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Mercury accumulation and attenuation at a rapidly forming delta with a point source of mining waste

Bryce E. Johnson[a,*], **Bradley K. Esser**[b], **Dyan C. Whyte**[c], **Priya M. Ganguli**[c], **Carrie M. Austin**[c], and **James R. Hunt**[a]

[a]Civil and Environmental Engineering, University of California, Berkeley, CA 94720

[b]Chemical Sciences Division, 7000 East Avenue, Lawrence Livermore National Laboratory, Livermore CA 94550

[c]California Regional Water Quality Control Board, 1515 Clay St., Suite 1400, Oakland, CA 94612, USA

Abstract

The Walker Creek intertidal delta of Tomales Bay, California is impacted by a former mercury mine within the watershed. Eleven short sediment cores (10 cm length) collected from the delta found monomethylmercury (MMHg) concentrations ranging from 0.3 to 11.4 ng/g (dry wt.), with lower concentrations occurring at the vegetated marsh and upstream channel locations. Algal mats common to the delta's sediment surface had MMHg concentrations ranging from 7.5 to 31.5 ng/g, and the top 1 cm of sediment directly under the mats had two times greater MMHg concentrations compared to adjacent locations without algal covering. Spatial trends in resident biota reflect enhanced MMHg uptake at the delta compared to other bay locations. Eighteen sediment cores, 1 to 2 meters deep, collected from the 1.2 km^2 delta provide an estimate of a total mercury (Hg) inventory of 2500 ± 500 kg. Sediment Hg concentrations ranged from pre-mining background conditions of approximately 0.1 μg/g to a post-mining maximum of 5 μg/g. Sediment accumulation rates were determined from three sediment cores using measured differences of ^{137}Cs activity. We estimate a pre-mining Hg accumulation of less than 20 kg/yr, and a period of maximum Hg accumulation in the 1970s and 1980s with loading rates greater than 50 kg/yr, corresponding to the failure of a tailings dam at the mine site. At the time of sampling (2003) over 40 kg/yr of Hg was still accumulating at the delta, indicating limited recovery. We attribute observed spatial evolution of elevated Hg levels to ongoing inputs and sediment re-working, and estimate the inventory of the anthropogenic fraction of total Hg to be at least 1500 ± 300 kg. We suggest ongoing sediment inputs and methylation at the deltaic surface support enhanced mercury levels for resident biota and transfer to higher trophic levels throughout the Bay.

Keywords

Sediments; Mercury; Methylmercury; Contaminant Accumulation; Bioaccumulation; Biota; Natural Attenuation; Tomales Bay

*Corresponding author. Tel: 650 888 4855 bjohnson@ce.berkeley.edu (B. Johnson).

1. Introduction

Sediment systems are important to the transport and fate of anthropogenic mercury and terrestrial sediments with enhanced Hg levels can accumulate within estuarine bottom sediments. Accumulating estuarine sediment layers can record Hg removal from the overlying water column via sediment deposition and the timing of historical releases can be resolved through radionuclide distributions (Santschi et al., 1999; Santschi et al., 2001). Recovery for many sites relies on natural attenuation achieved by the burial and isolation of cleaner sediments on top of the contaminated layers. However, burial times can be slow due to ongoing and episodic inputs, and mixing processes can re-work and re-distribute the contaminated surface. In the time it takes contaminated layers to become effectively isolated from the biologically active sediment-water interface, mercury can become incorporated within benthic and pelagic food webs with concentrations magnifying at higher tropic levels (Lawson and Mason, 1998; Coelho et al., 2008). In many systems, modeling mercury-laden sediment accumulation is complicated by multiple sources. The Walker Creek Delta on Tomales Bay presents an opportunity to investigate mercury accumulation and recovery from a point source, and assess the impact of mercury mining on Bay biota.

The Gambonini mercury mine is a point source of mercury mining waste located within the Walker Creek watershed (Whyte and Kirchner, 2000). Discharge from the mine site enters Walker Creek approximately 29 km upstream from the delta. The Gambonini mine is one of many mercury mines along the California Coast Range mercury mineral belt. The mine is a hot spring type cinnabar deposit where mineralization occurs during the cooling of fluids containing trace levels of mercury that are transported upwards from the subsurface as a result of geothermal forcing (Rytuba, 2000). Mineral exploration of the Gambonini Ranch began in 1945, however the land was not developed into a working mine until 1964. Buttes Gas & Oil Company operated the mine, and between 1964 and 1970 produced 5000 flasks (170,000 kg) of liquid mercury. The mining company disposed onsite approximately 300,000 m^3 of mining wastes and tailings with an average mercury concentration of 320 μg/g (Whyte and Kirchner, 2000). The inventory of total Hg at the mine site is estimated to be approximately 100,000 kg. The remnant mercury in the calcines produced during roasting is composed of 58 percent metacinnabar (HgS, cubic) and 48 percent cinnabar (HgS, hexagonal) (Kim et al., 2004). Mercury sulfide mineral species are mobile and have been shown to dominate the transport of particulate mercury from tailings in California gold mines (Slowey et al., 2008). In 1970, a small dam was built below the mine site to reduce inputs of mining waste to the watershed. In closing the mine, Buttes Gas & Oil Company buried some of the tailings, contoured the remaining waste pile, and planted grass seed. A steep canyon and a small ephemeral stream hydrologically connect the waste pile to Walker Creek.

Before remediation in 1999, the waste pile was subject to significant erosion evident by numerous rills, large gullies, and debris flow scars (Whyte and Kirchner, 2000) (See Figure S-1). During the 1982 storm, the debris dam built by the mining company, located approximately 400 meters downstream from the mine, failed and released a sediment load of poorly sorted mine tailings into Walker Creek. Although the quantity of sediment discharged during this event is unknown, the amount was sufficient to partially bury automobiles in the adjacent property (personal communication with Doris Gambonini) and alter the channel morphology of Walker Creek near the point of debris input, as recorded in historical aerial photographs. In 1998, a study from January through February, which included a large storm event, showed a two thousand-fold variation in total mercury concentrations in the ephemeral stream downstream from the Gambonini mine (Whyte and Kirchner, 2000). Over the two-month period, 77 kg of mercury were released from the mine site and 99.9 percent of the total Hg measured was associated with particles (Whyte and Kirchner, 2000). The authors suggest that hundreds to thousands of kilograms of mercury have been discharged from the mine site

to downstream waters since mining operations ceased in 1972 (Whyte and Kirchner, 2000). In 1999, the U.S. Environmental Protection Agency and California Regional Water Quality Control Board (Water Board) remediated the mine site by filling in the excavation pit, re-contouring the waste rock pile, installing surface drains and planting vegetation (Smelser and Whyte, 2001). However, large floodplains kilometers downstream from the mine can possibly delay the arrival of eroded sediments to the Bay by 40 to 100 years (Rooney and Smith, 1999). The fate of the mercury-laden mine sediments discharged from the mining site remains a significant environmental concern. Over-bank and flood-plain deposits along Walker Creek, and the salt marshes and intertidal mudflats in the Walker Creek Delta, are potentially storing much of the mercury released from the Gambonini mine.

2. Materials and methods

2.1. Study Area

Tomales Bay, located in the Gulf of the Farallones National Marine Sanctuary, provides winter habitat for thousands of migratory waterfowl and is renowned for its fishery and oyster beds. The Bay is located approximately 64 km north of San Francisco and is about 20 km long, with an average width of 1.4 km and a highly variable bathymetry (see Figure 1, and Figure S-2). Tomales Bay occupies a rift-zone of the San Andreas fault, however the modern morphology of the Bay is dominated by anthropogenic activities that have resulted in increased sediment supply (Rooney and Smith, 1999). Sediments are supplied from the surrounding watershed covering an area of approximately 600 km^2 (Snidvongs, 1993). Two major streams flow into the Bay, Lagunitas Creek at the south end of the Bay, and Walker Creek located at the northern end, about 4 km from the Bay mouth. Terrigenous sediments within Tomales Bay are supplied primarily from the Lagunitas and Walker creek drainage systems (Daetwyler, 1966). Alterations in land use over the last 150 years have significantly increased sediment loading, reducing Tomales Bay in both length and depth through rapid sedimentation despite rising sea levels (Rooney and Smith, 1999). Relative to creek inputs, tidal exchange with upwelled waters off the coast provides only a small amount of organic particles to the estuary's sediment layers (Snidvongs, 1993). The estuary has been characterized by several previous studies, including nutrient dynamics (Smith et al., 1991;Smith and Hollibaugh, 1998), the spatial distribution of benthic fluxes of nutrients (Dollar et al., 1991), groundwater nutrient contribution (Oberdorfer et al., 1990), as well as carbon sources and sediment diagenesis (Chambers et al., 2000;Chambers et al., 1994). Seasonal and spatial distributions of phytoplankton production in the water column have been investigated (Cole, 1999) and seagrass populations throughout the Bay reflect distributions of nutrient availability (Fourqurean et al., 1997).

