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Reducing methylmercury accumulation in the food webs of San Francisco Bay and its local watersheds

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ABSTRACT

San Francisco Bay (California, USA) and its local watersheds present an interesting case study in estuarine mercury (Hg) contamination. This review focuses on the most promising avenues for attempting to reduce methylmercury (MeHg) contamination in Bay Area aquatic food webs and identifying the scientific information that is most urgently needed to support these efforts. Concern for human exposure to MeHg in the region has led to advisories for consumption of sport fish. Striped bass from the Bay have the highest average Hg concentration measured for this species in USA estuaries, and this degree of contamination has been constant for the past 40 years. Similarly, largemouth bass in some Bay Area reservoirs have some of the highest Hg concentrations observed in the entire US. Bay Area wildlife, particularly birds, face potential impacts to reproduction based on Hg concentrations in the tissues of several Bay species. Source control of Hg is one of the primary possible approaches for reducing MeHg accumulation in Bay Area aquatic food webs. Recent findings (particularly Hg isotope measurements) indicate that the decades-long residence time of particle-associated Hg in the Bay is sufficient to allow significant conversion of even the insoluble forms of Hg into MeHg. Past inputs have been thoroughly mixed throughout this shallow and dynamic estuary. The large pool of Hg already present in the ecosystem dominates the fraction converted to MeHg and accumulating in the food web. Consequently, decreasing external Hg inputs can be expected to reduce MeHg in the food web, but it will likely take many decades to centuries before those reductions are achieved. Extensive efforts to reduce loads from the largest Hg mining source (the historic New Almaden mining district) are underway. Hg is spread widely across the urban landscape, but there are a number of key sources, source areas, and pathways that provide opportunities to capture larger quantities of Hg and reduce loads from urban runoff. Atmospheric deposition is a lower priority for source control in the Bay Area due to a combination of a lack of major local sources. Internal net production of MeHg is the dominant source of MeHg that enters the food web. Controlling internal net production is the second primary management approach, and has the potential to reduce food web MeHg in some habitats more effectively and within a much shorter time-frame. Controlling net MeHg production and accumulation in the food web of upstream reservoirs and ponds is very promising due to the many features of these ecosystems that can be manipulated. The most feasible control options in tidal marshes relate to the design of flow patterns and subhabitats in restoration projects. Options for controlling MeHg production in open Bay habitat are limited due primarily to the highly dispersed distribution of Hg throughout the ecosystem. Other changes in these habitats may also have a large influence on food web MeHg, including temperature changes due to global warming, sea level rise, food web alterations due to introduced species and other causes, and changes in sediment supply. Other options for reducing or mitigating exposure and risk include controlling bioaccumulation, cleanup of contaminated sites, and reducing other factors (e.g., habitat availability) that limit at-risk wildlife populations.

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1. Introduction

Mercury (Hg) contamination of estuaries is a global concern. Global atmospheric transport of Hg leads to contamination of aquatic ecosystems even in areas that are far removed from sources (Fitzgerald et al., 1998). In the more populated regions of the planet, local Hg sources are often abundant near estuaries due to the dense human settlements and industrial activities that are common near these water bodies (e.g., Gill et al., 1999; Hope, 2006; Levinton and Pochron, 2008). Estuaries include habitats where conditions favoring methylmercury (MeHg) production and accumulation in the food web are prevalent, including tidal marshes and subtidal waters with low oxygen content (Lambertsson and Nilsson, 2006; Heim et al., 2007). Estuaries are also highly productive ecosystems that provide important habitat for wildlife and support fisheries that are a significant food source for humans. Coastal and estuarine fisheries are major vectors for human MeHg exposure (Sunderland, 2007).

San Francisco Bay (California, USA) and its local watershed (Fig. 1) present an interesting case study in estuarine Hg contamination. In many ways the Bay is representative of Hg-contaminated urban estuaries around the world. Hydrodynamics that favor retention of sediment particles and associated contaminants are one common feature of estuaries. San Francisco Bay is surrounded by the fourth largest metropolitan area in the United States, with an overall population of over seven million people. Urban and industrial land uses in the Bay Area are associated with sources of Hg and other contaminants and runoff from these areas contributes significant loads to the Bay (SFBRWQCB, 2006; Conaway et al., 2008; McKee et al., 2010). The Bay is a very productive ecosystem that supports a diverse and abundant array of wildlife species and provides a food supply for Bay Area residents. Contamination of aquatic food webs in the Bay Area with MeHg and other substances is a high priority concern for water quality managers (SFBRWQCB, 2006).

San Francisco Bay is also unique in many ways that add to its interest as a case study of MeHg contamination. The mix of Hg

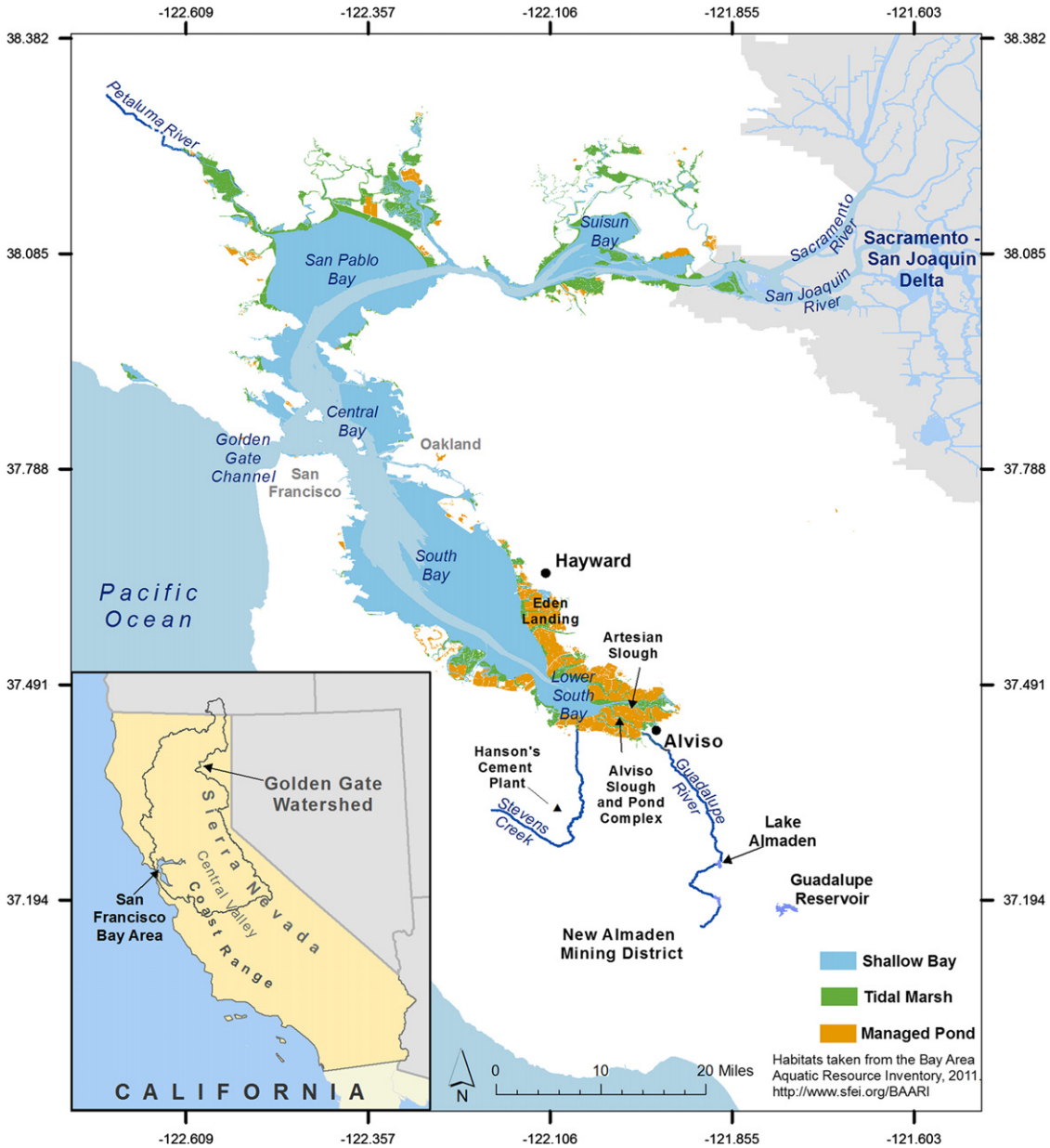

Fig. 1. San Francisco Bay and its watershed.

sources to the Bay is unusual, with inputs dominated by legacy contamination from Hg mines including the New Almaden Hg mining district (hereafter New Almaden), historically the nation's largest Hg mining region, in the Guadalupe River watershed that drains to Lower South Bay. In addition, extensive historic gold mining, which used Hg in the extraction process, occurred in the distant upstream portions of the watershed in the Sierra Nevada. Many reservoirs and riparian areas in the local watershed of the Bay have also been contaminated by historic Hg mining, some severely (Tetra Tech, 2005; Davis et al., 2010; Robinson et al., 2011). Hg concentrations are elevated throughout most of the Bay and in large portions of its watershed. Much of the Hg in the ecosystem is in the form of cinnabar or other sulfide-associated forms. The degree to which these highly insoluble sulfide-associated forms are available for Hg(II)-methylation has been a subject of debate. Atmospheric deposition of Hg is also likely to be important, but unlike many other parts of the USA, coal-fired power plants and waste incinerators are not significant local sources. There are only four coal-fired power plants in California, and none are in the Bay Area (California Energy Commission, 2011). Hg depositing in the Bay and its watershed is primarily attributable to emissions from various sources contributing to the global pool, with the largest contribution coming from Asia (Seigneur et al., 2004; Task Force on Hemispheric Transport of Air Pollution, 2010).

Other unique features of the Bay include extensive diversion of freshwater inflow, food web disruption due to introduction of nonnative species, and a vast degree of habitat alteration (primarily conversion of tidal marsh to other land uses). Due to the combination of all of these insults, the Bay is considered perhaps the most highly altered coastal ecosystem in the United States (Nichols et al., 1986). Another unusual feature of the Bay is a net erosional sedimentation regime, likely caused by a reduced supply of incoming sediment (Schoellhamer, 2011), which tends to prolong the influence of legacy deposits of Hg in buried sediment (Hornberger et al., 1999; Conaway et al., 2004). In recent years an ambitious program of estuarine wetland restoration has been initiated. One project in the South Bay alone is planning to restore over 15,000 acres of tidal marsh—the largest single tidal wetland restoration project on the Pacific Coast of the USA. This restoration activity is expected to generate a huge net benefit, but carries a potential risk of increasing MeHg in the food web on either a local or regional scale (Grenier and Davis, 2010). Finally, San Francisco Bay is fairly unique in the extent of contaminant monitoring that is performed, due primarily to the Regional Monitoring Program for Water Quality in the San Francisco Estuary (SFEI, 2010a) and long-term monitoring performed since the 1970s by the U.S. Geological Survey. Hg contamination in particular has been a topic of great interest and has been intensively studied by these and other programs in the past 10 years, making the Bay perhaps the most thoroughly studied estuary in the world with regard to Hg contamination.

The objective of this paper is to synthesize the continually growing body of information on Hg in the Bay. This synthesis updates and expands the reviews of Tetra Tech (2006) and Conaway et al. (2008), with a focus on the most promising avenues for reducing the MeHg contamination that is threatening the health of Bay Area anglers and wildlife, and identifying the scientific information that is most urgently needed to support these efforts. It is intended that this synthesis will inform efforts to address this challenging contaminant in other estuaries as well.

2. Setting

San Francisco Bay is the largest estuary on the Pacific coast of both North and South America (Fig. 1). The landward boundary of the Bay is at the confluence of the Sacramento and San Joaquin Rivers. The seaward boundary is the Golden Gate, where the Bay empties into the Pacific Ocean. The watershed of the Bay encompasses approximately 40% of the land area of California, including the expansive agricultural land of the Central Valley lying between the slopes of the Sierra Nevada to the east and the Coast Range to the west.

The Bay is a complex ecosystem, exhibiting considerable variability at multiple temporal scales due to tidal action, climatic variation, and strong seasonal and interannual variability in rainfall in a Mediterranean climate. The Bay is also heterogeneous spatially, with large differences in residence time and other physical, chemical, and biological properties among the major sub-embayments. The northern reach of the Bay (Suisun, San Pablo, and Central bays) receives greater than 95% of the Bay's total freshwater inflow and features a gravitational circulation pattern typical of partially mixed estuaries; surface currents of lower salinity flow toward the sea, while bottom currents of higher salinity flow landward. Mixing between upper and lower water masses results in a gradual transition from the low salinity of the freshwater sources to the higher salinity of Central Bay and the ocean. The southern reach of the Bay (South Bay) receives less than 5% of the fresh water entering the Estuary, and a high proportion of the freshwater input is from municipal wastewater effluent. Unlike the northern reach, freshwater inflows in the South Bay are rarely sufficient to drive gravitational circulation. During much of the year the South Bay resembles a tidally oscillating lagoon (Conomos et al., 1985). Although different processes are at play, the northern and southern reaches both effectively trap sediment particles, leading to long residence times for particle-associated contaminants such as Hg.

To promote a more holistic approach in management and study of Hg in the region, the geographic scope of this paper includes the Bay, adjoining tidal marshes and managed ponds, and reservoirs and riparian habitats further upstream in the local watersheds that drain directly to the Bay. As will be discussed throughout this paper, MeHg exposure and risk to humans and wildlife vary across these habitats, as do options for reducing MeHg exposure.

At its upstream end at the eastern edge of Suisun Bay, San Francisco Bay is connected to a tidal, freshwater, inland delta of the Sacramento and San Joaquin rivers ("the Delta"). The Delta has also been the subject of considerable study of Hg and MeHg (e.g., Marvin-DiPasquale and Agee, 2003; Heim et al., 2007; Davis et al., 2008). Inclusion of this region, however, was generally beyond the scope of this review. One exception to this is the consideration of Hg loads from the Delta to San Francisco Bay, which is discussed in Sections 4 and 5.

3. Human and wildlife exposure and risk

3.1. Human exposure

The potential for human health risk from consumption of San Francisco Bay fish contaminated with MeHg was first recognized in the 1970s following a multiagency survey of Hg in the California environment (Interagency Committee on Environmental Mercury, 1971). This survey found Hg in freshwater and estuarine fish throughout the state and higher levels in some fish in the Bay, the Delta, and nearby reservoirs downstream of New Almaden. A fish consumption advisory was issued for striped bass (*Morone saxatilis*) from the Bay and Delta in 1971, and further studies led to advisories for several reservoirs downstream of New Almaden, where no consumption of fish was advised due to very high levels of Hg (1 to >2 ppm wet weight—unless otherwise specified, all tissue

concentrations are presented on a wet weight basis) (California Department of Health Services, 1987). A more comprehensive survey of fish from San Francisco Bay in 1994 (Fairey et al., 1997) found mean Hg levels ranging from 0.07 to 1.26 ppm in nine sport fish species popular with consumers (SFEI, 2000). In response to this survey, a Bay-wide advisory for the general population to limit consumption of all fish to two meals per month was issued by the California Office of Environmental Health Hazard Assessment (OEHHA, 1994). Hg levels were an important determinant of advice for shark species (leopard shark [*Triakis semifasciata*] and brown smoothhound [*Mustelus henlei*]), white sturgeon (*Acipenser transmontanus*), and striped bass. Women of childbearing age and children were advised to eat only one meal of Bay fish per month, and not to consume large-sized shark and striped bass.

