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# Impairment Assessment for Mercury in Tomales Bay, CA

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# 1. Introduction

Tomales Bay is located in northwestern Marin County, California (Figure 1), approximately 64 km northwest of San Francisco. It is a drowned segment of the northwest trending rift zone formed by the San Andreas Fault. The Bay is approximately 20 km long, 2 km wide, and has an average depth of about 6 m. Its northern end opens to Bodega Bay and the Pacific Ocean while the southern end terminates in the watersheds of Lagunitas and Olema Creeks. In aggregate, all the watersheds draining to the Bay have an area of approximately 561 $km^2$.

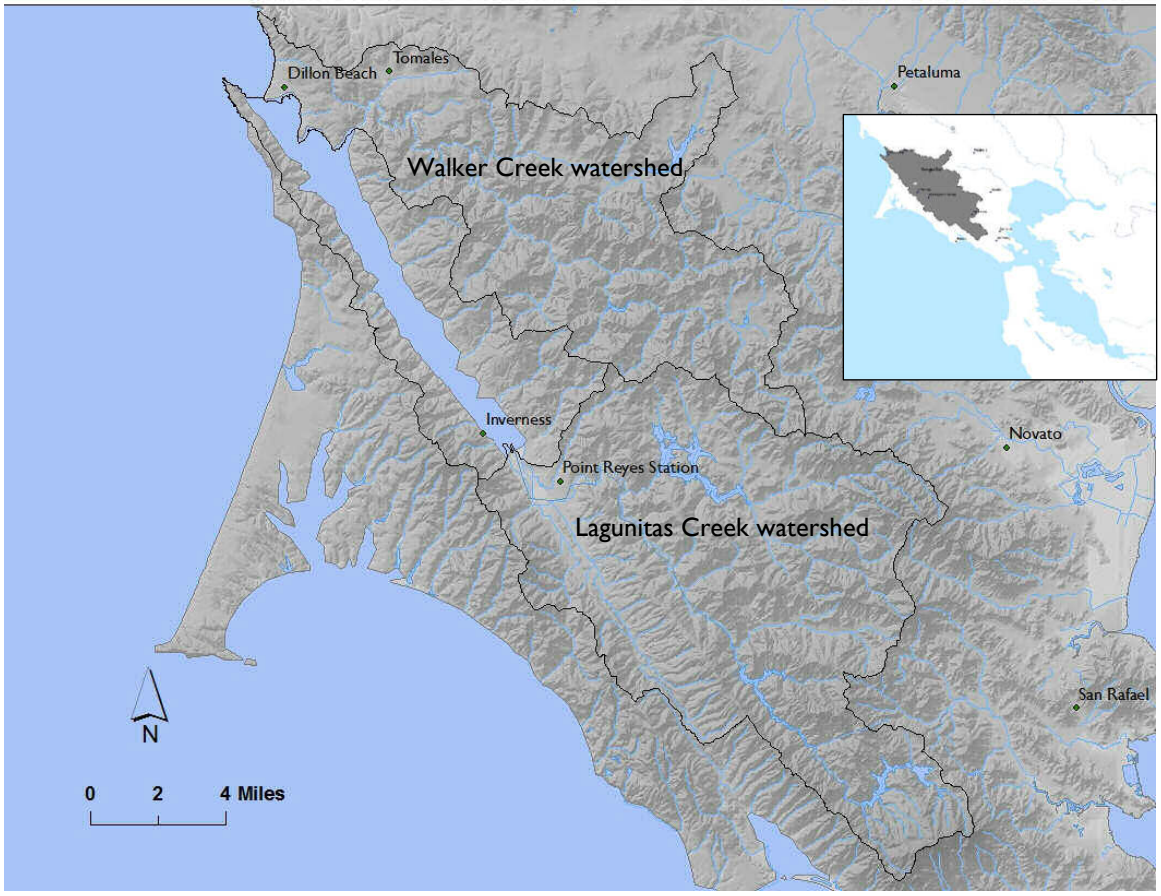



**Figure 1.** **Tomales Bay and its subwatersheds**. Location in San Francisco Bay Area in inset.

There is a concerted effort among local environmental interests to improve the Bay's ecological health. The Tomales Bay Strategic Plan envisions the Bay as *"... a vital ecosystem with clean water and diverse wildlife. Residents and visitors cherish its open waters, shoreline, scenic beauty and serenity. People enjoy diverse activities in a landscape that expresses rural and wilderness qualities, and supports limited and sustainable levels of use and development"* (Point Reyes National Seashore Association; http://www.tomalesbay.net/). The Tomales Bay Watershed Council provides a comparable but more specific vision addressing key elements of the Bay's good health (http://www.tomalesbaywatershed.org/stewardship_executive.pdf):

- *human activities in the watershed - including agriculture, recreation, commercial fishing, and residential use - coexist with high, sustainable or improving levels of ecosystem health and watershed function;*
- *natural habitats and a broad diversity of wildlife species, including salmonid populations, are restored throughout the watershed;*
- *water quality of the Bay and its tributaries meets State standards for shellfish mariculture (as a benchmark for clean water);*
- *sustainable agriculture is one of the primary land uses in the watershed;*
- *the rural character and quality of life for local residents and communities is preserved; and*
- *the public participates in planning and managing the watershed.*

One of the challenges to achieving these visions of a healthy Tomales Bay and Tomales Bay watershed has been the threat of mercury contamination of the Bay's food webs. The watersheds east of the Bay largely consist of Franciscan mélange, a heterogeneous geologic assemblage of dismembered sequences of graywacke, shale, and lesser amounts of mafic volcanic rocks, serpentinite, and blueschist. There are localized occurrences of mercury deposits throughout the Coast Ranges that have been mined since the mid 1800s (Rytuba 2000,Wiener and Suchanek 2008). The Gambonini Mercury Mine, which was located in the Walker Creek watershed of Tomales Bay, has been a major source of Tomales Bay's mercury (Johnson et al. 2009).

Due to the presence of mercury from mining waste in the Tomales Bay watershed, it is necessary to analyze the potential impacts and risks to ecological health that may have resulted from improper disposal of mercury mining waste. This report explores two major research questions and five hypotheses regarding the ecological health of Tomales Bay related to mercury, including the spatial distribution of elevated mercury in sediment, fish tissue, and water; temporal trends in mercury contaminated sediment; and risk to the aquatic food web. The San Francisco Bay Regional Water Quality Control Board (SFBRWQCB), the regulatory agency tasked with protecting water quality in waterbodies throughout the San Francisco Bay Area, will use the analysis presented in this report to determine impairment of Tomales Bay due to mercury, and whether management actions to improve water quality are warranted.

Tomales Bay and its tributaries appear several times on the 303(d) list of impaired waterbodies. Tomales Bay and Walker Creek are listed for mercury, nutrients, and sedimentation/siltation. Lagunitas Creek is listed as impaired by nutrients and sedimentation/siltation (SWRCB 2006, Table 1). The SFBRWQCB completed plans for improving water quality, Total Maximum Daily Loads (TMDLs) for pathogens (Ghodrati and Tuden 2005) for Tomales Bay and for mercury in Walker Creek upstream of tidal influence (Marshall 2006). The remaining listings require additional TMDLs to be developed.

**Table 1. TMDLs within the Tomales Bay watershed.**

| Pollutant | Location |
|---|---|
| Pathogens | Tomales Bay |
| Mercury | Walker Creek and Tomales Bay |
| Sedimentation/siltation | Tomales Bay, Walker and Lagunitas Creeks |
| Nutrients | Tomales Bay, Walker and Lagunitas Creeks |

The purpose of this report is to characterize if, and the degree to which, mercury currently impairs Tomales Bay. A separate report submitted to the SFBRWQCB (Ridolfi and McKee 2009) addressed impairment of Tomales Bay by sedimentation/siltation. Similar to the sediment impairment assessment, this report has been organized in the following sections:

- Problem statement
- Project setting
- Existing research and data summary
- Methods, including suggested numeric targets to protect wildlife
- Results
- Source analysis
- Conclusions and data gaps

# 2. Problem statement

## 2.1. Beneficial uses

Beneficial uses "define the resources, services, and qualities of…aquatic systems that are the ultimate goals of protecting and achieving high water quality" (SFBRWQCB 2007, Chapter 2). Ideally, beneficial uses should be protected from human activities and other outside influences. Thus, water quality guidelines are designed to protect beneficial uses, which are adversely affected in impaired water bodies. The designated beneficial uses for Tomales Bay are:

- **Ocean, commercial, and sport fishing (COMM):** uses of water for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including, but not limited to, uses involving organisms intended for human consumption or bait purposes.
- **Estuarine habitat (EST):** including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (e.g., estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
- **Marine habitat (MAR):** uses of water that support marine ecosystems, including, but not limited to, preservation or enhancement of marine habitats, vegetation such as kelp, fish, shellfish, or wildlife (e.g., marine mammals, shorebirds).
- **Fish migration (MIGR):** habitats necessary for migration, acclimatization between fresh water and salt water, and protection of aquatic organisms that are temporary inhabitants of waters within the region.
- **Navigation (NAV):** shipping, travel, or other transportation by private, military, or commercial vessels.

- **Preservation of rare and endangered species (RARE):** habitats necessary for the survival and successful maintenance of plant or animal species established under state and/or federal law as rare, threatened, or endangered.
- **Shellfish harvesting (SHELL)**: uses of water that support habitats suitable for the collection of crustaceans and filter-feeding shellfish (e.g., clams, oysters, and mussels) for human consumption, commercial, or sport purposes.
- **Fish spawning (SPWN):** high quality aquatic habitats suitable for reproduction and early development of fish.
- **Water contact recreation (REC1):** recreational activities involving body contact with water where ingestion of water is reasonably possible. These uses include, but are not limited to, swimming, wading, water-skiing, skin and scuba diving, surfing, whitewater activities, fishing, and uses of natural hot springs.
- **Non-water contact recreation (REC2):** recreational activities involving proximity to water, but not normally involving contact with water where water ingestion is reasonably possible. These uses include, but are not limited to, picnicking, sunbathing, hiking, beachcombing, camping, boating, tide pool and marine life study, hunting, sightseeing, or aesthetic enjoyment in conjunction with the above activities.
- **Wildlife habitat (WILD):** including, but not limited to, the preservation and enhancement of vegetation and prey species used by wildlife, such as waterfowl (SFBRWQCB 2007, Chapter 2).

Of these beneficial uses listed for Tomales Bay, there is the potential for eight of them to be adversely affected by mercury (Table 2).

**Table 2. Beneficial uses impaired by mercury in Tomales Bay (marked with a "✓").**

| Beneficial Use | Potentially impaired by mercury? |
|---|---|
| COMM | ✓ |
| EST | ✓ |
| MAR | ✓ |
| MIGR | ✓ |
| NAV | |
| RARE | ✓ |
| REC1 | ✓ |
| REC2 | |
| SHELL | ✓ |
| SPWN | ✓ |
| WILD | ✓ |

## 2.2. Water quality guidelines

In order to assess impairment for Tomales Bay, it is important to examine the available water quality objectives. Numeric water quality objectives define the maximum concentration at which certain pollutants can be present in an aquatic system without degrading any beneficial use. A major goal of the SFBRWQCB is to ensure that all water bodies meet these water quality objectives. There are two current numeric water quality objectives for mercury (Table 3). In addition, a suggested fish tissue numeric target was developed specifically for this project (discussed in Section 4). In this report, impairment of Tomales Bay by mercury will be assessed using these water quality objectives and the fish tissue target.

**Table 3. Current water quality objectives for total mercury in water.**

| Target | Guideline | Source |
|---|---|---|
| Aquatic Life | 2.1 µg/L (1-hour avg) | SFBRWQCB 2007 |
| Aquatic life and human health | 0.051 µg/L (30-day avg) | USEPA 2000 |

## 2.3. Potential impairment of beneficial uses by mercury

### 2.3.1. Mercury bioaccumulation

Mercury occurs naturally in the Tomales Bay watershed, primarily in mineral form as cinnabar or metacinnabar (HgS). HgS is the predominant form present in runoff from the mercury mining regions of the Coast Range. HgS must be transformed to dissolved $Hg^{2+}$ or a dissolved Hg-sulfide complex before it can be converted to methylmercury. This is a slow process because HgS is extremely insoluble, although the process of mining and roasting mercury ore increases its solubility. Dissolved organic carbon also increases the solubility of HgS (Ravichandran et al. 1999). Local and global anthropogenic activities such as mining, coal combustion, and industrial uses have released mercury in excess of concentrations present in the pre-industrial period, generally in the form of elemental mercury (Hg(0)) or ionic (Hg(II)) mercury species.