Walker Creek is a coastal stream with a watershed drainage area of approximately 200 km^2. The modern stream bed is incised into a 4000 to 5000-year-old alluvial terrace composed of clays, silts, sands, and coarse gravel (Haible, 1976). Hillside erosion within the watershed was likely accelerated by the introduction of non-native grasses and farming practices in the late-1800s, and the high density of dairy farms in the early-1900s. The delta at the mouth of Walker Creek has undergone significant geomorphologic changes in the last 200 years. From 1852 to 1870, the town of Tomales, now four kilometers upstream from the current delta, was once part of the estuary and was utilized as a port where small barges and steamers docked to load local produce (Haible, 1976). By the late 1800s, accretion along the lower reaches of the watershed made the waterway to the town of Tomales impossible to navigate, forcing the port to move (Haible, 1976). Daetwyler (1966) estimated that between 1860 and 1930, approximately 2.5×10^6 m^3 of sediment was deposited at the site of the current delta.

The Walker Creek Delta covers an area of approximately 1.2 km^2 and has variable fresh water inflow and an intertidal zone. Large storms are responsible for a significant portion of the sediment accumulation at the delta. The storm from January 3 to 5, 1982, for example, produced

over 25 cm of rainfall in the town of Tomales (Anima et al., 1984). Sediment cores collected from the intertidal surface of the delta one month after the storm contained flood deposits with 6 to 7 cm of sandy sediment atop muddy sand that was abundant with mollusks (Anima et al., 1984). These sediment cores did not reveal stratifications, probably as a result of mixing during previous storms. The authors of the study suggest that sediments accumulate during large storms and undergo a process of re-working during the intervals between major events. Tidal and wind driven currents at the delta likely re-work deposited sediments and drive exchange between the delta and the Bay. Since available bathymetric studies of the Bay showed poor resolution at the delta, we developed a bathymetry data set of the intertidal zone in 2003 and merged our data with a recent bay-wide survey (Rooney and Smith, 1999). An interesting feature of the delta is the bifurcation of the creek channel at the creek mouth. The main channel splits sharply to the northwest near Location H and passes between Locations 24 and G, and between Locations 17 and 18. A smaller channel turns to the southeast, and passes through Location 12 and exits the intertidal zone near Location 8. Both channels become significantly less defined with distance from the creek mouth and demonstrate decreased channel depth and increased width in proximity of the Bay. This trend likely represents a transition from creek dominated flows to tidally driven currents.

2.2 Sampling and analysis

We conducted several sampling campaigns between 1998 and 2003 to evaluate total Hg and monomethylmercury (MMHg) levels in both sediment and biota within Tomales Bay (Table S-1). We used ultra-clean techniques after EPA method 1669 (this is for trace metals in water, but we followed similar guidelines with respect to sediment handling). Our initial survey of total Hg in surface sediments was conducted at 13 intertidal locations along the axis of the Bay to provide an assessment of Hg distributions in sediment within the Bay. Samples were collected by hand in 1999 and 2000, using acid-clean jars dipped into the top 5 cm of the sediment layer. Any surface detritus was removed from the collected sample and the sample was placed on dry ice and shipped to Sequoia Analytical for total Hg determination by EPA method 7471A.

We completed three sediment coring campaigns within the Walker Creek Delta. Total mercury and methylmercury spatial distributions were determined from eleven short cores (10 cm length) collected from both intertidal and vegetated regions of the delta, and at a location 4 km south of the delta. A follow-up study investigated the influence of microbial mats atop sediment cores. A third sediment coring initiative determined historical total Hg loading and inventories at the intertidal delta through eighteen sediment cores 1-2 meters in length. Figure 1b shows the sampling locations for sediment cores collected from the Walker Creek Delta.

Total Hg and MMHg distributions in short cores were evaluated at eleven locations by collecting 2 to 3 cores separated by a distance of approximately 5 meters and sectioning the cores into 0-1 cm, 2-5 cm, and 6-10 cm depth intervals from the surface (a total of 98 samples). Figure 1b shows the sampling locations for the short-cores. Cores were collected between 5/16/2000 and 6/5/2000 at intertidal locations along the creek channel (Locations A, B, and C), on vegetated marsh regions (Locations D and E), intertidal locations bayward from the creek mouth (Location F, G, H, I, and J), and 4 km south of the delta at McDonald (Location K). Samples were recovered from the sediment layers using ultra clean techniques at low tide by pushing two plastic tubes each 5 cm in length into the mud and removing the mud surrounding the tubes by hand. A follow-up study (6/17/2002) investigated the role of microbial mats. Three short-cores were collected near Location I where algal mats were present and a duplicate core was collected within 3 m at a location with no algal covering. Algal mats (3 mm thick) were removed by hand and placed into a plastic bag and sediment cores were collected with a 10 cm tube and sectioned at 0-1 and 2-10 cm intervals. Cores from all short core sampling

events were extruded from the tubes and sediment samples were trimmed to remove smearing effects before packing on dry ice and shipping to Frontier Geoscience for analysis of total Hg, MMHg, and nutrient concentrations.

Eighteen vibra-cores were collected in October 2003 at high spring tides from a large raft capable of navigating the shallow mudflat. The cores were 9 cm in diameter and 1 to 2 meters in length and were separated by a range of spatial scales, from 50 to 1000 meters (see Figure 1b). Sampling locations were selected based on criteria for geostatistical analysis, with the goal of sampling the variety of Hg distributions found within the deltaic sediments and identifying the spatial correlation between sampled locations. Eight cores were collected along the perimeter of the intertidal zone (Locations 8, and 17-23) in an effort to identify to what extent Hg accumulation was confined to the intertidal region of the delta. Three cores were collected at the mouth of Walker Creek (Locations 10, 12, and 15), and in the middle of the mudflat and adjacent to the two channels that bifurcate at the creek mouth (Locations 13 and 24). Five cores were collected along the northeast shoals (Locations 1, 4, 6, 7, and 11) because results from surface sediment samples identified large gradients in this region. Collected cores were kept in a vertical position during retrieval of the core from the coring device and frozen on-site in a wooden box packed with dry ice. Cores were transported to the laboratory and stored in freezers. Frozen sediment cores were sliced into 2 cm sections. The bulk density of the sediment was determined by assuming a grain density of 2.5 g/cm^3 and calculation of the porosity through a change in weight upon freeze-drying. The average dry bulk density was 1.3 g/cm^3 and the average porosity was 0.5. Dried slices were loosened with a mortar and pestle, then sieved through a 63-micron mesh screen and weighed, allowing the calculation of both the fine and the coarse mass fraction of sediment. Total Hg was assessed by cold vapor atomic fluorescence spectroscopy (Gill and Fitzgerald, 1987). Multiple analyses (n=14) of PACS-2 sediment standards obtained from the National Research Council of Canada, Institute for National Measurements Standards, resulted in an average Hg concentration of 3.0 μg/g with a standard deviation of 0.5 μg/g, which compared well with the reported value of 3.0 ± 0.3 μg/g. A sample with elevated Hg concentration at Location 13 and at a depth of 53 cm was analyzed on eight consecutive analysis days (n=8). The error as defined by one standard deviation was less than 30%, and the average concentration on the fine fraction was 5.5 ± 1.5 μg/g. The larger uncertainty associated with the field sample, compared to the PACS-2 standard, is attributed to the greater heterogeneity of the deltaic sediments, and the difficulties of obtaining a representative sample, particularly at sandy locations, where the fraction of fines was visibly heterogeneous. The activity of ^{137}Cs was established at a low level gamma counting facility at Lawrence Livermore National Laboratory (Bandong et al., 2001; Volpe et al., 2002). ^{137}Cs activities of the bulk sample of surface sediments at sandy locations were less than the detection limit of approximately 0.02 pCi/g, hence ^{137}Cs was profiled for the fine fraction of sediment since the finer material has a larger capacity to bind cesium. Using the sediment accumulation rates obtained from ^{137}Cs profiling, the age that corresponds to the bulk density at given depths was identified. Bulk densities were largely uniform with depth, and small variability was found in cores where sediment type changed from mud to sand over the length of the core.

2-D maps of Hg distributions were generated by ordinary kriging (Journal and Huijbregts, 1978; Caeiro et al., 2003). Spatial interpolations were generated for (1) the mass flux of sediment, calculated as the sediment accumulation rate multiplied by the dry bulk density; (2) the concentration of Hg on the fine fraction; (3) the concentration of Hg on the coarse grains; (4) the total Hg concentration; and (5) the fraction of fines. These estimates were generated at 2 cm intervals and for each year between 1940 and 2003 using a rectangular estimation grid in the shape of the delta and a grid size of 30 meters. The spatial correlation structure of total Hg concentration was assessed by semivariograms, and the characteristic length scale of spatial correlation was determined to be approximately 400 meters. One of the profiled cores (Location 12) was not included in the kriging model. Location 12 was collected in a channel and its

attributes likely did not represent nearby profiles on the intertidal shelf. The uncertainty of the kriging estimates was determined through the kriging variance. 2-D maps of kriging variance were generated with each spatial interpolation (see Figure S-3). The areal integration of the kriging variance defined the uncertainty of the loading rate, and the temporal and depth integration defined the uncertainty for the areal inventories. Overall, the uncertainty from the kriging variance for total Hg loading and areal inventories ranged from 10 to 40%, and 20 to 30%, respectively.

