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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 δ^{202}Hg of -0.98 ± 0.06‰ and Δ^{199}Hg of 0.17 ± 0.03‰ (1 s.d.; $n = 5$). The δ^{202}Hg of subtidal sediment in SF Bay systematically changed between pre-mining, circa 1960, and surface sediment. In circa 1960 sediment δ^{202}Hg ranges from -0.63 to -0.32‰ (± 0.10‰) with higher δ^{202}Hg in the south and lower δ^{202}Hg in the north; however in surface sediment δ^{202}Hg is nearly constant and averages -0.52 ± 0.04‰ (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 δ^{202}Hg of -0.57 ± 0.10‰ and Δ^{199}Hg of 0.05 ± 0.01‰ (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 ~0.6‰ in δ^{202}Hg, presumably reflective of various anthropogenic Hg sources. The three sediment endmembers (metallic Hg, Hg mining and background Hg) were defined using δ^{202}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.

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^2 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 ^{137}Cs and ^{210}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 ^{137}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 ^{137}Cs appearance in subtidal locations marks the maximum depth of downward migration of ^{137}Cs, and that sediment below this maximum depth has not been exposed to the