}\text{Hg}$  of  $0.05 \pm 0.01\text{‰}$  (1 s.d.;  $n = 2$ ) and are consistent with sediment contaminated by a metallic Hg source that was derived from Hg ore in the California Coast Ranges and used in Sierra Nevada gold mining. Wetlands adjacent to south and central SF Bay have high THg in deeper sediment layers ( $>3000$  ng/g) that vary by  $\sim 0.6\text{‰}$  in  $\delta^{202}\text{Hg}$ , presumably reflective of various anthropogenic Hg sources. The three sediment endmembers (metallic Hg, Hg mining and background Hg) were defined using  $\delta^{202}\text{Hg}$  and THg concentrations. Based on the estimated contribution of endmember sediment to subtidal and intertidal locations, we suggest that the subtidal Hg stable isotope record in sediment cores is consistent with historical sediment transport to, and deposition in, SF Bay. Thus, Hg stable isotopes can be used to trace sediment transport in locations that are impacted by multiple anthropogenic Hg sources.

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## 1. Introduction

A wide variety of contaminants have been delivered to the San Francisco (SF) Bay estuary over the past 150 years (Conomos et al., 1979; Nichols et al., 1986; van Geen and Luoma, 1999; Conaway et al., 2008). Mercury (Hg) appears as one of the first anthropogenic metals present in the sediment record (Hornberger et al., 1999; van Geen and Luoma, 1999; Conaway et al., 2004), with Hg mining and gold (Au) mining considered the most likely early sources of Hg in the Bay (Nriagu, 1994; Thomas et al., 2002; Marvin-DiPasquale et al., 2003; Conaway et al., 2004; Alpers et al., 2005; Bouse et al., 2010). Rich deposits of the Hg ore mineral cinnabar (HgS) in the California Coast Range allowed the growth of an industry to mine and process Hg ore into metallic elemental Hg (Hg(0)), which was widely used to enhance

Au recovery through amalgamation during hydraulic mining of placer deposits in the Sierra Nevada Mountains (Nriagu, 1994; Rytuba, 2003; Alpers et al., 2005). Although the use of Hg in Au mining decreased in California during the 20th century, especially following the Sawyer decision that stopped hydraulic Au mining in 1884, the use of Hg by other industries (e.g., chloralkali, petrochemical) and in products such as fungicides and slimicides, became more common (Conaway et al., 2008). Throughout SF Bay, total mercury (THg) concentrations in surface sediment remain elevated 2 to 8 times pre-mining levels (Hornberger et al., 1999; Marvin-DiPasquale et al., 2003; Conaway et al., 2004, 2007; Bouse et al., 2010; Gehrke et al., 2011a). A portion of the Hg in sediment may be converted to neurotoxic monomethyl mercury (MMHg), contributing to elevated Hg concentrations in various trophic levels of aquatic biota and posing a risk to humans and wildlife (Greenfield et al., 2005; Davis et al., 2008; Greenfield and Jahn, 2010; Gehrke et al., 2011b; OEHHA, 2011; Davis et al., 2012). Estimating the contribution of Hg to sediment in SF Bay from an array of sources is complicated because of its widespread use and changes in sediment transport as a result of watershed modification during the past 150 years (Conaway et al., 2007; James and Singer, 2008; Singer et al., 2008; James et al.,

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2009; Singer et al., submitted for publication). This study utilizes Hg stable isotopes to assess the spatial and temporal distribution of Hg in SF Bay sediment and builds on prior work in the region by providing a discriminant tracer of various sediment sources.

Mercury has seven stable isotopes (196, 198, 199, 200, 201, 202, and 204 amu), and the isotopic composition of Hg in environmental matrices can now be determined with high precision (Blum and Bergquist, 2007; Foucher et al., 2009). Mercury stable isotopes are becoming a useful tool to characterize sources and identify biogeochemical transformations of Hg in the environment. For example, the isotopic composition of a variety of Hg-bearing ores has been determined (Smith et al., 2008; Foucher et al., 2009; Stetson et al., 2009; Feng et al., 2010; Sonke et al., 2010; Gehrke et al., 2011a; Yin et al., 2013) along with commercially available metallic Hg (Blum and Bergquist, 2007; Sonke et al., 2008; Estrade et al., 2009; Laffont et al., 2011). Stable isotopes of mercury have also been employed to trace geogenic, urban, industrial and atmospheric sources of Hg in the environment (Gehrke et al., 2009; Feng et al., 2010; Senn et al., 2010; Sonke et al., 2010; Estrade et al., 2011; Liu et al., 2011; Foucher et al., 2013; Yin et al., 2013) and to estimate the relative contribution of different Hg sources using endmember mixing calculations (Foucher et al., 2009; Liu et al., 2011; Yin et al., 2013).

An initial study of Hg stable isotopes in SF Bay sediments was conducted by Gehrke et al. (2011a). These authors measured Hg in intertidal surface sediment throughout SF Bay and investigated the isotopic composition of roasted Hg mine waste (calcine) and unroasted Hg ore from a mine in the California Coast Range. Gehrke et al. (2011a) also documented a present-day spatial gradient in Hg isotopic composition throughout SF Bay and demonstrated that calcine and unroasted Hg ore have significantly different Hg isotopic compositions. Based on this spatial gradient the authors suggested that Hg in SF Bay intertidal surface sediment is dominated by two regional anthropogenic sources: Hg mining (entering southern SF Bay) and Au mining (entering northern SF Bay). Gehrke et al. (2011a) did not constrain the pre-mining sediment Hg isotopic composition, nor did they explore historical variations in the isotopic composition of Hg in SF Bay. In this study, we use eight sediment cores, dated from pre-1900 to 2006, to constrain the pre-mining sediment Hg isotopic composition. We use Yuba River terrace sediment to characterize the Hg isotopic signature of sediment predominantly contaminated by Au mining. To assess the influence of Hg from precipitation on sediment Hg stable isotopes, we analyzed precipitation collected at three locations in the SF Bay area. Finally, we use the variation in Hg stable isotope composition in sediment cores to estimate the present day and historical contribution of sediment to locations in SF Bay.

## 2. Materials and methods

### 2.1. Environmental setting

San Francisco Bay is a large estuary with a surface area of 1240 km<sup>2</sup> and an average water depth of 6 m (Conomos et al., 1985). It is separated into two hydrologic regions, the northern reach and the southern reach, which converge and open to the Pacific Ocean in the Central Bay (Conomos et al., 1979). The northern reach can be divided into three sub-basins: the Sacramento–San Joaquin Delta, Suisun Bay, and San Pablo Bay. The southern reach includes two sub-basins: South Bay and Lower South Bay (Conomos et al., 1985). The watersheds that contribute to SF Bay are important because changes in freshwater flow and suspended sediment delivery can significantly alter circulation and sediment dynamics within the Bay (McKee et al., 2006; Jaffe et al., 2007; Schoellhamer, 2011). The Sacramento–San Joaquin (SSJ) watershed, which flows into north SF Bay, covers nearly 40% of the land area of the state of California and has been the source of up to 90% of freshwater input and 80% of sediment input to SF Bay (Conomos et al., 1985). However, as a result of water diversion projects, freshwater discharge from the SSJ watershed is now less than 40% of pre-1850 levels (Nichols

et al., 1986) and the SSJ delta contributes only 40–60% of the total sediment delivered to SF Bay (McKee et al., 2006; McKee and Lewicki, 2009). There is much evidence of large-scale sediment deposition in floodplains and floodways of the Sacramento Valley well upstream of the delta (Singer et al., 2008; Singer and Aalto, 2009; Springborn et al., 2011; Singer et al., submitted for publication). The south SF Bay watersheds, including Guadalupe River and Coyote Creek, provide less than 10% of freshwater input to SF Bay (Conaway et al., 2008); however, small tributaries surrounding SF Bay are important sources of sediment to wetlands and near shore locations (McKee and Lewicki, 2009).