Although health impacts of industrial exposure to high levels of mercury have been documented, the primary environmental concern at lower ambient concentrations is with methylmercury, the most bioavailable and bioaccumulative form of mercury. Methylmercury is produced through addition of a methyl group to $Hg^{2+}$, a process referred to as methylation. Methylation is performed primarily by sulfate-reducing bacteria (Compeau and Bartha 1985, Regnell et al. 1996 Gilmour et al. 1998), which are found at zones of transition from oxic to anoxic conditions in the water column or sediment (Watras et al. 1994, Slotton et al. 1995, Choi and Bartha 1993, Devereux et al. 1996; Gilmour et al. 1998, Bloom et al. 1999). Net methylmercury production, or methylmercury production in excess of degradation, is the critical parameter that leads to food web accumulation.

Excessive concentrations in the food web arise when methylmercury is taken up by organisms faster than it can be excreted. The strong reactivity of methylmercury with sulfhydryl groups of proteins is responsible for its high degree of bioaccumulation

(Beckvar et al. 1996). Phytoplankton can concentrate dissolved methylmercury in the water column approximately 100,000 times, making this a critical step in the bioaccumulation process (Watras et al. 1994). After this initial step, methylmercury concentrations increase approximately three-fold with each additional step in the food chain (Watras et al. 1994), in a process known as biomagnification. In this process consumers retain and further concentrate much of the methylmercury of their prey and subsequently pass this on to the next trophic level. Species at high trophic positions in the aquatic food web, such as predatory fish, attain concentrations that are approximately a million times higher than concentrations in water. Concentrations of methylmercury in fish also increase with increasing age or size because of the very slow rate of elimination relative to the rapid rate of uptake and because larger fish can consume larger prey with higher concentrations of methylmercury. Because methylmercury biomagnifies, trophic position is one of the primary factors influencing observed tissue concentrations. Species highest on the food chain, such as sport fish, piscivorous birds, or humans, are at the highest risk for mercury exposure.

Methylmercury production and bioaccumulation are affected by climate, hydrology, food web structure, and many other environmental factors, making it difficult to predict biomagnification factors across ecosystems from measurements of mercury or methylmercury in water or sediment. Because of this variability, bioaccumulation monitoring and selection of appropriate biological indicators is important. Sampling of species at risk, or diet items of species at risk, provides the most reliable means of assessing risk.

Although methylmercury is the primary form of toxicological concern, in many studies only total mercury is measured. In some tissues of some taxa (such as fish muscle or avian eggs or feathers), it is well established that the vast majority of mercury is present as methylmercury (Wiener et al. 2007, Eagles-Smith et al. 2009). Once it has been reliably established that a majority of mercury in the tissue of an indicator species is present as methylmercury, total mercury can serve as a proxy for methylmercury in fish.

### 2.3.2. **Mercury toxicity**

**Human toxicity**

Klasing and Brodberg (2008) summarized human exposure and toxicity of methylmercury. The primary route of methylmercury exposure in humans in the USA is fish consumption. When ingested, methylmercury in fish tissue is almost completely absorbed from the gastrointestinal tract. Once absorbed, methylmercury is distributed throughout the body. Its ability to cross the placenta as well as the blood-brain barrier allows methylmercury to accumulate in the brain and fetus, which are known to be especially sensitive to the toxic effects of this chemical. Primarily based on an epidemiological study in the Faroe Islands, USEPA has established a reference dose for humans of 0.1 μg Hg/ kg body weight per day.

A major concern about methylmercury exposure in humans is its potential to cause toxic effects in the central nervous system, including sensory and motor deficits and behavioral impairment. In humans and other mammals, methylmercury causes

lesions in the cerebrum and the cerebellum, which accompany symptoms such as anorexia, ataxia, difficulty moving, neurasthenia (generalized weakness), impairment of hearing and vision, and tremors, followed by convulsions and death (Wolfe et al. 1998). These more acute effects generally only manifest at higher doses, however. More subtle effects were documented in the studies of Faroe Islands residents, where chronic, lower-dose maternal exposures were associated with neurobehavioral effects in children, such as problems with attention, fine-motor function, and verbal memory (Klasing and Brodberg 2008). In humans and other mammals, methylmercury is easily transferred across the placenta, and selectively concentrates in the fetal brain. Methylmercury also can cause immune system impairment, biochemical and enzyme impairment, and genotoxicity.

**Bird toxicity**

In birds, reproduction is generally the most sensitive endpoint to methylmercury contamination (Wolfe et al. 1998, Davis et al. 2003, Schwarzbach et al. 2006, Eagles-Smith et al. 2009). Methylmercury is readily transferred from the maternal bloodstream to albumen (egg white) proteins. Developmental effects in birds include decreased weight, developmental abnormalities, and embryo mortality. In adults, methylmercury can reduce reproductive success through effects on parental behavior. In Mallard embryos, effects range from decreased embryo weight to developmental abnormalities and, eventually, death, with increasing methylmercury concentrations (Heinz 1979; Wolfe et al. 1998). Reproductive effects can persist beyond the embryo, and affect juvenile survival rates, causing brain lesions in hatched Mallard ducklings. In adults, mean prey concentrations of 0.3 to 0.4 µg/g wet corresponded with Common Loons establishing fewer territories and laying fewer eggs (Scheuhammer 1991).

Heinz (1979) described the reproductive effects of methylmercury in a laboratory study used to establish the reference dose for Mallards of 21 µg/kg/day. Though this is one of the few reference doses available, Mallards later were shown to be less sensitive to mercury than other bird species. Therefore, this threshold may not be protective of all wild bird species. In the more recent study, Heinz et al. 2009) injected methylmercury into eggs of 26 bird species to characterize the relative sensitivity of embryos. The species (including some that occur in Tomales Bay) were categorized into low, medium, and high sensitivities (Table 4).

**Table 4. Relative sensitivity to methylmercury among bird species (after Heinz et al. 2009).**

| Relative Sensitivity to Methylmercury | Tomales Bay Species | Other Species |
|---|---|---|
| Low | Double-crested Cormorant | Mallard, Hooded Merganser, Lesser Scaup, Canada Goose. Laughing Gull |
| Medium | Caspian Tern, Great Egret | Clapper Rail, Brown Pelican, Sandhill Crane, Ring-necked Pheasant, Chicken, Common Grackle, Herring Gull, Tree Swallow, Common Tern, Royal Tern, Brown pelican, Anhiga |
| High | Osprey, Snowy Egret | Tri-colored Heron, American Kestrel |

Though the Heinz et al. (2009) study was not designed to develop dose/response thresholds for wild birds, the work suggests that many west coast and Tomales Bay species could experience methylmercury effects at levels lower than the Mallard reference dose of 21 μg/kg/day. Thus, this reference dose may not be sufficiently protective for these species. In San Francisco Bay, methylmercury exposure is considered a significant concern for populations of Clapper Rail (Schwarzbach et al. 2006), Forster's Tern (Eagles-Smith et al. 2009), and Least Tern (Austin and Looker 2006). None of these species, however, regularly breed in Tomales Bay at present.

**Fish toxicity**

Fewer studies on the toxic effects of methylmercury, at environmentally relevant concentrations, have been performed on fish. Direct mortality is only known to occur at very high concentrations, observed in severely contaminated environments (Sandheinrich and Wiener 2009) such as Minamata Bay, Japan, and Clay Lakes in Ontario, Canada (Sandheinrich and Wiener 2009). However, laboratory studies have shown impairment of fish behavior at concentrations typical of fish found in mercury-impacted habitats (Scheuhammer et al. 2007). Studies on fathead minnows found that average concentrations of 0.9 μg/g wet, due to diets containing 0.87 μg/g dry total Hg dry caused reduced spawning success, suppression of gonadal development, and decreases in sex hormones (Drevnick and Sandheinrich 2003). A similar effect on sex hormones caused by tissue methylmercury concentrations of about 0.7 μg/g wet was observed in white sturgeon (Scheuhammer et al. 2007). In general, Sandheinrich and Wiener (2009) found that changes in biochemical processes, damage to cells and tissues, and reduced reproduction in fish occur at methylmercury concentrations of about 0.3 to 0.7 μg/g wet in the whole body and about 0.5 to 1.2 μg/g wet in axial muscle. We were unable to find any specific studies of effects of mercury on fish species common to Tomales Bay.

## 2.4. Existing impairment information

### 2.4.1. Historic mercury mining

Mercury is naturally present in large quantities in California's Coast Range mountains (Rytuba 2000). At the peak of mining activity in the state (the Gold Rush era of the 1800s), there were about 320 mercury mines, primarily producing mercury to aid processing of gold that was mined from the Sierra Nevada and Klamath-Trinity Mountains. About 90% of the mercury produced in the United States between 1850 and 1980 was mined from the Coast Range (Davis et al. 2003). Of the 100,000 metric tons of mercury produced from the Coast Range mines, nearly 12,000 metric tons were transported to gold mines. Thus, tens of thousands of metric tons have been lost to the environment and have caused widespread contamination throughout California (Alpers et al. 2005). After a large drop in mercury production following the Gold Rush, another small peak occurred in the 1960s due to the use of mercury in the manufacturing of caustic soda and paint, as well as electrical applications (Jasinski 1994).

The Gambonini Mercury Mine, located in the Walker Creek watershed approximately 13 km upstream from the confluence of Walker Creek and Tomales Bay, is one of many mercury deposits in the mercury belt of the California Coast Range (Figures 2a,b; Rytuba 2000, 2003), and is the major point source of mercury to Tomales Bay (Johnson et al. 2009). In addition to active mining, Gambonini was also the processing location for three other, smaller mines in the watershed during the second wave of mercury mining in the 1960s and 1970s. The waste ore was deposited in a pile loosely secured by a dam along hillslopes and channels of a small tributary to Walker Creek. It was estimated that the Gambonini site contained over 300,000 $m^3$ of mercury-contaminated soil, with an average total mercury concentration of 320 μg/g (Whyte and Kirchner 2000). A dam was built by the mining company about 400 m downstream of the tailings pile in an attempt to prevent water quality impairment. However the dam failed in 1982, and by 1990, the ravine was incising through the toe of the waste pile resulting in failure, as indicated by a 5 m landslide at the top of the pile (Whyte and Kirchner 2000). The surrounding area and Walker Creek were subsequently flooded with the mercury-laden sediment (Whyte and Kirchner 2000).

Water sampling in the winter of 1998 indicated that mercury was closely associated with particles. Thus there was a strong correlation between sediment transport (measured by total suspended solids, TSS) and mercury concentrations ($R^2 = 0.98$, $p = 0.001$; Whyte and Kirchner 2000). Releases of mercury-contaminated sediment were mostly a product of intense bursts of rain and resulting erosion. During the two month period sampled (Jan-Feb 1998), 1,300 metric tons of sediment and 82 kg of mercury flowed downstream from the mine site. The authors concluded that stabilizing the waste pile and establishing vegetation would reduce transport of mercury to creeks. In 1999, following Whyte and Kirchner's study, the SFBRWQCB and USEPA remediated the waste pile using a combination of geotechnical engineering, revegetation, biostabilization,

channel reconfiguration, and runoff control techniques to reduce erosion of mercury-contaminated sediment (Marshall 2006).