In 2011 OEHHA used data collected between 1997 and 2009 (Table 1) to develop an updated and more comprehensive fish consumption advisory for the Bay (Gassel et al., 2011). The advisory included new species – Chinook salmon (*Oncorhynchus tshawytscha*), jacksmelt (*Atherinopsis californiensis*), brown rockfish (*Sebastes auriculatus*), and red rock crab (*Cancer productus*) – all of which had relatively low Hg levels. Only shark species exceeded OEHHA's MeHg advisory threshold for no consumption (0.44 ppm). The advisory allowed at least one serving per week (32 g d^{-1}) of all other species by women 18–45 and children 1–17 if MeHg was the only contaminant in Bay fish. Local data indicate that consumption rates are generally below these OEHHA guidelines (SFEI, 2000). Asians (from many countries) and African Americans had the highest consumption rates, with a highest average for any ethnic group of 22.4 g d^{-1} for Pacific islanders (SFEI, 2000).

Striped bass are a relevant and useful indicator species for comparing MeHg contamination across USA estuaries due to several factors: their popularity for consumption (this is the most popular species for consumption in San Francisco Bay—SFEI, 2000); their dependence on estuaries (Able, 2005); their broad spatial integration across the estuaries in which they reside due to their variable use of fresh, brackish, and saline habitat (Secor and Piccoli, 2007); and their wide distribution on the east, west, and Gulf coasts. Striped bass from San Francisco Bay have the highest average Hg concentration measured for this species in USA estuaries (Table 2). The average Hg concentration measured in 2009 in San Francisco Bay (a length-adjusted mean of 0.44 ppm at 60 cm—Davis et al., 2011) was higher than average concentrations recently reported for five other USA coastal areas. The New Jersey coast (Burger and Gochfeld, 2011) had the second highest average concentration (0.39 ppm—based primarily on fish greater

Table 1
Fish Hg statistics used in the 2011 San Francisco Bay advisory (Gassel et al., 2011). All species analyzed as muscle without skin, except white croaker (with skin) and shiner surfperch (whole body without head, tail, and viscera). Samples collected from 1997 to 2009. Surf and seaperch were combined in the advisory. Polychlorinated biphenyl data were also used to determine advice for some species. The statistics for striped bass in this table are based on data not adjusted for size (in contrast to the text and Table 2).

Species name	Common name	Number of individuals	Average Hg (ppb wet), (SD)	Hg range (ppb wet)	Average length (mm)	Length range (mm)
Triakis semifasciata	Leopard shark	76	951 (300)	320–2020	1041	NA
Mustelus henlei	Brown smoothhound shark	9	677 (368)	240–1380	719	NA
Morone saxatilis	Striped bass	253	419 (199)	130–1850	NA	450–1150
Rhacochilus toxotes	Rubberlip seaperch	9	349 (65)	270–430	378	350–400
Amphistichus argenteus	Barred surfperch	6	346 (59)	290–410	262	180–310
Paralichthys californicus	California halibut	32	329 (325)	170–2060	732	NA
Acipenser transmontanus	White sturgeon	43	312 (170)	150–910	1337	NA
Genyonemus lineatus	White croaker	190	222 (65)	120–380	NA	190–340
Hyperprosopan argenteum	Walleye surfperch	16	155 (35)	80–180	268	170–340
Cancer productus	Red rock crab	60	133 (25)	100–150	117	100–150[a]
Sebastes auriculatus	Brown rockfish	30	129 (35)	100–200	247	200–360
Embiotoca jacksoni	Black surfperch	33	118 (34)	70–180	252	200–300
Cymatogaster aggregata	Shiner surfperch	902	103 (42)	40–200	NA	90–200
Atherinopsis californiensis	Jacksmelt	20	84 (11)	70–100	NA	200–300
Oncorhynchus tshawytscha	Chinook (King) salmon	57	83 (26)	40–110	814	560–1040

NA=not available due to missing composite details.

[a] Crab carapace width.

Table 2
Mercury concentrations measured in striped bass in U.S. estuaries.

		N	Hg (ppm wet)	Statistic	Years	Comments
San Francisco Bay	Davis et al. (2011)	18	0.44	Length-adjusted mean	2009	Mean at 60 cm. Annual length-adjusted means for 1994, 1997, 1999, 2000, 2003, and 2006 were similar
New Jersey	Burger and Gochfeld (2011)	178	0.39 (0.02)	Mean (SE)	2003–2008	Mean length or weight not provided. Median size approximately 84 cm
South Carolina	Glover et al. (2010)	81	0.23	Mean at 58 cm	1993–2007	Estimated mean at 58 cm. 42% below detection. Censored interval regression model used to account for large number of values below reporting limits
Narragansett Bay	Piraino and Taylor (2009)	66	0.16 (0.01)	Mean (SE)	2006–2007	Mean at 49 cm
Louisiana	Katner et al. (2010)	38	0.14 (1.64)	Geometric mean (log SD)	1994–2008	Mean length or weight not provided
Chesapeake Bay	Mason et al. (2006)	79	0.12	Mean	2002–2004	Mean length or weight not provided

than 85 cm). Average Hg concentrations in striped bass from other USA coastal areas ranged from 0.12 to 0.23 ppm (Mason et al., 2006; Piraino and Taylor, 2009; Glover et al., 2010; Katner et al., 2010; Burger and Gochfeld, 2011).

Largemouth bass (*Micropterus salmoides*) is an important indicator species for human consumers of fish caught in lakes and reservoirs in California and across the USA (Davis et al., 2008, 2010; Stahl et al., 2009). Largemouth bass in some reservoirs in the Guadalupe River watershed have some of the highest Hg concentrations observed in the entire USA. USEPA recently published results from a national probabilistic survey of contaminants in fish from lakes based on sampling conducted in 2000–2003 (Stahl et al., 2009). A largemouth bass composite sample from Guadalupe Reservoir had a Hg concentration of 6.60 ppm (not size-adjusted, average length for the composite was 449 mm)—the highest concentration measured in the entire country. Another recent survey in California found that Almaden Lake had the highest average Hg concentration among 272 lakes sampled from across the state—2.15 ppm in largemouth bass size-normalized to 350 mm (Davis et al., 2010). It should be noted, however, that these two reservoirs represent a special case of Hg contamination as they are situated downstream of the New Almaden Hg mining district and, as a result, their sediment has exceptionally high total Hg concentrations (Tetra Tech, 2005). Many other reservoirs in the region have also been found to have high concentrations of Hg (greater than 0.8 ppm) in largemouth bass (Davis et al., 2010); including some that are known to be downstream of historic Hg mining and others that are not. Possible causes of high bass Hg in reservoirs not known to be downstream of mines include limnological properties that favor net production of MeHg, Hg from geological sources, and atmospheric deposition of Hg.

3.2. Exposure and risk in birds

Bay Area wildlife species are also at risk from MeHg in the estuarine food web. Birds are particularly sensitive to MeHg, especially during early development as embryos and chicks (Scheuhammer et al., 2007), and they face potential impacts to reproduction based on the concentrations documented in the tissues of several Bay species. The Bay and its wetlands are a vital refueling stop for large populations of migrating waterbirds on the Pacific Flyway and also support many species of breeding birds, including threatened and endangered species and other endemics. Potential MeHg impacts are a significant concern for several special-status species, including the federally endangered California Clapper Rail (*Rallus longirostris obsoletus*) and California Least Tern (*Sterna antillarum browni*). The control plan for Hg in San Francisco Bay (the Total Maximum Daily Load, or TMDL—described further in Section 4) includes a concentration target for prey fish to protect piscivorous birds, particularly the California Least Tern.

MeHg exhibits habitat-specific patterns of bioaccumulation in the Bay (Greenfield and Jahn, 2010; Grenier et al., 2010), likely due to variation in MeHg cycling among habitats. As birds are adapted to forage in particular habitats, each species tends to reflect bioaccumulation of MeHg in the food web of one or two primary habitat types. Varying sensitivity among the species relying on each habitat combine with the variation in MeHg cycling to produce a mosaic of risk to wildlife across the region.

MeHg exposure is a major concern for birds in two of three main estuarine habitats—managed ponds and tidal marshes—but exposure to harmful levels is less likely in open Bay habitat (defined in this paper as Bay shallows, intertidal flats, and subtidal sloughs). Eggs of the piscivorous Double-crested Cormorant (*Phalacrocorax auritus*) have been monitored for more than a decade as an indicator of accumulation of Hg and other contaminants in the open Bay. While Hg concentrations in eggs from San Pablo and Suisun Bays (ranging from 0.28 to 0.70 ppm wet weight in composite samples) have tended to be at or below adverse effects thresholds for reproductive impairment in Mallards and Ring-necked Pheasants (0.5–0.8 ppm fww; Fimreite, 1971; Heinz, 1979), eggs from South Bay (ranging from 0.56 to 1.05 ppm) have tended to exceed those levels (Grenier et al., 2011). Cormorants are relatively insensitive to MeHg toxicity compared to other species (Heinz et al., 2009), so it does not appear likely that these concentrations are harmful to the population. California Least Terns are also piscivores that forage extensively in the shallows of the open Bay (Ehrler et al., 2006). Limited data are available for Hg in eggs of California Least Terns because of their small population and endangered status. Three fail-to-hatch eggs collected in 2000 had an average Hg concentration of 0.3 ppm (Schwarzbach and Adelsbach, 2003), which is below the effects thresholds for mallards and pheasants. However, terns as a group may be somewhat more sensitive to MeHg than those species (Heinz et al., 2009).

Managed ponds are habitats on the margin of the Bay that were originally tidal marsh, were converted to ponds used for salt production, and are now managed to support waterbirds. Forster's Tern (*Sterna forsteri*), Caspian Tern (*Sterna caspia*), American Avocet (*Recurvirostra americana*), and Black-necked Stilt (*Himantopus mexicanus*) all feed and breed primarily in and around managed ponds. The terns are piscivores, while stilts and avocets feed on invertebrates in shallower ponds. Eagles-Smith and Ackerman (2008) and Eagles-Smith et al. (2009) have conducted extensive studies of Hg exposure and risk in these species, including sampling of eggs and blood. Nearly half (48%) of breeding Forster's Terns and approximately 5% of avocets, stilts, and Caspian Terns (Eagles-Smith et al., 2009) exceeded 3 ppm of Hg in blood, a concentration at which Common Loons (*Gavia immer*) experienced a 40% loss in reproduction (Evers et al., 2008). Estimated reproductive risks to these species based on egg Hg concentrations are very similar (Eagles-Smith et al., 2009). Annual mean Hg concentrations in Forster's Tern eggs ranged from 0.9 to 1.6 ppm from 2005 to 2009 (Eagles-Smith and Ackerman, 2010). Concentrations in blood and eggs have been consistently higher in Lower South Bay near the town of Alviso, which is downstream of New Almaden.

MeHg is also a significant concern for several species of tidal marsh birds in the Bay. Recovery of the endangered California Clapper Rail, found only in San Francisco Bay, may be impeded by MeHg contamination. A study from 1991 to 1999 concluded that MeHg was a likely cause of the unusually high rates (31%) of nonviable Clapper Rail eggs (Schwarzbach et al., 2006). MeHg was found in rail eggs above effects thresholds at all of the marshes studied; mean egg MeHg by marsh ranged from 0.3 to 0.8 ppm (Schwarzbach et al., 2006). Egg-injection studies have indicated that hatchability in Clapper Rails is relatively sensitive to MeHg (Heinz et al., 2009). Tidal marsh Song Sparrows (*Melospiza melodia*), a state species of special concern, had MeHg concentrations in blood that indicated potential risks of impaired reproduction. Average Song Sparrow blood MeHg concentrations in a probabilistic sampling of South Bay ranged from 0.1 to 0.6 ppm by marsh, and more than half the sparrows were above a 0.4 ppm threshold for a 5% reduction in songbird reproduction (Jackson et al., 2011) in both 2007 and 2008 (Grenier et al., 2010). Song Sparrow MeHg concentrations were lowest in marshes far from the Bay and highest in marshes near the Bay, which parallels the salinity gradient (Grenier et al., 2010). Sparrow MeHg exposure also correlated with the percent of Hg in sediment that was present as MeHg.

The risk to wildlife from MeHg exposure in non-estuarine wetlands of the watersheds that drain into the Bay is largely unknown. However, a recent study of riparian songbirds (Song Sparrows) found concentrations that may reduce reproductive success in some streams of the Bay Area (Robinson et al.,

2011). The greatest risk, where the mean adult Song Sparrow blood MeHg concentration (1.66 ppm) would be associated with a >25% loss in reproductive success based on the study by Jackson et al. (2011), occurred at a site downstream of New Almaden. However, sites upstream of the Hg mines also had elevated MeHg in blood, though to a lesser degree.

3.3. Exposure and risk in mammals

MeHg bioaccumulation in estuarine mammals of the Bay is less well studied than in birds. MeHg exposure has been best characterized in harbor seals (*Phoca vitulina*) that feed in the open Bay. Juvenile and adult harbor seals had blood MeHg concentrations averaging slightly over 0.3 ppm in samples from 2003 to 2005 (Brookens et al., 2007). The significance of these concentrations is unclear because effects thresholds have not yet been determined. However, forage fish Hg concentrations in San Francisco Bay are typically well below a lowest observed adverse effect threshold of 1.1 ppm wet weight developed by USEPA based on mink (*Mustela* spp.) (Scheuhammer et al., 2007; Greenfield and Jahn, 2010), suggesting low risk for harbor seals.

Small tidal marsh mammals, particularly endemic shrews (order *Insectivora*), could be at risk for MeHg effects. The only study of small mammal MeHg from San Francisco Bay focused on rodents and found that endangered salt marsh harvest mice (*Reithrodontomys raviventris*) were absent from marshes in which other rodent species had high MeHg exposure (Clark et al., 1992). No data are available for MeHg exposure in bats, otters, or terrestrial carnivores that feed in tidal marshes or managed ponds.

3.4. Exposure and risk in fish

Little information on the effects of MeHg on estuarine fish species is available (Wheeler et al., 2002; Dillon et al., 2010), and no studies on this have been performed in San Francisco Bay. In contrast, extensive data are available and have recently been reviewed for freshwater habitats (Dillon et al., 2010; Sandheinrich and Wiener, 2011). Thresholds for effects on fish have decreased substantially over the past 15 years as approaches for evaluating toxicity have advanced. Effects on biochemical processes, damage to cells and tissues, and reduced reproduction in fish have been documented at MeHg concentrations of about 0.3–0.7 ppm in the whole body and about 0.5–1.2 ppm in axial muscle (Sandheinrich and Wiener, 2011). Dillon et al. (2010) developed dose-response curves for Hg based on 11 tissue residue-toxicity studies (mostly using freshwater species) that predict a 50% rate of adverse response at a whole-body concentration of 3 ppm for juveniles and adults, and at a concentration of 0.4 ppm for effects on early life-stages. Concentrations of Hg in individuals of some species of Bay fish (in particular, leopard shark, striped bass, white sturgeon, and brown smoothhound shark) exceed 0.5 ppm in axial muscle. Whether estuarine species are as sensitive as freshwater species is unknown, but MeHg effects at present concentrations seem plausible. Concentrations well above the 1.2 ppm threshold for effects in freshwater species have been observed in largemouth bass muscle in some Bay Area reservoirs, as discussed in Section 3.1.