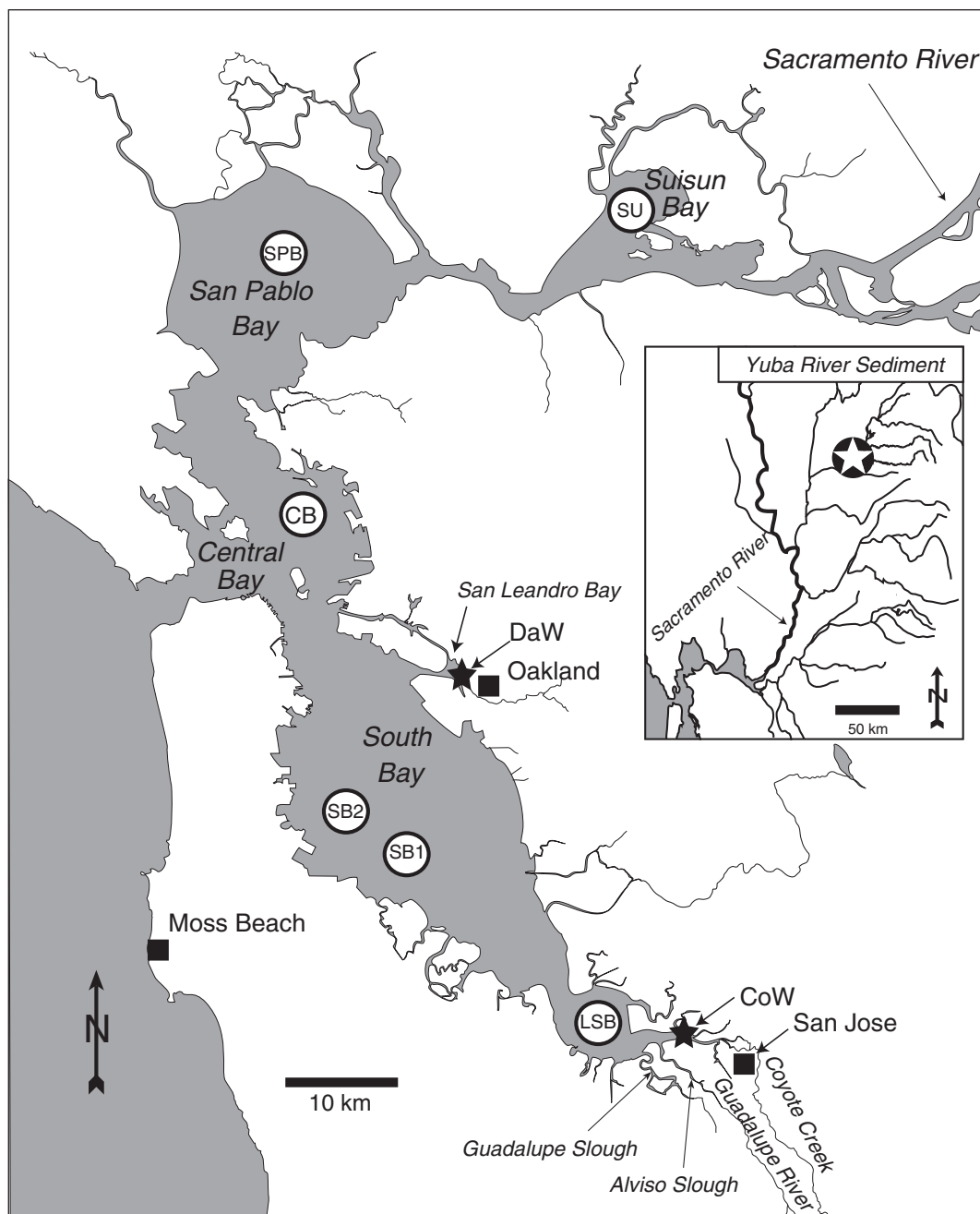
### 2.2. Sample locations

Six sediment cores from subtidal locations, with overlying water depths between 2.3 and 7.8 m, and two sediment cores from wetlands adjacent to SF Bay were analyzed for Hg stable isotope composition for this study (Fig. 1). Additional details on sediment coring and sampling are provided in Yee et al. (2011). One core was obtained from each subtidal site in Lower South Bay (LSB), Central Bay (CB), San Pablo Bay (SPB), and Suisun Bay (SU) and two subtidal cores were obtained from South Bay (SB1, SB2). One wetland core, termed Coyote Creek (CoW), is located in the southern slough region. This wetland is directly downstream of the New Almaden Hg mining district, the largest historical producer of Hg in the United States, which operated between 1847 and the early 1970s (Cargill et al., 1980; Thomas et al., 2002; Conaway et al., 2004). The second wetland core is located at the outlet of Damon Slough (DaW) and is adjacent to San Leandro Bay, a small tidally influenced sub-embayment in central SF Bay. To characterize the Hg stable isotope composition of sediment associated with Au mining in the Sacramento River watershed, sediment was collected at two locations within a large riverside terrace along the Yuba River. This site is a dissected mine tailings fan from a tributary basin (Dry Creek), which represents an early phase of hydraulic Au mining without subsequent remobilization (Singer et al., submitted for publication). The Yuba and Bear Rivers, tributaries of the Feather River, which eventually joins the Sacramento River and north SF Bay (Fig. 1), were sites of concentrated Au mining activity in the late 19th century. Hydraulic Au mining in the Yuba River watershed displaced large volumes of Hg-laden sediment into piedmont and lowland valleys, some of which remains upstream behind flood control structures or as debris fans (Hunerlach et al., 2004; James, 2005; Singer et al., 2008; James et al., 2009; Bouse et al., 2010; Fleck et al., 2011; Singer et al., submitted for publication). In addition to sediment, bulk precipitation samples were collected at three locations (Moss Beach, Oakland, San Jose) in the SF Bay area between December 2008 and March 2009 (Fig. 1).

### 2.3. Sample handling and analytical methods

#### 2.3.1. Core sample dating and selection for Hg isotope analysis

Sediment cores were dated using <sup>137</sup>Cs and <sup>210</sup>Pb radiometric methods and analyzed for a suite of trace elements (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn) and sediment quality parameters (e.g., moisture content, Total Organic Carbon, Total Nitrogen) as previously described by Yee et al. (2011). In each sediment core, at least three 2.5 cm depth intervals were measured for Hg stable isotopic composition. Typically, the three intervals consisted of surface sediment (0–2.5 cm), sediment at the greatest depth available in the core (greater than 67 cm), and sediment closest to the first appearance of <sup>137</sup>Cs, reflective of bomb (nuclear weapon) testing in the 1950s and 1960s. Because of the non-continuous depositional history of subtidal locations exact ages were not used for subtidal core intervals. However, Yee et al. (2011) suggested that the depth of <sup>137</sup>Cs appearance in subtidal locations marks the maximum depth of downward migration of <sup>137</sup>Cs, and that sediment below this maximum depth has not been exposed to the



**Fig. 1.** Sampling locations for subtidal sediment cores (open circles), wetland sediment cores (black stars), and bulk precipitation (black squares). The location of Yuba River terrace sediment (open star) is included on the inset map. Further description of the variety of Hg sources in the SF Bay region can be found in Conaway et al. (2008) and Alpers et al. (2005).

surface since at least the mid-1950s, when bomb testing began. Based on this interpretation, the sediment interval analyzed that is closest to the  $^{137}\text{Cs}$  appearance in subtidal cores will hereafter be referred to as “circa 1960” sediment or “c. 1960” sediment. For wetland cores there is evidence of a sharp  $^{137}\text{Cs}$  peak in subsurface sediment, suggesting little sediment re-suspension or bioturbation. In wetland cores, an approximate age was assigned to each sediment interval by Yee et al. (2011) based on estimated accumulation rates with the  $^{137}\text{Cs}$  peak representing deposition in the early 1960s – the period of maximum  $^{137}\text{Cs}$  deposition in the SF Bay area (Yee et al., 2011).

### 2.3.2. Sediment processing, combustion and THg concentration

Sediment intervals of SF Bay cores were stored frozen in glass containers and prior to Hg analysis, sediment was freeze-dried and ground

to a fine powder with a clean agate mortar and pestle. Terrace sediment from the Yuba River, CA was dried and then sieved to  $<63\ \mu\text{m}$  and stored in glass vials prior to analysis. For each sample analyzed, at least 200 mg of sediment was placed in a two-stage furnace and progressively heated to release all Hg, following previously described methods (Biswas et al., 2008; Gehrke et al., 2009; Blum, 2011; Gehrke et al., 2011a). In brief, Hg was released from the sample matrix as Hg(0) as the sample was gradually heated to 750 °C over 6 h. Mobilized Hg(0) was carried in a flow of  $\text{O}_2$ , through a second furnace held at 1000 °C, after which it was sparged into a 1%  $\text{KMnO}_4/1.8\ \text{M}\ \text{H}_2\text{SO}_4$  trapping solution, thus oxidizing Hg(0) to Hg(II). Sediment THg concentrations were determined using cold vapor atomic absorption spectroscopy (CV-AAS; Nippon MA-2000) based on the concentration of Hg in the trapping solution and the mass of dry sediment placed in the combustion furnace. The

sediment THg concentration for subtidal and wetland sediment cores via combustion typically yielded THg concentrations within 30% of reported THg concentrations for sub-samples of the same sediment measured by wet acid digestion at Moss Landing Marine Lab (Yee et al., 2011). The THg concentration of Yuba River sediment measured by combustion, as described here, agreed to within 10% of the THg concentration measured by cold vapor atomic fluorescence spectroscopy (CVAFS; Tekran) by EPA Method 1631 at the USGS in Menlo Park, CA. The sediment standard NRC MESS-3 (marine sediment reference material) was combusted and processed alongside samples in an identical manner. The combustion yield of Hg in NRC MESS-3 averaged  $94 \pm 4\%$  and was always within error of the certified THg concentration ( $91 \pm 9$  ng/g). Prior to isotopic analysis the original trapping solution was reduced with SnCl<sub>2</sub> and all Hg was purged from the original solution into a secondary trapping solution (1% KMnO<sub>4</sub>/1.8 M H<sub>2</sub>SO<sub>4</sub>) to minimize matrix effects during isotopic analysis that might be associated with combustion products. The yield for the secondary trapping procedure was always greater than 92%, and typically greater than 95%. The secondary purge and trap yield was at least 96% for all NRC MESS-3 aliquots that were analyzed.

### 2.3.3. Precipitation Hg separation and THg concentration

At each location, precipitation collectors were assembled using a borosilicate glass funnel (collection area of 181 cm<sup>2</sup>), Teflon adaptor with glass vapor lock (to prevent evaporation), and a 1 L Teflon bottle (Landis and Keeler, 1997). Collectors were located away from overhanging obstacles and funnels were left open for periods of 3 to 33 days, depending on rainfall amount, collecting multiple precipitation events into a single, pre-acidified (1 mL trace metal grade hydrochloric acid) 1 L Teflon bottle. A total of six bottles were collected at each site between December 2008 and March 2009, and each bottle was preserved to a final concentration of 1% BrCl upon return to the laboratory. A small (5 mL) aliquot from each collection bottle was analyzed by CV-AAS (Nippon MA-2000) to obtain a volume-weighted average THg concentration for each site. Precipitation samples from each site were combined using purge and trap methods, to obtain sufficient Hg for stable isotope measurements, as described elsewhere (Gratz et al., 2010). Briefly, the combination of precipitation samples required slowly pumping the entire sample into a mixing chamber with 5% SnCl<sub>2</sub> to reduce all Hg to Hg(0). The Hg(0) was separated using a frosted tip phase separator and carried into an oxidizing 1% KMnO<sub>4</sub>/1.8 M H<sub>2</sub>SO<sub>4</sub> trapping solution. For Oakland and San Jose collection locations, all six 1 L samples were combined into a single trap that represented the entire winter 2009 sampling period. Due to greater precipitation volume at Moss Beach, the six 1 L samples collected were combined into two separate traps representing the first half (MB1; January–February 2009) and the second half (MB2; March 2009) of the collection period. The THg concentrations of the final trap solutions were measured prior to Hg stable isotope analysis. Although we expect the whole sample THg concentration (in the oxidizing 1% KMnO<sub>4</sub> trap) to be the most accurate measurement, an estimated yield was calculated based on the initial volume weighted average and the final trap THg concentrations. Three of the four estimated sample yields were between 86% and 99% (MB-1, San Jose and Oakland), however one sample (MB-2) had an estimated yield of 152%. The high apparent yield suggests that the initial 5 mL aliquot measured had a lower THg concentration than the entire sample after processing, which can occur from incomplete reduction of Hg in the CV-AAS due to interferences in the original sample matrix.

### 2.3.4. Hg stable isotope analysis

The Hg isotopic composition of the trap solution for each sample was measured using Cold Vapor-Multi Collector-Inductively Coupled Plasma-Mass Spectrometry (CV-MC-ICP-MS; Nu-Instruments). Solutions were partially neutralized with NH<sub>2</sub>OH then diluted to a concentration between 1 and 5 ng/g. Hg(II) was reduced on-line by the addition of

SnCl<sub>2</sub> and Hg(0) was separated from the solution using a frosted tip liquid-gas separator. Instrumental mass bias was corrected by the introduction of an internal Tl standard (NIST 997) as a dry aerosol to the Ar gas stream and by sample-standard bracketing using NIST 3133 with the same concentration and solution matrix as that of the sample (Blum and Bergquist, 2007). The Hg stable isotope composition is reported in delta notation in units of permil (‰) and referenced to the NIST 3133 standard (Blum and Bergquist, 2007). Mass dependent fractionation (MDF) is calculated by comparing the <sup>202</sup>Hg/<sup>198</sup>Hg ratio of the sample to the <sup>202</sup>Hg/<sup>198</sup>Hg ratio of the NIST 3133 bracketing standards and is reported as δ<sup>202</sup>Hg using Eq. (1) (Blum and Bergquist, 2007). Mass independent fractionation (MIF) is a measurement of the deviation from the theoretical MDF and is reported in permil (‰) as Δ<sup>199</sup>Hg and Δ<sup>201</sup>Hg using Eqs. (2) and (3) (Blum and Bergquist, 2007):

$$\delta^{202}\text{Hg} = 1000 * \left( \left[ \left( \frac{{}^{202}\text{Hg}}{{}^{198}\text{Hg}} \right)_{\text{sample}} \right] / \left[ \left( \frac{{}^{202}\text{Hg}}{{}^{198}\text{Hg}} \right)_{\text{NIST3133}} \right] - 1 \right). \quad (1)$$

$$\Delta^{199}\text{Hg} = \delta^{199}\text{Hg} - (\delta^{202}\text{Hg} * 0.2520) \quad (2)$$

$$\Delta^{201}\text{Hg} = \delta^{201}\text{Hg} - (\delta^{202}\text{Hg} * 0.7520). \quad (3)$$

Procedural blanks and replicates of NRC MESS-3 (n = 4) were processed alongside sediment samples in an identical manner. Procedural blanks averaged 0.285 ng Hg per 24 gram trap solution (n = 5) whereas samples contained between 80 and 250 ng Hg. Total recovery of the NRC MESS-3 process replicates averaged  $95 \pm 4\%$  (n = 4) and the Hg isotopic composition of NRC MESS-3 was δ<sup>202</sup>Hg =  $-1.93 \pm 0.10\%$ , Δ<sup>201</sup>Hg =  $-0.02 \pm 0.07\%$  and Δ<sup>199</sup>Hg =  $0.01 \pm 0.02\%$  (mean ± 2 s.d.; n = 4). A procedural standard (NIST-3133) of similar Hg concentration as precipitation samples demonstrated no measurable fractionation upon pre-concentration into the trapping solution (1% KMnO<sub>4</sub>/1.8 M H<sub>2</sub>SO<sub>4</sub>) with an 85% process yield (δ<sup>202</sup>Hg of 0.02‰ and Δ<sup>199</sup>Hg of 0.02‰). Precipitation procedural blanks never accounted for more than 1% of Hg in the final trap solution.