Hg fluxes ($F_{Hg}(x,y,t)$) in units of g/m^2/yr were determined for the fine and coarse contributions and for total and anthropogenic contributions. The spatial inventory between 1940 and 2003 of Hg (M_{Hg}) is the integration of 2-D flux maps generated between 1940 and 2003 through:

$$M_{Hg}(x,y) = \int_{1940}^{2003} F_{Hg}(x,y,t)\,dt \quad (1)$$

The annual contaminant loading rate (L) was determined by integrating the contaminant flux over the areal extent of the delta:

$$L(t) = \int_{A} F_{Hg}(x,y,t)\,dA \quad (2)$$

where A represents the areal extent of the delta. The cumulative inventory (I) was determined as the temporal integration of the contaminant loading:

$$I(t) = \int_{1940}^{t} L(t)\,dt \quad (3)$$

Cross-validation was performed on total Hg concentrations by systematically removing individual coring locations from the kriging model, recalculating the statistics, and computing an estimate at the removed locations (Rubin, 2003). The average error associated with the cross-validation was large and underestimated the removed locations by 70 to 100%. This error likely results from sampling on a larger scale than the scale of areal variability.

In an effort to better elucidate the potential for Hg bioaccumulation in biota proximal and distal to the Walker Creek Delta, we sampled shore crabs, bivalves, oysters, and transplanted mussels at several locations. Five shore crabs (*Pachygrapsus*) were collected (6/5/2000) from both the Walker Creek Delta and at McDonald (4 km south of the delta). Sixteen to 23 resident bivalves *(Corbicula fluminea)* were collected (5/11/2000 and 7/28/2000) by a clam dredge from five different intertidal locations. The collection of the shore crabs and bivalves was coordinated with the collection of the 10-cm sediment cores at Locations I and K. Commercial oysters (*Crassostrea gigas*) were collected (4/15/1998 to 4/17/1998) from seven oyster farms throughout Tomales Bay, typically 9 to 15 per lease location. Mussels (*Mytilus californianus*) collected from Bodega Bay, a control site, were deployed (12/7/1999) at seven locations along the axis of Tomales Bay then retrieved after 100 days. The control site, Bodega Bay, is located approximately 16 km north of Tomales Bay and is well characterized with no known sources of Hg contamination. The transplanted mussels were placed in nylon mesh bags, each bag containing 36 specimens, divided into four equal sections. Room was left in each section to allow for growth and movement of the mussels within the bags. In addition to sampling invertebrates for Hg analyses, we sampled the nine most commonly caught and consumed fish species in Tomales Bay. Collected fish included jack smelt (*Atherinopsis californiensis*), shiner surfperch (*Cymatogaster aggregata*), redtail surfperch (*Amphistichus rhodoterus)*, halibut (*Paralichthys californicus*), angel shark (*Squatina californica)*, bat ray

(*Myliobatis californica)*, leopard shark (*Triakis semifasciata*), and the brown smoothhound shark (*Mustelus henlei)*. All collected biota was packaged on ice and delivered to Moss Landing Marine Laboratories, CA for trace metal analysis. The bivalves were not depurated prior to removal of the tissue for analysis and potential interferences of particulate mercury trapped within the bivalves are discussed in the results.

3. Results

3.1. Bay-wide total Hg distributions

The intertidal sediments at the mouth of Walker Creek exhibit significantly higher total Hg concentrations compared to other locations sampled within the Bay. Figure 2 shows the spatial variability of total Hg in the upper 5 cm of the intertidal sediment samples collected at the Walker Creek Delta compared to other locations within Tomales Bay. Average Hg concentrations at the Walker Creek Delta ranged from 0.9 to 3.1 μg/g, whereas other areas in Tomales Bay typically ranged from 0.05 to 0.5 μg/g. The total Hg concentration of 0.75 μg/g at Preston Pt. is likely due to inputs directly from Walker Creek and/or transfer of Hg through the delta. The unexpected peak of 1.1 μg/g at Millerton, located 13 km from Walker Creek could be due to transport from Walker Creek, however Millerton is adjacent to the mouth of Lagunitas Creek, and further studies are needed to identify the spatial extent and effects of mercury inputs from Walker Creek on the southern part of the Bay. The range of total Hg in surface sediments measured north and south of the Walker Creek Delta is typical of Hg concentrations found upstream from non-mined areas of the Walker Creek watershed, where the average Hg concentration in fines is 0.2 μg/g, dry wt. (SFBRWQCB, 2002). Tomales Bay sediments collected north and south of the Walker Creek Delta also have total Hg concentrations (Figure 2) similar to the typical range reported for nearby San Francisco Bay, 0.2 to 0.4 μg/g with a maximum measured value of 1.1 μg/g (Conaway et al., 2007). However, maximum levels of total Hg reported for San Francisco Bay are similar to the average mercury concentrations reported for the Walker Creek Delta (Heim et al., 2007;Conaway et al., 2007), indicating the significance of Hg contamination at this delta.

3.2. Total Hg accumulation at the Walker Creek Delta, 1940 to 2003

Total Hg concentrations for the long-cores were determined as a function of depth then age-dated to assess the accumulation history of total Hg. Figure 3 shows the depth profiles of total Hg on the fine fraction (Hg_f), total Hg on the coarse fraction (Hg_c), the fraction of fines (f_{fines}), the total Hg from both fractions (Hg_T), and ^{137}Cs profile for Locations 1, 13, and 24 respectively. Cores were selected for ^{137}Cs analysis based on their location, sediment characteristics, and total Hg inventories. Locations 13 and 24 had the highest inventories of total Hg of the collected cores and Location 1 represents a region along the northeast shoal of the delta with limited Hg accumulation. Total Hg was determined as the sum of mass-weighted contributions from the coarse and fine fractions but was dominated by the Hg on the fine fraction. This pattern was typical in cores collected from the delta.

Figure 3 shows the ^{137}Cs distributions for the three cores profiled in this study. The ^{137}Cs profiles did not demonstrate a clearly identifiable maximum ^{137}Cs corresponding to 1963. This could be due to the modest resolution of the depth profile, ongoing sediment inputs, and sediment re-working at the delta. The rounded profiles of cores at Locations 13 and 24 may suggest post-depositional mixing and/or diffusion. However, we suspect that diffusion of ^{137}Cs through the pore waters is limited based on comparison to studies of nearby San Francisco Bay that showed sediment accumulation rates determined from ^{137}Cs were within 5% of sediment accumulation rates determined from ^{239,240}Pu, known to be significantly less mobile (Fuller et al., 1999). The apparent immobility of cesium could be explained by strong binding with a micaceous clay mineral (namely illite) in eroded soils and sediments (Koning

and Comans, 2004;Sawhney, 1972). The Walker Creek watershed has geological features of the Franciscan mélange and contains illite formations (Blake et al., 2000;Oberdorfer et al., 1990;Cloos M., 1983). Illite strongly binds cesium (Bellenger et al., 2008;Guivarch et al., 1999), and desorption has been shown to decrease with increased contact time (Comans et al., 1991). Organic matter in marine sediments can compete with illite for cesium binding (Kim et al., 2006). Hence, we expect cesium diffusion through the pore waters is small and that the rounded ^{137}Cs profiles are due to limited sampling resolution and sediment mixing.

We assign the deepest occurrence of ^{137}Cs to the onset of large-scale atmospheric testing of nuclear weapons in 1952 (Beck et al., 1990) and this affords an estimate of bulk sediment accumulation rates. Locations 13 and 24, near the mouth of Walker Creek, had relatively high sediment accumulation rates, 2.3 ± 0.1 and 1.8 ± 0.2 cm/yr respectively, compared to Location 1 at the northeast shoal where the average sediment accumulation rate was estimated to be 0.3 ± 0.1 cm/yr. Location 1 also contains a significantly smaller inventory of ^{137}Cs than the other two sites. The small inventory and shallow depth of first appearance for ^{137}Cs are both consistent with significant erosion of sediment from this site in recent years or decades. An order of magnitude estimate of the mixing time of surface sediments before isolation from the water column by burial of newer deposits for the regions near the mouth of Walker Creek was approximately 3 years, based on a complete re-working of a 6-cm storm deposit (Anima et al., 1984) and a bulk sediment accumulation rate of 2 cm/yr. Nonetheless, for the three age-dated locations in this study, elevated Hg concentrations were found only at depths where ^{137}Cs was detected, demonstrating negligible Hg accumulation prior to the opening of the mine in 1964.

Sediment accumulation rates previously reported for the Bay are similar to rates we estimate for the delta. The bay-wide average accumulation rate since the onset of anthropogenic activities in the watershed (early 1800s) is approximately 0.5 cm/yr, based on historical bathymetric surveys (Rooney and Smith, 1999). Sediment cores collected in 1990 near the head of the Bay, suggested bulk sediment accumulation rates, through ^{137}Cs and ^{210}Pb profiling, of approximately 2 cm/yr (Snidvongs, 1992). The Lagunitas Creek Delta at the head of the Bay has also rapidly accumulated sediments, and over the last 150 years the tidal marsh at the mouth of Lagunitas Creek has grown at an average rate of 10 meters/yr (Niemi and Hall, 1996).