4. Existing control plans and their conceptual foundations

4.1. Existing control plan for San Francisco Bay

In 2006, in response to increased awareness of the risks to human and wildlife health associated with MeHg in the Bay food web, the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) required actions to reduce Hg loads to San Francisco Bay to make Bay fish safe for consumption by piscivorous wildlife and by humans who consume sport fish (SFBRWQCB, 2004, 2006).

The control actions are contained in a Total Maximum Daily Load (TMDL), which prescribes an acceptable maximum mass loading rate that the Bay can assimilate yet eventually attain water quality standards. The TMDL allocates this critical loading rate among all contributing sources and defines a program of implementation to achieve any necessary load reductions. The TMDL total Hg (THg) loading rate for the Bay is about 700 kg yr^{-1}, about 40% less than the estimated total load of 1200 kg yr^{-1} (SFBRWQCB, 2006). However, due to the large inventory of Hg already in the Bay, even if these load reductions are achieved in the 20 years mandated by the TMDL, it is expected to take more than 100 years to achieve target concentrations in sport fish (0.2 ppm in striped bass normalized to 60 cm) and prey fish (0.03 ppm in fish 3–5 cm in length) to protect human and wildlife consumers.

The TMDL mandates substantial load reductions from all contributing sources. It requires municipalities to reduce Hg loading in urban runoff by 80 kg yr^{-1} by implementing control measures such as Hg-containing light bulb and device recycling, improved operation and maintenance of stormwater infrastructure, and identification and clean-up of contaminated sites in the watersheds. The TMDL assumes a 110 kg yr^{-1} reduction in Delta outflow from control measures mandated by regulatory efforts upstream in the Central Valley to reduce the ongoing Hg loads associated with historic Hg and gold mining in the watersheds of the Sierra Nevada foothills and the Coast Range drained by the Sacramento and San Joaquin rivers. Wastewater treatment plants, through source control and facility upgrades, must reduce loads by about 40% to achieve about a 10 kg yr^{-1} reduction. The TMDL also assumes a 240 kg yr^{-1} Hg load reduction from reduced remobilization of the Hg source buried in Bay sediment. This reduction estimate for bed erosion was derived based on observed rates of erosion in Suisun Bay and San Pablo Bay coupled with the anticipated reduction of THg concentrations in sediment in these Bay segments from 0.42 to 0.20 ppm as a result of reductions of other loads. Lastly, the TMDL requires a 90 kg yr^{-1} (98%) reduction from the Guadalupe River watershed in the southern part of the Bay, which includes New Almaden. This reduction will be achieved by implementing the remedial and control measures mandated through a specific TMDL for the Guadalupe River watershed (described further below).

4.2. Existing control plan for the Guadalupe River watershed

In 2008, the SFBRWQCB required control actions for both MeHg and THg in the Guadalupe River watershed. The Guadalupe TMDL established concentration limits (rather than mass load limits) for MeHg in reservoir water and THg in suspended sediment in the Guadalupe River (SFBRWQCB, 2008).

Reservoirs in the Guadalupe River watershed produce prodigious quantities of MeHg, due to a combination of high Hg(II)-methylation rates resulting from the long summer dry season (and hence long period of thermal stratification that causes oxygen depletion in the hypolimnion) and pollution by local Hg mines and atmospheric sources. MeHg concentrations in reservoirs immediately downstream of (and highly polluted by) New Almaden reach a dry season peak of 10 to 50 ng L^{-1} in the hypolimnion. Further downstream in Lake Almaden, MeHg has been measured up to an astonishing 140 ng L^{-1} at mid-depth (SCVWD, 2009). In a nearby "reference" reservoir that does not receive runoff from historic Hg mining districts or any other local point sources (Lexington Reservoir), atmospheric deposition has increased bottom sediment THg to about 3 times

above pre-industrial levels (Sanders et al., 2008), and MeHg has reached 2.6 ng L^{-1}—still a high concentration (SFBRWQCB, 2008).

Hg concentrations in fish parallel the high MeHg concentrations in water (SFBRWQCB, 2008). THg in adult largemouth bass (standardized to 40 cm, n=18–20) in 2004 was 5.8 and 3.6 ppm in the two reservoirs adjacent to New Almaden (Guadalupe Reservoir and Almaden Reservoir, respectively), 2.1 ppm downstream (Almaden Lake), and 0.6 ppm in a reference reservoir (Lexington Reservoir). The concentration in largemouth bass in the reference reservoir was still three times higher than the human health target included in the TMDL (0.2 ppm to protect consumers eating 32 g d^{-1}) (SFBRWQCB, 2008), probably due to conditions favoring net Hg(II)-methylation.

Therefore, because source control alone, such as reducing erosion of Hg mining wastes at mines and in creeks downstream, will not achieve fish tissue MeHg targets (based on observations from the reference reservoir), the Guadalupe River TMDL also calls for measures to reduce MeHg production and bioaccumulation in reservoirs. Previously, owners of the New Almaden property cleaned up the most contaminated mine sites, and the TMDL calls for additional erosion controls at mine sites within 10 years and in downstream creeks within 20 years. Erosion control will likely reduce THg loads to San Francisco Bay by 90% (Kirchner et al., 2011), which is less than the 98% THg load reduction required by the Bay TMDL (SFBRWQCB, 2006); additional measures, such as control of urban Hg sources and runoff, will also be needed. The Santa Clara Valley Water District has also started pilot testing of controls on MeHg production in reservoirs adjacent to and downstream of New Almaden. They reported a 90% reduction in MeHg concentrations measured at mid-depth in the downstream reservoir (Almaden Lake) in response to mechanical aeration and circulation of the hypolimnion (unpublished data).

4.3. Conceptual models supporting management

4.3.1. Existing conceptual models

The TMDL for San Francisco Bay is based on a simple conceptual model of how THg moves into the ecosystem and accumulates in the food web. Regulators often rely on simple models of complex phenomena for a variety of reasons. First, in order to support the imposition of regulatory requirements, regulators generally try to achieve broad consensus on the underlying science. The regulations themselves and supporting scientific documentation are both subject to review by scientists and the interested public, which tends to create scientific conservatism in regulatory agencies that would rather rely on a simplified, but essentially correct, conceptual understanding of a phenomenon than on novel, but not universally accepted, concepts. Even when regulators can make limited use of qualitative results of recent scientific studies, quantitative application is not always possible. For example, there is evidence from studies of experimental lakes in Canada (Hintelmann et al., 2002) that some chemical species of Hg (e.g., uncomplexed Hg[II] deposited from the atmosphere) may be more readily available to organisms at the base of the food web than other chemical forms (e.g., cinnabar from mine tailings). However, there was not enough support in the literature to apply this finding quantitatively to load reduction requirements in the TMDL for the Bay.

The simple conceptual model underlying the Bay TMDL defines the ecosystem as the water in the Bay and the top 15 cm of bottom sediment. Hg in sediment below 15 cm is not considered to be in circulation. The conceptual model assumes that any atom of inorganic Hg in the system has an equal chance of being converted into MeHg and incorporated into the food web, so reducing the THg in the system will have a proportional effect on food web Hg concentrations. Reducing loads of Hg from 1200 to 700 kg yr^{-1} is therefore predicted to eventually (in about 100 years) reduce THg in the system by approximately 40%, and the TMDL assumes food web Hg concentrations will decrease by the same percentage (SFBRWQCB, 2006).

A somewhat more elaborate conceptual model was developed for the Hg TMDL for the Guadalupe River watershed. The Guadalupe River watershed is dominated by Hg mining sources, and biogeochemical conditions in reservoirs play a large role in Hg methylation. The conceptual model underlying the Guadalupe River watershed Hg TMDL (SFBRWQCB, 2008) posits that the magnitude and severity of Hg problems in reservoirs are controlled by three factors: (a) sources of Hg, (b) chemical and physical conditions that control Hg(II)-methylation and MeHg-demethylation rates in reservoirs, and (c) composition and complexity of reservoir food chains. Some Hg sources are diffuse and difficult to control, such as atmospheric deposition from global industrial emissions and naturally occurring Hg in soils. Other sources are local and more controllable, such as erosion of Hg-laden sediment from mines. Reservoirs in the Guadalupe River Watershed (there are no natural lakes) undergo a long period of thermal stratification, which creates conditions favoring the conversion of inorganic Hg to MeHg, in the deep, anoxic portion of the water body. Food web composition and complexity also affect bioaccumulation rates. Reservoirs with low productivity, like those in the Guadalupe River watershed, tend to have higher MeHg concentrations in phytoplankton. Reservoir food webs are also highly manipulated by introductions of prey and predator fish and other species, and these changes can have a strong influence on bioaccumulation.

Regulators addressed all three of these factors in the Guadalupe TMDL, and also incorporated an adaptive management framework. Hg mining waste control actions are phased so that Hg discharges from upstream (i.e., mines) will be eliminated or significantly reduced before downstream projects (i.e., streambank stabilization) are undertaken. Reservoir MeHg control studies will be completed in the first decade, and reservoir management will be changed accordingly in the second decade. The goal is to attain safe MeHg levels in prey and sport fish in these reservoirs within 20 years (SFBRWQCB 2008). Because there are already feasible strategies for reducing reservoir MeHg concentrations without necessarily reducing THg concentrations, it is possible to achieve more rapid improvements in fish tissue concentrations. This is in contrast to the situation for the Bay, where the slow trajectory of recovery in fish tissue concentrations was based on the assumed time frame for reductions in THg concentrations in Bay sediment.

4.3.2. Developing improved conceptual models to support management strategies

The San Francisco Bay TMDL report discussed the limitations of its conceptual model as well as the technical and scientific information needed by water quality regulators to improve the effectiveness of the TMDL. These information needs fall into three categories. First, improving the effectiveness of source control actions requires a better understanding of when and where in the Bay Hg(II) is converted to MeHg and taken up into the food web. Second, designing strategies to intervene in the series of processes by which net production and bioaccumulation of MeHg occurs requires detailed understanding of these complex processes. Filling these first two categories of information gaps will help identify opportunities for management intervention. The third category is evaluating the effectiveness of implemented control strategies, which will enable water quality managers to revise and refine their approach as implementation proceeds.

5. External sources and potential controls

5.1. General concepts

Controlling sources of either THg or the various forms of Hg is one of the primary possible approaches for attempting to reduce MeHg accumulation in Bay Area aquatic food webs. Understanding the relative influence of the different quantities and forms of Hg emanating from different sources is essential to efficient and effective source control. The influence on MeHg bioaccumulation of the Hg entering the aquatic ecosystem as cinnabar and related insoluble forms has long been a question. Recent findings indicate that although in the short term there may be differences in the relative availability of different Hg inputs to Hg(II)-methylation and eventual MeHg bioaccumulation, the decades-long residence time of particle-associated Hg in the Bay is sufficient to allow significant conversion of even the insoluble forms of Hg into MeHg. Therefore, the large pool of Hg already present within the ecosystem dominates the fraction converted to MeHg and accumulating in the food web. In other words, a small bioavailable portion of a very large pool (Hg in Bay sediment) appears to outweigh the influence of a likely highly bioavailable but small input (i.e., atmospheric deposition). Decreasing Hg inputs can be expected to reduce MeHg in the food web, but it will likely take a long time before those reductions are seen due to the large pool already in the ecosystem. Furthermore, sediment particles currently entering the Bay from many local watersheds (both with and without historical mining) have comparable or higher Hg concentrations than those already in the Bay, so unless these concentrations are decreased, the problem of Hg contamination will likely continue indefinitely even without the legacy inventory in surface sediment.

5.2. Hg mining sediment as a source to the Bay and upstream ecosystems

5.2.1. Linkage to impairment

Several lines of evidence indicate that transport of sediment particles from historic Hg mines forms a substantial contribution to MeHg contamination of Bay Area aquatic food webs. First, Hg stable isotopes exhibit spatial gradients indicating that mining legacy Hg in sediment, including that from both Hg mines in the Bay Area and Sierra Nevada gold mines in the upper watershed, contribute significantly to biotic MeHg exposure in the ecosystem (Gehrke et al., 2011a,b). δ^{202}Hg isotope values in Bay sediment exhibited a north-south spatial gradient. South Bay values were similar to δ^{202}Hg of Hg mine calcine (roasted ore) waste materials, suggesting New Almaden mining waste as a primary source. North Bay values were more similar to the Hg(0) used in Sierra Nevada gold mines (Gehrke et al., 2011a), although the causal link to gold mining is less certain as Hg(0) from modern use in products and industrial processes as well as atmospheric Hg would have the same signature. Forage fish δ^{202}Hg paralleled the spatial gradient found in sediment, suggesting that the legacy Hg, including that derived from mining, contributed a substantial portion of the MeHg tissue burden (Gehrke et al., 2011b). The isotope pattern in fish was not as uniform and isotopically light as it would be if atmospheric Hg were the primary source throughout the Bay (Gratz et al., 2010).

Another line of evidence indicating that Hg-enriched sediment from Hg mining districts can be a source of MeHg to aquatic food webs is the very high concentrations of MeHg in biota observed in reservoirs downstream of New Almaden, discussed previously in Sections 3.1 and 4.2. The reservoirs with exceptionally high concentrations are hydrologically connected to the historic mining district.

MeHg in water (Fig. 2), sediment (Fig. 3), and multiple species (Ackerman et al., 2007a,b; Greenfield and Jahn, 2010) are highest in the region where the Guadalupe River drains into the South Bay, but at the regional scale this appears to be due to conditions that favor net Hg(II)-methylation rather than high THg inputs from New Almaden. THg concentrations in open Bay sediment in this region are not elevated relative to the rest of the Bay (Fig. 3). The relatively homogeneous spatial distribution of THg in open Bay surface sediment is a function of thorough mixing and the distribution of fine-grained sediment. The imprint of historic inputs from New Almaden is evident on a finer scale in managed ponds in Lower South Bay: Hg concentrations in Bay surface water and sediment in adjacent managed ponds decline with distance from the Guadalupe River (Conaway et al., 2003; Miles and Ricca, 2010) and this has an effect on bioaccumulation in these habitats at a local scale. Multiple factors could explain the relatively high net MeHg production in the Lower South Bay. Potential drivers include increased primary productivity and anaerobic bacterial respiration, perhaps associated with large volumes of wastewater discharge, smaller subtidal Bay volume, and relatively long residence time, in comparison to other portions of the Bay (Conomos, 1979; Conaway et al., 2003).

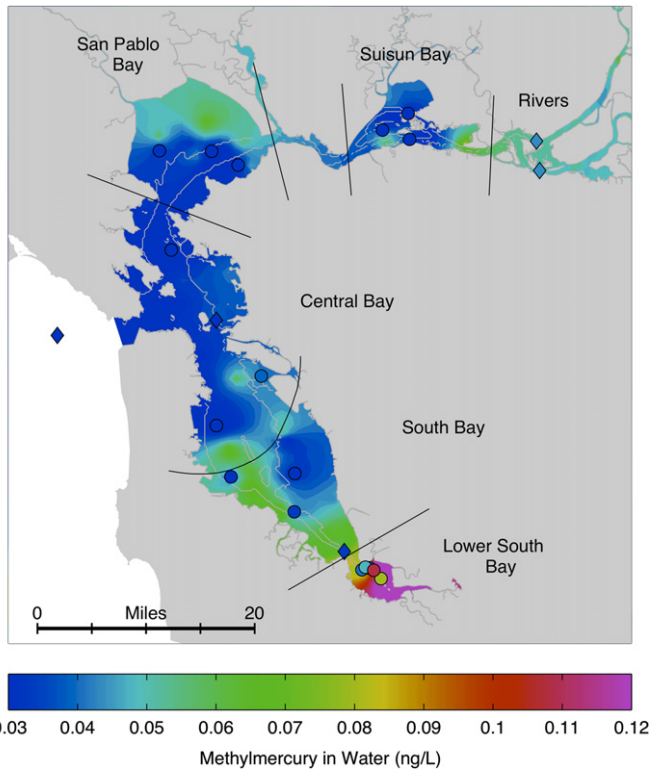

Fig. 2. MeHg in Bay surface waters. Map plot based on 97 RMP data points from 2006 to 2009. Data are for total MeHg. Colored symbols on map show results for samples collected in 2009. Circles represent random sites. Diamonds represent historic fixed stations.