The in-house standard UM-Almaden was monitored over the course of 46 analytical sessions during which sediment analyses were completed and had a long-term average isotopic composition of δ<sup>202</sup>Hg =  $-0.58 \pm 0.05\%$ , Δ<sup>201</sup>Hg =  $-0.03 \pm 0.04\%$  and Δ<sup>199</sup>Hg =  $-0.02 \pm 0.04\%$  (mean ± 2 s.d.; n = 46). The uncertainty associated with sediment Hg stable isotope measurements is reported as the greater of either the uncertainty of replicate analysis of NRC MESS-3 or the long-term analytical uncertainty associated with UM-Almaden. Therefore, the 2 s.d. analytical uncertainty for sediment Hg stable isotope measurements in this study is δ<sup>202</sup>Hg =  $\pm 0.10\%$ , Δ<sup>201</sup>Hg =  $\pm 0.07\%$ , and Δ<sup>199</sup>Hg =  $\pm 0.04\%$ . UM-Almaden was analyzed multiple times at identical Hg concentrations as the precipitation samples that were analyzed (1.7 and 3.1 ng/g) during the same session. UM-Almaden at a Hg concentration of 1.7 ng/g had an average isotopic composition of δ<sup>202</sup>Hg =  $-0.56 \pm 0.14\%$ , Δ<sup>201</sup>Hg =  $-0.12 \pm 0.15\%$  and Δ<sup>199</sup>Hg =  $-0.03 \pm 0.11\%$  (mean ± 1 s.d.; n = 4). UM-Almaden at a concentration of 3.1 ng/g had an average isotopic composition of δ<sup>202</sup>Hg =  $-0.57 \pm 0.05\%$ , Δ<sup>201</sup>Hg =  $-0.04 \pm 0.05\%$  and Δ<sup>199</sup>Hg =  $0.00 \pm 0.04\%$  (mean ± 1 s.d.; n = 5).

## 3. Results and discussion

### 3.1. Mercury isotopic composition of subtidal sediment

In five of six subtidal sediment cores the THg concentration is between 28 and 58 ng/g at sediment depths greater than 100 cm (Fig. 2; Table 1). The THg concentration in these five subtidal cores agrees with established pre-mining THg concentrations from north SF Bay sediment cores ( $60 \pm 10$  ng/g; Hornberger et al., 1999), San Pablo Bay sediment cores (30 to 80 ng/g; Bouse et al., 2010) and in wetland

sediment cores from south SF Bay ( $80 \pm 30$  ng/g; Conaway et al., 2004). In the five subtidal cores with THg less than 60 ng/g,  $\delta^{202}\text{Hg}$  is  $-0.98 \pm 0.06\text{‰}$  and  $\Delta^{199}\text{Hg}$  is  $0.17 \pm 0.03\text{‰}$  (1 s.d.;  $n = 5$ ) with no measurable difference in Hg isotopic composition among the five different locations. The  $\delta^{202}\text{Hg}$  of pre-mining sediment is within error of pre-anthropogenic Mediterranean sapropels ( $-0.91 \pm 0.15\text{‰}$ ; 1 s.d.,  $n = 5$ ; Gehrke et al., 2009) and off-shore sediment from the Gulf of Mexico ( $-1.00 \pm 0.11\text{‰}$ ; 1 s.d.,  $n = 6$ ; Senn et al., 2010). In the subtidal sediment core from Suisun Bay (SU), the THg concentration is greater than 140 ng/g throughout the core (Fig. 2) and there is uncertainty in depositional age estimates (Yee et al., 2011). Due to lack of age control, and because THg does not reach a pre-mining concentration at depth, results from this core are not included in further discussion.

In c. 1960 and surface sediment intervals from subtidal locations, the THg concentration is enriched 2 to 6 times over that of pre-mining THg (Fig. 2; Table 1). There is no obvious spatial trend in THg concentrations, and THg concentration is independent of %TOC ( $r^2 = 0.09$ ,  $p = 0.33$ ). The Hg stable isotope composition of subtidal sediment systematically changes between pre-mining, c. 1960 and surface sediment. In c. 1960 sediment,  $\delta^{202}\text{Hg}$  has a range between  $-0.63$  and  $-0.32\text{‰}$  with the highest  $\delta^{202}\text{Hg}$  in LSB and lower  $\delta^{202}\text{Hg}$  in SPB and CB (Fig. 3), following the same geographic trend as observed in intertidal surface sediment (Gehrke et al., 2011a). The spatial and temporal changes in sediment  $\delta^{202}\text{Hg}$  are not correlated with %TOC ( $r^2 = 0.02$ ,  $p = 0.53$ ) or other ancillary sediment chemistry parameters. Interestingly, subtidal surface sediment does not exhibit any spatial variation in  $\delta^{202}\text{Hg}$ . Rather, subtidal surface sediment has consistent  $\delta^{202}\text{Hg}$  ( $-0.52 \pm 0.04\text{‰}$ ) and  $\Delta^{199}\text{Hg}$  ( $0.07 \pm 0.03\text{‰}$ ) (1 s.d.;  $n = 6$ ) regardless of location or THg concentration.

### 3.2. Mercury isotopic composition of wetland sediment

#### 3.2.1. Coyote Creek wetland

In the deepest core samples from the Coyote Creek wetland (CoW), in sediment deposited pre-1943, the THg concentration is 660 ng/g, which is significantly higher than the pre-mining THg concentration throughout SF Bay (<110 ng/g). In sediment deposited between the early 1940s (98.75 cm) and the mid-1950s (78.75 cm), THg increases from 720 ng/g to a maximum of 3200 ng/g and then decreases to 330 ng/g near the surface (Fig. 4). The elevated THg concentration in CoW subsurface sediment is consistent with other wetlands in south SF Bay, such as Alviso Slough and Triangle Marsh (Conaway et al., 2004; Marvin-DiPasquale and Cox, 2007; Gehrke et al., 2011a). In Triangle Marsh, peak THg (~1200 ng/g) also occurs in mid-20th century sediments and has been attributed to a combination of increased Hg mining activity, changes in watershed hydrology, and land subsidence in the area (Conaway et al., 2004). In CoW sediment, the THg peak coincides with a 0.4‰ shift in  $\delta^{202}\text{Hg}$  from  $-0.20\text{‰}$  to  $+0.21\text{‰}$  (Fig. 4). The  $\delta^{202}\text{Hg}$  in the highest THg sediment measured in CoW (this study) and in Alviso Slough (Gehrke et al., 2011a) is ~0.2‰ higher than the only Hg mine waste analyzed from the region (Fig. 5; Gehrke et al., 2011a). During the leaching of Hg mine waste the more soluble byproduct species of Hg are mobilized (Rytuba, 2000). Leachates of calcine may contain Hg with up to ~1.2‰ higher  $\delta^{202}\text{Hg}$  than the parent calcine (Stetson et al., 2009). Soluble Hg will associate quickly with particles, such as iron oxyhydroxides, and travel downstream via the particulate phase (Rytuba, 2000). As a result, the  $\delta^{202}\text{Hg}$  of sediment in CoW can be explained by the isotopic variation of the calcine and its leachates that have been mobilized and transported to downstream wetlands. Thus, we suggest that the subsurface sediment in the Coyote

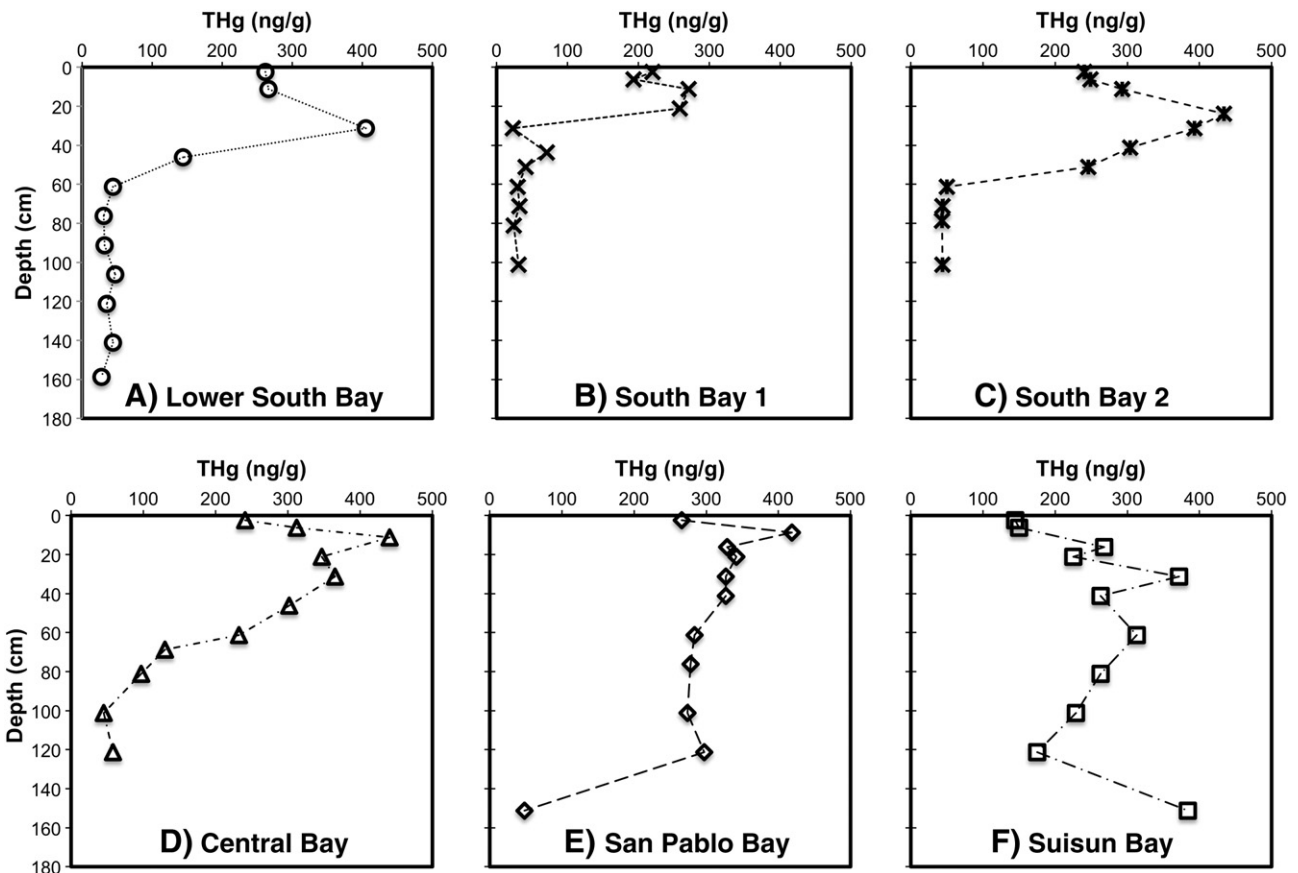


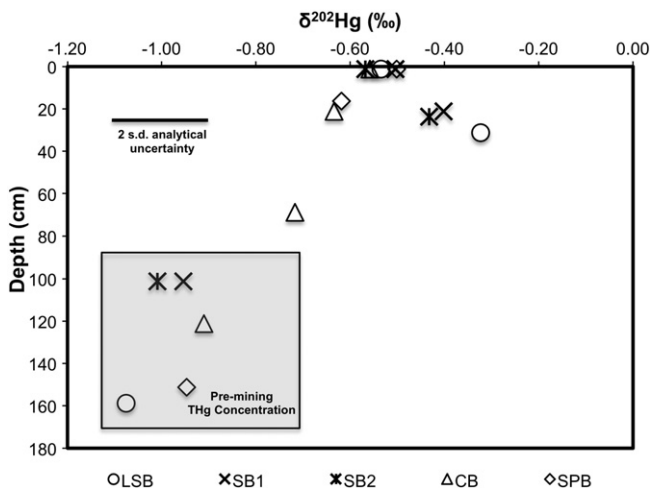
Fig. 2. Depth vs. THg concentration for the six subtidal sediment cores selected for Hg stable isotope analysis (A–F; from Yee et al., 2011). Pre-mining THg concentration is approximately <80 ng/g (Hornberger et al., 1999; Bouse et al., 2010).