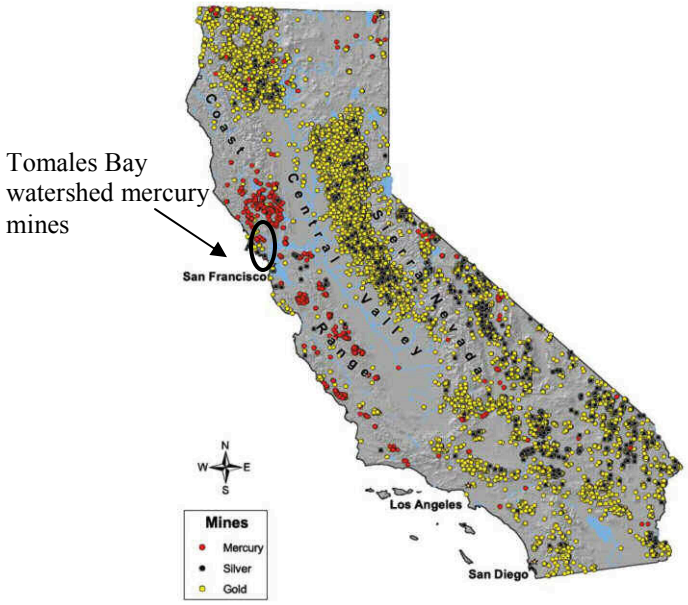



**Figure 2a.** **Gold, silver, and mercury mining in California. Mercury mines are indicated by red dots (Wiener and Suchanek 2008).**

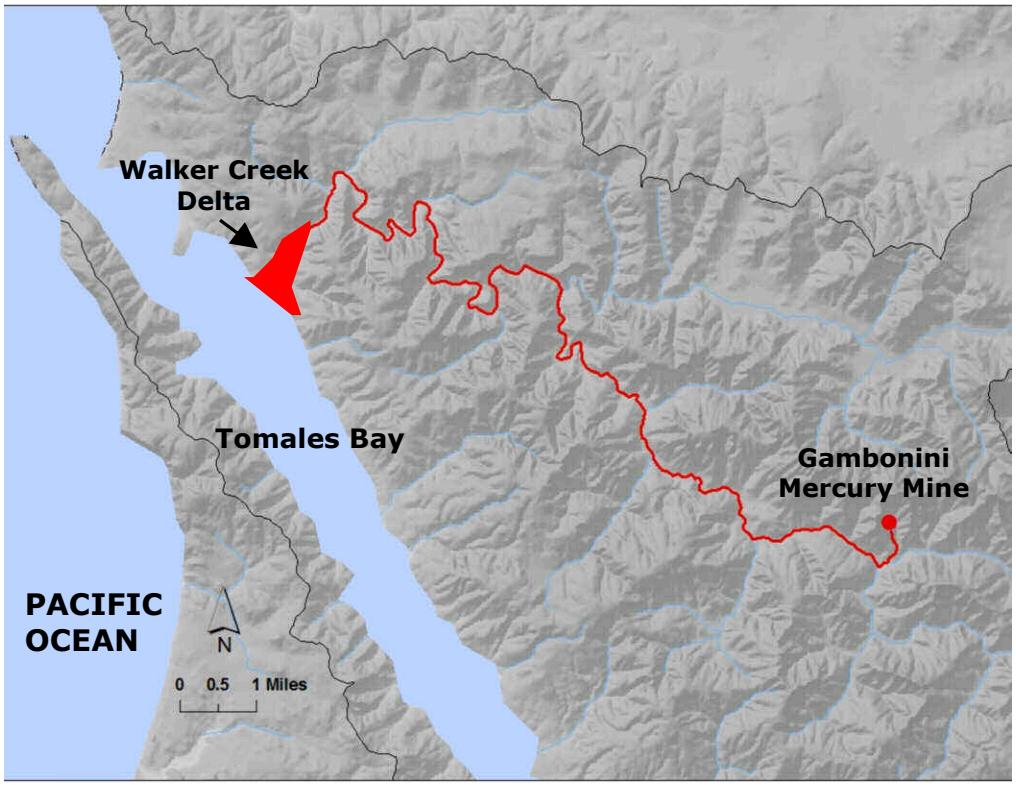



**Figure 2b.** **Mercury mines in the Walker Creek watershed.** The Gambonini Mine was the largest mine, and also the processing facility for other mines in the area.

### 2.4.2. **Existing data on mercury contamination**

**Human health risks from sport fish and shellfish in Tomales Bay**

Available data for sport fish, aquatic invertebrates, birds, and sediment indicate that there are moderately elevated concentrations of methylmercury in the Tomales Bay food web. Data collected by the California Office of Environmental Health Hazard Assessment (OEHHA) and the State Water Resources Control Board under the Coastal Fish Contamination Program indicated that several sport fish species had methylmercury concentrations above a criterion (0.3 µg/g wet) set by USEPA (2001) and the target for mercury concentrations in sport fish tissue (0.2 µg/g wet) established for the San Francisco Bay Mercury TMDL to protect human health (Austin and Looker 2006; Figure 3). Several species of sport fish (California halibut, redtail surfperch, shiner perch, pile surfperch, jacksmelt, leopard shark, brown smoothhound shark, Pacific angel shark, and bat ray); as well as red rock crabs and clams were collected from Tomales Bay in 1999-2001. The three shark species sampled had the highest mercury concentrations (0.47-1.4 µg/g wet), whereas halibut, perches, and jacksmelt had lower concentrations below the EPA criterion (0.07-0.2 µg/g wet). Red rock crab (claw muscle) had a mean methylmercury concentration of 0.14 µg/g/ wet. Methylmercury concentrations in clams averaged 0.06 µg/g wet at Hamlet and 0.03 µg/g wet at four other locations.

These data on fish and shellfish prompted OEHHA to issue *Guidelines for Consumption of Fish and Shellfish from Tomales Bay (Marin County)* (OEHHA 2004). The guidelines advise people who fish in Tomales Bay to limit the number of servings of sport fish and red rock crab consumed to reduce exposure to methylmercury. The advisory is particularly stringent for women of child-bearing age and children, the populations that are most at risk from methylmercury exposure. The guidelines indicate that concentrations of methylmercury in commercial shellfish were low enough that consumption limits were not needed (OEHHA 2004).

**Comparison to sport fish and shellfish from other locations**

Methylmercury data for sport fish and shellfish are available from other locations in California, and help to provide context for interpretation of data from Tomales Bay. In general, Tomales Bay tissue methylmercury concentrations are in the same range or lower than other estuaries in California (Table 5). Several important indicator species had relatively low average concentrations in Tomales Bay. The average concentration in California halibut from Tomales Bay (0.18 µg/g wet) was similar to the average for other coastal locations included in the Coastal Fish Contamination Program (CFCP) database (0.19 µg/g wet; OEHHA, unpublished data), and much lower than the average for San Francisco Bay (0.60 µg/g wet). Topsmelt are a key indicator species for the Regional Monitoring Program (RMP) for Water Quality for San Francisco Bay. The average mercury concentration for topsmelt in Tomales Bay (0.12 µg/g wet) was much lower than the average for San Francisco Bay (0.23 µg/g wet). Shiner perch are another primary indicator species in the RMP. Shiner perch collected from Tomales Bay in 2009 had an average concentration of 0.02 µg/g wet, considerably lower than the San Francisco Bay average of 0.10 µg/g wet. Shiner perch collected in 1999 and 2001 included the CFCP, however, had an average (0.09 µg/g wet), similar to San Francisco Bay.

Two species (jacksmelt and brown smoothhound shark) appeared to have relatively high mercury concentrations in Tomales Bay, however small sample sizes and other issues confounded comparisons for these species. Jacksmelt collected in Tomales Bay by OEHHA (2004) in 1999 and 2001 had an average concentration of 0.06 µg/g wet (n=18 fish). The average for jacksmelt in the present study was 0.08 µg/g wet, but this was based on only two composites and a total of 6 fish (3 per composite). There was only one other jacksmelt sample (collected off of White's Point, near Long Beach, CA) and it had a significantly lower mercury concentration (0.02 µg/g wet) than the jacksmelt caught from Tomales Bay. Jacksmelt from San Francisco Bay in 2003 (n=20 fish) were a bit lower than jacksmelt from Tomales Bay (averaging 0.05 µg/g wet). The jacksmelt averages based on a reasonable sample size (OEHHA data for Tomales in 1999 and 2001 and RMP in 1993) were very similar in Tomales Bay and San Francisco Bay.

Brown smoothhound shark were only sampled from one other location in California, according to the CFCP. Brown smoothhound from Mission Bay (near San Diego, CA) and San Francisco Bay had much lower mean mercury concentrations (0.18 and 0.63 µg/g wet, respectively) compared to Tomales Bay (1.3 µg/g wet). The differences in mercury concentration can be explained largely by fish length, since the Mission and San Francisco Bay sharks were on average much smaller than those from Tomales Bay. Overall, crabs and sport fish in Tomales Bay tend to have similar or lower mercury concentrations than have been observed in other estuaries, with the possible exception of brown smoothhound shark.

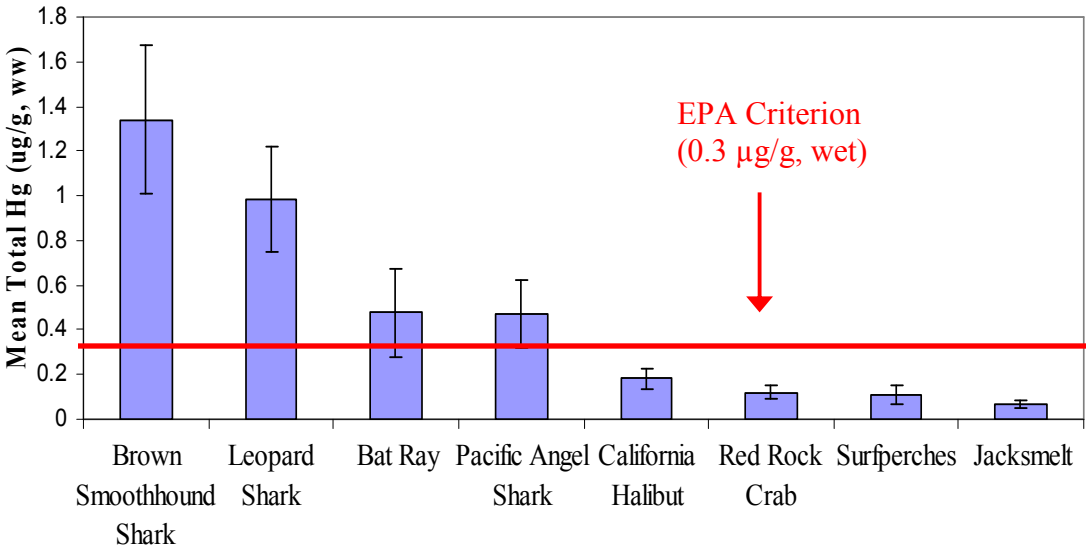



**Figure 3.** **Tomales Bay fish and crustacean mercury concentrations (µg/g wet) collected in 1999 and 2001 (OEHHA 2004).** USEPA criterion 0.3 µg/g wet (USEPA 2001) indicated by the red line. Error bars indicate one standard deviation. Reported in THg with the exception of red rock crab, which is reported in MeHg. For sport fish, THg and MeHg concentrations are assumed to be equivalent. See Appendix, Tables 21a-g for detailed data on total length and 'n' per species.

**Table 5. Methylmercury in sport fish and shellfish in other estuaries, compared to Tomales Bay**. The only species that are higher in methylmercury in Tomales Bay are Brown smoothhound and leopard sharks. See Appendix, Tables 21a-g for more detailed data.

| Species | MeHg higher in Tomales Bay compared to other estuaries? |
|---|---|
| Red rock crabs | No |
| Brown smoothhound shark | Yes |
| California halibut | No |
| Leopard shark | Yes |
| Jacksmelt | Yes |
| Shiner perch | No |
| Staghorn sculpin | No |
| Threespine stickleback | No |
| Topsmelt | No |

**Mercury in Invertebrates**

Mussels transplanted into Tomales Bay, commercial oysters, and wild resident clams and crabs were sampled by the SFBRWQCB 1996-2000 and indicated that methylmercury concentrations were higher in the Walker Creek Delta compared to other sites in Tomales Bay (Figure 4). With regard to impairment, the methylmercury data are most relevant. SFBRWQCB sampled resident bivalves and crabs of the size that wildlife consume. Methylmercury concentrations in bivalves (n=30) from the Walker Creek Delta were approximately 0.06 µg/g wet, higher than concentrations at the other three locations which ranged from 0.03-0.04 µg/g wet. Consistent with the bivalve data, total mercury in crabs (shown to be 90% methylmercury by OEHHA [2004]), was also clearly elevated at the Walker Creek Delta (0.45 µg/g dry) relative to 0.07µg/g dry at McDonald, a few miles south.