To what extent, and at what time scale, reduction of Hg loading from New Almaden will result in reduced biota concentrations remains a subject of considerable uncertainty (Rothenberg et al., 2008). Hg is anticipated to remain elevated in sediment for many decades. Even relatively insoluble Hg forms such as cinnabar, metacinnabar, and calcines appear to be available to bacteria for methylation, so the substantial mass of Hg in sediment could constitute a sufficient pool available for net MeHg production and bioaccumulation long after source curtailment from the watershed.

5.2.2. Potential source control actions

Extensive efforts to reduce loads of Hg mining waste from New Almaden to the Bay have been underway for over a decade and

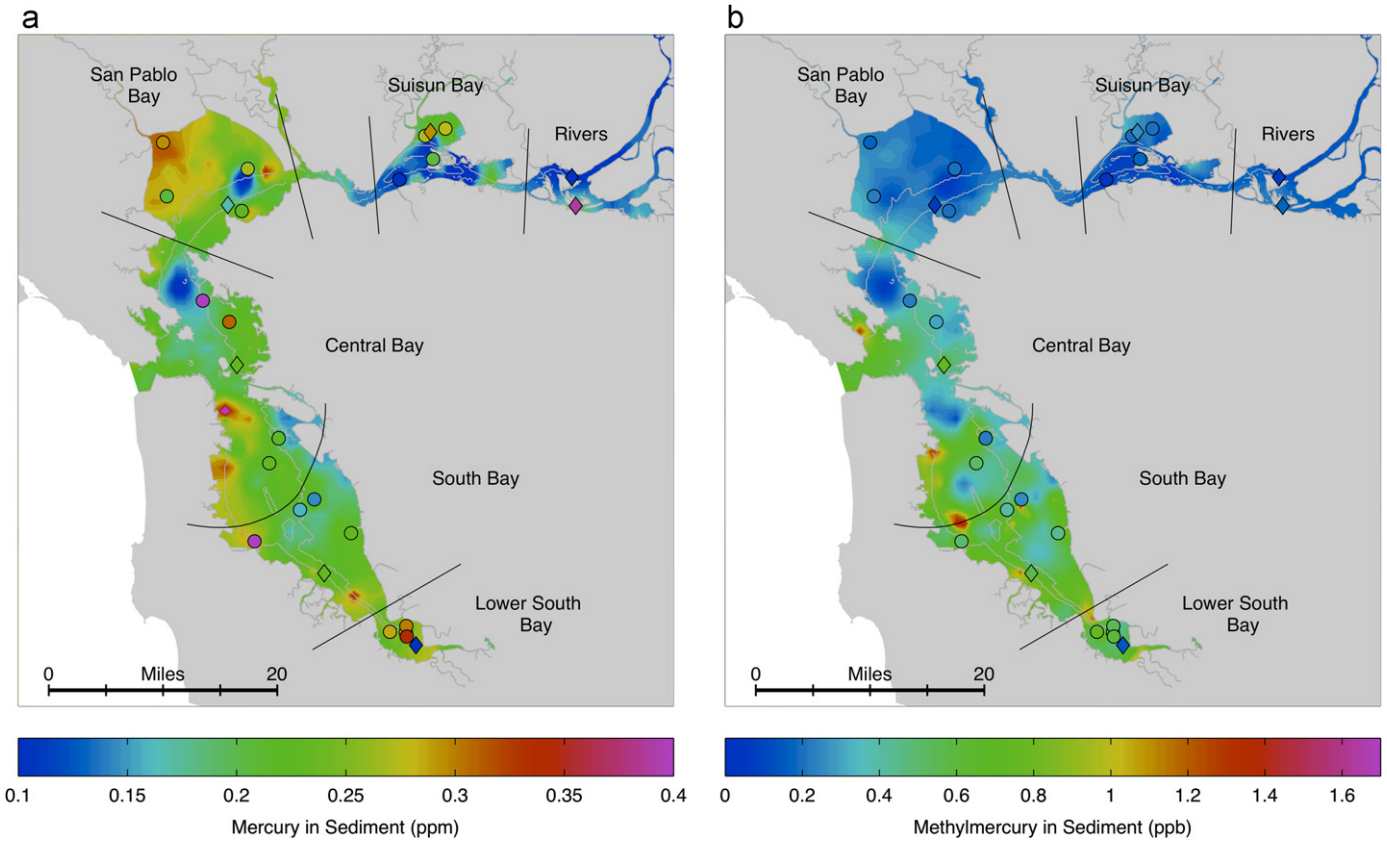

Fig. 3. THg and MeHg in Bay surface sediment. Map plots based on 378 samples collected in summer over an eight-year period from 2002 to 2009. Colored symbols show results for samples collected in 2009. Circles represent random sites. Diamonds represent historic fixed stations.

are planned to continue for at least another two decades. As mentioned above, Hg mining waste control actions will be phased so that Hg discharges from upstream will be eliminated or significantly reduced before downstream projects are undertaken. This phasing should prevent upstream sites from re-contaminating downstream sites-which previously happened at a mitigation site at the bottom of Guadalupe Creek, where prey fish accumulated high Hg levels after upstream control measures were implemented (SFBRWQCB, 2008).

The five largest processing areas and associated waste dumps at New Almaden (i.e., the most polluted mine sites) have already been cleaned up and the contaminated material has been placed in on-site landfills. It is cost-prohibitive to dispose of wastes in off-site hazardous waste landfills. The Guadalupe TMDL requires that erosion controls be implemented for numerous other sites at New Almaden by 2018. For example, Hg-contaminated calcines were used to pave dirt mine roads many decades ago. Improved management of these roads will reduce erosion of Hg-laden sediment. Additionally, proper grading and re-vegetation of uncontrolled waste dumps will reduce erosion rates.

From 2018 to 2028, the Guadalupe TMDL will target a severely polluted creek downstream of one facility where most of the New Almaden ore was processed. The banks of this downstream reach remain severely contaminated, are a continuing source to the Bay, and present a regulatory challenge because it is private, residential property. The current strategy relies on developing a cooperative effort among several local agencies and property owners and seeking outside funding to cover estimated costs of several hundred million US dollars for a comprehensive creek bank stability and habitat restoration project. Many other creeks that drain New Almaden are also polluted, but to a lesser extent, and these will be addressed opportunistically, through construction permits.

Within the Guadalupe River watershed, reservoirs polluted by New Almaden have exceptionally high fish Hg concentrations. Therefore, controlling net Hg(II)-methylation and MeHg bioaccumulation will be necessary measures for decades to come, until erosion from the mines is stopped and natural erosion of cleaner hillsides buries contaminated sediment in reservoirs.

5.2.3. *Key information gaps for Hg mining sediment*

One critical category of remaining information gaps pertains to MeHg cycling in reservoirs within the watershed (discussed further in Section 6.3.5). Another important information gap concerns trends in loading to downstream ecosystems. Monitoring is essential to track decreases in Hg discharges from New Almaden resulting from mining waste control actions at the mine and downstream sites. Such monitoring of management effectiveness is not a simple undertaking, because loads of Hg discharged from mine sites and downstream creeks are driven by infrequent, large storm events (Kirchner et al., 2011). However, measurements of Hg concentrations on suspended sediment are less variable and can provide evidence of effectiveness in spite of interannual climatic variability. Hg loads and concentrations discharged from the Guadalupe River have been intensively monitored over the past decade (McKee et al., 2010); this information can serve as a basis for evaluating trends in loads from the New Almaden region over time. Estimated annual Hg loads from the Guadalupe River from 2003 to 2010 have ranged from a minimum of 2.3 kg in 2007 to a maximum of 113 kg in

2003. Loads fluctuate greatly from year to year due to variation in rainfall intensity, water flow, and other factors.

5.3. Urban runoff

5.3.1. Linkage to impairment

Hg in urban runoff originates from a variety of sources, ranging from atmospheric deposition to improper disposal of products. The Hg loads that enter urban runoff all have similar isotopic signatures, since most Hg-containing products utilize refined elemental Hg, which is isotopically light and thus has similar composition as Hg from atmospheric sources (Gratz et al., 2010). The spatial trend of increasingly lighter Hg isotopes in sediment and fish moving away from the Lower South Bay suggests that the lighter isotopes contribute in proportion to their local presence in Bay sediment, so Hg from urban runoff is likely a portion of the MeHg produced and bioaccumulated in the Bay food web. Even in Alviso Slough, a heavily mine-impacted area, surface layers of core samples taken show a lighter isotope signature than deeper (presumably more mine-impacted) sections (Gehrke et al., 2011a), indicating the importance and influence of current Hg inputs from atmospheric and urban sources.

5.3.2. Potential control actions

Due to a long history of thousands of uses and various processes of dispersion, Hg is now spread widely across the urban landscape, and this broad distribution poses a challenge for management. However, there are key sources, source areas, and pathways that can be identified and provide opportunities to capture larger quantities of Hg and potentially have a greater influence on food web concentrations.

Measures to prevent Hg from entering stormwater runoff offer some potential for load reductions. The largest single pathway of Hg into urban stormwater in the Bay Area, contributing an estimated 51%, is atmospheric deposition (Fig. 4) (SFEI, 2010b). Another large source is Hg from electrical products (instruments, switches, thermostats, and fluorescent lighting), that accounts for an estimated 37% of the load to stormwater. With wind and vehicles moving dust and soils off of contaminated industrial lots onto roadways, spillage of Hg onto pavements during incorrect disposal or transport to recycling facilities, and the use of Hg in car lights (only banned recently in California), the main pathway for Hg entry into stormwater is via runoff from impervious surfaces. A combination of institutional controls (that change civic behavior and municipal operations), source controls (including correct disposal of products containing Hg), and careful application of best management practices (BMPs) during demolition and remodeling together have the potential to capture about 45% of the Hg load presently entering stormwater (SFEI, 2010b).

Stormwater loads of Hg can also be reduced via treatment controls after the Hg has entered the stormwater transport pathway. Treatment control is a challenge in the Bay Area, however, where, on average, rain occurs on just 60 days of the year and may periodically overwhelm the capacity of engineered controls. These rainy periods also account for over 90% of the annual transport of Hg and other contaminants (McKee et al., 2010; Gilbreath et al., 2012). Although climate change models for California suggest small increases in annual precipitation, the increase may occur in the form of less frequent but more intense rainfall (Cayan et al., 2008; Trenberth, 2011). However, there are some indications that the coast range may experience an increased frequency of rainfall (Pan et al., 2011) that could result in both increased annual runoff as well as increased peak flows, making treatment control even more challenging. Bio-retention control, found in many low-impact development projects, shows promise (David et al., 2011), with design, implementation, and maintenance all being important components of successful application. Given the association of Hg with fine sediment particles, treatment controls that use settling alone are unlikely to achieve cost-effective load reductions (Yee and McKee, 2010). Treatment of runoff from contaminated industrial areas at municipal wastewater plants during dry weather and first flush winter storms is being tested on a pilot-scale in the Bay Area, with the hope of

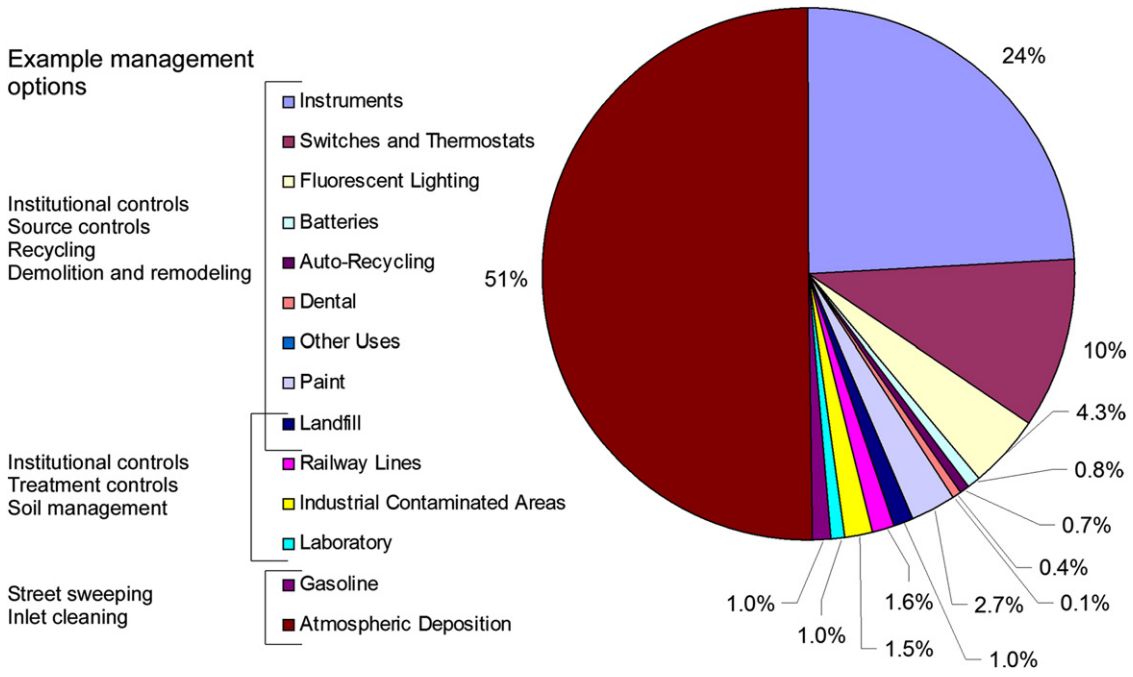

Fig. 4. Estimated mass contributions of Hg entering storm drains and creeks in the Bay Area. Levels of confidence in the quantification differ for each section of the pie. The order of confidence for Hg from greatest to least is as follows: high—switches and thermostats, fluorescent lighting, and instruments; medium—dental, landfill, paint, laboratory, atmospheric deposition, batteries, gasoline, other uses (mainly cell phones, LCD TVs and other modern use devices), and railway lines; low—industrial contaminated areas and automobile recycling.

capturing highly-contaminated small volumes of runoff without having to build additional treatment plant capacity.

Consistent with accumulated local knowledge on the largest sources and pathways of Hg, a San Francisco Bay municipal regional stormwater discharge permit issued in 2009 contains specific provisions for control of Hg. These include increased effort to collect and recycle Hg-containing devices and equipment, identification of contaminated areas for abatement, and enhanced municipal sediment removal, along with investigations of the effectiveness of on-site stormwater retrofit treatment, treatment in wastewater plants, and bio-retention.

Information on the speciation of Hg in urban runoff is valuable in evaluating control options and may also be useful in selecting watersheds for actions. Most of the stormwater sampling of local watersheds has focused on THg concentrations, but a subset of samples in several urban tributaries has also been analyzed for dissolved Hg in the filtered (<0.45 μm) fraction. In a 100% urban tributary, on average, the dissolved phase was 8% of THg, with a maximum of 59% during low flow conditions in spring (Gilbreath et al., 2012). A large dissolved THg component during low flows poses a treatment challenge.