**Table 1**

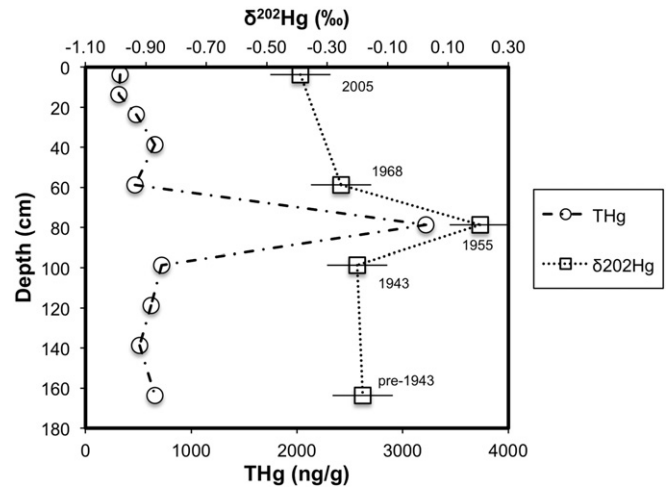
The THg Concentration and Hg stable isotope composition of sediments. All THg concentrations reported here are from Yee et al. (2011) except for Yuba River sediment (a/b), which is based on the combustion solution concentration (see Section 2.3.2)

Location	Latitude (N)	Longitude (W)	Depth interval cm	THg	$\delta^{202}\text{Hg}$	$\Delta^{201}\text{Hg}$	$\Delta^{199}\text{Hg}$
				ng/g	‰	‰	‰
Suisun Bay	38.1025	122.0459	0–2.5	145	−0.48	0.00	0.04
			30–32.5	372	−0.45	0.02	0.01
			120–122.5	175	−0.65	0.02	0.09
San Pablo Bay	38.072	122.3871	0–2.5	266	−0.50	0.00	0.05
			15–17.5	329	−0.62	−0.01	0.01
			150–152.5	48.0	−0.95	0.04	0.13
Central Bay	37.8761	122.3619	0–2.5	241	−0.56	0.06	0.07
			20–22.5	347	−0.63	0.03	0.05
			67.5–70	130	−0.72	0.01	0.04
South Bay 2	37.626	122.347	0–2.5	241	−0.57	0.05	0.07
			22.5–25	434	−0.43	0.05	0.06
			100–102.5	44.0	−1.01	0.12	0.19
South Bay 1	37.6121	122.265	0–2.5	220	−0.50	0.03	0.07
			20–22.5	258	−0.40	−0.05	0.04
			100–102.5	31.0	−0.95	0.08	0.20
Lower South Bay	37.4791	122.0785	0–2.5	262	−0.53	0.08	0.13
			30–32.5	405	−0.32	0.05	0.09
			157.5–160	28.0	−1.08	0.11	0.18
Coyote Creek wetland	37.4624	121.9997	2.5–5	329	−0.39	0.05	0.07
			57.5–60	469	−0.25	0.05	0.06
			77.5–80	3220	0.21	0.00	−0.02
			97.5–100	719	−0.20	0.03	0.06
			162.5–165	657	−0.18	0.02	0.01
			67.5–70	23.0	−1.08	0.13	0.24
Damon slough wetland	37.7536	122.2133	2.5–5	533	−0.50	0.14	0.16
			17.5–20	3140	−0.42	0.05	0.11
			22.5–25	1440	−0.39	0.12	0.17
			27.5–30	193	−0.65	0.04	0.11
			37.5–40	71.0	−0.80	0.09	0.17
Yuba River (a)	39.21874	121.29905	67.5–70	5440	−0.64	0.05	0.05
			Yuba River (b)	3180	−0.50	0.01	0.04

Creek wetland is most representative of the isotopic composition of sediment heavily impacted by Hg mine waste that has been transported to SF Bay.



**Fig. 3.** Depth vs.  $\delta^{202}\text{Hg}$  for the six subtidal sediment cores. Sediment intervals with pre-mining THg concentration are enclosed by the shaded rectangle.

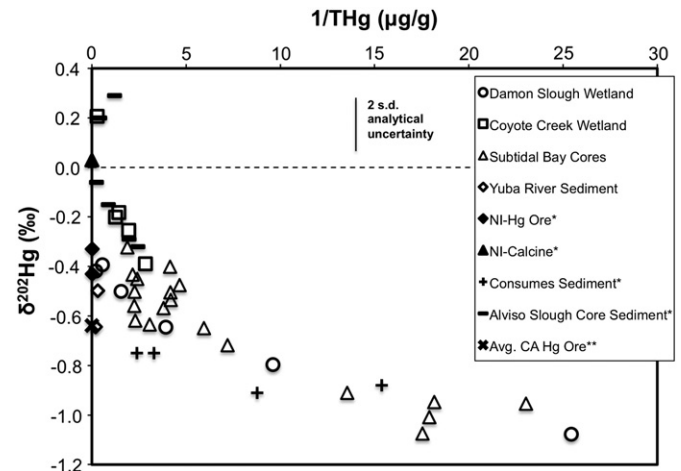


**Fig. 4.** THg concentration (circles) and  $\delta^{202}\text{Hg}$  (squares) vs. depth for Coyote Creek wetland (CoW) sediment. Approximate radiometric ages are included from Yee et al. (2011) and error bars for  $\delta^{202}\text{Hg}$  represent the 2 s.d. analytical uncertainty ( $\pm 0.10\%$ ).

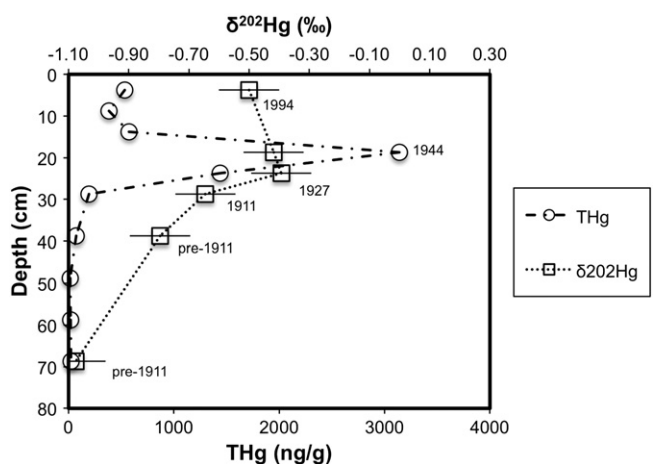
### 3.2.2. Damon slough wetland

Sediment at 69 cm depth, and with THg of 23 ng/g, in Damon slough wetland (DaW) was deposited prior to 1911 and has  $\delta^{202}\text{Hg}$  of  $-1.08\%$  and  $\Delta^{199}\text{Hg}$  of  $-0.24\%$  (Fig. 6), which is nearly identical to subtidal sediments with similar THg concentrations (Figs. 5 & 7). An indistinguishable Hg isotopic composition for low THg (23 ng/g) wetland sediment and low THg (<60 ng/g) subtidal sediment suggests a similar origin for pre-mining Hg in sediment. Sediment is enriched above pre-mining THg concentrations at depths shallower than 40 cm, with the highest THg concentration in DaW (3100 ng/g) occurring at 19 cm (~1940s), followed by a decrease up-core to 600 ng/g in near-surface sediment (Fig. 6). The THg maximum in DaW coincides with a shift in  $\delta^{202}\text{Hg}$ ; the highest THg sediment (1440 and 3140 ng/g) has the highest  $\delta^{202}\text{Hg}$  ( $-0.39$  and  $-0.42\%$ , respectively; Fig. 6). Subsurface sediment with high THg concentration in DaW is consistent with previously reported high concentration subsurface sediments in nearby San Leandro (SL) Bay (Daum et al., 2000) and the  $\delta^{202}\text{Hg}$  of DaW surface sediment ( $-0.50\%$ ) is within error of previously measured intertidal surface sediments in San Leandro Bay ( $-0.53\%$  and  $-0.59\%$ ; Gehrke et al., 2011a).

Although peak THg concentrations in DaW and CoW are observed in similar age sediment (between 1940 and 1960), and peak THg concentrations are similar (3140 and 3220 ng/g, respectively), the  $\delta^{202}\text{Hg}$  of high THg DaW sediment is  $\sim 0.6\%$  lower than high THg sediment in



**Fig. 5.**  $\delta^{202}\text{Hg}$  vs.  $1/\text{THg}$  for all SF Bay sediment measured in this study. Included is New Idria (NI) Hg ore and calcine, Consumes River surface sediment, Alviso Slough sediment cores (\*Gehrke et al., 2011a) and California (CA) Hg ore (\*\*Smith et al., 2008).



**Fig. 6.** THg concentration (circles) and  $\delta^{202}\text{Hg}$  (squares) vs. depth for Damon slough wetland (DaW) sediment. Approximate radiometric ages are included from Yee et al. (2011) and error bars for  $\delta^{202}\text{Hg}$  represent the 2 s.d. analytical uncertainty ( $\pm 0.10\%$ ).

CoW ( $-0.42\%$  and  $+0.21\%$ , respectively; Table 1). The lower  $\delta^{202}\text{Hg}$  of DaW subsurface sediment could be the result of the accumulation of Hg from a discrete Hg source in DaW at the same time as Hg accumulation in CoW. Alternatively, the  $\delta^{202}\text{Hg}$  of DaW sediment could be explained by the mixing of regional Hg sources, with significantly different  $\delta^{202}\text{Hg}$ , emanating from north and south SF Bay, followed by rapid deposition in wetlands adjacent to SF Bay. If rapid deposition of regional Hg sources is responsible for the high THg wetland sediment, we would expect high THg in similarly aged sediment in other wetlands adjacent to SF Bay. However, sediment THg peaks are small or not observable in the other wetlands sampled for this study (Yee et al., 2011). Comparatively high THg concentration in intertidal sediments from SL Bay (Gehrke et al., 2011a), coupled with high subsurface THg in DaW (this study) and SL Bay (Daum et al., 2000), suggests that at some time a local Hg source may have contributed Hg to sediment in SL Bay and DaW.