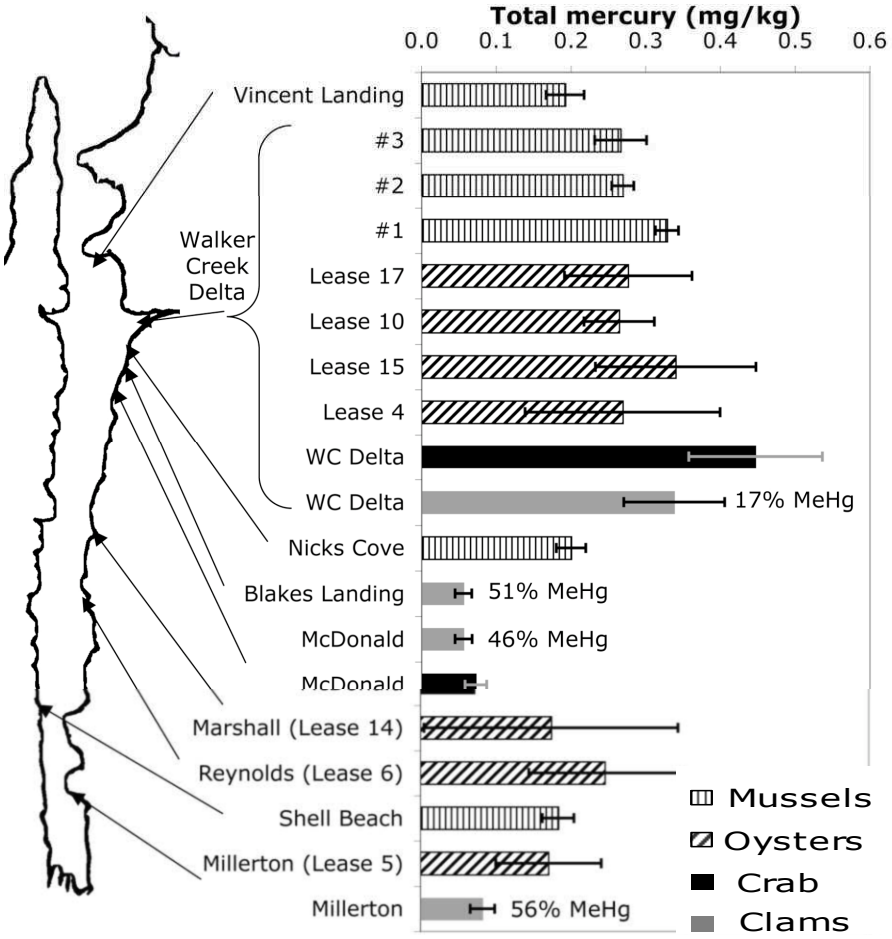



**Figure 4.** **Total mercury and methylmercury concentrations in invertebrates.** All reported in µg/g dry except for clams, reported in wet weight. Crabs sampled June 2000 (State Mussel Watch), resident clams sampled 1996 and 1997 (5 per location), farmed oysters sampled April, 1998 (5 per location; SFBRWQCB unpublished data). Error bars for mussels and crabs represent 2*SD; error bars for crabs and bivalves represent ±20%. After Johnson et al. (2009).

**Mercury in birds**

Birds in Tomales Bay may be at risk due to methylmercury exposure, but little work has been done in this ecosystem. Hoffman et al. (1998) recorded total mercury concentrations in the livers of Greater Scaup (19 µg/g dry; n=11), Surf Scoter (19 µg/g dry; n=10), and Ruddy Duck (6 µg/g dry; n=10) from Tomales Bay. These concentrations were higher than total mercury concentrations in livers of the same species from Suisun Bay (Hoffman et al. 1998). However, it is important to note that these species of birds do not breed in Tomales Bay, and thus bioaccumulation of mercury may occur at other locations.

**Mercury in sediment**

Data for sediment samples collected between 1999 and 2004 provide further information regarding potential risks to wildlife, since it is likely that sediment is a major pathway for methylmercury production and uptake into the food web. Sediment samples collected in 1999 and 2000 had total mercury concentrations ranging from 0.05-3.1 µg/g dry (Figure 5). Most of the samples exceeding the background level of mercury in sediment upstream of mined areas (0.2 µg/g dry; Marshall 2006) were collected around the Walker Creek Delta. One exception was a sample collected at Millerton, near the confluence with Lagunitas Creek in the southern portion of the Bay, which had an average concentration of 1.1 µg/g (Johnson et al. 2009).

Cores of sediment around the Walker Creek Delta were analyzed for methylmercury at 0-1, 2-5, and 6-10 cm depths, and ranged between 0.2 and 11.4 ng/g (Johnson et al. 2009; Figure 6).

In summary, existing data for sport fish, invertebrates, birds, and sediment indicate that humans and wildlife may face health risks in Tomales Bay due to methylmercury exposure. However, the degree of food web contamination in Tomales Bay is moderate. Methylmercury contamination of Tomales Bay is of concern due to the biological significance of the wildlife in the area, which is discussed in the next section.

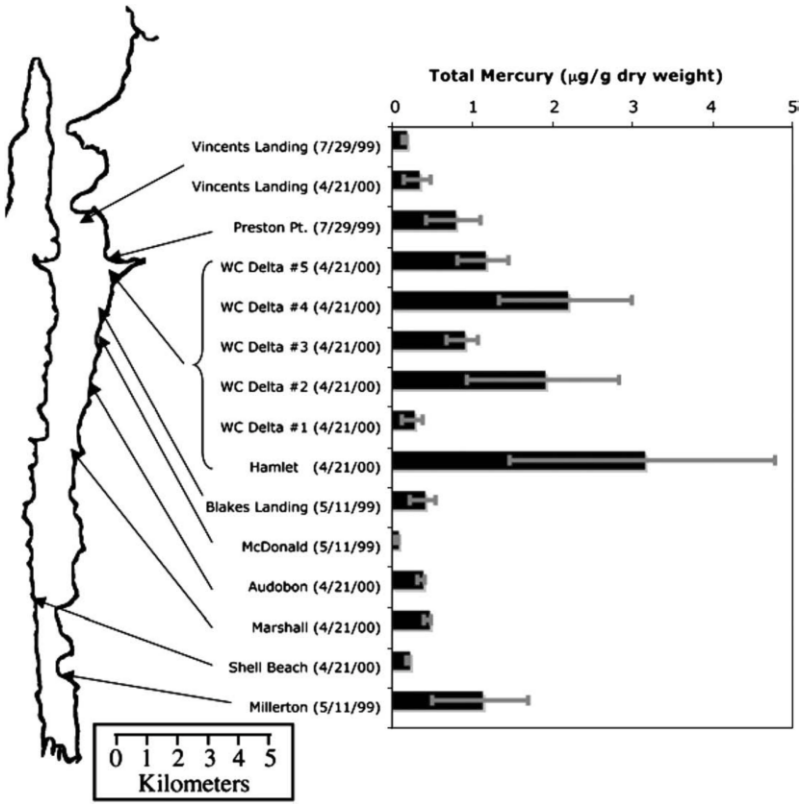



**Figure 5. Total mercury in surface sediment (~0-5cm) 1999-2000 (Johnson et al., 2009).**

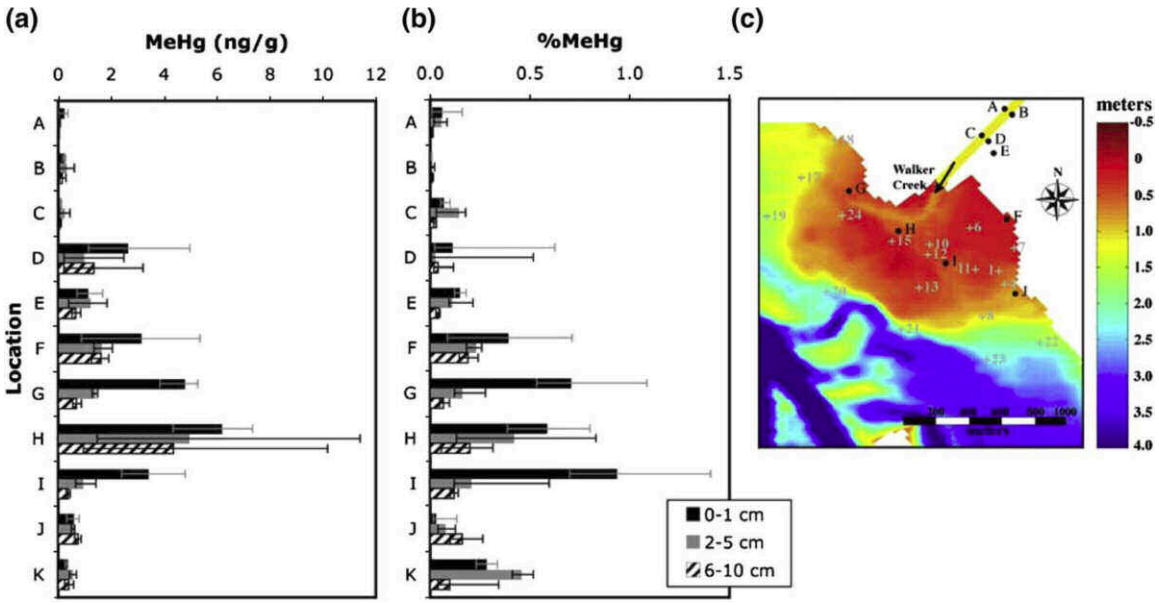



**Figure 6.** **Methylmercury concentrations (a) and percent methylmercury (b) in the top 1, 2-5, and 6-10 cm of sediment cores. Results are averaged from three cores for each site taken at locations in the Walker Creek Delta area (c). After Johnson et al. (2009).**

# 3. Project setting

## 3.1. Ecological Significance

Tomales Bay is renowned for its wildlife, herring fishery, and commercial shellfish industry. It is included in four protected areas due to its ecological significance: the Gulf of the Farallones National Marine Sanctuary, Golden Gate National Recreation Area, Point Reyes National Seashore, and Tomales Bay State Park (Figure 7). Nearly 2000 species, including many threatened and endangered species, were recently recorded in a study of biodiversity within Tomales Bay (Tomales Bay Biodiversity Partnership 2004). The Bay is also an important migratory stop along the Pacific Flyway and supports approximately 20,000 shorebirds and 22,000-25,000 waterfowl (Kelly 1992). Nearly half the bird species of North America have been spotted in this region (Tomales Bay Watershed Council 2003).

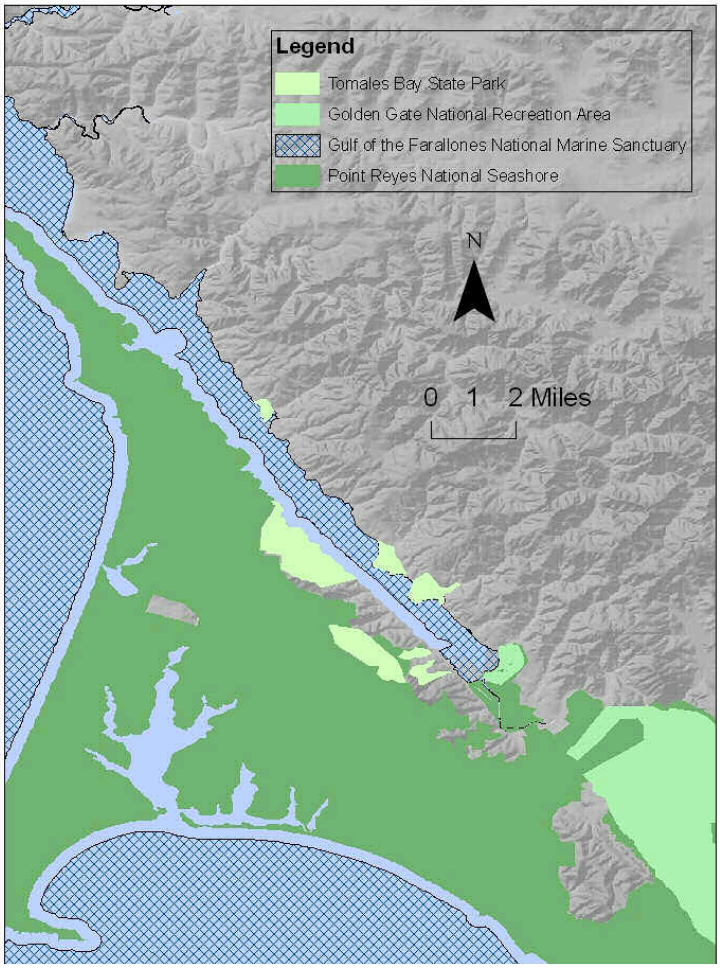



**Figure 7.** **Protected areas around Tomales Bay.** The Gulf of the Farallones National Marine Sanctuary extends much further into the Pacific Ocean for a total of 966 square nautical miles (not all pictured here).