Some local data on tributary concentrations of MeHg have been collected for urban and mixed land use watersheds, with MeHg concentrations averaging around 0.5–1.5% of THg (e.g., Gilbreath et al., 2012). This is generally slightly higher than ratios found in the Bay water column and sediment (0.1–1%). In dry weather however, up to 15% of the THg load enters the Bay as MeHg, and MeHg may be an even greater portion of the THg load in agriculturally dominated watersheds (Dean and Mason, 2007). In one urban watershed, reactive Hg ($Hg(II)_R$-the fraction of inorganic Hg(II) that is available to methylating bacteria) ranged between 0.3 and 2.1% of THg (Gilbreath et al., 2012).

Once Hg enters the Bay, partitioning and speciation generally become less important. New inputs of Hg(II) will rapidly partition to available fine particulate and organic matter, which can then settle out and persist for decades in bottom sediment. These new inputs then become part of the overall sediment Hg pool available for Hg(II)-methylation and subsequent MeHg bioaccumulation. However, in the immediate vicinity of the mouths of small tributaries and in semi-enclosed embayments, urban runoff inputs of MeHg and $Hg(II)_R$ may contribute a significant portion of the MeHg present locally (Yee et al., 2011). Evaluating the degree of concern over risks to sensitive species in the local vicinity of these inputs versus more general concern about Bay-wide impairment can help in determining whether to quantify MeHg and $Hg(II)_R$ loads from specific tributaries.

5.3.3. Key information gaps for urban stormwater

Despite considerable advances in understanding over the past decade, there are still a number of key information gaps related to management of Hg loads from urban runoff. The present regional urban stormwater loading estimate of 160 kg THg in the Hg TMDL for the Bay (SFBRWQCB, 2006) is highly uncertain because it was determined by multiplying average suspended sediment loads (310,000 metric t) by Hg concentrations in bottom sediment from tributaries. A more recent estimate of suspended sediment load entering the Bay from local small tributaries is about 3 times greater (Lewicki and McKee, 2010). In addition, the amount of data on urban soil and bed sediment Hg concentrations has doubled (Yee and McKee, 2010) and there have also been many more measurements of Hg in storm water (e.g., Gilbreath et al., 2012). Therefore, there is increasing information available to identify which urban watersheds are delivering disproportionately large loads to sensitive areas on the Bay margin. There is a reasonable understanding of the timing and speciation of Hg loads from these types of watersheds, but only a rudimentary understanding of the linkage of these loads to key biological cycles in wetlands and mudflats on the Bay margin. The habitats where these inputs enter the Bay may be as important as the magnitude and speciation of incoming loads. As the most influential watersheds are identified, another key information gap is the most cost-effective suite of management practices to reduce loads of Hg or other constituents affecting net MeHg production. Modeling of Hg fate in Bay receiving waters is needed to inform decisions on the best way to apply controls. Monitoring to determine the effectiveness of control measures will also be essential.

In response to these key information gaps and uncertainties, the Bay Hg TMDL and the municipal regional stormwater discharge permit call for continued monitoring of loads and gathering of other information. To identify the watersheds which contribute most to Bay impairment, a recent reconnaissance study of 16 urban drainages found relatively high concentrations of Hg on particles in runoff from watersheds with older industrial land use (McKee, unpublished data). Further reconnaissance of this type would be valuable in prioritizing among the hundreds of small local watersheds that drain to the Bay. To estimate loads to the Bay at a regional scale, a model that combines rainfall with either land use or imperviousness based runoff coefficients with event mean concentrations associated with land use or source areas is being developed (Lent and McKee, 2011). Load data are also being collected in specific watersheds using a turbidity surrogate methodology (Quémerais et al., 1999; Wall et al., 2005; Gilbreath et al., 2012).

Continued acquisition of Hg speciation data (dissolved, methyl, and reactive) will enhance the present understanding based on just a few local datasets and literature from elsewhere. Ideally these data would be acquired as models are developed that quantify the link between management actions in the watersheds, resulting loading changes, and reduced biological uptake in sensitive areas of the Bay margin.

To evaluate long-term (decadal-scale) trends, selected watersheds where management actions are occurring will be monitored periodically to track concentrations of Hg on sediment particles. To evaluate the projected impacts of management actions, pilot projects will be conducted to find and abate contaminated soil and sediment in stormwater conveyances and to evaluate the effectiveness of Hg removal through enhanced sediment management including street sweeping and inlet maintenance. In addition, municipalities will evaluate the effectiveness of on-site treatment installations and further investigate Hg capture through diversion of dry weather flow and first-flush urban stormwater to municipal wastewater treatment plants. In addition to the immediate benefits from these activities, these efforts will help determine the scope and focus of further actions in subsequent permit terms (2014 and beyond).

Although the Bay TMDL addresses Hg issues on an ecosystem-wide basis, managers are initially attempting to identify smaller and potentially more manageable portions of the ecosystem that are most critically impacted and where a clear linkage to specific pathways exists. These cases may also present opportunities to test management actions at a scale where observable effects are more easily measured.

Studies of stable Hg isotopes in Bay sediment and fish have demonstrated utility in differentiating between various sources of Hg (Gehrke et al., 2011a,b). It may be worthwhile to investigate the isotopic variability of sources of urban runoff to ascertain whether isotopes could help identify which are most important and which are most prone to Hg(II)-methylation and MeHg bioaccumulation.

5.4. Atmospheric deposition

5.4.1. Linkage to impairment

San Francisco Bay represents an ecosystem where available data do not indicate impairment due primarily to atmospheric sources. Globally, atmospheric deposition is established to be a primary source of bioavailable Hg to water bodies, and has been directly linked to ecosystem and human health impairment. As discussed in the mining section, Hg stable isotopes are most consistent with a Hg mine-dominated signal in the South Bay and either atmospherically deposited Hg or elemental Hg(0) from gold mining or modern products and industrial processes in the North Bay (Gehrke et al., 2011a, 2011b). However, even though mining inputs appear to have a primary role, the influence of atmospheric deposition on future rates of MeHg accumulation in the food web is a critical question for managers. In addition to direct deposition to Bay Area water bodies, analysis of wet and dry deposition of Hg in the Bay Area indicated that atmospheric deposition (Tsai and Hoenicke, 2001) is a substantial component (about one-third) of ongoing watershed loads for many areas of the Bay.

5.4.2. Potential control actions for atmospheric deposition

China is currently the world's largest Hg emitter (Dastoor and Larocque, 2004, Pacyna et al., 2010), and monitoring studies have detected enhanced Hg deposition on the west coast of North America (Jaffe et al., 2005). Regional-scale modeling suggests that around one-fourth of North American air Hg concentrations (mostly as Hg[0]) are from emissions in Asia (USEPA, 1997a, 1997b; Seigneur et al., 2004; Task Force on Hemispheric Transport of Air Pollution, 2010). Regulators in California have little control over these sources, but federal officials may be able to negotiate limits through international agreements. However, global Hg transport models suggest that changes in Hg deposition in the Bay Area in response to reductions of Asian emissions would be much smaller than the percent change in emissions (Task Force on Hemispheric Transport of Air Pollution, 2010).

Reduction of local atmospheric emissions does not appear likely to yield significant reductions in MeHg in Bay Area aquatic food webs. As an upper bound estimate of the benefit of reducing atmospheric Hg inputs, Tsai and Hoenicke (2001) estimated that 27 kg THg yr^{-1} are deposited directly on the Bay's surface, and 55 kg yr^{-1} are deposited in the local watersheds draining to the Bay. About one-third of atmospheric Hg deposition in the western USA is from "natural" sources (Seigneur et al., 2004), so total elimination of atmospheric deposition is not possible. Global modeling studies have indicated that Hg from non-USA global anthropogenic and natural sources constitutes about two-thirds of atmospheric Hg deposition in North America, and about 70–90% of deposition in the Bay Area (Seigneur et al., 2004; Task Force on Hemispheric Transport of Air Pollution, 2010). The Bay Area has no sources immediately to its west, so local contributions (which may include sources outside of the nine Bay Area counties) are likely to be smaller than in other parts of the USA. However, several studies suggest that some local contribution is likely. Comparisons of other urban areas to nearby upwind rural locations have found measurably higher urban concentrations and deposition (Landis et al., 2002; Rutter et al., 2008), indicating ground-level contributions from regional urban sources. In addition, nearby coastal wet deposition was generally lower than that in the urbanized Bay area (Steding and Flegal, 2002). Sanders et al. (2008) found higher Hg concentrations in sediment cores from lakes in inland California compared to a lake on the California coast, and attributed the elevated concentrations at the inland lakes to urban and industrial emissions and legacy contamination from mining.

The potential for further reduction of local Hg emissions through controls on stationary sources is limited. The California Air Resources Board (CARB) estimated that emissions from stationary point sources in the nine Bay Area counties totaled about 200 kg yr^{-1} in 2008 (CARB, 2008). The two largest stationary Hg air source categories in the Bay Area are the five petroleum refineries located in the North Bay and a cement plant in the South Bay (USEPA, 2005). In 2005, the petroleum refineries directly measured air emissions totaling about 20 kg yr^{-1}, much less than the earlier emissions inventory (ERM, 2009) and CARB estimates. Emissions from the cement plant in South Bay have not been directly measured, but a study conducted in 2009 found a possible impact on local atmospheric Hg concentrations, in particular for reactive gaseous Hg and particulate Hg concentrations at a nearby site (Rothenberg et al., 2010b). Atmospheric wet deposition also showed local impact of plant emissions with greatly diminished deposition at a site in the immediate nearfield (1 km away) of the plant during one month of plant closure for maintenance (Rothenberg et al., 2010b). In contrast, however, recent stormwater sampling in the nearby Stevens Creek watershed did not indicate elevated Hg concentrations (McKee, unpublished data). The cement plant is now subject to more stringent USEPA regulation that will cut emissions from this facility by about 90% by 2014 (BAAQMD, 2010).

Other local Hg air sources are smaller, such as gasoline (about 5 kg yr^{-1} from combustion of automobile fuel (Conaway et al., 2005)), and crematoria (about 12 kg yr^{-1} from dental amalgam (BAAQMD, 2003)). The American Dental Association has reported a 30% decrease in the number of Hg amalgam fillings used between 1990 and 1999 (Berthold, 2002); if this trend continues crematoria emissions will likely decrease proportionally.

Given the dominance of non-local sources and other factors, controlling local Hg air emissions has not been a top priority for Bay water quality regulators. Regulation of local air sources is complicated by the fact that water quality regulators do not directly regulate air sources. CARB's allowable air emissions are based almost exclusively on protection of public health based on human exposure via inhalation. Water quality regulators would need to provide compelling evidence that local air sources of Hg were substantially contributing to water quality impairments before air quality regulatory authorities would be able to require emission reductions.

Atmospheric deposition (combined from global and local sources) likely does contribute significantly to loads of Hg and subsequent MeHg accumulation in Bay Area aquatic food webs. Although legacy mining sediment is the dominant source of Hg in the Guadalupe watershed and Lower South Bay, for other watersheds loads from atmospheric deposition may be of a similar magnitude to loads from urban and industrial uses of Hg. Thus, decreases in atmospheric Hg pollution would reduce both direct deposition and indirect loads to the Bay from deposition in the watershed. Although in the short-term efforts are best directed at more readily controllable sources associated with mining legacies in the watershed and urban runoff, if insufficient progress is made toward reducing impairment through those efforts, additional efforts to control atmospheric Hg emissions or co-factors affecting deposition (e.g., atmospheric photochemistry of other pollutants) should be considered.

5.4.3. Key information gaps for atmospheric deposition

Information gaps for atmospheric sources remain, especially concerning the extent to which long-range atmospheric Hg transport contributes both to local atmospheric deposition and MeHg accumulation in local food webs. Resolving these questions could be important because reductions in global Hg emissions

may be difficult to achieve in the short-term, and increases in emissions are possible (Pacyna et al., 2010), and management of other sources may appear less effective as a result. Studies that can discriminate between current atmospheric deposition and legacy watershed Hg sources—using chemical tracers of Asian coal, sophisticated Hg isotope studies, deposition monitoring upwind and downwind of local Hg air sources, or other approaches—could be very valuable in this regard.

Locally-derived atmospheric oxidants may be more controllable, potentially affecting atmospheric Hg speciation (Rothenberg et al., 2010a) and thus local atmospheric deposition of Hg through control of the fraction that adsorbs to surfaces and settles out with particulate matter. However, this indirect linkage makes it unlikely that specific actions will be taken with decreased Hg deposition as a goal; rather, attempts to control atmospheric oxidants primarily as risks for human inhalation exposure may have side benefits of reducing local Hg deposition and subsequent ecosystem impacts, even if those were not primary driving factors in the decision-making. Available information from the literature and local data on atmospheric deposition may provide sufficient technical support for understanding the likely impacts of control on atmospheric oxidants.

5.5. Other sources and pathways

Other sources and pathways are considered to be smaller contributors to MeHg accumulation in the food web or to offer fewer options for control.

5.5.1. Legacy Hg and gold mining in the Central Valley watershed

The Hg load conveyed to the Bay by the Sacramento and San Joaquin Rivers through the Delta, which drain Sierra Nevada foothills and Coast Range mountains contaminated by Hg and gold mining, is among the largest inputs of THg to the Bay in terms of annual mass load—estimated by the TMDL to be 440 kg yr^{-1} (SFBRWQCB, 2004). This load estimate was derived by multiplying the average concentration of Hg on suspended sediment in these rivers (0.26 ppm) by the estimated total suspended sediment load (1.6 Mt—SFBRWQCB, 2004). This Hg concentration on suspended sediment is similar to the TMDL sediment Hg target of 0.2 ppm and is below the median Hg concentration in Bay surface sediment (0.3 ppm). This Hg pathway therefore represents a large amount of moderately contaminated sediment entering the Bay.

A more detailed and more recent estimate prepared by McKee et al. (2006) suggests that the suspended sediment load to the Bay from the Delta averages 1 Mt—35% less than the estimate used to compute the TMDL load estimate. Combining this with the improved monitoring data on Hg loads entering the Bay via the Delta (David et al., 2009), which indicate an average annual Hg load of 260 kg, suggests particle concentrations average about 0.23 ppm. Moreover, this sediment load may decrease further due to the cessation of the hydraulic mining sediment pulse, increased sediment trapping in reservoirs, smaller floods, and enhanced bank protection (Schoellhamer, 2011). On the other hand, the anticipated increase in frequency of intense storms associated with climate change may act to increase floods and sediment mobilization (McKee et al., submitted). Overall, it is anticipated that sediment entering the Bay from the Central Valley should become less contaminated by Hg as control measures targeting the Sierra foothills mining legacy sources are implemented.

5.5.2. Industrial and municipal wastewater

The combined THg load from the approximately 60 wastewater treatment facilities ringing the Bay constitutes less than 2% of the overall load to the Bay (SFBRWQCB, 2004). These point sources have been subject to strict end-of-pipe concentration-based effluent limits for decades. Municipal wastewater facilities, in particular, have successfully reduced their Hg loads in the last five years to the point where they are already discharging below their TMDL mass allocation (about a 40% mass reduction). These reductions have been achieved through a combination of effective plant operation and source control efforts aimed at the largest sources in their service areas. For example, there have been aggressive efforts, with a target of 85% compliance, to make sure that dental offices have separators to prevent amalgam Hg from entering the sanitary sewers.