A wide variety of sediment types, from coarse sands to fine mud, were found at the intertidal delta (Table 1). Locations 1, 4, 6, 7, 8, 22, and 23 along the eastern shoal and Locations 18 and 19 contained mostly fine mud, while the remaining locations particularly near the creek mouth contained coarser-grained deposits. The focusing of sandy sediment in proximity of the creek mouth suggests that this region is predominantly formed from bedload discharged by Walker Creek. Locations 11, 13, 21, and 24 were sandy with layers of mixed mud and sand. Locations 17 and 20 were characterized by a mixture of silty sand and mud. These cores demonstrate a winnowing of sandy deposits with distance from the creek discharge, with fine grained deposits largely constrained to the margins of the delta. Cores collected near the creek mouth (Locations 10, 12, and 15) also demonstrate a sharp transition from poorly sorted mud in the top 20-30 cm to sandy sediment throughout the bottom parts of the core. Two of the cores (Locations 11 and 13) showed isolated layers of mixed mud and silt among otherwise sandy deposits, and Locations 21 and 24 showed large layers of sandy deposits on top of mud and silt. These findings highlight the complexity of delta formation at the mouth of Walker Creek and suggest rapid transitions of geomorphology within the delta.

Greater ^{137}Cs resolution and alternative fallout isotopes are needed to constrain accumulation to annual time scales, hence the ^{137}Cs profiles in this study are applied to generalized decadal trends in Hg accumulation. Sediment accumulation rates at locations without ^{137}Cs data were interpolated based on similarity of sediment characteristics and distance from one of the dated

cores. The error associated with the spatial interpolation was particularly important at locations with elevated mercury, hence the two cores (Locations 13 and 24) with the greatest measured mercury inventories (2.48 and 1.72 g/cm^2, respectively) were gamma counted for ^{137}Cs. The choice of interpolation technique did not strongly impact the general accumulation trends at the delta, and a simple nearest neighbor approach was adopted in favor of a more elaborate technique. Table 1 shows the assigned sediment accumulation and interpolated accumulation rates. Locations 4, 6, and 7 were all near Location 1, and had similar sediment characteristics, predominantly mud with layers of mixed mud and lesser amounts of silty sand. Locations 17, 18, 19, and 20 were in close proximity and assigned to Location 24. Location 15 was also grouped with Location 24 because both cores have similar characteristics of sand with layers of silty mud. Locations 8, 10, 11, 12, 21, and 23 were in proximity of and assigned to Location 13. Although Location 11 is near Location 1, its sediment characteristics are more similar to Location 13′s. Location 22 is far from any of the dated cores, but was assigned to Location 13 because the first occurrence of excess Hg occurs at similar depth, at approximately 90 cm.

We estimate anthropogenic excess Hg for the Walker Creek Delta sediments by subtracting background Hg concentration from the measured total Hg concentration. A background concentration for a bulk sample of 0.2 μg/g was assigned based on measured total Hg concentrations in non-mined areas within the watershed (SFBRWQCB, 2007). A threshold of 0.6 μg/g (three times background) was applied to reduce outliers and only samples with measured total Hg values greater than 0.6 μg/g were assumed to contain excess mercury, thus providing a conservative estimate of anthropogenic mercury. Mercury concentrations at the bottom of the sediment cores were typically ≤ 0.1 μg/g, indicating that the pre-mining background concentration of total Hg at the Walker Creek Delta was more than a factor of 2 smaller than the current background reported for the watershed. Increased background levels in surface sediments distant from the delta are likely due to growing inputs from regional and longer-range atmospheric sources.

Figure 4 shows the depth profiles for both total Hg and excess total Hg, and the historically reconstructed fluxes of total Hg. Locations 13, 15, and 24 had the largest total Hg inventories (see Table 1). Locations 10, 12, 8, and 22 showed the largest Hg concentrations near the surface, with generally decreasing trends with sediment depth. All of the cores were deep enough to sample the complete distribution of anthropogenic mercury, and most of the anthropogenic mercury was found within the top 100 cm. Excess Hg appears in the reconstructed profiles starting after 1970. Peak Hg loadings occurred between 1975 - 1985 (see Locations 13, 24, and 15) and a smaller peak occurred in the late 1990s (see Locations 15, 8, 11, and 22). These peaks probably represent inputs during major storm events. Trends of increasing total Hg concentrations with greater depths, as found in proximity of the creek mouth (Locations, 13, 15, and 24), may imply reduction of anthropogenic sources in recent years, while locations along the eastern shoal reflect increases of sources (Mahler et al., 2006). However, long-term sediment re-working and erosion could also explain the peaks reported in the late 1990s. The combination of ongoing inputs (Whyte and Kirchner, 2000) and mixing processes are likely delaying the natural attenuation of Hg concentrations in surface sediments.

Focusing factors determined as the ratio of measured ^{137}Cs in the sediment to the expected fallout were calculated to compare sediment trapping efficiencies (Fuller et al., 1999). For the Walker Creek Delta, focusing factors ranged from 0.4 at Location 1, to 2.5 at Location 13, with an average value of 1.7 (median 2.2, n=3). A focusing factor of 9.0 was determined for the southern portion of the Bay (Snidvongs, 1992), and this indicates that the southern reaches of the Bay by comparison act as a good sink for sediments, whereas sediments deposited at the Walker Creek Delta are more likely to undergo processes of sediment re-working. Focusing factors for ^{137}Cs have been shown to be significantly smaller than those determined from other fallout isotopes (Fuller et al., 1999), and this is likely due to cesium desorption from weaker

ligands prior to deposition. Nonetheless, the relatively low focusing factor at Location 1, compared to Locations 13 and 24, may suggest erosion of recent sediment and/or long-term sediment re-working along the northeast shoal compared to location in the central regions of the mudflat. Alternatively, the northeast shoal may be maintaining an equilibrium surface that has neither accumulated nor eroded a significant amount of material over the last several decades (Olsen et al., 1993).

Areal inventories of sediment accumulation were determined through the temporal integration of the mass flux of accumulating sediment (see Figure S-4). The sediment fill is thinnest along the eastern shoal and thickest at the creek mouth where terrigenous sediments discharged by Walker Creek rapidly accumulated. Overall, an estimated 4×10^6 tons of sediment (approximately 3 million cubic meters) accumulated within the intertidal delta between 1940 and 2003, indicating sediment accumulation between 1940 and 2003 was approximately 40% greater than the accumulation rate over the period between 1860 to 1930 (Daetwyler, 1966).

Figure 5a shows the inventory calculated from equation (1) for Hg associated with fine grains (< 63 μm) and Figure 5b shows the inventory associated with coarse grains (> 63 μm). The spatial inventory of Hg on fine particles is focused along the shoals of the delta's two channels. A majority of the inventory on the fines is located within 600 meters of the channel bifurcation. However, Hg on fine particles was transported through the intertidal zone and accumulated along the edge of the delta (Locations 22 and 23). The occurrence of significant fine-grained Hg deposits at the margin of the sampled region suggests a larger range of transport of fine particles than resolved in this investigation. The highest concentrations of total Hg in the coarse fraction were found at the mouth of Walker Creek and decreased to background levels within 1 km from the creek mouth. This suggests that bedload Hg has not traveled far from the creek channel.

Figure 6a shows the accumulation history of Hg and Figure 6b shows the areal inventory of excess Hg between 1940 and the time of sampling. The total inventory of Hg (Figure S-5) was estimated as 2,500 ± 500 kg, and over 80% of this Hg was associated with the fine fraction of sediment. Mercury loading prior to the opening of the mine in 1964 was approximately 20 kg/yr and may reflect erosion from numerous small scale mining operations in the Walker Creek watershed prior to the opening of the Gambonini mine. We estimate the pre-mining loading rate was ≤ 5 kg/yr based on a background concentration of 0.1 μg/g. A peak loading rate between 60 to 70 kg/yr was estimated for the late 1970s to early 1980s. Large storm events are responsible for a majority of the annual runoff and two large consecutive wet years in 1982 and 1983 in concert with the failure of the tailings dam in 1982 correlate well with the reconstructed peak of Hg accumulation in the delta. Overall, approximately 1500 ± 300 kg of excess Hg has accumulated in the delta between 1960 and 2003, and excess Hg contamination is largely confined to the intertidal region of the delta. Sharp decreases of total Hg with distance from the creek mouth compare well to observed trends in other estuaries with historic mercury mining activities (Covelli et al., 2001). The inventory of total Hg in the delta is likely significantly smaller than the mass released from the mine site. Whyte and Kirchner (2000) estimate a release rate of 77 kg/yr from the mine, however this study estimates a range of 45 to 55 kg/yr of excess mercury accumulating at the delta during the similar period. The apparent discrepancy between the inventory discharged from the mine site and Hg accumulating at the delta could be explained by known storage of Hg along the floodplains of Walker Creek (SFBRWQCB, 2007), discharge from the creek directly to the Bay, and loss of deposited sediments from the delta to the Bay through reworking by tidal and wind-driven flow.