## 3.2. Land use

Land use influences the amount of rainfall that becomes runoff and enters Tomales Bay (Fischer et al. 1996). It also directly influences the retention and release of mercury. Furthermore, the percentage of wetlands in a watershed generally correlates with methylmercury production (Grigal 2002). Mercury sources are often attributed to specific land uses such as industrial, urban (local fossil fuel combustion and commercial products), and agricultural (fertilizers and pressure sensing, temperature sensing, and electrical components; DTSC 2002). Major land uses in the Tomales Bay watershed are livestock grazing and dairy farming (55%) and park and open space (42%; Figure 8). There are six small, unincorporated communities (Point Reyes Station, Tomales, Woodacre, Lagunitas-Forest Knolls, Inverness and Dillon Beach) with a combined population of about 11,000 people. An additional 2.5 million visitors visit the National Seashore annually (National Park Service 2008). Given these land uses, nearby industrial and urban land uses are unlikely to be significant sources of mercury.

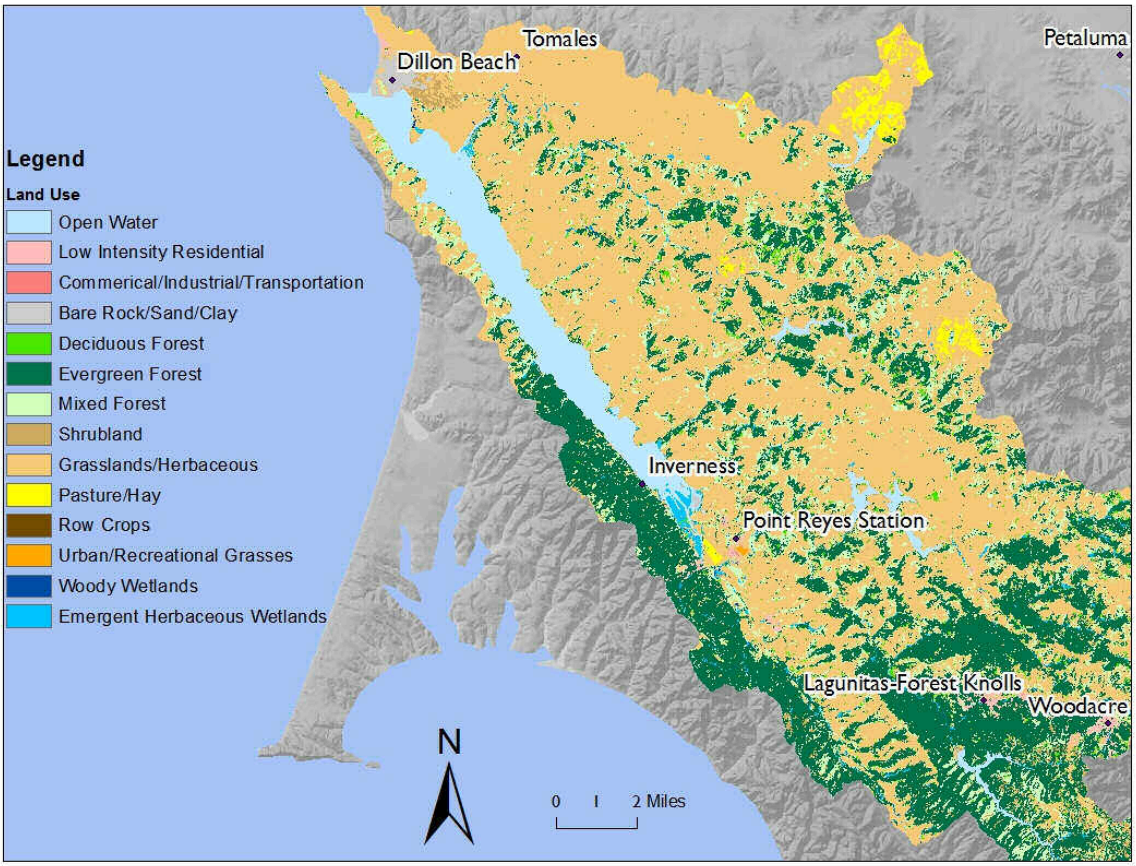



**Figure 8. Land use of the Tomales Bay watershed (ABAG 2000).**

## 3.3. Climate

Tomales Bay experiences a two season (one wet and one dry season) Mediterranean-style climate typical of much of California. Intense, episodic rainfall occurs during the winter months, with average annual rainfall varying between 60 cm (in the north and east portions of the watershed) and 130 cm in the south (Fischer et al. 1996). Another important component of the climate is fog, produced by the meeting of the cold coastal ocean currents and the warmer air coming from inland during the summers. Large blankets of fog can extend for over 80 km offshore to inland. This cooling effect and up to 25 days/month of fog cover creates a mild temperature along the coast, while temperatures inland are warmer (Evens 1993).

## 3.4. Hydrology

The Mediterranean climate of the area significantly impacts the hydrology, since runoff is episodic in the winter months. Fischer et al. (1996) demonstrated that rainfall and runoff are well correlated for Tomales Bay watershed since human alteration of the landscape and water resources is much less than for more urbanized landscapes in the San Francisco Bay Area. There are two major freshwater inputs to Tomales Bay: Lagunitas and Walker creeks. Lagunitas Creek accounts for about two-thirds of the total watershed runoff, Walker Creek accounts for one quarter, and small tributaries account for the

remaining runoff (Table 6). Stream discharge is currently measured at two gaging stations maintained by USGS (Lagunitas Creek at Samuel P. Taylor Park and Lagunitas Creek at Point Reyes Station), though historically others were in operation. This seasonal rainfall contributes to higher salinity and residence times of up to 120 days in the southern portions of the Bay during the summer when freshwater inputs are close to zero (Hollibaugh et al. 1988). Episodic rainfall also correlates with mercury fluxes as demonstrated by Whyte and Kirchner (2000), who found that during a 200 minute period a 2.6-fold increase in streamflow resulted in an 82-fold increase in mercury flux. The northern portion of the Bay maintains conditions much like that of the Pacific Ocean. Upwelling is greatest in the summer months and tends to depend on northerly winds (Bakun 1975). Processes of upwelling, tidal currents, and natural geology contribute to the Bay's variable bathymetry ranging from 1-18 m (Figure 9).

**Table 6. Annual runoff in the Tomales Bay watershed based on USGS gaging records, and including discharge from reservoirs (Ghodrati and Tuden 2005).**

| Watershed | Runoff (% of total) |
|---|---|
| Lagunitas Creek | 66% |
| Walker Creek | 25% |
| Other small tributaries | 9% |
| TOTAL | 100% |

## 3.5. Geology

It is important to consider the underlying geology of the Tomales Bay region in order to understand the natural geologic processes that generate sediment in the watershed, and the transport of pollutants such as mercury which are mostly bound to sediment particles during fluvial transport. Tomales Bay occupies the rift zone of the San Andreas Fault, which separates the Pacific and North American plates. It is the most significant geologic feature of the area, and has shaped the topography and geology of the landscape since Tomales Bay was filled with glacial melt water 15,000 to 5,000 years ago at the end of the last ice age (Wahraftig and Wagner 1972). Evidence suggests that since the Cretaceous period, the Point Reyes Peninsula has been moving northward at an average rate of 1-5 cm per year (Galloway 1977). The 1906 earthquake, however, resulted in horizontal displacement on the peninsula of up to six meters in a matter of seconds (Galloway 1977) providing a reminder that much of the movement on the fault is punctuated rather than a gradual continuous creep.

The San Andreas Fault serves as a dividing line between two distinct geologic regions of the watershed. The western side of the Bay is underlain by the late Cretaceous Inverness Ridge formation (granodiorite and granite) and Tomales Point (tonalite) and its soils are more coarse-grained and well drained (Anima et al. 2008). In contrast, the eastern shore has much finer-grained soils that originate from the Wilson Grove Formation (north of Walker Creek only) and the Franciscan Formation, where most of the mercury mining took place (Figure 10). Geologic and mining-related mercury sources therefore are present only in the eastern portion of the watershed. Both of these formations are highly erodible, and produce soils susceptible to landslides and gullies

(Warhaftig and Wagner 1972). This underlying geology and orientation to the Pacific Ocean results in the substrate of the northern portion of Tomales Bay (to just below Hog Island) being made up of sandy deposits, while the southern half is dominated by clay and silt (Daetwyler 1962).

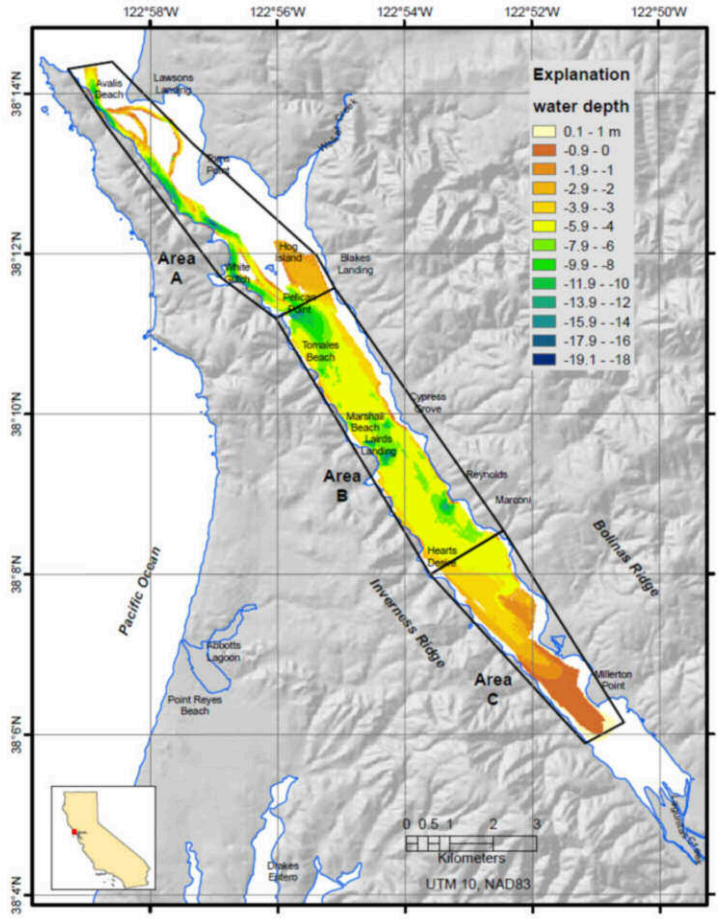



**Figure 9.** **Bathymetry of Tomales Bay (Anima, et al. 2008).** Note black outline indicates where bathymetry was measured, which does not include much of the Walker and Lagunitas Creek deltas.

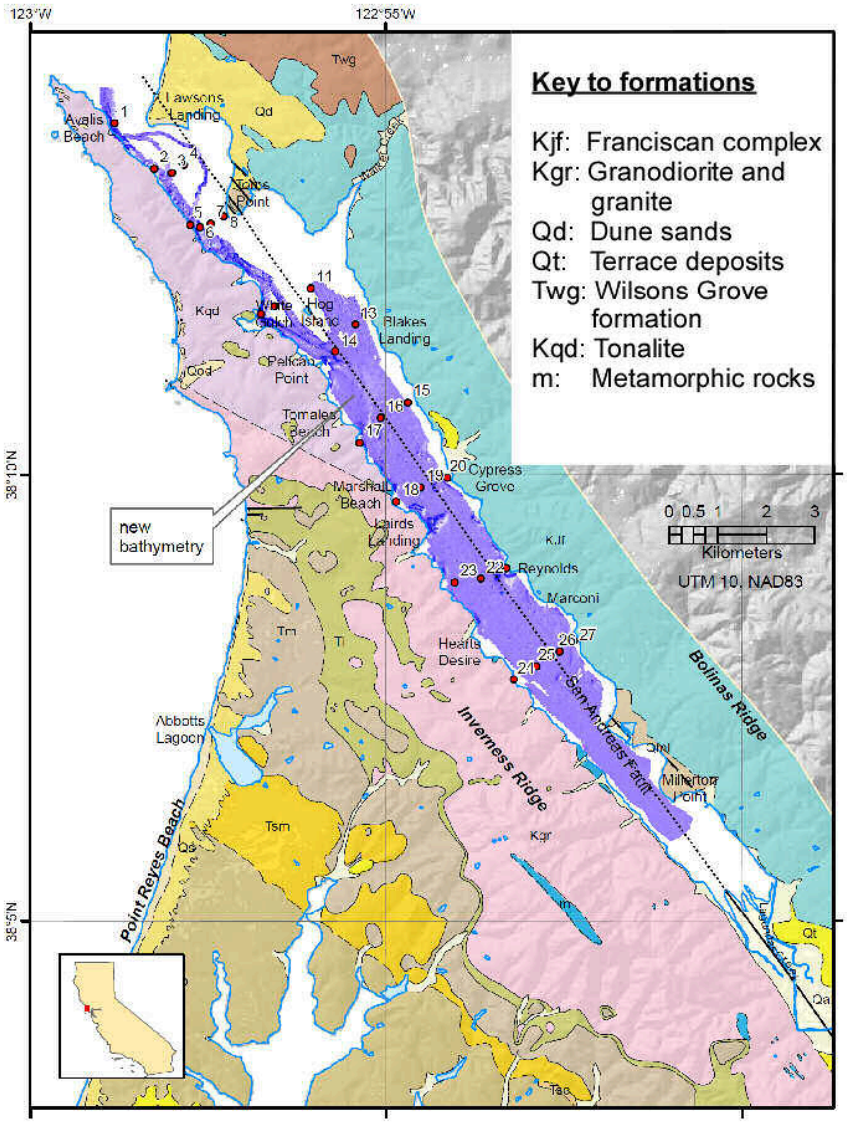



**Figure 10.** **Geology of Tomales Point Reyes National Seashore and Vicinity.** Purple area indicates area where USGS mapped bathymetry in 2008 (Figure 9). Adapted from Clark and Brabb (1997) in Anima et al. (2008).