5.5.3. Non-urban runoff

The Hg concentration on suspended sediment draining non-urban watersheds (about 0.06 ppm) is well below the TMDL suspended sediment target concentration of 0.2 ppm. In fact, these concentrations are similar to Hg concentrations on buried sediment that pre-dates Hg and gold mining (Hornberger et al., 1999; Conaway et al., 2004), so no control measures are anticipated for these uncontaminated non-urban watersheds.

5.5.4. Dredged material disposal

Dredged material disposal activities generate an overall net loss of Hg from the Bay, because a substantial portion of the dredged material is used as fill material for wetland restoration or is transported to an open-ocean disposal site (SFBRWQCB, 2004). Disposal of dredged material is unlikely to be releasing new Hg into the system but instead removes (when disposed out of the Bay) or re-distributes Hg within the Bay. In response to sea level rise and reduced sediment supply from the Delta, regional managers will likely increasingly seek opportunities for dredged material use in local wetland restoration, levee repair, and other "beneficial re-uses" rather than ocean disposal. Dredged material already routinely undergoes testing to determine appropriate disposal methods, so material from more contaminated sites (i.e., greater than in-Bay disposal limits, currently 0.47 ppm Hg dry weight) can be disposed of or reused (e.g., at ocean, upland, or landfill sites) in a manner that makes it unavailable to Bay biota.

5.5.5. Key information gaps for other sources and pathways

Wastewater inputs are small relative to other Hg loads in most other areas of the Bay, so there are few needs for additional data. Similarly, sediment loads from the Delta already have concentrations near the Bay TMDL target, so aside from periodic measurement to assure continued improvement, little additional information is needed. Regulators do need to know how to use dredged material safely as fill for wetland restoration so as not to cause increased food web uptake. Although the most contaminated sediment can be excluded from use in potentially sensitive habitats, more moderately contaminated sediment (i.e., similar to Bay ambient concentrations) may be best managed by use in habitat restoration while addressing other factors influencing bioavailability and bioaccumulation.

6. Fate processes, internal net production of MeHg, and potential controls

6.1. General mass budgets for Hg and MeHg

Much of the concern about Hg in the Bay is derived from past mining in New Almaden and its historic use in gold mining in the Sierra Nevada. During the period of peak production between 1850 and 1890, annual Hg production from New Almaden was in excess of 500,000 kg (up to 1.6 million kg at its peak) for most

years (Bailey and Everhart, 1964), with much lower production ($<100{,}000$ kg yr^{-1}) during later periods of renewed demand for Hg in World War II and in the 1960s (Cargill et al., 1980). An estimated 4.5 million kg of Hg was released from placer gold mining operations in California, of which 80 to 90% was in the Sierra Nevada (Churchill, 2000), with another 1.3 million kg lost in gold lode ore milling operations. These historical uses and releases created a large inventory of Hg contamination in the Bay.

Some locations in the subtidal North Bay (consisting of San Pablo and Suisun Bays) and Central Bay (Hornberger et al., 1999) and tidal wetlands in Lower South Bay (Conaway et al., 2004) have been found to contain elevated Hg concentrations in deep cores, with subsurface Hg profiles indicating anthropogenic releases of Hg beginning in the late 1800s. However, strong peaks were found in only a handful of the subtidal sites, suggesting that much of the Hg either dispersed to yield widespread but lower concentrations, washed out of the Bay to the ocean, never reached the Bay (remaining in upstream watersheds), or some combination of these. Where Hg peaks were found, maximum concentrations in both subtidal and wetland cores were associated with layers deposited during the 1940s and later periods, suggesting either similar delays in delivery from the mining districts despite the vastly different sizes of the North Bay and South Bay watersheds (the Sacramento and San Joaquin river watersheds for Hg from gold mining in the Sierra Nevada, and the Guadalupe River watershed for Hg mining in New Almaden), or a greater contribution from more recent uses and releases. Remixing of sediment after it enters the Bay or diversion of flows into the South Bay salt ponds are also possible explanations for the patchy distribution of Hg in buried sediment.

A more recent survey of subtidal and tidal marsh cores yielded similar results (Yee, 2009). Most cores showed more recent THg concentrations being elevated compared to pre-industrial background levels, but with maxima around or after the 1950s, and concentrations in deeper sections of subtidal cores similar to or only slightly higher than current surface sediment concentrations. Based on these cores, the inventory of excess Hg (over pre-industrial levels) in the Bay is about 320,000 kg, with 40,000 kg in the top 11 cm. Overall, this is a small percentage of the THg estimated to have been lost in Gold Rush era mining operations. Some of the Gold Rush Hg has passed through the Bay to the ocean, but much has been delayed in arriving due to sedimentation in the floodplains of upstream tributaries (Singer et al., 2008).

A regional mass balance of Hg (MacLeod et al., 2005) combining Delta, local watershed, and point source loads estimated that 740 kg of Hg enters Bay waters annually, a small percentage of the sediment inventory. A similarly small mass (510 kg) was estimated to leave the Bay through advection out the Golden Gate. More recent data (Section 4) suggest that loads from the Delta and local watersheds are lower than previously estimated, but even if new inputs ceased entirely, it would be decades before the current THg inventory in the Bay is cut in half. The other major loss pathway in the Hg mass balance was burial of surface sediment below the biologically active layer. Although continued supply of sediment from the Delta and local watersheds could theoretically bury contaminated surface sediment, unless the newly deposited sediment is appreciably cleaner than that currently in place, the problem is likely to continue indefinitely into the future. Furthermore, declines in sediment supply appear to limit the prospects for burial as a substantial pathway for removal.

Regional mass balance models for MeHg indicate that internal production accounts for most of the inventory of MeHg in the Bay. MacLeod et al. (2005) estimated loads of MeHg entering the Bay using data on concentrations in Delta outflow (Choe and Gill, 2003) and postulated an internal source based on observed steady state concentrations higher than could be accounted for from external loads. A subsequent MeHg mass balance (Yee et al., 2011) considered loads from additional non-point sources, such as local tributaries and tidal marshes, as well as taking into account Hg(II)-methylation and MeHg-demethylation rates for subtidal environments in North Bay (Marvin-DiPasquale et al., 2003) and applying them to the rest of the Bay. Ambient concentrations and inventories of MeHg in both Bay sediment and water were very sensitive to (and almost linearly dependent on) Hg(II)-methylation and MeHg-demethylation rates, particularly in sediment, where the bulk of the MeHg inventory is found. Although in limited areas of high water and sediment throughput, such as fluvial channels, external loads of MeHg will play a larger role, for most areas of the Bay long residence times of water and sediment compared to in-Bay Hg(II)-methylation and MeHg-demethylation rates result in a small influence of external loads on the local MeHg mass balance.

6.2. Internal net production of MeHg

Net production of MeHg within the Bay is the dominant source of MeHg that enters the food web. Net production of MeHg is the result of Hg(II)-methylation and MeHg-demethylation, and information on how the rates at which these processes occur vary across Bay habitats is useful for understanding patterns in food web uptake and risk, and in evaluating options for controlling internal net MeHg production. The dynamics of MeHg production, and consequently opportunities for managers to intervene, vary considerably among the Bay habitat categories (open Bay, tidal marsh, and managed pond).

Extensive studies by Marvin-DiPasquale and coworkers have documented variation in Hg speciation and the activity of Hg(II)-methylating bacteria in multiple habitats throughout the Bay and its watershed (Grenier et al., 2010; Kieu, 2004; Marvin-DiPasquale et al., 2003, 2007, 2009a,b, 2011; Marvin-DiPasquale and Cox, 2007; Topping et al., 2004; Windham-Myers et al., 2009, 2010a, 2010b; Yee et al., 2008). The approach used in these studies of benthic MeHg production in the Bay (and elsewhere) is based on three assumptions: (1) the activity of Hg(II)-methylating bacteria (k_{meth}) is a primary driver of benthic MeHg production; (2) the availability of inorganic Hg(II) to those bacteria (assessed as tin-reducible 'reactive' mercury ($Hg(II)_R$)) is a second primary driver; and (3) spatial and temporal variation in both benthic MeHg concentrations and production rates are best understood by the examination of independent k_{meth} and $Hg(II)_R$ data, both of which are used to calculate MeHg production potential (MPP) rates, and both of which vary as a function of habitat-specific geochemical and physical conditions.

Drawing upon data from the studies cited, as well as unpublished data collected by Marvin-DiPasquale and coworkers, a graphical analysis was conducted on k_{meth} and $Hg(II)_R$ data for surface sediment sampled throughout the Bay between 2000 and 2010. The data were grouped into two regions (North and Central Bay [combined] and South Bay) and four sub-habitat types (open Bay [subtidal and mudflat], tidal marsh plain, tidal marsh slough, and managed pond), resulting in seven unique region/habitat categories (no managed pond data were available for the North/Central Bay region). The complete data set was not normally distributed, thus a non-parametric approach (quartile distribution) was used to assess the central tendency of the various Hg parameters in each region/habitat category. The 25–75% interquartile range of k_{meth} and $Hg(II)_R$ data for each region/habitat type was plotted and compared to the median values for the complete dataset (Fig. 5). The median k_{meth} and $Hg(II)_R$ values for the complete dataset bisect the X and Y axes and result in four

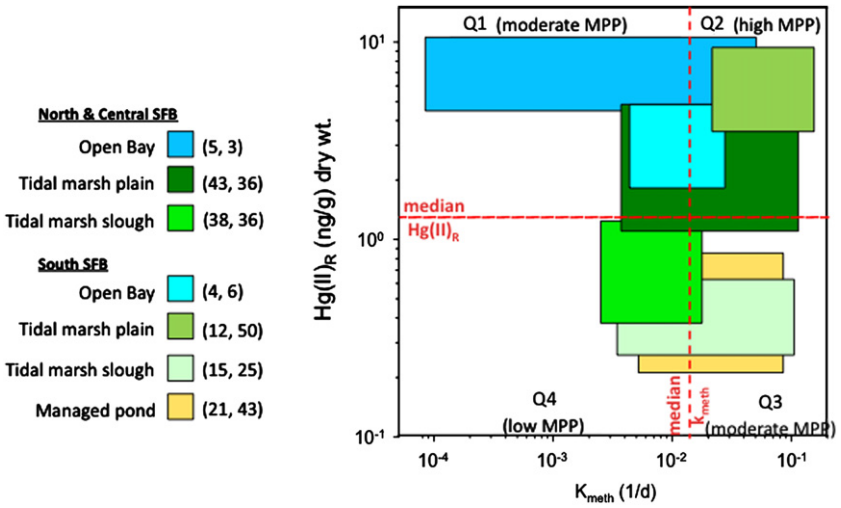

Fig. 5. Hg methylation rate constant (k_{meth}) versus inorganic 'reactive' Hg ($Hg(II)_R$) concentration for surface sediment collected throughout San Francisco Bay, grouped by region (North and Central Bay; South Bay) and habitat type. Each box width and height represents the 25–75% quartile interval for k_{meth} and $Hg(II)_R$, respectively, of the data for a region/habitat grouping. The vertical and horizontal dashed lines represent the median k_{meth} and $Hg(II)_R$ values for complete dataset, dividing the *X*–*Y* space into four quadrants (Q1 thru Q4). MeHg production potential (MPP) is calculated as a function of k_{meth} and $Hg(II)_R$, measured independently. Q1 reflects a zone of moderate MPP (low k_{meth} and high $Hg(II)_R$); Q2 a zone of high MPP (high k_{meth} and high $Hg(II)_R$); Q3 a zone of moderate MPP (high k_{meth} and low $Hg(II)_R$); and Q4 a zone of low MPP (low k_{meth} and low $Hg(II)_R$). The number of observations for each region/habitat specific dataset is given to the right of the color coded boxes in the legend (*X*,*Y*). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

quadrants defined as: Q1—low k_{meth} and high $Hg(II)_R$, a zone of moderate MeHg production; Q2—high k_{meth} and high $Hg(II)_R$, a zone of high MeHg production; Q3—high k_{meth} and low $Hg(II)_R$, a zone of moderate MeHg production; and Q4—low k_{meth} and low $Hg(II)_R$, a zone of low MeHg production. These data indicate that South Bay tidal marsh plains (vegetated zone) tend to have high MPP (Q2). North/Central Bay tidal marsh plains straddle the range of moderate to high MPP, with a wide range of k_{meth} values, but generally high concentrations of $Hg(II)_R$ (Q1 and Q2). North/Central Bay tidal marsh sloughs tend to have low MPP. Open Bay (subtidal) regions tend to have moderate MPP (Q1), with high $Hg(II)_R$ concentrations, but generally low to median rates of microbial activity (k_{meth}). Managed ponds and tidal marsh sloughs in the South Bay straddle the range of moderate to low MPP (Q3 and Q4), with a wide range of k_{meth} values, but generally low concentrations of $Hg(II)_R$. This last result may seem counter-intuitive, as South Bay sloughs and former salt ponds have some of the highest THg concentrations in the ecosystem (e.g., median values of 420 and 530 ng g^{-1} dry weight, respectively, compared to a median value of 250 ng g^{-1} for the South Bay 'open-Bay' habitat), based on the same dataset. However, only a small fraction of the THg in these two south Bay habitats was present as $Hg(II)_R$ (median values of $< 0.1\%$ $Hg(II)_R$ for both tidal sloughs and salt ponds) compared to the South Bay tidal marsh plains (median = 1.9% of THg as $Hg(II)_R$) and open-water habitats (median = 1.3% of THg as $Hg(II)_R$). This order of magnitude difference in % $Hg(II)_R$ among South Bay habitat types is at least partially due to the fact that the slough and pond sediment tends to be more chemically reducing than the open-Bay and marsh plain sediment, and $\%Hg(II)_R$ has been shown to be positively correlated with the sediment redox status and negatively correlated with measures of solid phase reduced-sulfur compounds (Marvin-DiPasquale et al, 2009a,b). Further, since almost all of the slough samples came from Alviso Slough and the ponds have been largely hydrologically isolated from the rest of Bay for many decades, the THg signal in these two habitats likely reflects Hg largely originating from the New Almaden mining district (e.g., associated with fine calcines), which may be less chemically available to the Hg(II)-reduction assay. In contrast, the more contemporary THg (e.g., from urban runoff or atmospheric deposition) is likely an important component of open-Bay and tidal plain surface sediment, and may be more 'available' as assessed by the $Hg(II)_R$ assay.

MeHg-demethylation is also an important process that can be expected to vary regionally and across habitat types. However, far fewer empirical data are available on these processes and the conditions that drive MeHg-degradation in the Bay. And while rate constants for MeHg degradation (k_{deg}) in sediment have been measured via radiotracer approaches, there is no comparable metric for the pool of total MeHg in sediment that is most readily available for microbial degradation (Marvin-DiPasquale et al., 2000, 2003; Marvin-DiPasquale and Agee, 2003), which points to an important area for future research.

A similar statistical analysis as presented above for k_{meth} and $Hg(II)_R$ was used to examine THg and MeHg data for the same seven region/habitat categories (Fig. 6). However, in this case qualitative categories of low, moderate and high were calculated from the percentile distribution of the complete data set, based on three percentile bins: low- $< 33\%$; moderate-33–67%; and high- $> 67\%$. In addition to the datasets from Marvin-DiPasquale and co-workers summarized in Fig. 5, 744 more THg and 438 more MeHg data points collected between 1993 and 2010 were added to the analysis for subtidal regions throughout the North, Central, and South Bay, as well from as South Bay marsh sloughs (SFEI, 2012).