Hg concentrations at the intertidal sediment surface have slowly decreased through deposition of cleaner sediments. Figure 7 shows the areal distribution of total Hg concentration averaged over 50 to 74, 25 to 49, and 0 to 24 cm depth intervals, and these depths roughly correspond

to the 1970s, 1980s, and 1990s, respectively. Mercury accumulated first near Location 13 in the middle of the intertidal zone. Mercury inventories are found at shallower and younger sediment layers to the northwest and southeast, along the vector of the two channels that cross the delta. Our findings suggest storm events before 1990 (depths greater than 25 cm) resulted in different areal distributions of Hg accumulation compared to post-1990, and demonstrate the spatial evolution of Hg accumulation at the forming delta (see Figure S-6). At locations near the creek mouth (13, 15, and 24), surface sediments show elevated concentrations at depths greater than 25 cm (prior to 1990) and were later isolated by cleaner sediments. Rapid episodic sediment accumulation at the Walker Creek Delta is dominated by bedload material (Anima et al., 1984) that armor finer grained particle-bound Hg. Mercury in the surface sediments of the Walker Creek Delta are largely being isolated by accumulation of cleaner upstream material in the period after 1990 (see Figure 7c). The only exceptions are at Locations 6, 8, and 22 along the southeast shoreline in the muddy areas of the delta. At these locations the average excess Hg concentration appears to have increased since 1990, and does not show evidence of the 1982 storm event (Figure 4). The areal distribution of total Hg in the shallowest interval (Figure 7c) also suggests sediment reworking, fines resuspension and transport to these muddier locations where the Hg levels are highest in the surface sediments. However, in the absence of multiple chronological markers it is not possible to distinguish on going inputs from mixing.

3.3. Mercury methylation and algal mats at the delta

The relatively large intertidal mudflat at the Walker Creek Delta may be a significant component of the Bay's monomethylmercury production. Figure 8 shows the spatial distribution of MMHg and percent MMHg for short sediment cores analyzed at 0-1 cm, 2-5 cm, and 6-10 cm intervals. Total Hg concentrations for the short cores ranged from 0.06 to 7.6 μg/g. Monomethylmercury concentrations were less than 0.6 ng/g in the creek channel upstream of the mouth (Locations A, B, C). In vegetated marsh locations, MMHg concentrations ranged from 0.2 to 5.0 ng/g (Locations D and E), and bayward of the creek mouth ranged from 0.3 to 11.4 ng/g (Locations F, G, H, I, J). At an intertidal location 4 km south of the delta, MMHg concentrations ranged from 0.2 to 0.7 ng/g (Location K at McDonald). The highest values for MMHg and percent MMHg were found at the intertidal regions of the delta with the highest inventory of anthropogenic particle-bound mercury. However, total Hg concentrations were not well-correlated to MMHg concentrations, $r^2 < 0.1$ for individual samples. Intertidal regions at the Walker Creek Delta had the largest MMHg concentrations and highest percent MMHg ratio. This may indicate greater MMHg production at intertidal locations compared to vegetated marsh lands as suggested by Drott et al. (2008). Monomethylmercury concentrations were also higher in the top 1 cm of sediment and were typically low at 6-10 cm depths. This pattern may correspond to methylation at depths conducive to sulfate reducing bacteria. Methylmercury levels in sediments are controlled by competing methylation and demethylation reactions (Martín-Doimeadios, et al., 2004). Observed decreases in MMHg with sediment depth could also be explained by net demethylation within the delta where MMHg was transported from upstream locations. However, the relatively low MMHg concentrations found in cores along the creek channel do not support an upstream source of MMHg to the delta. Although further studies are necessary to resolve methylation/demethylation dynamics and the role of upstream sources, we expect, based on analogy to sites in nearby San Francisco Bay (Marvin-DiPasquale et al, 2003), that conditions at the Walker Creek Delta support net methylation of mercury. Regions with high MMHg concentrations also had the largest sediment accumulation rates (proximity of core Locations 13 to I, and 24 to G), and regions with low sediment accumulation rates had comparatively small MMHg concentrations (proximity of core Locations 1 to J). We suggest that ongoing sediment inputs with excess Hg may be an important parameter driving Hg methylation at the delta. However, further investigations are needed to clarify the role of mercury methylation at the Walker Creek Delta on other regions of the Bay. If peak methylation

at the delta occurs in summer periods then transport to other locations in the Bay may be limited because mixing between the northern and southern waters of the Bay is known to be minimal in summer, and greatest during winter (Smith and Hollibaugh, 1998).

While some previous studies have reported a correlation between Hg methylation and organic carbon content in estuarine sediments (Lamberstson and Nilsson, 2006), this relationship does not appear to hold for Walker Creek Delta sediments. Total organic carbon concentrations from the short cores collected in the delta ranged from 0.04 to 2.5 % (dry wt.) and showed a weak correlation with MMHg concentrations, $r^2 \sim 0.3$. Furthermore, MMHg concentrations were weakly correlated to nutrient concentrations, $r^2 \sim 0.4$ with sulfur, $r^2 \sim 0.4$ with nitrogen, $r^2 \sim 0.3$ with sulfate, and $r^2 \sim 0.2$ with phosphorous. Tomales Bay as a whole has relatively low nutrient concentrations and terrestrial and marine sources bring in more fixed carbon than is created photosynthetically in the Bay (Smith et al., 1991; Smith and Hollibaugh, 1998). However, despite low micronutrient and carbon concentrations, the shallow warm waters of the delta may afford conditions with increased methylation within the Bay. The intertidal region of the delta stores the majority of anthropogenic Hg and has the largest MMHg concentrations and highest %MMHg found, so far, within the Bay (Figure 8).

Intertidal zones along the shoreline of Tomales Bay, and particularly at the Walker Creek and Lagunitas Creek deltas, are colonized by microbial mats composed primarily of cyanobacteria (Joye and Paerl, 1993). Microbial mats can be highly productive communities with biomass regenerated, respired, buried, and sloughed off to the Bay (Joye and Paerl, 1994). Figure 9 shows a comparison total Hg and MMHg distributions in sediments directly under algal mats compared to adjacent locations with no algal covering. The elevated MMHg concentrations in the top 1 cm were more pronounced at stations where green algal mats occurred. The total Hg concentrations of the algal mats ranged from 0.4 to 0.8 μg/g and MMHg concentrations ranged from 7.5 to 31 ng/g. For these reasons, we suggest that algal mats promote mercury methylation at the delta.

3.4. Mercury uptake by Tomales Bay biota

Hg concentrations in Tomales Bay biota suggest a strong spatial trend in Hg uptake consistent with sediment total Hg and MMHg distributions in the sediment profile. Figure 10 shows total Hg concentrations and sampling localities for biota including bivalves, crabs, transplanted mussels, and farmed oysters. Resident bivalves harvested from the Walker Creek Delta (Location I) contained 0.34 μg/g total Hg (wet wt.) and 0.07 μg/g (wet wt.) MMHg. In comparison, resident bivalves harvested from locations south of the delta (Location K and “Millerton”) contained total Hg concentrations of 0.04 to 0.07 μg/g (wet wt.) and MMHg concentrations of 0.02 to 0.04 μg/g (wet wt.). Sediments have been shown to be a significant source of Hg to marine bivalves (Gagnon and Fisher, 1997). Although bivalves were not depurated prior to analysis, potential sediment grains contained within the analyzed tissue does not support reported concentrations. At the delta, total Hg in the bivalves is less than 10% of the total mercury levels reported in the surface sediment, and bivalve MMHg concentrations are over an order of magnitude greater than MMHg levels found in the surface sediment at the same location. Shorecrabs collected from the delta (Location I) contained 6 times more MMHg than shorecrabs from McDonald (Location K) 4 km south of the delta (360 vs. 64 ng/g) and possibly reflect the order of magnitude difference in sediment MMHg concentrations in the top 0-1 cm between Locations I and K (3.4 vs. 0.32 ng/g); %MMHg in shorecrabs from these two locations was similar (81% at Location I; 88% at Location K). Total Hg concentrations in mussels transplanted to the Walker Creek Delta ranged from 0.23 to 0.30 μg/g (dry wt), while transplanted mussels deployed at locations south of the delta ranged from 0.10 to 0.15 μg/g (dry wt), and transplanted mussels deployed less than 2 km north of the delta at Vincent Landing contained 0.24 μg/g total Hg (dry wt). Total Hg concentrations in commercial oysters grown

in floating bags or on platforms in Tomales Bay for 1-2 years ranged from 0.16 - 0.44 μg/g (dry wt.) at the delta and 0.09 to 0.30 μg/g (dry wt.) south and north of the delta. Growing conditions among oyster farms varies from grow bags suspended in the water column to bags anchored to the sediment bed. The small variability measured between farms on the delta to other Bay locations could also be explained by variability of exposure associated with growing conditions. Overall, these results suggest the Walker Creek Delta is an important location of Hg uptake for Tomales Bay biota.

Sediments contaminated with Hg at the Walker Creek Delta are likely an important pathway for Hg uptake in benthic organisms and subsequent Hg accumulation in higher trophic level organisms living in Tomales Bay. A study of leopard shark diets demonstrated that cancer crabs were found in 87% of the stomachs of sharks collected near Hog Island (less than 3 km from Walker Creek Delta) and Urechis worms were found in 82% of the stomachs of sharks collected from inner bay locations (Webber and Cech, 1998). In addition to uptake of MMHg, deposit feeders can extract sediment-bound inorganic Hg through gut fluids, particularly cysteine-containing proteins (Zhong and Wang, 2006). This may be an important mechanism of mercury uptake for some species, such as bivalves, where elevated MMHg only accounts for about half of the measured total Hg.