## 3.6. Commercial and recreational fishing

The California Department of Fish and Game (CDFG) regulates the Pacific herring fishery and commercial shellfish farming operations in Tomales Bay. The Bay's oysters have been farmed since the early 1900s, and now occupy 463 acres in the north and central-eastern areas of the Bay (Figure 11). The aquaculture industry (which includes small quantities of mussels and clams, in addition to oysters) contributes an estimated $2.49 million annually to the local economy (Ghodrati and Tuden 2005). Commercial production of the native oyster *(Ostrea lurida)* began around 1875; however the fishery is now mostly comprised of Pacific oysters *(Crassostrea gigas)* and Bay mussels *(Mytilus edulis* and *M. galloprvincialis)* due to their higher growth rate and size. In addition, there are small amounts of Eastern *(O. virginica)*, European *(O. edulis)*, and

Kumumoto *(C. gigas kumomoto)* oysters and Manila clams *(Tapes semidecussata)* in production (Conte and Moore 2001). Oysters grow in bags or in wooden trays placed on the substrate of intertidal areas in the Bay.

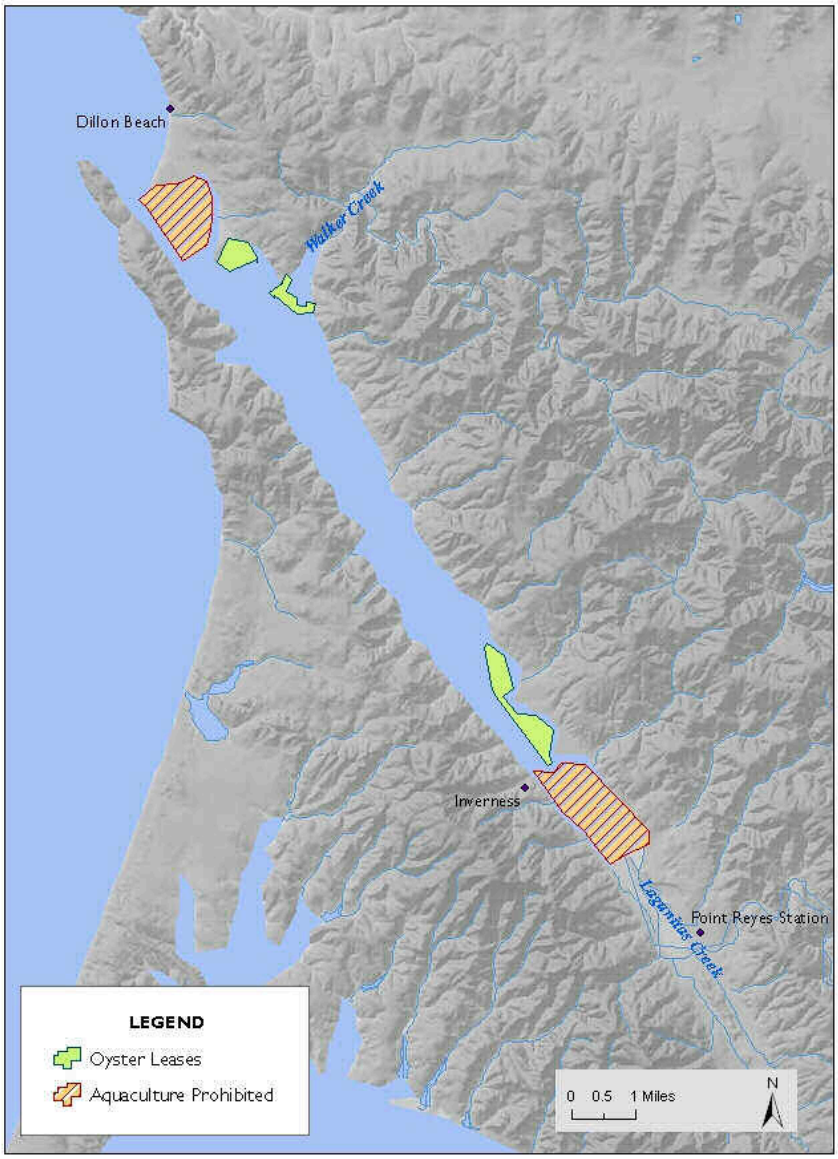



**Figure 11. Areas of current shellfish leases in Tomales Bay, and where aquaculture is prohibited.** For more detailed maps of individual leases, see Ghodrati and Tuden (2005).

In winter, the Bay is a major spawning ground for Pacific herring (*Clupea pallasi*), which is almost exclusively harvested for its roe and exported to Japan. Records of spawning biomass (measured in tons of eggs deposited during the winter spawning season) are available starting in 1973. Based on these records, the greatest biomass was observed in 1979 at over 20,000 tons, but later dropped to nearly zero tons in 1989 (Figure 12). This trend was similar in San Francisco Bay. Subsequently, the fishery was closed for three seasons. Since then strict quotas have been assigned, and are roughly

equivalent to 15-20% of the estimated biomass for the coming year (Moore and Mello 1995). The most recent catch, and the last time the fishery was open (2006-7), yielded only 1.2 tons of herring despite a quota set at 350 tons. About 12% of the total tonnage was roe. The low catch, compared to an average of 163.3 tons per year since 1992-3, was attributed to low market price and high operating costs (Bartling 2007).

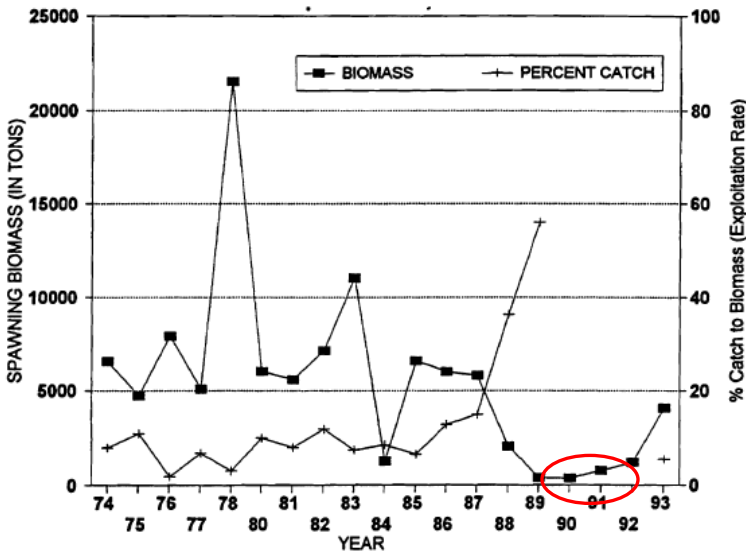



**Figure 12. Spawning biomass (tons) of Pacific herring, 1974-1993 (Moore and Mello 1995). Red circle indicates years that the fishery was closed for three seasons (1990, 1991, & 1992).**

In addition to the commercial herring fishery and aquaculture industry, Tomales Bay supports a thriving recreational fishery, with halibut and clams being the two most popular organisms taken each year by anglers (TBWC 2003). Other fish commonly caught include Dungeness and rock crabs, jacksmelt, perches, sole, striped bass, sturgeon, sharks, and rays (TBWC 2003).

# 4. Previous research programs

Tomales Bay has been the subject of numerous research and monitoring programs over the past few decades (Table 7). In the first major effort, Tomales Bay was one of five estuaries studied through the Land Margin Ecological Research (LMER) program to better characterize the exchange of nutrients between oceans and land. Several papers were produced through this program (see http://lmer.marsci.uga.edu/tomales/briepubs.html). The focus of these papers was nutrient dynamics, and they did not report any mercury analysis. Other research and monitoring programs are summarized in Table 7, and include studies by a range of regulatory agencies, non-profit groups, and academic institutions. This document draws on findings from many of these research programs in order to better interpret information about mercury and potential impairment of Tomales Bay.

**Table 7.** **Research and monitoring programs in Tomales Bay.** Programs highlighted in gray indicate mercury data collected and cited in this report. LMER= Land Margin Ecological Research; TBWC=Tomales Bay Watershed Council; PEEIR=Pacific Estuarine Ecological Indicator Research;.

| Organization or Researcher | Matrices and Parameters Analyzed | Frequency | # Sites, Locations | Reference(s) |
|---|---|---|---|---|
| Johnson (UC Berkeley) | Sediment: THg and MeHg in 1-2m cores<br>Algal mats and surface sediment: THg and MeHg | Cores taken in 2003; algal mats and surface sediment sampled in Aug 2002 | Around Walker Creek Delta | Johnson et al. 2009 |
| LMER | Nutrients cycling, sedimentation and water circulation | Varied by research component; 1985-1999 | varies | 60+ publications; see http://lmer.marsci.uga.edu/tomales/briepubs.html |
| Moss Landing Marine Pollution Studies Laboratory | Water: MeHg for 11 months; THg for 2 months | May 2007-May 2008 | 2 sites: near Walker Creek Delta and Shell Beach | Moss Landing Marine Pollution Studies Laboratory 2008 |
| National Park Service (Giacomini Wetland Restoration) | Topography and cross-sections, water level, sediment quality (nutrients), sedimentation on floodplains, biota, vegetation, water quality (salinity, conductivity, conductance, pH, DO, temperature and turbidity; nutrients, pathogens, and productivity indicators at a smaller subset of stations). | varying frequency over 20 years post-construction | 35 sites in the Project Area; 16 reference sites in 3 wetlands including the Walker Creek marsh) | Parsons 2005 |
| OEHHA | Biota: MeHg and THg in clams; THg in crabs | April-June 2000 | Around Walker Creek Delta | OEHHA 2004 |
| OEHHA | Biota: THg in sportfish | May 1999 (8 species), May 2001 (7 species; 6 of the same from 1999) | Mid-Bay | OEHHA 2004 |
| PEEIR | Range of studies to demonstrate utility of resident indicator species in salt marshes for ecosystem-wide management | Varied by study; 2001-2006 | 7 estuaries in CA, including Walker Creek | Various, see www-bml.ucdavis.edu/peeir/docs/PEEIRPubsto2009.pdf |
| RWQCB | Water: TSS, Hg (filtered and unfiltered), and MeHg | Feb and March 2001 | 17 sites, high and low tide at 6 | Marshall 2006; Johnson et al. 2009 |

| | | | | |
|---|---|---|---|---|
| | | | sites | |
| RWQCB | Water: TSS, Hg (filtered and unfiltered), and MeHg | Dec 2000 and April 2001 | 8 sites sampled at both dates except for one; 6 sites around WC delta | Marshall 2006; Johnson et al. 2009 |
| RWQCB | Sediment: THg | Spring and summer random years | Same as above mostly | Marshall 2006; Johnson et al. 2009 |
| RWQCB | Biota: THg in mussels, oysters, bivalves | Winter 1996-97, spring 99 | Around Walker Creek Delta | Marshall 2006; Johnson et al. 2009 |
| RWQCB | Sediment: MeHg and THg | Spring 2004 | Around Walker Creek Delta | Johnson et al. 2009 |
| TBWC (Long Term Trend Monitoring) | Water: fecal coliform, transparency, turbidity, conductivity/salinity, pH, dissolved oxygen, ammonia, and temperature, tidal stage, discharge, cumulative precipitation *nutrients added for 2008-2010 | Weekly during wet season and twice a month during dry season 2003-2005; 2008-2010 | 4 bay and 9-12 tributaries | http://www.tomalesbaywatershed.org/waterquality.html |
| TBWC (source area monitoring for septic tanks) | Water: temperature, DO, conductivity, pH, fecal coliform, ammonia, and others | 2-3 storm events per winter (increased to 3-4 in 2008) 2003-2005; 2008-2010 | 50 "hotspots" throughout watershed and bay | http://www.tomalesbaywatershed.org/waterquality.html |
| UC Davis | Sediment cores: microfossils Water: temp, salinity, pH, DO, chlorophyll, DIC, stable isotopes, nutrients, alkalinity. | Cores every 6-9 months; water every month starting in spring 2009 | Mid-bay | http://www.bml.ucdavis.edu/facresearch/hill_research.html#change |

# 5. Methods

## 5.1. Development of Numeric Targets to Protect Wildlife

One of the first steps in determining impairment of Tomales Bay by methylmercury was to estimate a numeric target for the protection of wildlife. We evaluated existing numeric targets for mercury and provided information to support their use as appropriate standards to protect the wildlife-related beneficial uses of Tomales Bay. Guidance documents describe numeric targets as a necessary component of a TMDL because they provide a reference from which to assess risk of a pollutant to biota (e.g., Ghodrati and Tuden 2005). This section will review the technical analysis performed in developing an estimated target for protection of wildlife from methylmercury in Tomales Bay.