One prominent feature of this plot (Fig. 6) is a general increase in MeHg with increasing THg across the different habitat categories. However, this does not necessarily imply a cause and effect relationship, as many factors are known to control MeHg production and concentrations. This apparent positive relationship between THg and MeHg concentration in sediment may have more to do with habitat differences in labile organic matter loading to surface sediment (affecting k_{meth}) and the pool size of $Hg(II)_R$. Coupled with knowledge regarding dominant Hg sources (e.g., cinnabar mines in the South Bay versus a mix of sources in the North Bay) and relative amounts of organic loading in the various sub-habitats (high in the tidal marshes and managed ponds, and lower in the open Bay and tidal sloughs), the summaries presented in Figs. 5 and 6 provide a foundation for understanding Hg(II)-methylation potential across key habitats of the ecosystem.

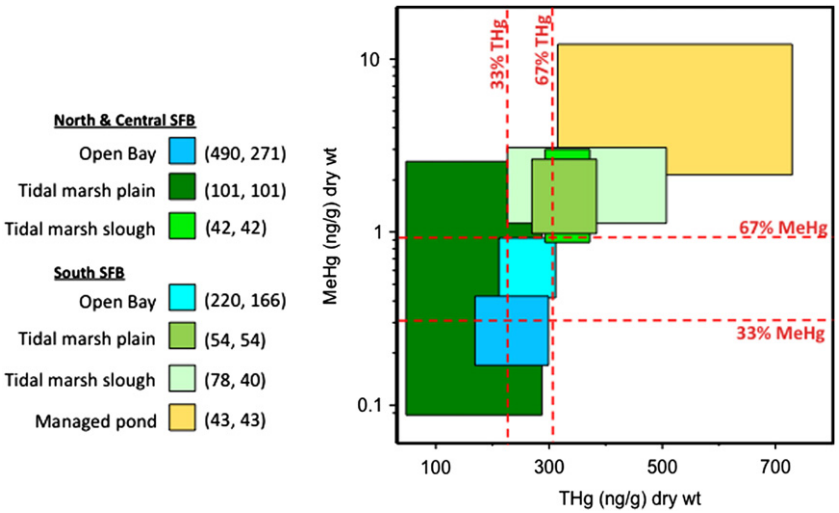

Fig. 6. THg versus MeHg concentration for surface sediment collected throughout San Francisco Bay, grouped by region (North and Central Bay; South Bay) and habitat type. Each box width and height represents the 25–75% quartile interval for THg and MeHg of the data for that region/habitat grouping. The vertical and horizontal dashed lines represent the 33rd and 67th percentiles for the complete data set, allowing THg and MeHg concentrations to be qualitatively described as low ($<33\%$), moderate (33–67%) or high ($>67\%$). The number of observations for each region/habitat specific is indicated to the right of color coded boxes in the legend (*X*,*Y*). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6.2.1. Open Bay

Sediment THg and MeHg concentrations in the open Bay (subtidal and mudflats) portions of the North/Central Bay are low to moderate, while sediment THg and MeHg concentrations in the South Bay are moderate (Fig. 6). In addition to slightly higher THg concentrations in the South Bay, this regional difference in MeHg concentration may be driven by higher levels of phytoplankton production and deposition in South Bay (Cole and Cloern, 1984; Cloern, 1996; Cloern and Dufford, 2005), which would tend to increase benthic microbial activity (i.e., k_{meth}). While k_{meth} data for the open Bay are limited for both regions, the 25–75% interquartile range for k_{meth} is indeed generally lower in North/Central Bay (Fig. 5). This hypothesis is consistent with recent observations of increased dissolved MeHg concentration occurring in overlying water during phytoplankton bloom senescence (Luengen and Flegal, 2009). However, higher rates of phytoplankton production and subsequent deposition in the South Bay would also tend to make the surface sediment in this region more reducing than in the North/Central Bay. Such a regional difference in redox potential may affect Hg(II) availability for methylation and explain the generally lower sediment $Hg(II)_R$ concentrations in the South Bay (Fig. 5), as more oxidized sediment tends to have higher $Hg(II)_R$ concentrations (or $\%Hg(II)_R$) (Marvin-DiPasquale and Cox, 2007; Marvin-DiPasquale et al., 2007; Yee et al., 2008; Marvin-DiPasquale et al., 2009a,b; Grenier et al., 2010; Windham-Myers et al., 2010a). This trend in $Hg(II)_R$ with sediment redox is thought to reflect the strong chemical binding of Hg(II) to solid-phase reduced-sulfur compounds (e.g., FeS and Fe_2S) which are more abundant in reduced sediment.

6.2.2. Tidal marshes

Tidal marsh regions were sub-categorized into slough channels and marsh plains (largely vegetated), due to distinct differences in hydrology, frequency of inundation, and emergent vegetation. It was recently estimated that Alviso Slough and it is fringing vegetated marsh contain approximately 1650 kg of THg in the top 2 m of sediment (Marvin-DiPasquale and Cox, 2007). The vast majority of this THg inventory is associated with New Almaden, which drains into Alviso Slough.

Sediment THg and MeHg concentrations were quite similar among three of the four tidal marsh region/habitat types: North/Central Bay marsh sloughs, South Bay marsh plains, and South Bay marsh sloughs had high THg concentrations and moderate to high MeHg concentrations (Fig. 6). In contrast, the North/Central Bay marsh plain had low to moderate THg concentrations and a wide range (low to high) in MeHg concentrations. Hg inputs from New Almaden undoubtedly play a dominant role in the South Bay marsh plains and sloughs. While the North/Central Bay sloughs had high MeHg concentrations compared to the corresponding marsh plains for that region, the k_{meth} and $Hg(II)_R$ data (Fig. 5) would suggest that the marsh plains are an area of moderate to high MPP rates, while the sloughs are an area of comparatively low MPP rates. This lack of correspondence of MPP rates and MeHg concentrations suggests that MeHg degradation processes (generally not measured) may be very rapid in North/Central Bay tidal marsh surface sediment (Marvin-DiPasquale et al., 2003), thus mitigating MeHg production in this habitat to some degree.

6.2.3. Managed ponds

Managed ponds are present throughout the Bay, but have been most intensively studied in the South Bay. The South Bay salt ponds are interesting in several respects: (a) they are located within the region of the Bay most directly impacted by Hg inputs from New Almaden; (b) the ponds themselves have been largely hydrologically isolated since their construction between 1854 and the 1950s, a period that overlaps with mining at New Almaden (1846–1976); (c) birds feeding and nesting in the ponds have among the highest Hg body burdens in the region (Ackerman et al., 2007a,b; Ackerman et al., 2008a,b); and (d) restoration activities have begun to hydrologically reconnect the ponds to either muted or full tidal flushing. The impact of restoration on bioaccumulation of Hg in the South Bay food web is an area of intense research.

The first comprehensive assessment of sediment THg and MeHg concentrations within the South Bay ponds was conducted between 2003 and 2007 (Miles and Ricca, 2010), and included both the Alviso pond complex and the Eden Landing complex along the eastern edge of South Bay. Average THg concentration was significantly greater in the Alviso pond complex (0.74 ppm

prior to restoration and 1.03 ppm after restoration), compared to the Eden Landing pond complex (0.11 ppm before and after restoration). Average MeHg concentrations were more similar for the two South Bay pond complexes (2.6–3.0 ppb for Alviso and 1.0–2.2 ppb for Eden Landing).

The present analysis includes data from the Alviso pond complex only, with a majority of the data (72%) from a single pond (Pond A8), as it is the focus a number of recent (Marvin-DiPasquale and Cox, 2007; Grenier et al., 2010) and ongoing process studies associated with the return of muted tidal flow that occurred in June 2011. The remaining 28% of the South SFB Salt Pond data comes from four other ponds (A3N, A5, A7 and A16). THg and MeHg concentrations for the South Bay ponds fall into the high range (Fig. 6). In contrast, calculated MPP rates fall in to the low to moderate range (Fig. 5), due to moderate-high values of k_{meth} but low $Hg(II)_R$ concentrations. The low $Hg(II)_R$ concentrations are consistent with the South Bay ponds having the lowest surface sediment redox (E_h) values among all of the region/habitat groupings. These results suggest that while the South Bay ponds are quite active with respect to microbial populations capable of carrying out Hg(II)-methylation, only a small percentage of the total Hg(II) pool is available to those microbes. This is also consistent with the observation that primary production and organic loading to the benthos is particularly high in these ponds, compared to the open waters of South Bay and Alviso Slough (Thébault et al., 2008; Grenier et al., 2010). The moderate-high MeHg concentrations (Fig. 6) may suggest that MeHg degradation processes are particularly slow, relative to MeHg production, in this sub-habitat.

6.3. Controlling internal net production of MeHg

For several reasons, controlling internal net MeHg production is a strategy that must be considered, especially for ecosystems like the Bay that face widespread legacy contamination, for short to mid-term management of MeHg bioaccumulation. First, MeHg is the form of Hg that causes toxicity. Second, controlling net MeHg production would help address the difficult problem of the large THg inventory already present in Bay sediment, and would potentially yield faster results than the long (multi-decadal to century) time-frame for recovery if controlling THg loads is the only option. In addition, the degree to which external THg loads contribute to food web concentrations is unclear, as much of the Bay is already so contaminated that the external supply of THg may not be the primary factor limiting methylation and bioaccumulation.

6.3.1. Open Bay

There are several candidate strategies for controlling internal net MeHg production in open Bay habitats, but each presents formidable challenges of feasibility and scale. In this section, two broad categories of control are considered: elective strategies that are purposefully employed by resource managers; and non-elective changes that will come about through global warming and other broad-scale phenomena.

One group of elective strategies to consider for controlling net MeHg production in the open Bay relies on isolating Hg-contaminated sediment from overlying water (capping) or removing this sediment altogether (dredging). Sediment capping isolates contaminated sediment by covering it with stable layers of clean sediment, gravel, rock, or synthetic materials. Capping reduces contaminant mobility and interaction between aquatic organisms and the contaminants. Capping has been investigated for controlling metals flux from sediment in a shallow tidal estuary (Mohan et al., 2000; Simpson et al., 2002). Capping may be feasible for well-defined, highly-contaminated regions at the Bay margins not subject to strong physical mixing forces, but implementation may be challenging in many portions of the Bay where tide and wind-driven currents would make it very difficult to keep the overlying cap material in place.

Targeted dredging has been implemented in a few well-defined, highly-contaminated areas on the margins of the Bay. Dredging is likely to be of limited benefit in widespread areas where Hg is distributed at lower concentrations because of the large volume of material that would need to be removed to impact the reservoir of sediment-bound Hg.

Another conceivable strategy for control of open Bay net MeHg production is to control factors that may influence bacterially-mediated Hg(II)-methylation. In this regard, nutrient control stands out as worthy of consideration. Food web shifts (Cloern et al., 2010), increasing water clarity due to declining suspended sediment concentrations (Schoellhamer, 2011), and increasing phytoplankton biomass (Cloern et al., 2007) have all raised concern recently about the potential for eutrophication in the nutrient-rich waters of the Bay. If excessive nutrient loads cause eutrophic conditions and subsequent oxygen depletion in bottom sediment, increased sulfate-reducing bacteria activity may lead to enhanced Hg(II)-methylation. Conversely, increased productivity may enhance growth dilution, which could decrease MeHg bioaccumulation (Chen and Folt, 2006; Driscoll et al., this issue). The net effect will depend on the processes at particular locations and times; for example, whether a net increase in productivity will outpace increased Hg(II)-methylation in a eutrophic condition.

If a link between eutrophication and increased MeHg in the food web is established, controlling anthropogenic nutrient inputs may be particularly effective in specific areas. In the extreme South Bay, anthropogenic nutrient inputs from municipal wastewater treatment plants are the dominant nutrient source (McKee and Gluchowski, 2011). These South Bay wastewater treatment plants discharge to the Bay through slough channels, so nutrient control could potentially impact redox conditions and MeHg cycling in the immediate discharge zone.

Non-elective phenomena include ecosystem-level changes due to global warming and other developments beyond the control of water quality managers. First, climate change will bring about a number of alterations—only some of them anticipated. One impact of climate change is sea level rise, which will tend to make the Bay more saline. Predicting how this will impact Hg in Bay food webs is a challenge. A second effect of climate change is a general increase in temperatures, which will impact snow pack and precipitation patterns (California Climate Change Center, 2006). In the Bay Area, climate change may lead to lower temperatures if the general warming intensifies the local summer pattern of inland movement of cool marine air. How changes in salinity, temperature, and precipitation may affect freshwater delivery, vegetation, and phytoplankton distribution and abundance, and, in turn, the distribution of MeHg in the food web is too complex to accurately predict. Some researchers have shown that increased salinity reduced the activity of sulfate-reducing bacteria (Compeau and Bartha, 1987; Blum and Bartha, 1980). Changing air and water temperatures may affect rates of phytoplankton growth and microbial activity, but whether this will increase or decrease net Hg(II)-methylation and food web uptake of MeHg is not certain.

In addition to global warming and sea level rise, other broad-scale changes and cycles may affect food web dynamics and MeHg bioaccumulation, including decadal-scale climatic variation in the Pacific that appears to have driven food web shifts in the Bay (Cloern et al., 2010), the continued introduction of exotic species that have caused major shifts in the Bay food web in the past (Cohen and Carlton, 1998), a trend of increasing transparency

of Bay waters due to a reduction in suspended sediment concentrations (Schoellhamer, 2011), and a trend of increasing phytoplankton blooms and biomass (Cloern et al., 2007). Water quality managers must not only grapple with what is within their control to remedy the MeHg problem, they must also contend with these non-elective changes and adapt their control strategies as necessary in response. Some of these non-elective phenomena (i.e., temperature, precipitation, and species introductions) can also be expected to affect MeHg dynamics in all of the habitat types discussed in this Section.

6.3.2. Tidal marsh

Tidal marshes have distinct subhabitats, each with its own elevation, inundation regime, and plant community (or lack thereof). This organization is driven by the physics of the tides and their interaction with plants in the vegetated low marsh and marsh plain. Based on the information generated to date, which is less extensive than that available for open water habitats, MeHg cycling and biomagnification vary among tidal marsh subhabitats (Grenier et al., 2010), and the food webs among the subhabitats are also relatively separate. Some strategies for MeHg control in marshes to be restored therefore relate to design of the overall layout of subhabitats. However, when the extent of one subhabitat is increased, then the extent of another must concomitantly be decreased, causing some species to benefit more than others.

Creating salinity gradients through restored marshes from the upland edge to the Bay edge may be a good strategy for reducing wildlife exposure to MeHg in tidal marshes. The strongest dataset available for understanding spatial patterns in resident marsh wildlife MeHg exposure showed that MeHg in tidal marsh Song Sparrow blood decreased with distance from the Bay edge (Grenier et al., 2010). The decrease of nearly an order of magnitude ($n=20$ marshes, range 0.07–0.64 ppm), which was consistent across years, was observed over a distance of several km. Birds with low MeHg were from more brackish marshes, while those near the Bay with higher MeHg were from salt marshes.

While other parameters covary with salinity (e.g., inundation frequency, average water table depth), there is evidence that differences in plant community composition along the salinity gradient (i.e., among brackish and fresh marshes) could be a primary driver of differences in MeHg production. Field experiments have indicated that pickleweed (*Sarcocornia pacifica*), which dominates local salt marsh plains, has greater root surface area compared to more brackish marsh vegetation, and this surface area creates appropriate redox zones for methylating bacteria near the sediment surface (Windham-Myers et al., 2009). Furthermore, pickleweed also exudes a greater amount of acetate and other labile organic matter that these bacteria can use as fuel to drive their metabolic activity, thus increasing MeHg production. This plant-driven mechanism may explain the high MPP observed in tidal marsh plain habitat in general compared to unvegetated Bay habitats (Fig. 5).