Top-level predators and bottom dwelling fish contained higher Hg concentrations than other species. Mean Hg concentrations were highest in brown smoothhound sharks (1.31 ± 0.07 μg/g wet wt.) and leopard sharks (1.09 ±0.08 μg/g), followed by bat rays (0.56 ±0.08 μg/g), angel sharks (0.43 ±0.06 μg/g), halibut (0.26 ±0.02 μg/g), redtail surf perch (0.16 ±0.04 μg/g), shiner surf perch (0.10 ±0.01 μg/g), and jack smelt (0.06 ± 0.01 μg/g). These concentrations are similar to Hg concentrations measured in fish from San Francisco Bay (Greenfield et al., 2005; Davis et al., 2008), an estuary impaired by historic gold and mercury mining. It is possible that some of these species migrate between the two bays. Total mercury concentrations for Tomales Bay may also reflect mercury from atmospheric loading (Hammerschmidt and Fitzgerald, 2006). Hence, linking elevated Hg levels in higher-trophic level fish from within Tomales Bay to anthropogenic Hg from the Gambonini mine remains a challenge.

4. Conclusions

A point source of Hg released to an intertidal estuary over a limited time period illustrates the complexity of deltaic systems. There are a variety of influences on Hg distribution and accumulation rates, such as the interactions of upstream releases, transport by large storm events, and reworking within sediments by tidal currents and wind-generated waves. While the mine site has been remediated to eliminate waste material erosion at the source, the legacy of the relatively small Hg mine can be found within the delta. The hot spot of Hg contamination at the delta is slowly undergoing burial by cleaner sediments, with sediment re-working and ongoing inputs likely explaining the slow attenuation of mercury concentrations within deltaic sediments. The elevated concentrations of background total Hg within the watershed over the last century indicates the recovery of the delta to pre-mining conditions is unlikely, regardless of management actions. Although higher sampling density is needed to better constrain the areal variability, the sediment cores analyzed provided a conservative estimate of total Hg loading and inventory. Dredging the biologically active Hg inventory is likely unrealistic due to sensitive delta habitat and the large spatial extent. Without further work to address inputs of excess Hg to surface sediments from upstream flood deposits, benthic organisms at the Walker Creek Delta will likely continue to support the transfer of Hg up the food chain.

The spatial extent of anthropogenic mercury released from the Gambonini mine throughout Tomales Bay is not well understood, and requires further investigation. Our studies suggest that while much of the inventory at the Walker Creek Delta appears to be confined to the

intertidal regions of the delta, an unknown portion has likely deposited outside the area sampled in this study. It is possible that the delta is actually a relatively poor sink for fine sediments discharged from Walker Creek, and significant portions of mercury discharged by the creek are transported to the Bay and coastal ocean. The regular occurrence of wind-driven waves and strong tidal flows at the delta suggests re-suspension of surface sediments and loss through exchange with the Bay. The region near the creek mouth stores the majority of the Hg inventory at the delta, and is characterized by significant fractions of coarser grained deposits. We suspect a portion of suspended particulates accumulates as fines on the delta and becomes armored by coarser deposits. A more detailed investigation of the delta's geochemistry could enhance understanding of the sediment accumulation history and better quantify mixing effects relevant to the transfer of particulate Hg through the delta and natural attenuation of contaminated bottom sediments.

Algal mats were sites of MMHg production and suggest a link to the food chain. Localized MMHg production and bioaccumulation were demonstrated at the intertidal parts of the delta. However, the factors controlling MMHg production and bioaccumulation within the delta are not well understood. A comparative study of MMHg from creek inputs and methylation/demethylation rates at the delta and other bay locations are needed to identify the overall importance of the Walker Creek Delta on bay-wide MMHg production. The effects of atmospheric mercury on Tomales Bay were not assessed in these investigations. A comparative study of the other major delta within the Bay (Lagunitas) that has no regional Hg sources could help to delineate methylation of mercury from mining waste and atmospheric sources. Further characterization studies are planned in support of regulatory efforts to assess total maximum daily loads (TMDLs) for mercury and sedimentation to protect wildlife and human health.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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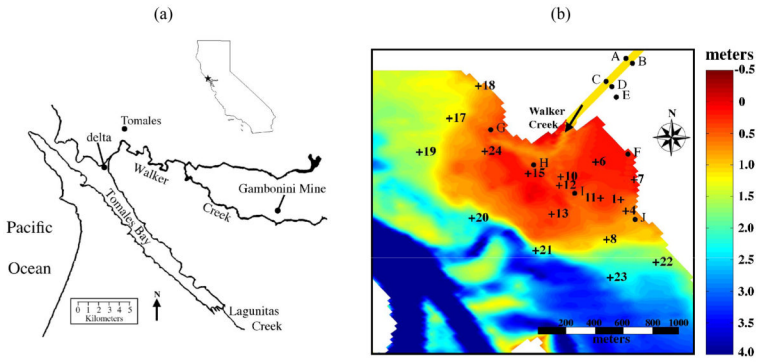

Figure 1.

(a) Gambonini mercury mine on Walker Creek and delta on Tomales Bay, California. (b) Bathymetry of the Walker Creek Delta with sampling locations for long cores (numbered), and short cores (letters). Note: Location K, is at McDonald, 4 km south of the mouth of the Walker Creek Delta.

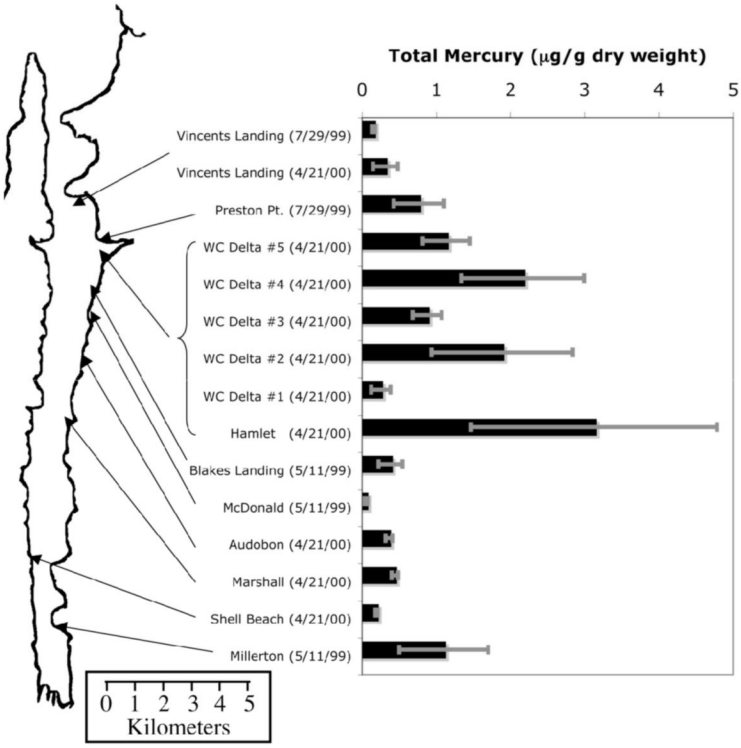

Figure 2.
Tomales Bay average surface sediment (upper 5 cm) total Hg distributions (µg/g, dry wt.). Error bars are two times the standard deviation, 3 to 5 samples per location.