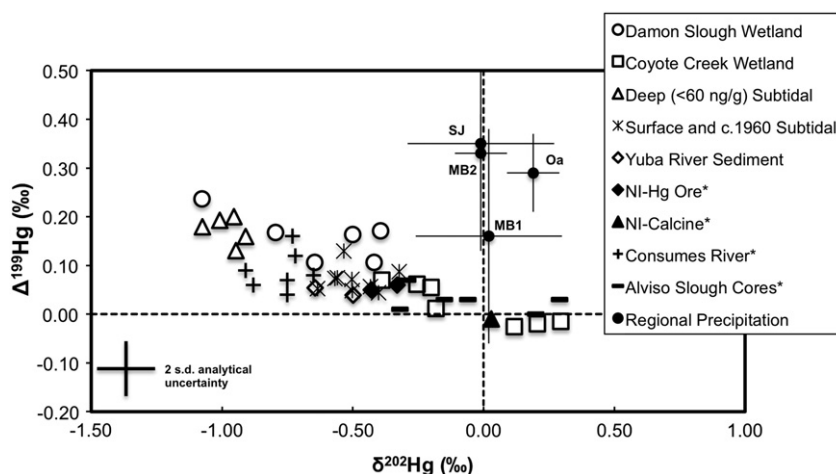
No Au or Hg mines are present in the four small watersheds that contribute to San Leandro Bay. Instead, most of the surrounding land use is urban or industrial and a variety of industries that use Hg have been present since the mid-19th century. For example, the Oakland, CA Clorox plant, located  $\sim 0.6$  km from San Leandro Bay, used an electrolytic Hg cell (containing Hg(0)) to produce chlorine and caustic soda from 1919 to 1957 (Conaway et al., 2008; Jemison, 2009). Although the Hg-cell process ceased operation in 1957, Hg

contamination of a perched groundwater zone exists below the facility and high THg concentrations persist in the surrounding soil (Jemison, 2009). The Oakland Clorox facility is one example of the possible remnant industrial Hg sources that surround San Leandro Bay, however we do not have evidence that this is the primary source of Hg in San Leandro Bay.

If the Hg in DaW is from the industrial use of metallic Hg then DaW sediment should reflect the Hg isotopic composition of the metallic Hg source plus any additional MIF or MDF that might have been imparted by biogeochemical transformation and loss of Hg from the sediment (e.g., volatilization). When the recovery of Hg(0) from Hg ore is efficient, the isotopic composition of the metallic Hg product will be indistinguishable from the Hg ore itself (Yin et al., 2013). The isotopic composition of Hg ores from across California is  $-0.64 \pm 0.84\%$  (1 s.d.,  $n = 91$ ; Smith et al., 2008) and Hg ore specifically from the New Idria Hg mine has  $\delta^{202}\text{Hg}$  of  $-0.38 \pm 0.07\%$  (1 s.d.,  $n = 2$ ; Gehrke et al., 2011a). Thus, the high THg subsurface sediment in DaW (with  $\delta^{202}\text{Hg}$  of  $-0.4\%$ ) is consistent with metallic Hg recovered from California Coast Range Hg ore. The DaW wetland sediment core is an example of the challenge in tracing Hg in sediment when local Hg sources are present but regional Hg sources have been spatially distributed.

### 3.3. Mercury isotopic composition of Yuba River sediment

The Yuba River is the tributary basin of the Sierra Nevada foothills most heavily impacted by Au mining (Gilbert, 1917). We analyzed two sediment samples from a riverside terrace along the Yuba River, CA. In Yuba River terrace sediment the THg concentration is 3180 and 5440 ng/g,  $\delta^{202}\text{Hg}$  is  $-0.50\%$  and  $-0.64\%$  and  $\Delta^{199}\text{Hg}$  is  $0.04\%$  and  $0.05\%$ , respectively (Fig. 5; Table 1). Metallic Hg was used for placer Au mining in the Sierra Nevada and most of the Hg used came from California Coast Range Hg ore (Alpers et al., 2005). The Hg stable isotope composition of Yuba River sediment is similar to the average isotopic composition of Hg ore deposits from throughout the California Coast Range ( $\delta^{202}\text{Hg}$  of  $-0.64 \pm 0.84\%$ ; 1 s.d.,  $n = 91$ ; Smith et al., 2008). As mentioned, efficient recovery of Hg(0) from Hg ore would result in no difference in  $\delta^{202}\text{Hg}$  between the Hg(0) product and the Hg ore (Yin et al., 2013). Mercury released to the environment as Hg(0) during Au mining will undergo biogeochemical transformations (i.e. vaporization, dissolution, evaporation, oxidation, etc.) as it becomes particle bound and is incorporated into sediment. The Hg stable isotope composition of sediments contaminated by Au mining could therefore be affected by fractionation during loss of mercury from sediments. Nonetheless, the Hg stable isotope composition of Yuba River sediments is consistent with what can be expected of metallic Hg(0) recovered



**Fig. 7.**  $\Delta^{199}\text{Hg}$  vs.  $\delta^{202}\text{Hg}$  of Yuba River terrace sediment, SF Bay subtidal and wetland sediments, and regional precipitation. Precipitation collection sites are denoted by abbreviations (Moss Beach = MB; San Jose = SJ and Oakland = Oa) and precipitation analytical uncertainty is depicted as the 2 s.d. of individual measurements of UM-Almaden as described in Section 2.3.4. Also included is New Idria (NI) ore and calcine, Cosumnes River surface sediment, and Alviso Slough sediment cores (\*from Gehrke et al., 2011a).

from California Coast Range Hg ore that was used in Sierra Nevada placer Au mining and became well mixed with displaced hydraulic mining sediments.

Sediment from the Cosumnes River, a tributary of the Mokelumne River that flows into the Sacramento/San Joaquin Delta farther south, was previously used to estimate the stable isotope composition of Hg used during Au mining in the Sierra Nevada foothills (Gehrke et al., 2011a), but this system was far less impacted by hydraulic mining. Surface sediment from the Cosumnes River has THg between 65 and 419 ng/g and  $\delta^{202}\text{Hg}$  between  $-0.75$  and  $-0.91\%$  (Gehrke et al., 2011a). Although THg in sediment from marshes adjacent to the Cosumnes River is elevated (303 and 419 ng/g), streambed sediment THg is much lower (65 and 114 ng/g). Yuba River terrace sediment THg concentrations are at least seven times higher (3180 and 5440 ng/g) than any Cosumnes River sediment previously analyzed. The  $\delta^{202}\text{Hg}$  of Cosumnes River streambed sediment has lower  $\delta^{202}\text{Hg}$  ( $-0.88$  and  $-0.91\%$ ) when compared to the marsh sediment ( $-0.75\%$ ) and  $\delta^{202}\text{Hg}$  is significantly lower than Yuba River terrace sediment ( $-0.57 \pm 0.10\%$ ; 1 s.d.,  $n = 2$ ). Only the Cosumnes River marsh sediment is enriched above pre-mining THg concentration, and the  $\delta^{202}\text{Hg}$  of Cosumnes River streambed sediment resembles pre-mining sediment in subtidal SF Bay (Fig. 5). Therefore, Cosumnes River sediment is not an ideal representation of highly contaminated sediment predominantly impacted by Au mining. Instead, we suggest that Yuba River terrace sediment is consistent with, and a better representation of, the Hg stable isotope composition of sediment contaminated by metallic Hg that was used for Au mining.

#### 3.4. Mass independent fractionation in SF Bay sediment

The  $\Delta^{199}\text{Hg}$  observed in sediment is the sum of the Hg isotopic composition of Hg released to the environment and any additional MIF that has occurred in the environment. The magnitude of  $\Delta^{199}\text{Hg}$  is directly proportional to the amount of photochemical reduction that has taken place during environmental exposure (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009). The  $\Delta^{199}\text{Hg}$  observed in pre-mining, low THg ( $<60$  ng/g), downcore ( $>100$  cm) SF Bay sediment ( $0.17 \pm 0.03\%$ ; 1 s.d.,  $n = 5$ ) is similar to open ocean sediment on the Central Portuguese Margin ( $0.09 \pm 0.04\%$ ; 1 s.d.,  $n = 8$ ; Mil-Homens et al., 2013) and mid-Pleistocene sapropels from the Mediterranean Sea ( $0.11 \pm 0.03\%$ ; 1 s.d.,  $n = 5$ ; Gehrke et al., 2009), neither of which is impacted by anthropogenic Hg sources. We suggest that the isotopic composition of Hg in deep, pre-mining SF Bay sediment is consistent with Hg in seawater that has undergone significant photoreduction ( $>10\%$ ), enriching the odd isotopes of Hg in the residual Hg(II) pool such that positive  $\Delta^{199}\text{Hg}$  is preserved in sediment (Gehrke et al., 2009; Mil-Homens et al., 2013).

In all sediment from CoW,  $\Delta^{199}\text{Hg}$  is between  $-0.03$  and  $0.07\%$  and consistent with adjacent sediment in Alviso Slough and upstream mine waste. In DaW, however, all sediment has significant positive  $\Delta^{199}\text{Hg}$  ( $0.11$  to  $0.24\%$ ; Fig. 7). Metallic Hg used in industrial processes and Au mining around SF Bay is likely derived from CA Coast Range Hg ore that has not previously been exposed at the Earth's surface and is, therefore, unlikely to exhibit significant  $\Delta^{199}\text{Hg}$ . However,  $\Delta^{199}\text{Hg}$  has been observed in some Hg-bearing ore minerals (Stetson et al., 2009) and sphalerite ores (Sonke et al., 2010) and we cannot rule out the possibility that a metallic Hg source, with positive  $\Delta^{199}\text{Hg}$ , contributes Hg to DaW. The photochemical cycling of Hg in SF Bay wetlands likely varies in response to tidal resuspension, periodic drying, variable sunlight exposure and changing chemical conditions. If the  $\Delta^{199}\text{Hg}$  in DaW sediments is purely the result of photochemical reduction then, based on experimental data (Bergquist and Blum, 2007), we infer that 10 to 25% of the Hg(II) pool has been photochemically reduced and evaded. It is plausible that significant photochemical reduction of Hg occurs during transport to the wetland, during resuspension within the wetland or during seasonal drying that

increases sunlight exposure to wetland surfaces. Although both CoW and DaW likely experience similar periodic sunlight exposure, there is a much higher sediment accretion rate in CoW (Yee et al., 2011), which may reduce the time that sediment remains in the photochemically active zone prior to burial. Additionally, DaW sediment has a smaller proportion of fine ( $<63 \mu\text{m}$ ) sediment and greater %TOC compared to CoW (Yee et al., 2011). The presence of DOC can facilitate Hg photoreduction (Amyot et al., 1997; Ravichandran, 2004) and differences in the type or amount of organic material could lead to enhanced photochemical cycling in DaW. Although it is unclear whether the significant  $\Delta^{199}\text{Hg}$  in DaW is inherited from the Hg source or a result of photochemical reduction in the environment, the Damon slough wetland demonstrates that significant  $\Delta^{199}\text{Hg}$  can be present in sediment with high THg concentration ( $>1000$  ng/g).