Routing flows from incoming streams and other watershed drainage through restored marshes, rather than directing these waters to the Bay through pipelines or between levees (as is often currently the case), would create gradual transitional zones of salinity from fresh to brackish to tidal marsh. Although this arrangement could create water quality problems within the marshes themselves if the inputs are polluted, the potential advantages include decreased net MeHg production, sequestration and degradation of other pollutants, and increased habitat value.

Creating marshes with less interior area and greater channelization is another approach to marsh design that might reduce MeHg bioaccumulation. Interior marsh sediment (far from channels) has been observed to have higher MeHg concentrations (Yee et al., 2008). These would have to be highly constructed marshes, as natural physical and biological regimes create a channel density that varies predictably with salinity. Therefore, this approach might be expensive and ultimately not very successful. There is also anecdotal evidence that better drainage (e.g., fully tidal versus managed marsh) and more frequent tidal inundation (e.g., low marsh versus marsh plain) are associated with lower MeHg bioaccumulation. Lower marsh elevations are more constantly wetted, which may keep them from drying out to the point that re-wetting releases a pulse of MeHg. These observations fit with a basic conceptual model of conditions conducive to Hg(II)-methylation: frequent inundation in saline environments can help maintain highly reduced sulfidic conditions which can limit Hg solubility and availability for methylation (previously described in Section 6.2, and as opposed to episodic inundation often associated with swings between oxic and anoxic conditions which can increase methylation), and frequent flushing may also disperse and dilute any produced MeHg.

The support for these approaches is based on limited datasets, and studies focused on these topics should be conducted in lab and field trials before attempting to implement such measures on a large scale. Generating and evaluating additional ideas for designing marshes to minimize net production and bioaccumulation of MeHg represents one of the best available avenues for addressing the MeHg problem.

6.3.3. Managed ponds

Managed ponds around the Bay vary greatly in their physiochemical characteristics, management regimes, THg and MeHg concentrations in abiotic matrices, and MeHg accumulation in wildlife (Grenier et al., 2010; Miles and Ricca, 2010). This variability offers opportunities to identify the conditions, and the management approaches that promote those conditions, that minimize MeHg exposure in the food web. Studies indicate that the availability of labile organic matter (i.e., algae in particular) is positively correlated with MeHg production and bioaccumulation in some ponds (Grenier et al., 2010). There is also anecdotal evidence that seasonal ponds with large surface areas that slowly dry out over weeks and months are associated with greater MeHg bioaccumulation. The most feasible management of both of these potential driving factors would be through hydrology. Allowing at least some tidal flushing on a regular basis may keep organic matter from building up and sediment from becoming too dry. Another approach might be to place seasonal ponds only in areas with the lowest THg in sediment, since this particular habitat type is critical for some species.

6.3.4. Reservoirs

As discussed in Sections 4.2 and 4.3.1, the Guadalupe River TMDL includes provisions requiring measures to reduce net MeHg production and bioaccumulation in reservoirs. Pilot testing has begun and the initial results are promising, with marked reductions in MeHg observed in the water column in response to mechanical aeration and circulation. Other properties of these highly manipulated ecosystems that can potentially be adjusted to minimize net MeHg production and accumulation include water level fluctuation, species composition, and nutrient concentrations.

6.3.5. Key information gaps

Managers are in the very early stages of considering options to control internal net production, so the information gaps are formidable. Controlling internal net MeHg production holds great promise in reservoirs. Controlling internal production is a more

viable strategy in tidal marshes or managed ponds compared to open water, as there are better opportunities to control water, sediment, and nutrient supplies in such environments. A number of candidate strategies have been presented in this section, but other approaches should be identified and evaluated. The feasibility of capping and dredging in the Bay seems limited because of the widespread Hg contamination and strong Bay mixing forces, but these strategies could be carefully pilot-tested and evaluated, particularly in areas posing higher than typical risk to resident biota or producing and exporting large amounts of MeHg to other areas of the ecosystem. Using nutrient control to control Hg(II)-methylation has some promise, but it should be confirmed that there are circumstances in the Bay where this makes sense before embarking on this strategy.

Significant information gaps pertain to Hg cycling in reservoirs, including Hg(II)-methylation, MeHg bioaccumulation, year-to-year variability, and natural variability between reservoirs. The Guadalupe TMDL incorporates efforts to resolve these gaps in its adaptive management framework. Pilot studies to control anoxia and hence reduce Hg(II)-methylation will shed light on these issues. They will also help identify what additional studies are needed to address potential biological controls, such as enhancing biodilution, in the reservoirs.

Key information gaps need to be addressed to improve wetland restoration design and management for reducing MeHg exposure in wildlife. Marsh restoration designers should work with scientists to design studies for ongoing restoration projects that test some of the ideas discussed above using biosentinel wildlife and abiotic measurements to better understand MeHg processes and patterns of risk. In particular, routing freshwater inputs through tidal marsh would be promising to investigate further.

A similar series of studies in managed ponds, where a higher degree of experimentation is possible, would support optimization of pond management for maximizing habitat value while minimizing MeHg accumulation in biota. Reducing algal production through tidal flushing is an important management technique to test.

The range of possible ecosystem-level changes that may come about as a result of climate change and other non-elective processes poses an enormous challenge for water quality managers. The list of information gaps concerning how these changes will impact net MeHg production and distribution in the food web is long. At a minimum, managers will need better information about how changes in sea level, temperature, and salinity will impact the conditions for net MeHg production and uptake and how fast these changes will take place. Unfortunately, much of this information will be obtained by careful monitoring as the changes occur, rather than through model prediction, because the complex physical, chemical, and biological features of the Bay make accurate predictions all but impossible.

7. Modalities of management

MeHg contamination of Bay Area aquatic ecosystems is a daunting problem that calls for broad consideration of possible solutions. This section presents an overarching summary of potential MeHg management strategies, placing many of the approaches mentioned previously into a broader context, and briefly considering a few more. There are five general management modalities that can be employed to remedy the MeHg problem in Bay Area aquatic ecosystems. Location and timing are critical for all of these approaches—efforts must be focused where and when they have the greatest effect on reducing MeHg in the food web.

7.1. Upstream source control

The first category of management strategies includes upstream source control actions that can address Hg directly, or address pollutants (nutrients) that indirectly influence bioaccumulation. These actions should be prioritized to address large, readily controllable loads that are discharged to areas with a high potential for net MeHg production and food web uptake (e.g., certain types of wetlands, or embayments with high productivity and low flushing leading to hypoxia). For example, responsible parties are already remediating Hg contamination from New Almaden and downstream creek channels that continue to discharge large loads to South San Francisco Bay, an area of high bioaccumulation. It is also possible to employ Hg controls for stormwater to reduce early fall "first flush" loads, but the large volumes of stormwater that would require treatment limit the utility of this method for larger storm events. Attempts to control runoff loads are best applied to periods when concentrations of both THg and MeHg may be higher and volumes lower so engineered control capacities are not overwhelmed. Control of loads delivered during later wet season months (April and May) should also be considered as they might directly impact biological uptake during spring algal blooms on the mudflats. Upstream source control actions will be most effective if source areas can be identified and controlled before contaminated sediment mixes with cleaner sediment during transport and then becomes widely distributed in the Bay.

Upstream management actions can also address large, controllable loads of MeHg and nutrients from major sources that would otherwise be discharged to areas with high potential for bioaccumulation, particularly during ecologically sensitive periods such as breeding season. Whether nutrient control would exacerbate or mitigate MeHg accumulation is unclear, and likely to vary spatially and temporally, as discussed previously in the section on internal controls.

7.2. Controls on internal net MeHg production

The second category of potential management actions involves manipulating physical and chemical features of habitats to constrain net MeHg production. These strategies include physical controls, like water circulators to reduce anoxia in reservoirs or changing the hydrological regime of a managed pond to keep organic matter from building up. Chemical controls might also be useful, such as using granular activated carbon to sequester Hg and iron amendment to perturb Hg speciation (by binding sulfur) away from forms that readily diffuse across bacterial cell membranes. Laboratory and pilot-scale testing of binding with carbon (Henneberry et al., 2011; Ghosh et al., 2011) and iron (Mehrotra et al., 2003; Ulrich and Sedlak, 2010) amendments show some promise, but the feasibility and ecological impacts of large-scale use in the natural environment are concerns. Such amendments may be impractical due to large cost and possible habitat damage caused if they require tilling into soil or sediment. An alternative approach that delivers the amendments as pellets that naturally mix into sediment over time through bioturbation and advection has recently been developed. Further advances in increasing effectiveness and minimize negative impacts may make these techniques viable.

Scientists and managers working on restoring San Francisco Bay wetlands are developing innovative design and management strategies that explicitly seek to minimize net MeHg production and food web uptake. Approaches that appear promising include optimizing the mix of subhabitats, creating salinity gradients, and routing flows through restored marshes rather than around them. Some of these design features may be self-sustaining, that is, not

requiring active management. In contrast, hydrological controls will always require active management. Water level controls are practical where tidal flow control structures are in place, such as in acreage owned and managed by duck hunting clubs. Controlling water levels can reduce MeHg production by increasing circulation and dissolved oxygen, flushing out algae, and controlling the timing and duration of flooding.

By affecting redox conditions and carbon supply for microbial activity, wetland vegetation manipulation (e.g., harvesting) may provide, in some circumstances, a way to suppress net MeHg production and bioaccumulation in tidal marshes. The expense and scale of such manipulation, habitat tradeoffs, and the degree to which MeHg bioaccumulation can be reduced are considerations for this technique.

7.3. Controlling bioaccumulation

MeHg bioaccumulation depends on several trophic transfers – the largest of which is the incorporation into the base of the food web (e.g., Stewart et al., 2008) – and the first two modalities addressed minimizing bioaccumulation at this step. Another management option would involve interrupting the food web transfer at higher trophic levels. For example, one possible stopgap strategy for locations with water control structures is to exclude prey (small fish) from wetlands or ponds known to have active net MeHg production during specific, critical times of year. If feasible, such exclusion may prevent the small fish from accessing the area when they would most likely be exposed to peak MeHg concentrations, and their reduced MeHg body burden could propagate and reduce MeHg concentrations throughout the food web. A second similar strategy is to prevent birds from feeding in methylating areas during specific times. There are established techniques using noise to exclude birds from airports, landfills, and contaminated areas. These habitat exclusion strategies would involve, by definition, a loss of productivity and wildlife habitat value. In some cases, wildlife populations might be able to sustain this reduction in food sources, but the management decisions would need to be carefully considered to prevent causing more harm than good. Similarly, human exposure to contaminated fish could be reduced by removing non-native top-level predator fish, such as largemouth bass. However, all of these techniques suffer from one or more drawbacks that may make them ecologically damaging, infeasible, or socially unacceptable. Although there are negative impacts associated with MeHg bioaccumulation, the negative impacts of reduced habitat and productivity are generally more significant; similar magnitudes of population impacts would be seen only in the most contaminated environments. Therefore habitat exclusion should be used only in the most extreme circumstances, with decisions made by managers in consultation with stakeholders.

7.4. Cleanup of contaminated sites

A fourth category is the cleanup of Hg-contaminated sediment at sites. As mentioned in the discussion on internal controls, discrete areas with very high sediment Hg concentrations are uncommon in the Bay because Hg is widely dispersed, and there are considerable technical challenges involved in cleanup. Nevertheless, managers should still consider this option if circumstances are identified where targeted cleanup is feasible.

7.5. Reducing other factors limiting at-risk wildlife populations

A final category of management options is not a MeHg or bioaccumulation control strategy at all. Rather, it is a strategy aimed at increasing populations of potentially impacted wildlife species - principally birds. Another way to ensure that bird populations thrive in spite of their exposure to MeHg is to increase the size of the populations themselves. This can be accomplished most directly through provision of suitable habitat, which is currently underway as tidal marsh habitat is being restored around the Bay. A tradeoff inherent in the restoration of estuarine wetlands is that the habitat being restored may create additional areas where Hg can be methylated and taken up into the food web. At the same time, the pre-restoration habitat type was also, in the majority of cases, a wetland that had some level of MeHg production and bioaccumulation. Therefore, the difficulty is to evaluate the net costs, including the newly created risk of MeHg in the restored habitat, versus the net benefits.

This discussion illustrates why MeHg presents such a challenging problem for water quality regulators and managers. The available management strategies are difficult, expensive, modestly effective, slow to bear fruit, challenging to monitor, and may expose a significant percentage of the wildlife population to concentrations associated with harm. Innovative techniques that seem impractical at the moment may become viable in the future. Resource managers have an obligation to do what is possible and feasible today, but also remain attentive to novel strategies that may become available. The optimal approach is to attack the problem with the most effective actions for which society is willing to pay and with tradeoffs that society is willing to accept.

8. Key conclusions and information needs

Available data indicate that MeHg contamination of aquatic food webs in the San Francisco Bay region poses significant risks to humans who consume sport fish and to wetland and aquatic wildlife, and that substantial exposure reduction is needed. All sources and forms of Hg are contributing to accumulation in the food web, with the highest exposures generally occurring in areas with known Hg mining contamination. THg load reductions are a long-term solution, but, due to the vast pool of THg already present in the ecosystem, it is likely to take decades or centuries for this to lead to the needed reduction of MeHg in the food web. Reducing net MeHg production is a potential shorter-term solution that appears most promising for managed ponds and reservoirs, and somewhat promising with regard to design of restored wetlands. Other approaches may also help reduce exposure or net impact, such as site cleanups, enhancing other factors that limit wildlife populations, food web manipulation (e.g., slot limits for fishing, fish population manipulation), and habitat exclusion.

Extensive study over the past 10 years has significantly advanced understanding of Hg and MeHg in Bay Area aquatic ecosystems. However, many important uncertainties related to reducing MeHg exposure remain. The highest priority information needs include the following.

- Data for additional popular sport fish species to enhance the consumption advisory.
- Quantitative information to track improvement in awareness in response to efforts to communicate the consumption advisory.
- Spatial surveys of exposure to promote a focus on areas of greatest impairment. The greatest information gaps exist for tidal marshes, managed ponds, reservoirs, and streams.
- Information to promote understanding of the potential benefits of management actions at local and regional scales, including:
  - conceptual and quantitative models of loading and fate that allow exposure forecasting and source apportionment;
  - surveys of stormwater loading from local watersheds to identify pollution sources and linkages to key habitat areas;

- process studies to support design of management actions; and
- population models for sensitive wildlife species to understand the relative importance of MeHg exposure and other key factors.

The relative contribution of atmospheric deposition to MeHg exposure is an example of an important specific area of uncertainty. How will Bay Area aquatic food webs respond to global changes in atmospheric Hg, or to local and regional management actions if global atmospheric Hg remains constant or increases?

- Evaluation of the effectiveness of management actions at local and regional scales. This should include regional trend monitoring of key indicator species, covering the major habitat types, as well as project-scale monitoring of pilot management actions (stormwater load reductions, manipulation of managed ponds and reservoirs, wetland design, dredged material reuse) supported by the development and application of effective monitoring tools and approaches.
- The overall potential for reduction of net MeHg production at a regional scale is a critical overarching question, given the limited availability of opportunities for management actions and the unproven degree of effectiveness of the actions.

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