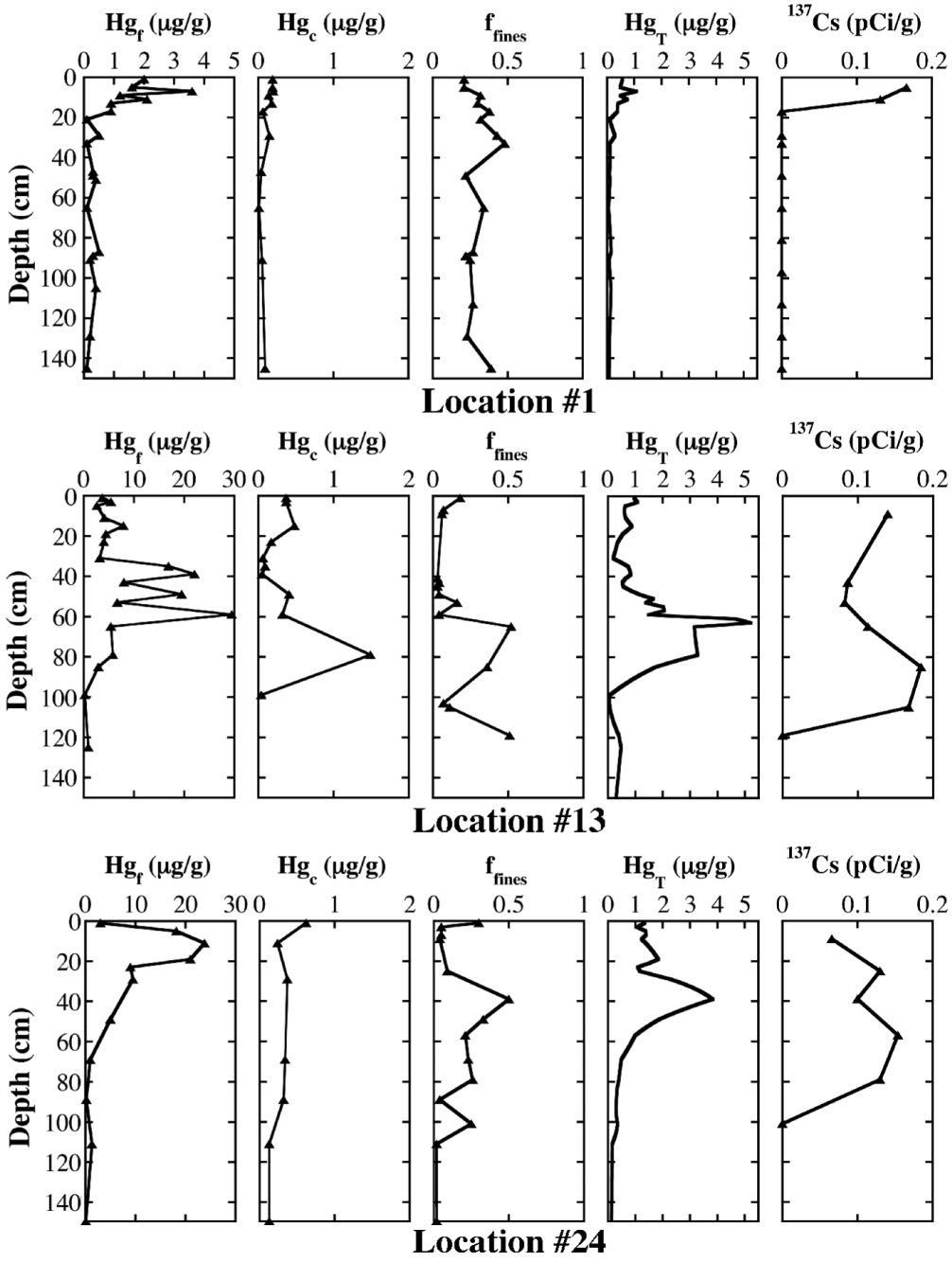

Figure 3.

Depth profiles of Hg concentrations on fine (< 63 μm) particles (Hg_f), the coarse fraction of sediment (Hg_c), and fraction of sediment associate with fines (f_{fines}), total Hg concentration from both the fine and coarse fractions (Hg_T), and ^{137}Cs determined accumulation histories for Locations 1, 13, and 24. Depths corresponding to the start of large scale atmospheric testing (1952) are 15 ± 5 cm, 115 ± 5 cm, 90 ± 10 cm for Locations 1, 13, and 24, respectively. ^{137}Cs activities shown as zero on the plot are < 0.02 pCi/g (the detection limit).

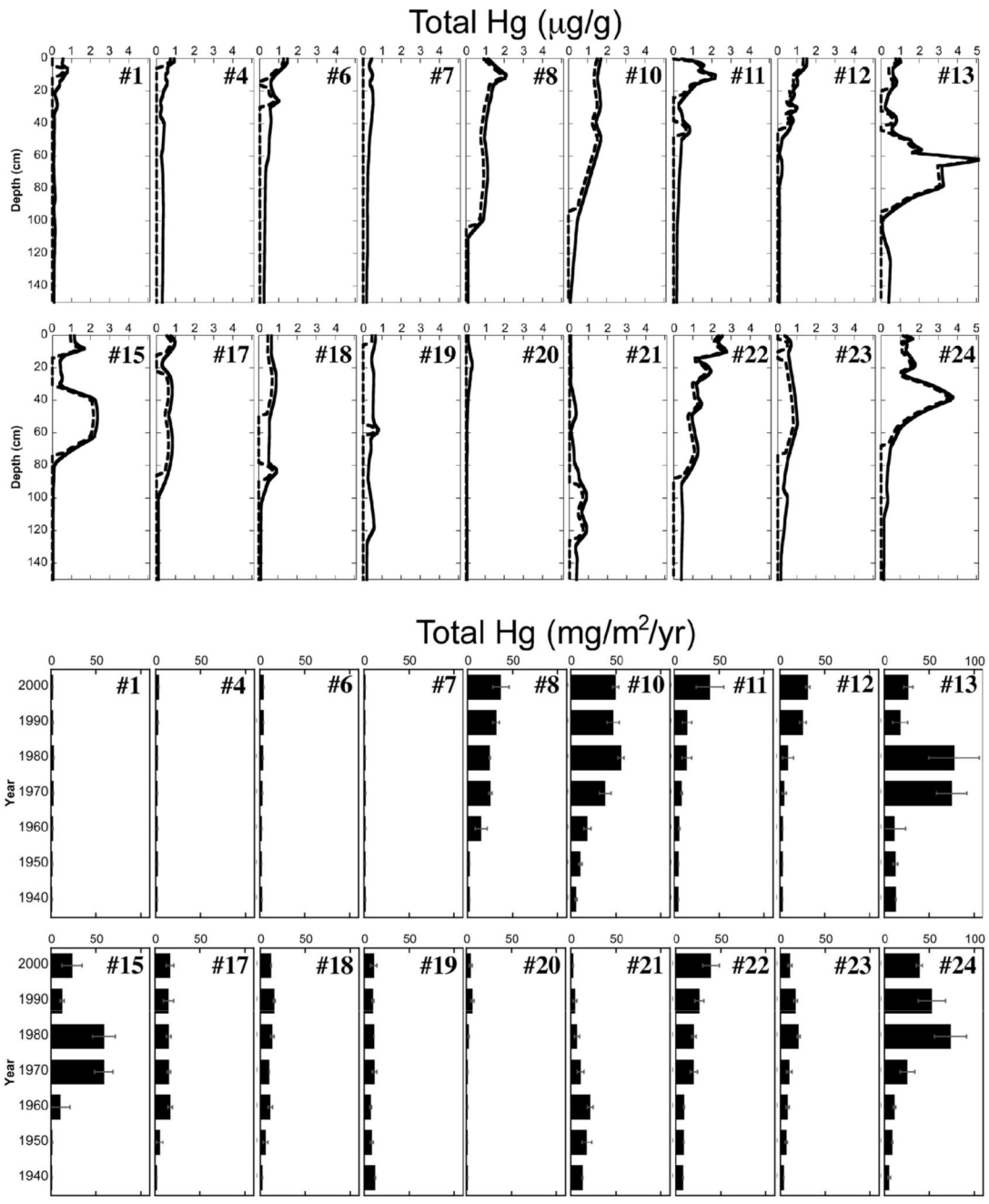

Figure 4.

Depth profiles (top) of total (solid line) and anthropogenic excess mercury (dashed line), and reconstructed accumulation fluxes (bottom) of total Hg averaged over ± 5 years increments, error bars represent one standard deviation.

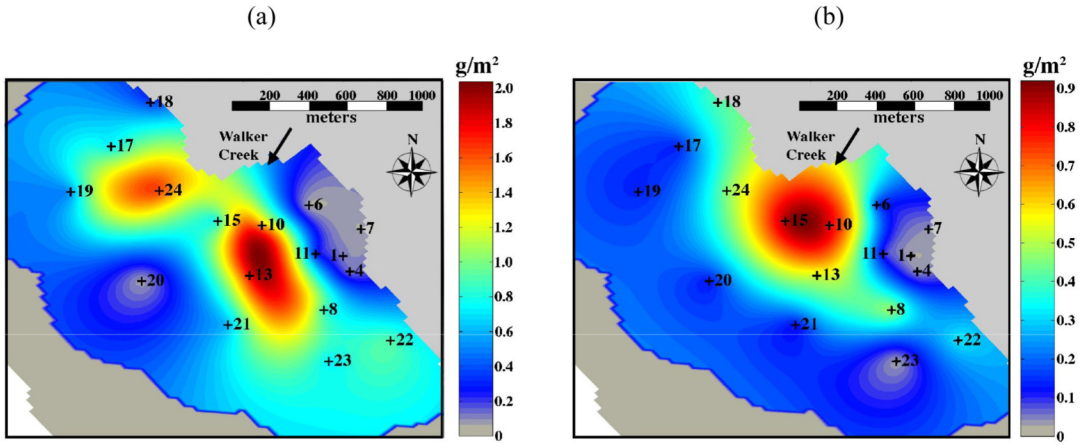

Figure 5.
(a) Spatial inventory of Hg on fine particles (<63 μm). (b) Spatial inventory of Hg on coarse particles (>63 μm).

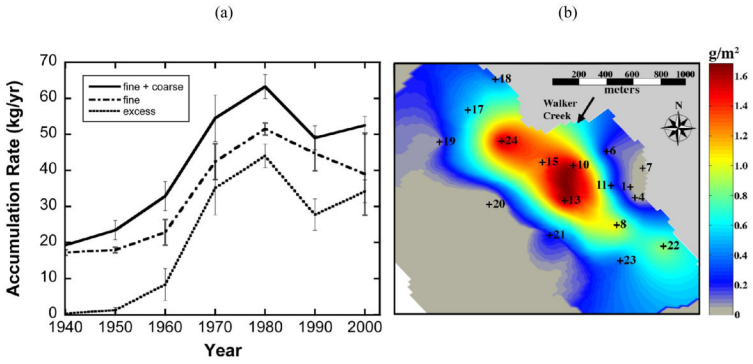

Figure 6.