#### 3.5. Mercury concentration and stable isotopes in SF Bay precipitation

The precipitation samples analyzed for Hg stable isotopes represent Hg from multiple events that were combined to integrate over one to three-month periods. The THg concentration of the precipitation samples for each site ranged from 4.7 to 9.0 ng/L and did not correlate with precipitation volume, distance from the Pacific Ocean, or site elevation. The narrow range of THg concentrations are consistent with previously reported measurements of Hg in SF Bay precipitation (6.6 to 9.7 ng/L; Hoenicke and Tsai, 2001) and similar to the average THg concentration of precipitation events from coastal California and south SF Bay (6.0 to 12 ng/L; Steding and Flegal, 2002). Precipitation from the three sites, integrated over the entire winter sampling period, had an average  $\delta^{202}\text{Hg}$  of  $0.06 \pm 0.11\%$  and an average  $\Delta^{199}\text{Hg}$  of  $0.30 \pm 0.05\%$  (mean  $\pm 1$  s.d.;  $n = 3$ ). The individual samples had a range for  $\delta^{202}\text{Hg}$  between  $-0.01\%$  and  $0.19\%$  and for  $\Delta^{199}\text{Hg}$  between  $0.16\%$  and  $0.35\%$  (Table 2; Fig. 7). The two Moss Beach samples represent Hg deposited on the California coast where a portion of the Hg is likely derived from long range transport over the Pacific Ocean (Steding and Flegal, 2002). Collection locations at San Jose and Oakland are in the SF Bay area and likely incorporate a mixture of long range and locally derived Hg. The Hg concentration and isotopic composition of precipitation from the coastal and SF Bay area sampling locations are similar, indicating that the long-term average Hg in precipitation at these locations is not greatly influenced by local Hg sources with distinct Hg stable isotope ratios. Thus, we interpret the range of  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  to be a reasonable estimate of the Hg stable isotope composition of precipitation during the winter season in the SF Bay region. A similar value for  $\delta^{202}\text{Hg}$  ( $0.13 \pm 0.13\%$ ) and  $\Delta^{199}\text{Hg}$  ( $0.35 \pm 0.10\%$ ) has been reported for precipitation collected on the west coast of Florida that was transported inland from the Gulf of Mexico and is believed not to have been impacted by local Hg emission sources (Sherman et al., 2011). Subtidal surface sediments in SF Bay have  $\delta^{202}\text{Hg}$  ( $-0.52 \pm 0.04\%$ ) and  $\Delta^{199}\text{Hg}$  ( $0.07 \pm 0.03\%$ ) values that are significantly different from the SF Bay area precipitation signal ( $\delta^{202}\text{Hg}$  of  $0.06 \pm 0.11\%$  and  $\Delta^{199}\text{Hg}$  of  $0.30 \pm 0.05\%$ ). In addition, precipitation Hg stable isotope ratios display no consistent spatial relationship with surface or subsurface sediments in SF Bay (Fig. 7). Mass balance calculations suggest that atmospheric inputs of Hg are a very minor source of the total Hg flux to sediments (MacLeod et al., 2005) and that sediment input contributes up to 100 times more Hg to SF Bay than precipitation (Hoenicke and Tsai, 2001; Conaway et al., 2008). The Hg stable isotope measurements of SF Bay area precipitation provide confirmation that Hg in precipitation is a relatively small input of Hg to sediments in SF Bay.

#### 3.6. Sediment endmembers in SF Bay from $\delta^{202}\text{Hg}$ and THg

Based on the results of sediment from subtidal, wetland and terrace locations, we have characterized three sediment endmembers



**Table 2**

Regional precipitation THg concentration and Hg stable isotope composition. The THg concentrations reported here are based on the combination of Hg from multiple bottles into a 1% KMnO<sub>4</sub> oxidizing trap solution. The "Moss Beach avg" THg concentration is the volume weighted mean that represents the entire winter 2009 sampling period.

Location	Latitude (N)	Longitude (W)	THg	$\delta^{202}\text{Hg}$	$\Delta^{201}\text{Hg}$	$\Delta^{199}\text{Hg}$
			ng/L	‰	‰	‰
Moss Beach 1	37.5316	122.51	6.2	0.02	0.19	0.16
Moss Beach 2	37.5316	122.51	9.0	-0.01	0.31	0.33
Moss Beach avg.			7.7	0.01	0.25	0.25
San Jose	37.4399	121.958	4.7	-0.01	0.19	0.35
Oakland	37.7416	122.206	7.9	0.19	0.27	0.29

present in SF Bay using Hg isotopic compositions and THg concentrations (Fig. 8). The proposed endmembers are:

- 1) Background sediment (Bk) represented by the average  $\delta^{202}\text{Hg}$  and THg concentration of five, low THg (<60 ng/g) subtidal sediment intervals ( $\delta^{202}\text{Hg} = -0.98\%$ ,  $1/\text{THg} = 18.0$ ). The THg concentration is consistent with pre-mining sediment THg concentration in SF Bay (Hornberger et al., 1999; Conaway et al., 2004; Bouse et al., 2010) and based on the isotopic composition we interpret the Hg to be of marine or background geologic origin.
- 2) Sediment contaminated by metallic Hg used during Au mining (Met) represented by the average  $\delta^{202}\text{Hg}$  and THg of terrace sediment from the Yuba River ( $\delta^{202}\text{Hg} = -0.57\%$ ,  $1/\text{THg} = 0.23$ ). The Yuba River had significant historical Au mining activity that used Hg(0) and mobilized large volumes of Hg-laden sediment. The Yuba River bulk sediment  $\delta^{202}\text{Hg}$  is most consistent with metallic Hg recovered from Hg ore in the California Coast Range that was later incorporated into sediment.
- 3) Sediment contaminated by Hg mine waste (HM) represented by subsurface sediment from the Coyote Creek wetland ( $\delta^{202}\text{Hg} = 0.21\%$ ,  $1/\text{THg} = 0.27$ ), which is directly downstream of the New Almaden Hg mining district (Thomas et al., 2002; Conaway et al., 2004).

Most of the Hg transported to SF Bay is associated with sediment and delivered during high flow conditions (Domagalski, 2001). Here we assume that Hg remains attached to sediment during river transport (Rytuba, 2000; Slowey et al., 2005; David et al., 2009) and that, within SF Bay, Hg is transported primarily adsorbed to suspended sediment (Schoellhamer et al., 2007). Based on this assumption, we

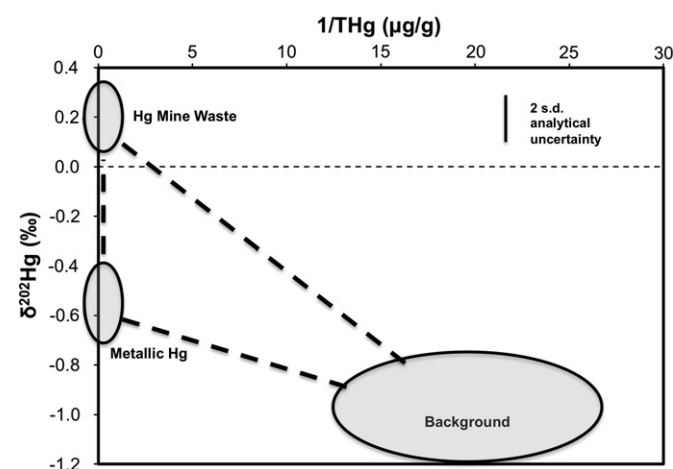


Fig. 8.  $\delta^{202}\text{Hg}$  vs.  $1/\text{THg}$  of three sediment endmembers identified for SF Bay.

have calculated the relative contribution of each endmember to subtidal locations using Eqs. (4)–(6) modified from Yin et al. (2013):

$$\delta^{202}\text{Hg}_{\text{SED}} = F_{\text{Bk}}\delta^{202}\text{Hg}_{\text{Bk}} + F_{\text{Met}}\delta^{202}\text{Hg}_{\text{Met}} + F_{\text{HM}}\delta^{202}\text{Hg}_{\text{HM}} \quad (4)$$

$$1/\text{Hg}_{\text{Sed}} = F_{\text{Bk}}/\text{Hg}_{\text{Bk}} + F_{\text{Met}}/\text{Hg}_{\text{Met}} + F_{\text{HM}}/\text{Hg}_{\text{HM}} \quad (5)$$

$$1 = F_{\text{Bk}} + F_{\text{Met}} + F_{\text{HM}} \quad (6)$$

We acknowledge that the calculation of the percent contribution of each endmember is only a rough approximation. Here we assume that the THg concentration and Hg isotopic composition of each endmember is invariant, however the concentration of the contaminated sediment endmembers delivered to SF Bay is likely influenced by variable amounts of dilution with uncontaminated sediment during transport to SF Bay. Nonetheless, the estimated mixtures of the sediment endmembers explain the Hg isotopic variation in all of the subtidal and intertidal sediments in this study and trends in the relative contribution of endmembers to all sediment samples appear robust.

In five subtidal cores, background sediment predominates in downcore (100–160 cm) samples (Fig. 9C). In c. 1960 sediment in subtidal locations, there was a small proportion (<22%) of background sediment, and sediment contaminated by metallic Hg accounted for 80% of the sediment deposited in Central Bay and San Pablo Bay locations. In c. 1960 sediment in South Bay and Lower South Bay there was a significant contribution of sediment contaminated by Hg mining (up to 37%; Fig. 9B). In surface sediment from subtidal locations, the proportion of each sediment endmember is relatively constant and dominated by metallic Hg contaminated sediment (57% or greater contribution; Fig. 9A). A significant contribution from both Hg mining and metallic Hg endmembers in surface sediment is evidence of a homogeneous surface sediment pool in open water locations. The application of the sediment endmembers proposed here to intertidal surface sediment reported by Gehrke et al. (2011a) suggests that in intertidal locations, sediment contaminated by Hg mining is present in South SF Bay (up to 40%) with a transition to sediment contaminated by a metallic Hg source(s) in Central Bay and northward. Thus, intertidal surface sediment and subtidal c. 1960 sediment appear to have the same spatial trend in sediment endmember contribution.

### 3.7. Insight into sediment transport from Hg stable isotopes

The Hg isotopic gradient in c. 1960 sediment is consistent with two Hg sources entering SF Bay and, based on the proposed endmembers in SF Bay sediment, the two sediment sources are similarly distributed in c. 1960 subtidal sediment and intertidal surface sediment (from Gehrke et al., 2011a). Erosion, deposition and sediment distribution in SF Bay are controlled by the amount of sediment delivered from surrounding watersheds (Schoellhamer, 2011). In addition, it is expected that the intertidal area would increase during periods of increased sediment supply and decrease when sediment supply decreased (Jaffe and Foxgrover, 2006; Jaffe et al., 2007).

Historical changes in sediment supply have changed erosional and depositional patterns in SF Bay. In brief, in the late 1800s large volumes of sediment were mobilized in the rivers leading to the Sacramento–San Joaquin delta due to hydraulic mining operations (Gilbert, 1917). As a result, a pulse of sediment was delivered to SF Bay and initially deposited in San Pablo Bay (Marvin-DiPasquale et al., 2003; Jaffe et al., 2007; Bouse et al., 2010). The sediment in SPB provided a large and easily eroded sediment pool (Schoellhamer, 2011) and gradual dispersion of the sediment pool led to net deposition in Central SF Bay between 1895 and 1947 (Fregoso et al., 2008) and in South SF Bay between 1858–1898 and 1931–1956 (Foxgrover et al., 2004). Beginning in the early 1900s, land use changes, water diversion projects and flood control projects reduced the sediment discharge from SF Bay tributaries including the Sacramento–San Joaquin Delta (Conomos et al., 1985; Wright and Schoellhamer, 2004; McKee et al., 2006; Singer et al.,