Methodologies for developing numeric targets used in mercury TMDLs were developed by the USEPA (1993), and evaluated by U.S. Fish and Wildlife Service (USFWS) and OEHHA. As mentioned in section 2.2, the current USEPA water quality criterion for mercury is a tissue residue concentration of methylmercury in edible fish and shellfish protective of humans (0.3 µg/g wet; USEPA 2001). Based on a request from USEPA, USFWS staff in Sacramento, CA evaluated this criterion for its ability to protect sensitive species of wildlife in California. This was not considered formal consultation under Section 7 of the Endangered Species Act, but instead guidance to the USEPA on the potential effectiveness of the methylmercury criterion (USFWS 2003). Subsequently, OEHHA reviewed the USEPA criterion, and evaluated its applicability to California water bodies (Sanborn and Brodberg 2006). They concluded that the methodology was broadly applicable in California, and that bioaccumulation factors and trophic level ratios that are water body-specific greatly strengthen the method and resulting targets

### 5.1.1. **Numeric Targets in Other Bay Area TMDLs**

There are three USEPA-approved mercury TMDLs in the San Francisco Bay and Central Valley Regions, and all have used the USEPA/USFWS methodology to develop numeric targets. Based on this precedent and a review of the methodology, we considered it appropriate to employ the same methodology for Tomales Bay. A review of existing targets developed for the approved TMDLs was conducted as a first step, to assist in evaluating whether the same targets could be applied to Tomales Bay.

A detailed comparison of local mercury TMDLs is provided in Ridolfi (2009). The Delta and San Francisco Bay mercury TMDLs proposed the same target (0.03 µg/g wet) for prey fish to protect the California Least Tern, while the Walker Creek TMDL proposed a slightly higher target (0.05 µg/g wet) to protect the Belted Kingfisher, as well as a second target for fish 15-35 cm (0.1 µg/g wet) to protect the Osprey (Table 8).

**Table 8. Summary of targets from other local mercury TMDLs.** Targets are methylmercury concentrations in prey fish to protect piscivorous wildlife.

| | Walker Creek | | San Francisco Bay | Delta |
|---|---|---|---|---|
| Numeric target (µg/g wet) | 0.05 | 0.1 | 0.03 | 0.03 |
| Species protected | Belted Kingfisher | Osprey | California Least Tern | California Least Tern |
| Prey fish size (Trophic Level) | 5-15 cm (TL3) | 15-35 cm (TL3) | 3-5 cm (TL2) | <5 cm (TL2) |

### 5.1.2. **Methylmercury Targets for Tomales Bay**

A review of the existing approved TMDLs in the Bay Area and Central Valley indicated that the targets and species that they protect are water body-specific, and that having local data is a necessary part of developing the most appropriate target for a given

watershed. The USEPA methodology used in other TMDLs and evaluated in California by USFWS and OEHHA uses five main components to calculate the threshold methylmercury concentrations using Equation 1 for each species on the list:

- A list of birds and mammal species that live in the water body,
- Body mass,
- Food ingestion rate (FIR),
- Diet, and
- Reference doses for sublethal effects of methylmercury.

$$\text{Threshold methylmercury concentration } (\mu g/g) = \frac{(\text{body mass [kg]})*(\text{FIR [g/day]})}{\text{Reference dose } (\mu g/kg/day)}$$

**Equation 1** (USEPA 1993)

A step-by-step summary of the calculations, assumptions, and local data used to develop estimated threshold methylmercury concentrations in each trophic level of prey consumed by piscivorous wildlife in Tomales Bay is provided below.

**Step 1. Bird and Mammal Species in Tomales Bay**

Wildlife that eat a mostly aquatic diet based on fish are considered to be most at risk (USEPA 1997), since methylmercury tends to be produced in aquatic habitats and biomagnify up the food chain to higher concentrations at higher trophic levels (USEPA 1997). Early life stages of vertebrates are the most sensitive to methylmercury effects.

Species that reside in Tomales Bay only a few months of each year (the winter for example) and then migrate to other locations to breed during the remainder of the year are not optimal indicators of the effects of methylmercury in Tomales Bay. They may be impaired by methylmercury from their breeding grounds or other locations, or have low body burdens of methylmercury and not be impaired. Since the goal of this project is to determine the impairment to wildlife from methylmercury from Tomales Bay, we focused on wildlife that reside and breed in the watershed, and are therefore more likely to be indicators for local methylmercury impairment. Based on this rationale, resident, breeding, piscivorous wildlife species were deemed most at risk for methylmercury exposure in Tomales Bay, and were used here to calculate numeric targets for methylmercury.

Tomales Bay is home to many piscivorous wildlife species. We consulted with local biologists (Jules Evens, Avocet Research Associates and John Kelly, Audubon Canyon Ranch) to determine which species of piscivorous wildlife breed in Tomales Bay. Based on their expert knowledge, there are 12 species of piscivorous birds and one piscivorous mammal species (harbor seal) to consider. Thus, of the 33 species of piscivorous wildlife that live at least part of their life cycle in Tomales Bay, the list was narrowed to 13 resident species that are likely to be at greatest risk for methylmercury accumulated directly from Tomales Bay.

Even though harbor seals are piscivores that breed in Tomales Bay, they were eliminated from the final list of species for which targets were developed for two reasons. First, although harbor seals maintain at least two colonies within Tomales Bay and many live there year-round, they tend to feed at least 20% of the time at locations outside of the Bay (Sarah Allen, Point Reyes National Seashore, *pers. comm.*). Brookens et al. (2007) tagged seven seals from Tomales Bay and found that they commonly traveled as far south as the Marin Headlands and Año Nuevo near Santa Cruz. Second, their diet from within the Bay is mostly herring and salmon, which are unlikely to indicate methylmercury impairment in Tomales Bay because these species spend much of their life history outside the Bay (S. Allen, *pers. comm.*). These two species of fish are anadromous and highly migratory. Salmon spend relatively short periods of time in the Bay while in transit between their adult lives in the ocean and their early life and spawning activities in upstream tributaries; thus, it is not possible to determine where the methylmercury in salmon consumed by seals is coming from (S. Allen, *pers. comm.*). Thus, Pacific harbor seals that reside year-round in Tomales Bay are not a good indicator species for bioaccumulation of methylmercury from sources within Tomales Bay. The list of possible indicator species was thus narrowed to 12 species of piscivorous birds (Table 9).

**Table 9.** **Piscivorous wildlife species in Tomales Bay.** These 12 species are likely to be at greatest risk for methylmercury exposure in Tomales Bay. There is one California Species of Special Concern, indicated by bold text.

| Species (common name) | Scientific Name |
|---|---|
| Pied-billed Grebe | *Podilymbus podiceps* |
| Double-crested Cormorant | *Phalacrocorax auritus* |
| Great Blue Heron | *Ardea herodias* |
| Great Egret | *Ardea alba* |
| Snowy Egret | *Egretta thula* |
| Black-crowned Night-Heron | *Nycticorax nycticorax* |
| Green Heron | *Butorides virescens* |
| American Bittern | *Botaurus lentiginosus* |
| **Least Bittern** | ***Ixobrychus exilis*** |
| Caspian Tern | *Hydroprogne caspia* |
| Osprey | *Pandion haliaetus* |
| Belted Kingfisher | *Megaceryle alcyon* |

**Step 2. Body Mass**

Body mass is an important component for determining risk of methylmercury exposure since it helps in determining relative ingestion rates between species. We consulted the literature (e.g., Dunning 1993), and compiled a list of typical body masses for adult female birds (Table 10). As explained earlier in this report, female birds at the time of breeding are likely to pass methylmercury on to their eggs, which are the most

sensitive life stage for methylmercury effects. Thus, it is important to protect female birds from having high methylmercury exposure just before and during breeding.

**Step 3. Food Ingestion Rates**

Food ingestion rates (FIRs) provide information about the mass of food consumed per day, which helps to determine the potential mass of methylmercury consumed. As explained in detail in USFWS (2003), FIRs (Table 10) are calculated using the free-living metabolic rate (FMR), metabolized energy (ME), and body mass of birds. FMRs for many types of birds and mammals have been studied extensively, and following Nagy (2001) we used an FMR averaged from 95 species of birds for 11 of the 12 species. FMRs specific to some orders of birds, including Charadriiformes (e.g., Caspian Terns) were available (Nagy 2001). Nagy found that FMR was more correlated to body mass than taxonomic group, with the exception of passerines. None of the birds under consideration in this report were passerines, so an "all birds" FMR was deemed appropriate, especially since body mass is factored into the FIR equation and would reduce any variability attributed to body mass.

Metabolized energy (ME) rates are specific to the class of animal and what it eats. For all species except the Black-crowned Night-Heron (*Nycticorax nycticorax*), we used the ME for birds whose diet consists of fish only. Since the Black-crowned Night-Heron consumes some birds as part of their diet, we computed the ME from eating fish separately from the ME from eating birds, based on methodology explained in USFWS (2003). Thus the Black-crowned Night-Heron has a different FMR than the other 11 birds.

**Step 4. Typical Diet**

Diet information is important in determining methylmercury exposure since different types of prey may contain different concentrations of methylmercury and may be metabolized in different ways (USFWS 2003). A literature review of the 12 species of piscivorous birds found in Tomales Bay provided the typical diets consumed (Table 10). It is important to note that many literature studies were not conducted locally in Tomales Bay, and since many species are opportunistic feeders (i.e., they change their diet based on what is available to eat), the diets and the percentage indicated for each trophic level (% of diet) are approximations. In addition, fish diets often change as they grow larger, so an individual can move up in trophic position over a lifetime, adding to the complexity. Improved information could be developed through additional local data collection and the development of a map of the food web for Tomales Bay. In the meantime, based on the dietary intake studies from the literature, example lists in other TMDLs (e.g., Wood et al 2008), the literature on fish for the West coast and Tomales Bay (Moyle 2002, Pettigrew 2004), and work done in San Francisco Bay to begin to develop an understanding of the food web (Jahn 2008), we assigned approximate trophic levels to the prey of each of the 12 birds species based on the types of food they consume. The literature indicates that most of the prey fish in Tomales Bay are at trophic level three (Pettigrew 2004). Many birds eat aquatic invertebrates and crustaceans, which are included in Table 10 under trophic level two. Some species also consume nestling birds or small mammals, indicated under the bird prey and "other" categories, respectively, in Table 10. This delineation of

diets among species is important for estimating the threshold methylmercury concentration by trophic level, which is used to provide a basis for the magnitude of numeric targets (Step 7 of this summary).