(a) Accumulation history of total Hg: Hg associated with both fines and coarse fractions (fine + coarse), Hg associated with the fines (fine), and anthropogenic excess (excess). Reported values are ± 5 year averages of the annually reconstructed rates, error bars are one standard deviation. (b) Inventory of excess Hg in October 2003 (time of sampling).

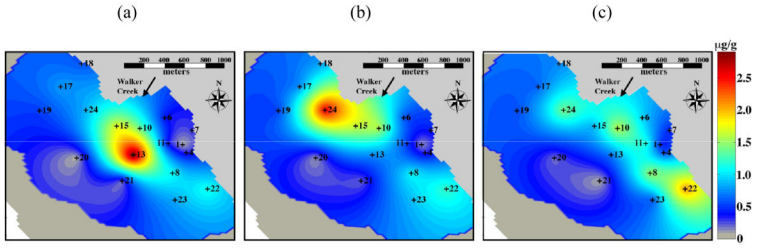

Figure 7.
Spatial average total Hg (fine + coarse) in sediments from (a) 50 to 74 cm (~1970s), (b) 25 to 49 cm (~1980s), and (c) 1 to 24 cm (~1990s) intervals.

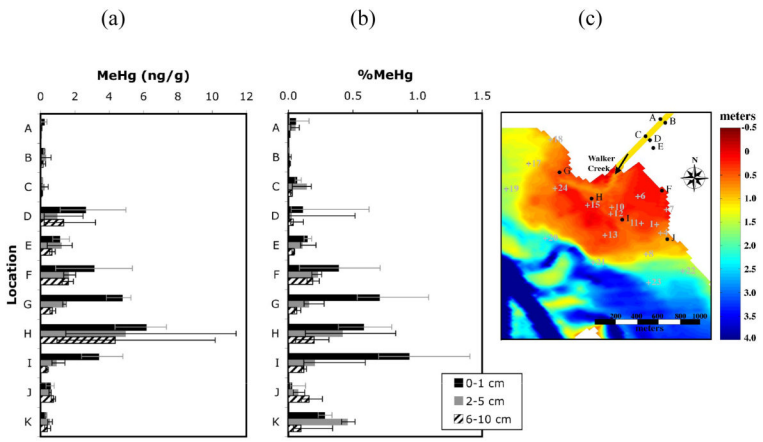

Figure 8.
(a) MMHg in sediment (ng/g), and (b) % MMHg in sediment. Plotted values are the average from three sets of cores, and error bars represent range of measurements. (c) Map of sample locations, color bar bathymetry (meters).

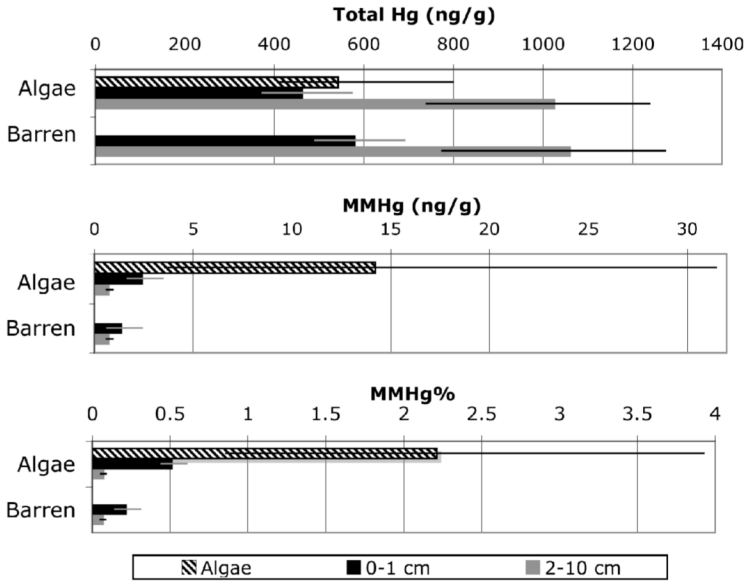

Figure 9.

Vertical distributions of total Hg, and MMHg concentrations, and % MMHg in surface sediments with algal mats (Algae) and adjacent location with no algal covering (Barren). Plotted values are the average from three sets of cores, and error bars represent range of measurements.

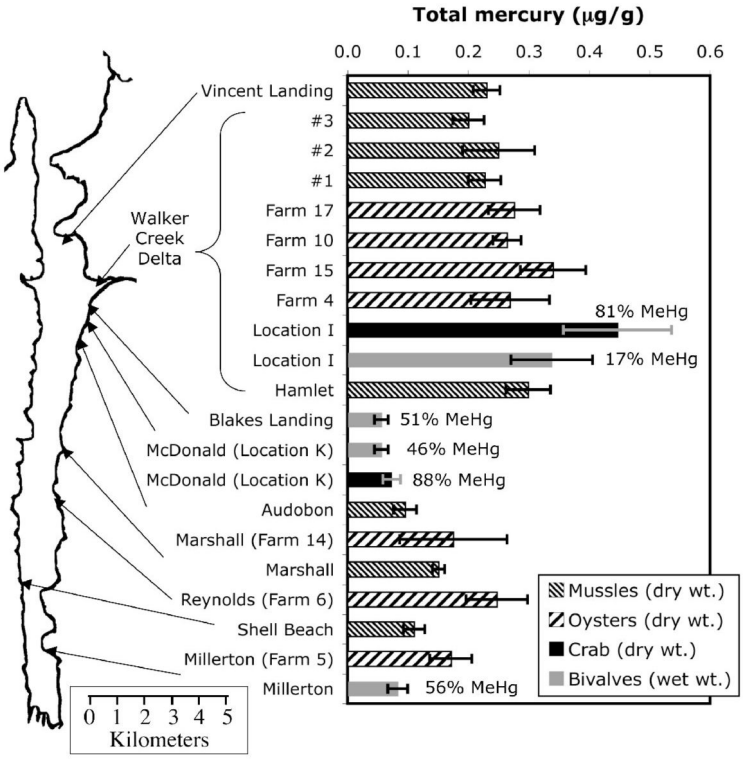

Figure 10.

Comparison of mean total Hg concentrations for non-migrating biota; crab with %MMHg, resident bivalves with %MMHg, mussels transplanted in Tomales Bay for 100 days, and farmed oysters. Error bars are two times the standard deviation.

Table 1

Sediment characteristics and total mercury abundance from 1-2 m sediment cores collected from Walker Creek Delta, 2003.

Core ID	Sediment Type[a]	f_{fines}[b] avg.	$[Hg]_{avg}$ (ug/g)		Total Hg Inventory (g/m^2)	Excess Hg Inventory (g/m^2)	w_{sed}[c] (cm/yr)
			0-25 cm	25-75 cm			
1	Mud w/ silt	0.35	0.45	0.12	0.40	0.04	0.3
4	Mud w/ silt	0.30	0.55	0.31	0.92	0.05	0.3*
6	Mud w/ silt	0.28	0.91	0.49	1.02	0.22	0.3*
7	Mud w/Silt	0.29	0.44	0.36	0.67	0.00	0.3*
8	Mud	0.42	1.54	1.08	1.40	1.06	2.3*
10	Sandy Mud w/silt @1-30 cm	0.40	1.60	1.47	2.25	1.62	2.3*
11	Sandy Mud w/silt @1-20, 60-70, and 92-94 cm	0.16	1.25	0.43	0.96	0.38	2.3*
12	Sandy Mud w/silt @1-30 cm	0.08	1.12	0.41	0.85	0.43	2.3*
13	Silt Mud w/silt @ 60-70, 80-90, & 107-123 cm	0.32	0.68	1.86	2.48	1.67	2.3
15	Sandy Mud w/silt @ 1-25 cm	0.05	0.85	1.62	1.70	1.29	1.8*
17	Mud w/silt Silty sand @ 1-50 cm	0.53	0.63	0.78	0.94	0.52	1.8*
18	Mud Mud w/ silt @ 1-40 cm	0.32	0.73	0.67	0.78	0.34	1.8*
19	Mud	0.35	0.54	0.52	0.88	0.07	1.8*
20	Sand w/silt	0.04	0.21	0.09	0.27	0.00	1.8*
21	Sandy Mud w/ silt @ 80-120 cm	0.17	0.08	0.20	0.94	0.24	2.3*
22	Mud	0.79	2.10	1.21	1.39	0.87	2.3*
23	Mud	0.64	0.61	0.85	0.83	0.36	2.3*
24	Sand Mud w/silt 30-100 cm	0.09	1.45	1.74	2.30	1.65	1.8

a) Sediment types assigned through direct observation.

b) Fraction of fines (f_{fines}) defined as the mass fraction of sediment that past a 63 μm mesh sieve.

c) Bulk sediment accumulation (W_{sed}) defined by ^{137}Cs depth profile.

*) Sediment accumulation rate based on nearest neighbor extrapolation.