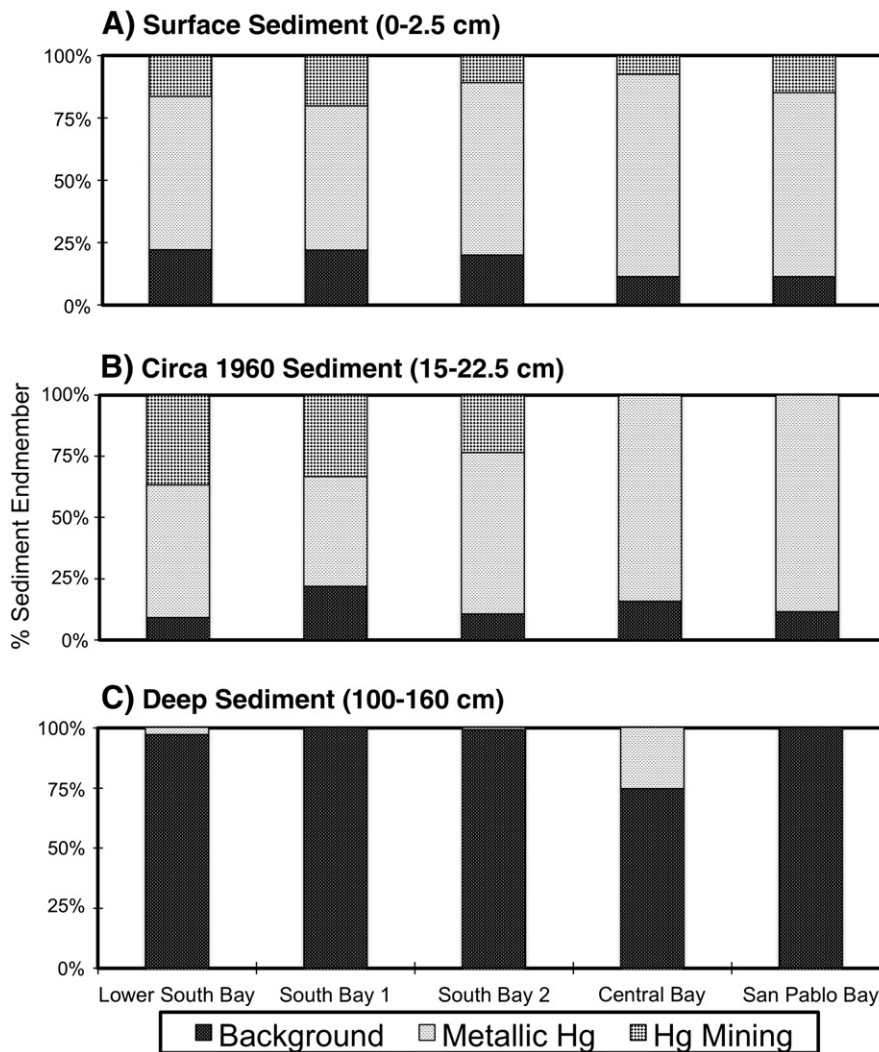


Fig. 9. Estimated endmember sediment contribution to (A) surface, (B) circa 1960, and (C) deep sediment in subtidal locations.

2008; McKee and Lewicki, 2009). Sub-basins within SF Bay shifted from depositional to erosional after depletion of the sediment pool and San Pablo Bay, Central Bay and South Bay all became erosional by the late 1950s (Foxgrover et al., 2004; Jaffe et al., 2007; Fregoso et al., 2008).

Because intertidal area growth is dependent on sediment supply (Jaffe and Foxgrover, 2006; Jaffe et al., 2007) it is likely that the intertidal area in SF Bay generally increased until the mid-1950s. Since the 1950s SPB, CB and SB became erosional, and surface sediment in subtidal regions became well homogenized with respect to Hg isotopic composition. As a result, only the c. 1960 subtidal sediment, and not subtidal surface sediment, retained the spatial trend in  $\delta^{202}\text{Hg}$  that was observed in intertidal surface sediment by Gehrke et al. (2011a). Therefore, we suggest that the sediment remaining in intertidal zones throughout SF Bay, and measured by Gehrke et al. (2011a), was likely deposited during the last period of intertidal growth in SF Bay, probably in the mid-20th century or earlier.

#### 4. Conclusion

This study documents the Hg isotopic composition and THg concentration of eight sediment cores around SF Bay, Yuba River terrace sediment and precipitation from the San Francisco Bay region. We propose three sediment endmembers with distinct Hg sources, based on Hg isotopic composition and THg concentration, to explain the distribution of sediment within SF Bay. In wetlands adjacent to SF Bay in two separate locations, high subsurface THg concentrations correlate with

shifts in  $\delta^{202}\text{Hg}$ . In the Coyote Creek wetland, we interpret the high THg sediment, deposited in the 1950s, to be the result of Hg that was leached and transported from calcine located upstream. In the Damon slough wetland, high THg sediment, deposited in the 1940s, is consistent with sediment contaminated by metallic Hg used in industry, but we have not attempted to identify the specific industrial source(s). We use low THg (<60 ng/g) subtidal sediment to identify the Hg isotopic composition of uncontaminated, downcore sediment. The positive  $\Delta^{199}\text{Hg}$  of pre-mining sediment is consistent with Hg that has undergone significant photoreduction. We suggest that at least some of the pre-mining Hg in SF Bay sediment is of marine origin; however the contribution of marine Hg relative to geogenic Hg is unknown.

We have calculated the contribution of three sediment endmembers to subtidal and intertidal locations using a mixing model. The estimated contribution of sediment endmembers to c. 1960 subtidal sediments and present day intertidal surface sediments is similar, suggesting that intertidal sediment was deposited in the mid-20th century or earlier. The sediment endmember mixing calculations suggest that sediment contaminated by metallic Hg was delivered to SF Bay via the SSJ delta and was gradually transported throughout SF Bay, possibly supplemented with sediment contaminated by metallic Hg of industrial, non-Au mining, origin. In south SF Bay the metallic Hg contaminated sediment mixed with sediment contaminated by Hg mining (with higher  $\delta^{202}\text{Hg}$ ) that had been delivered to south SF Bay. The relative homogeneity of surface sediment in all subtidal locations is interpreted as the result

of continual mixing of the subtidal surface sediment pool. From this study, we suggest that Hg stable isotopes can be a useful tool to assess spatial and temporal trends in sediment deposition when multiple, isotopically distinct Hg sources are present.

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## References

- Alpers, C.N., Hunerlach, M.P., May, J.T., Hothem, R.L., 2005. Mercury contamination from historical gold mining in California. Fact Sheet — U. S. Geological Survey, p. 1.
- Amyot, M., Mierle, G., Lean, D., Mc Queen, D.J., 1997. Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes. *Geochimica et Cosmochimica Acta* 61 (5), 975–987.
- Bergquist, B.A., Blum, J.D., 2007. Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* 318 (5849), 417–420.
- Biswas, A., Blum, J.D., Bergquist, B.A., Keeler, G.J., Xie, Z.Q., 2008. Natural mercury isotope variation in coal deposits and organic soils. *Environmental Science & Technology* 42 (22), 8303–8309.
- Blum, J.D., 2011. Applications of Stable Mercury Isotopes to Biogeochemistry. Springer-Verlag, Berlin Heidelberg 229–245.
- Blum, J.D., Bergquist, B.A., 2007. Reporting of variations in the natural isotopic composition of mercury. *Analytical and Bioanalytical Chemistry* 388 (2), 353–359.
- Bouse, R.M., Fuller, C.C., Luoma, S., Hornberger, M.L., Jaffe, B.E., Smith, R.E., 2010. Mercury-contaminated hydraulic mining debris in San Francisco Bay. *San Francisco Estuary and Watershed Science* 8 (1).
- Cargill, S., Root, D., Bailey, E., 1980. Resource estimation from historical data: mercury, a test case. *Mathematical Geology* 12 (5), 489–522.
- Conaway, C.H., Watson, E.B., Flanders, J.R., Flegal, A.R., 2004. Mercury deposition in a tidal marsh of south San Francisco Bay downstream of the historic New Almaden mining district, California. *Marine Chemistry* 90 (1–4), 175–184.
- Conaway, C.H., Ross, J.R.M., Looker, R., Mason, R.P., Flegal, A.R., 2007. Decadal mercury trends in San Francisco Estuary sediments. *Environmental Research* 105 (1), 53–66.
- Conaway, C.H., Black, F.J., Grieb, T.M., Roy, S., Flegal, A.R., 2008. Mercury in the San Francisco estuary. *Reviews of Environmental Contamination and Toxicology*, 194. Springer, New York, pp. 29–54 (Reviews of Environmental Contamination and Toxicology).
- Conomos, T.J., American Association for the Advancement of Science, American Society of, L., Oceanography, 1979. San Francisco Bay: The Urbanized Estuary: Investigations into the Natural History of San Francisco Bay and Delta with Reference to the Influence of Man: Fifty-eighth Annual Meeting of the Pacific Division/American Association for the Advancement of Science held at San Francisco State University, San Francisco, California, June 12–16, 1977. The Division, San Francisco, Calif (493 pp.: [1] leaf of plates pp.).
- Conomos, T.J., Smith, R.E., Gartner, J.W., 1985. Environmental setting of San Francisco Bay. *Hydrobiologia* 129 (1), 1–12.
- Daum, T., Lowe, S., Toia, R., Bartow, G., Fairey, R., Anderson, J., Jones, J., 2000. Sediment Contamination in San Leandro Bay, CA. San Francisco Estuary Institute, Oakland, CA.
- David, N., McKee, L.J., Black, F.J., Flegal, A.R., Conaway, C.H., Schoellhamer, D.H., Ganju, N.K., 2009. Mercury concentrations and loads in a large river system tributary to San Francisco Bay, California, USA. *Environmental Toxicology and Chemistry* 28 (10), 2091–2100.
- Davis, J.A., Greenfield, B.K., Ichikawa, G., Stephenson, M., 2008. Mercury in sport fish from the Sacramento–San Joaquin Delta region, California, USA. *Science of the Total Environment* 391 (1), 66–75.
- Davis, J.A., Looker, R.E., Yee, D., Marvin-DiPasquale, M., Grenier, J.L., Austin, C.M., McKee, L.J., Greenfield, B.K., Brodberg, R., Blum, J.D., 2012. Reducing methylmercury accumulation in the food webs of San Francisco Bay and its local watersheds. *Environmental Research* (0).
- Domagalski, J., 2001. Mercury and methylmercury in water and sediment of the Sacramento River Basin, California. *Applied Geochemistry* 16 (15), 1677–1691.
- Estrade, N., Carignan, J., Sonke, J.E., Donard, O.F.X., 2009. Mercury isotope fractionation during liquid–vapor evaporation experiments. *Geochimica et Cosmochimica Acta* 73 (10), 2693–2711.
- Estrade, N., Carignan, J., Donard, O.F.X., 2011. Tracing and quantifying anthropogenic mercury sources in soils of northern France using isotopic signatures. *Environmental Science & Technology* 45 (4), 1235–1242.
- Feng, X.B., Foucher, D., Hintelmann, H., Yan, H.Y., He, T.R., Qiu, G.L., 2010. Tracing mercury contamination sources in sediments using mercury isotope compositions. *Environmental Science & Technology* 44 (9), 3363–3368.
- Fleck, J.A., Alpers, C.N., Marvin-DiPasquale, M., Hothem, R.L., Wright, S.A., Ellett, K., Beaulieu, E., Agee, J.L., Kakouros, E., Kieu, L.H., Eberl, D.D., Blum, A.E., May, J.T., 2011. The effects of sediment and mercury mobilization in the south Yuba River and Humboldt Creek confluence area, Nevada County, California: concentrations, speciation, and environmental fate; part 1, field characterization. Open-File Report — U. S. Geological Survey, p. 1.
- Foucher, D., Ogrinc, N., Hintelmann, H., 2009. Tracing mercury contamination from the Idrija Mining Region (Slovenia) to the Gulf of Trieste using Hg isotope ratio measurements. *Environmental Science & Technology* 43 (1), 33–39.
- Foucher, D., Hintelmann, H., Al, T.A., MacQuarrie, K.T., 2013. Mercury isotope fractionation in waters and sediments of the Murray Brook mine watershed (New Brunswick, Canada): Tracing mercury contamination and transformation. *Chemical Geology* 336, 87–95.
- Foxgrover, A.C., Higgins, S.A., Ingracia, M.K., Jaffe, B.E., Smith, R.E., 2004. Deposition, erosion, and bathymetric change in South San Francisco Bay; 1858–1983. Open-File Report — U. S. Geological Survey, p. 1.
- Fregoso, T.A., Foxgrover, A.C., Jaffe, B.E., 2008. Sediment deposition, erosion, and bathymetric change in central San Francisco Bay; 1855–1979. Open-File Report — U. S. Geological Survey, p. 1.
- Gehrke, G.E., Blum, J.D., Meyers, P.A., 2009. The geochemical behavior and isotopic composition of Hg in a mid-Pleistocene western Mediterranean sapropel. *Geochimica et Cosmochimica Acta* 73 (6), 1651–1665.
- Gehrke, G.E., Blum, J.D., Marvin-DiPasquale, M., 2011a. Sources of mercury to San Francisco Bay surface sediment as revealed by mercury stable isotopes. *Geochimica et Cosmochimica Acta* 75 (3), 691–705.
- Gehrke, G.E., Blum, J.D., Slotton, D.G., Greenfield, B.K., 2011b. Mercury isotopes link mercury in San Francisco Bay forage fish to surface sediments. *Environmental Science & Technology* 45 (4), 1264–1270.
- Gilbert, G.K., 1917. Hydraulic-mining Debris in the Sierra Nevada. US Gov't Print Off.
- Gratz, L.E., Keeler, G.J., Blum, J.D., Sherman, L.S., 2010. Isotopic composition and fractionation of mercury in great lakes precipitation and ambient air. *Environmental Science & Technology* 44 (20), 7764–7770.
- Greenfield, B.K., Jahn, A., 2010. Mercury in San Francisco Bay forage fish. *Environmental Pollution* 158 (8), 2716–2724.
- Greenfield, B.K., Davis, J.A., Fairey, R., Roberts, C., Crane, D., Ichikawa, G., 2005. Seasonal, interannual, and long-term variation in sport fish contamination, San Francisco Bay. *Science of the Total Environment* 336 (1–3), 25–43.
- Hoenicke, R., Tsai, P., 2001. San Francisco Bay Atmospheric Deposition Pilot Study Part 1: Mercury. San Francisco Estuary Institute, Richmond, CA.
- Hornberger, M.L., Luoma, S.N., van Geen, A., Fuller, C., Anima, R., 1999. Historical trends of metals in the sediments of San Francisco Bay, California. *Marine Chemistry* 64 (1–2), 39–55.
- Hunerlach, M.P., Alpers, C.N., Marvin-DiPasquale, M.C., Taylor, H.E., De Wild, J.F., 2004. Geochemistry of Mercury and Other Trace Elements in Fluvial Tailings Upstream of Daguerre Point Dam, Yuba River, California, August 2001.
- Jaffe, B., Foxgrover, A., 2006. A history of intertidal flat area in south San Francisco Bay, California: 1858 to 2005. Open-File Report — U. S. Geological Survey, p. 1.
- Jaffe, B.E., Smith, R.E., Foxgrover, A.C., 2007. Anthropogenic influence on sedimentation and intertidal mudflat change in San Pablo Bay, California: 1856–1983. *Estuarine, Coastal and Shelf Science* 73 (1–2), 175–187.
- James, L.A., 2005. Sediment from hydraulic mining detained by Englebright and small dams in the Yuba basin. *Geomorphology* 71 (1–2), 202–226.
- James, L.A., Singer, M.B., 2008. Development of the lower Sacramento Valley flood-control system: historical perspective. *Natural Hazards Review* 9 (3), 125–135.
- James, L.A., Singer, M.B., Ghoshal, S., Megison, M., 2009. Historical channel changes in the lower Yuba and Feather Rivers, California: long-term effects of contrasting river-management strategies. *Management and Restoration of Fluvial Systems with Broad Historical Changes and Human Impacts: Geological Society of America Special Paper* 451, 57–81.
- Jemison, C., 2009. 2008 Annual Inspection Report: Clorox Company Oakland Plant Site. In: Control, D.o.T.S. (Ed.), Department of Toxic Substances Control, State of California, p. 7.
- Laffont, L., Sonke, J.E., Maurice, L., Monroy, S.L., Chincheros, J., Amouroux, D., Behra, P., 2011. Hg speciation and stable isotope signatures in human hair as a tracer for dietary and occupational exposure to mercury. *Environmental Science & Technology* 45 (23), 9910–9916.
- Landis, M.S., Keeler, G.J., 1997. Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations. *Environmental Science & Technology* 31 (9), 2610–2615.
- Liu, J., Feng, X., Yin, R., Zhu, W., Li, Z., 2011. Mercury distributions and mercury isotope signatures in sediments of Dongjiang, the Pearl River Delta, China. *Chemical Geology* 287 (1–2), 81–89.
- MacLeod, M., McKone, T.E., Mackay, D., 2005. Mass balance for mercury in the San Francisco Bay area. *Environmental Science & Technology* 39 (17), 6721–6729.
- Marvin-DiPasquale, M., Cox, M.H., 2007. Legacy Mercury in Alviso Slough, South San Francisco Bay, California Concentration, Speciation and Mobility. U.S. Dept. of the Interior, U.S. Geological Survey, Reston, VA (pp. 99 p.).
- Marvin-DiPasquale, M.C., Agee, J.L., Bouse, R.M., Jaffe, B.E., 2003. Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. *Environmental Science & Technology* 43 (3), 260–267.
- McKee, L.J., Lewicki, M., 2009. Watershed Specific and Regional Scale Suspended Sediment Load Estimates for Bay Area Small Tributaries, Oakland Ca.
- McKee, L.J., Ganju, N.K., Schoellhamer, D.H., 2006. Estimates of suspended sediment entering San Francisco Bay from the Sacramento and San Joaquin Delta, San Francisco Bay, California. *Journal of Hydrology* 323 (1–4), 335–352.

- Mil-Homens, M., Blum, J., Canario, J., Caetano, M., Costa, A.M., Lebreiro, S.M., Trancoso, M., Richter, T., de Stigter, H., Johnson, M., Branco, V., Cesario, R., Mouro, F., Mateus, M., Boer, W., Melo, Z., 2013. Tracing anthropogenic Hg and Pb input using stable Hg and Pb isotope ratios in sediments of the central Portuguese Margin. *Chemical Geology* 336, 62–71.
- Nichols, F.H., Cloern, J.E., Luoma, S.N., Peterson, D.H., 1986. The modification of an estuary. *Science* 231 (4738), 567–573.
- Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. *Science of the Total Environment* 149 (3), 167–181.
- OEHHA, 2011. Health advisory and safe eating guidelines for San Francisco Bay fish and shellfish. In: California, E.P.A. (Editor).
- Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter—a review. *Chemosphere* 55 (3), 319.
- Rytuba, J.J., 2000. Mercury mine drainage and processes that control its environmental impact. *Science of the Total Environment* 260 (1–3), 57–71.
- Rytuba, J.J., 2003. Mercury from mineral deposits and potential environmental impact. *Environmental Geology (Berlin)* 43 (3), 326–338.
- Schoellhamer, D.H., 2011. Sudden clearing of estuarine waters upon crossing the threshold from transport to supply regulation of sediment transport as an erodible sediment pool is depleted: San Francisco Bay, 1999. *Estuaries and Coasts* 34 (5), 885–899.
- Schoellhamer, D.H., Mumley, T.E., Leatherbarrow, J.E., 2007. Suspended sediment and sediment-associated contaminants in San Francisco Bay. *Environmental Research* 105 (1), 119–131.
- Senn, D.B., Chesney, E.J., Blum, J.D., Bank, M.S., Maage, A., Shine, J.P., 2010. Stable isotope (N, C, Hg) study of methylmercury sources and trophic transfer in the northern Gulf of Mexico. *Environmental Science & Technology* 44 (5), 1630–1637.
- Sherman, L.S., Blum, J.D., Keeler, G.J., Demers, J.D., Dvonch, J.T., 2011. Investigation of local mercury deposition from a coal-fired power plant using mercury isotopes. *Environmental Science & Technology* 46 (1), 382–390.
- Singer, M.B., Aalto, R., 2009. Floodplain development in an engineered setting. *Earth Surface Processes and Landforms* 34 (2), 291–304.
- Singer, M.B., Aalto, R., James, L.A., 2008. Status of the lower Sacramento Valley flood-control system within the context of its natural geomorphic setting. *Natural Hazards Review* 9 (3), 104–115.
- Singer, M.B., Aalto, R., James, L.A., Kilham, N.E., Higson, J.L., Ghoshal, S., 2013. Enduring Legacy of Toxic Fans: Episodic Redistribution of California Gold Mining Debris (submitted for publication).
- Slowey, A.J., Rytuba, J.J., Brown, G.E., 2005. Speciation of mercury and mode of transport from placer gold mine tailings. *Environmental Science & Technology* 39 (6), 1547–1554.
- Smith, C.N., Kesler, S.E., Blum, J.D., Rytuba, J.J., 2008. Isotope geochemistry of mercury in source rocks, mineral deposits and spring deposits of the California Coast Ranges, USA. *Earth and Planetary Science Letters* 269 (3–4), 398–406.
- Sonke, J.E., Zambardi, T., Toutain, J.-P., 2008. Indirect gold trap-MC-ICP-MS coupling for Hg stable isotope analysis using a syringe injection interface. *Journal of Analytical Atomic Spectrometry* 23 (4).
- Sonke, J.E., Schafer, J., Chmeleff, J., Audry, S., Blanc, G., DuprÉ, B., 2010. Sedimentary mercury stable isotope records of atmospheric and riverine pollution from two major European heavy metal refineries. *Chemical Geology* 279 (3–4), 90–100.
- Springborn, M., Singer, M.B., Dunne, T., 2011. Sediment-adsorbed total mercury flux through Yolo Bypass, the primary floodway and wetland in the Sacramento Valley, California. *Science of the Total Environment* 412, 203–213.
- Steding, D.J., Flegal, A.R., 2002. Mercury concentrations in coastal California precipitation: evidence of local and trans-Pacific fluxes of mercury to North America. *Journal of Geophysical Research-Atmospheres* 107 (D24), 4764.
- Stetson, S.J., Gray, J.E., Wanty, R.B., Macalady, D.L., 2009. Isotopic variability of mercury in ore, mine-waste calcine, and leachates of mine-waste calcine from areas mined for mercury. *Environmental Science & Technology* 43 (19), 7331–7336.
- Thomas, M.A., Conaway, C.H., Steding, D.J., Marvin-DiPasquale, M., Abu-Saba, K.E., Flegal, A.R., 2002. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. *Geochemistry* 2 (3), 211.
- van Geen, A., Luoma, S.N., 1999. The impact of human activities on sediments of San Francisco Bay, California: an overview. *Marine Chemistry* 64 (1–2), 1–6.
- Wright, S.A., Schoellhamer, D.H., 2004. Trends in the sediment yield of the Sacramento River, California, 1957–2001. *San Francisco Estuary and Watershed Science* 2 (2).
- Yee, D., Bemis, B., Hammond, D., Heim, B., Jaffe, B., Rattonet, A., van Bergen, S., 2011. Age Estimates and Pollutant Concentrations of Sediment Cores from San Francisco Bay and Wetlands, Oakland, CA.
- Yin, R., Feng, X., Wang, J., Li, P., Liu, J., Zhang, Y., Chen, J., Zheng, L., Hu, T., 2013. Mercury speciation and mercury isotope fractionation during ore roasting process and their implication to source identification of downstream sediment in the Wanshan mercury mining area, SW China. *Chemical Geology* 336, 72–79.
- Zheng, W., Hintelmann, H., 2009. Mercury isotope fractionation during photoreduction in natural water is controlled by its Hg/DOC ratio. *Geochimica et Cosmochimica Acta* 73 (22), 6704–6715.