**Step 5. Reference Dose**

A "reference dose" is defined as the "daily exposure to a toxicant at which no adverse effects are expected" (USFWS 2003). Heinz (1979) identified the reference dose for methylmercury in Mallards (21 μg/kg/day). Although Mallards are not considered an important species in Tomales Bay for the purpose of defining numeric methylmercury targets, they are the only bird species for which a specific numeric methylmercury toxicity threshold is available. Thus, in a similar manner to the other mercury TMDLs summarized above (Table 8), this is the reference dose we used as an estimate of the concentration at which we estimate no adverse effects would be observed in Tomales Bay bird species. As mentioned earlier in this report, more recent work by Heinz (2009) indicates that other birds that reside in Tomales Bay may be more sensitive to methylmercury than Mallards, so this reference dose may be too high.

**Table 10. Exposure parameters for piscivorous wildlife in Tomales Bay.** California Species of Special Concern is indicated by bold text. Sources: Dunning (1993), Nagy (2001). Other sources listed in "size of prey" column.

| Species | Total Food Ingestion Rate (g/day wet wt.) | Body Mass of Adult Female (kg) | Trophic Level 2 Aquatic Prey (% of diet) | Trophic Level 3 Aquatic Prey (% of diet) | Trophic Level 4 Aquatic Prey (% of diet) | Omni-vorous Bird Prey (% of diet) | Other foods (% of diet) | Size of Prey |
|---|---|---|---|---|---|---|---|---|
| Pied-billed Grebe | 118 | 0.36 | 80% | 20% | | | | Mostly aquatic invertebrates and crustaceans; some fish <3 cm (Muller and Storer 1999) |
| Double-crested Cormorant | 325 | 1.74 | | 100% | | | | "Size range 3–40 cm, but commonly <15 cm" (Hatch & Weseloh 1999) |
| Great Blue Heron | 368 | 2.11 | | 90% | | | 10% | 5-15 cm in breeding season; otherwise up to 30 cm or larger (Willard 1977); can also take birds such as Virginia Rails, and small mammals like muskrats (Evens pers.comm.) |
| Great Egret | 200 | 0.81 | 10% | 85% | | | 5% | Most fish are <5 cm in length, but a small portion can be >10 cm in length (Schlorff 1978). |
| Snowy Egret | 121 | 0.37 | 40% | 60% | | | | Most prey <10 cm (Parsons and Master 2000) |
| Black-crowned Night-Heron | 188 | 0.81 | 35% | 40% | 10% | 5% | 10% | Mostly fish >3 cm; also predate on eggs or chicks of other herons, terns and Franklin's Gulls (Davis 1993; Post 2008) |
| Green Heron | 78 | 0.19 | 45% | 45% | | | 10% | Mostly crustaceans, aquatic invertebrates, and fish up to 10cm (Davis and Kushlan 1994) |
| American Bittern | 183 | 0.71 | 60% | 30% | | | 10% | TL2 and TL3 fish but no size class given; also garter snakes, small mammals, frogs, and tadpoles (Gibbs et al 1992a) |
| **Least Bittern** | 48 | 0.09 | 60% | 40% | | | | Mostly aquatic invertebrates and fish less than 10 cm (Gibbs et al 1992b) |
| Caspian Tern | 296 | 0.66 | | 100% | | | | Fish include jacksmelt, shiner perch, and staghorn sculpin; some as big as 15 cm (Gill 1976) |
| Osprey | 305 | 1.57 | | 90% | 10% | | | Prey almost exclusivley on topsmelt (up to 15 cm) or jacksmelt(up to 28 cm), but sometimes starry flounder (up to 8 cm) or large carp (>7 cm) (Jules Evens, Avocet Research Assoc., *pers. comm.* ) |
| Belted Kingfisher | 67 | 0.15 | | 100% | | | | Generally less than 10.5 cm; up to 18 cm (Hamas, 1994) |

**Step 6. Calculate Estimated Threshold Methylmercury Concentrations in Total Diet**

To calculate estimated threshold methylmercury concentrations in total diet for piscivorous birds of Tomales Bay, it is necessary to use food ingestion rate (FIR), reference dose, and body mass in Equation 1 for each species (summarized in Table 11). As summarized in previous steps, FIR represents the total mass of food consumed per day, reference dose refers to the intake rate at which toxic effects are not observed (based on Mallard duck feeding studies, Heinz 1979), and body mass is defined as the mass of adult female birds. Using the resulting estimated threshold methylmercury concentration in total diet (Table 11) and the distribution of diet among trophic levels (Table 10), threshold methylmercury concentrations were estimated for each trophic level of prey for the piscivorous birds of Tomales Bay in Step 7.

**Table 11. Estimated threshold methylmercury concentrations in total diet to protect Tomales Bay wildlife.** Analysis is based on methods described in USEPA (1993). Note: local dose response studies are not available to refine these estimates. Bold text indicates a California Species of Special Concern.

| Species | Reference Dose (µg/kg body weight/day) | Body Mass of Adult Female (kg) | Food Ingestion Rate (g/day) | Threshold MeHg Concentration in Total Diet (µg/g ) |
|---|---|---|---|---|
| Pied-billed Grebe | 21 | 0.358 | 118 | 0.063 |
| Double-crested Cormorant | 21 | 1.74 | 325 | 0.112 |
| Great Blue Heron | 21 | 2.11 | 368 | 0.120 |
| Great Egret | 21 | 0.812 | 200 | 0.085 |
| Snowy Egret | 21 | 0.371 | 121 | 0.064 |
| Black-crowned Night-Heron | 21 | 0.810 | 188 | 0.091 |
| Green Heron | 21 | 0.187 | 78.0 | 0.050 |
| American Bittern | 21 | 0.706 | 183 | 0.081 |
| **Least Bittern** | 21 | 0.086 | 47.6 | 0.038 |
| Caspian Tern | 21 | 0.655 | 296 | 0.047 |
| Osprey | 21 | 1.57 | 304 | 0.108 |
| Belted Kingfisher | 21 | 0.148 | 67.2 | 0.046 |

**Step 7. Estimated Threshold Concentrations of Methylmercury by Prey Trophic Level**

Using the estimated threshold methylmercury concentrations in total diet from Table 11, the diets of piscivorous birds from Table 10, and all the assumptions outlined above, threshold methylmercury concentrations for each trophic level of prey consumed were estimated (Equation 2). This last step is important because trophic level and size of prey correlate with methylmercury concentrations.

Total diet MeHg =(% diet TL2*TL2conc)+(%diet TL3*TL3conc)+( %diet TL4*TL4conc)

**Equation 2** (USFWS 2003)

To solve Equation 2 for the three unknowns (the estimated threshold methylmercury concentrations in each trophic level of prey) we used the following method explained in Wood et al. (2008):

> "In order to solve…for the desired concentrations in TL2, TL3 and TL4 biota, concentrations in two trophic levels are put in terms of the concentration in the lowest trophic level. Equation [2] is then rearranged to solve for the lowest trophic level concentration. In order to express the concentration in a higher trophic level (i.e., TL4) in terms of TL2 concentrations, staff used two types of translators: food chain multipliers (FCM) and trophic level ratios (TLR). A food chain multiplier (FCM) is the ratio of methylmercury concentrations in fish of different trophic levels. A FCM represents the biomagnification of mercury between 2 successive levels of the food chain. The FCM is determined using mercury concentration data in fish in a predator-prey relationship. [With a FCM, the predator and prey can be in different size classes.] A trophic level ratio (TLR) is the ratio of methylmercury concentrations in fish of different trophic levels, but is derived using data for fish in the same size classification. For example, an Osprey may consume sunfish (TL3) and bass (TL4). A 350 mm sunfish, though, is too large to be preyed upon by an equivalently-sized smallmouth bass. Therefore, the ratio of mercury concentration in TL4 to TL3 fish eaten by Osprey is termed a TLR rather than a FCM."(p. 38)

To estimate the difference in methylmercury concentrations between TL2 and TL3 organisms, we used an FCM derived from a national dataset since TL2 and TL3 organisms have a predator-prey relationship in Tomales Bay (Jahn 2008). From what is known of the Tomales Bay food web from the literature, TL2 organisms are almost entirely aquatic invertebrates, and not fish. Aquatic invertebrates may not have the same amount of methylmercury in their tissue as TL2 fish (Suchanek et al 2008, Wiener et al. 2007). As there are insufficient data to characterize methylmercury concentrations in prey species of Tomales Bay, we used the national dataset to calculate the FCM for TL3/TL2. In this dataset, concentrations of methylmercury in TL3 fish were on average 5.7 times the concentrations in TL2 fish (USEPA 1993). Seven of the 12 piscivorous bird species (Pied-billed Grebe, Great Egret, Snowy Egret, Black-crowned Night-Heron, Green Heron, American Bittern, and Least Bittern) in Tomales Bay eat aquatic invertebrates, and the national FCM 3/2 was used to calculate the threshold methylmercury concentrations in their TL2 and TL3 prey.

Two species of birds in Tomales Bay consume TL4 fish (Osprey and Black-crowned Night-Heron), so it was necessary to use the TLR for TL4/TL3 to calculate their threshold methylmercury concentrations. As stated above, a TLR was used instead of an FCM because from what we know of TL3 and TL4 prey, they are of similar size and do not have a predator-prey relationship. Instead, TLRs are calculated as a ratio of bioaccumulation factors (BAFs) between trophic levels of fish (in the following examples we use *a* and *b* to stand for 2 different trophic levels):

$(BAF_{TLa}) / (BAF_{TLb}) = TLR\ a/b$ **Equation 3**

BAFs are ratios of dissolved methylmercury concentrations in water and methylmercury concentrations in fish, and characterize the bioaccumulation of aqueous methylmercury from water into the food chain.

For estimating the difference between trophic level three and four (TLR TL4/TL3) it is more important to have local BAFs, rather than relying on the national dataset (USFWS 2003, Sanborn and Brodberg 2006). A TLR was available from the Delta TMDL (Wood et al. 2008) based on data collected in the Delta. While the Delta is geographically close to Tomales Bay, it is mostly a freshwater system with different species of fish and different sources of mercury, and thus it is likely that there are different levels of methylmercury in both fish and water. San Francisco Bay is also a neighboring ecosystem, but a better comparison than the Delta because it is, like Tomales Bay, an estuary. We used data from San Francisco Bay collected through the Regional Monitoring Program (RMP) to estimate a TLR for TL4/TL3.

Field studies to determine the accuracy of these assumptions would be valuable. There were some assumptions used to calculate the BAFs and TLR for TL4/TL3 for San Francisco Bay, detailed by Ridolfi (2009). These include assumptions that mercury in fish tissue is assumed to be 95% methylmercury, even though only total mercury data are available, and that trophic levels assigned to fish are appropriate in spite of the limited information available on the food web study of San Francisco Bay. BAFs for trophic level four (represented by striped bass) and three (represented by shiner perch) were calculated, and the resulting TLR for TL4/TL3 for San Francisco Bay, and by proxy, Tomales Bay, is 3.4. While we used the information available to estimate BAFs for San Francisco Bay and assumed these might be applicable to Tomales Bay, further study in Tomales Bay to confirm that the San Francisco Bay BAFs and TLR for TL4/TL3 are appropriate for Tomales Bay would be valuable.

The estimated threshold methylmercury concentrations in prey consumed by piscivorous wildlife vary from consumer to consumer and with trophic level (Table 12). A threshold concentration is proposed for each of the 12 species of birds, and for each of the trophic levels at which they feed. For example, the Black-crowned Night-Heron diet is composed of prey from all four columns in Table 12: TL2, TL3, TL4, and omnivorous bird prey, and thus there are four separate estimated threshold methylmercury concentrations for that species. The lowest TL2 (representing aquatic invertebrates) methylmercury concentration is for the Black-crowned Night-Heron (0.01 µg/g ), the lowest TL3 (fish 3-30 cm in length) concentration is for the Belted Kingfisher , Caspian Tern, and Black-crowned Night-Heron (0.05 µg/g ), the lowest TL4 (fish greater than 15 cm in length) and omnivorous bird prey concentration are both for the Black-crowned Night-Heron (0.17 and 0.09 µg/g , respectively).

**Table 12. Estimated threshold methylmercury concentrations in prey fish to protect Tomales Bay piscivorous birds (all reported in µg/g wet).** Threshold concentrations are based on the methods described in the preceding paragraphs (USEPA, 1993) drawing from data from many sources inside and outside Tomales Bay. The target for trophic level three fish 5-15cm in length is likely protective of all piscivorous bird species since it was chosen to protect the species most sensitive to mercury (indicated by *). California Species of Special Concern is indicated by bold text; there are no threatened or endangered piscivorous birds in Tomales Bay. TL2= estimated threshold concentration in trophic level two organisms (mostly aquatic invertebrates); TL3= estimated threshold concentration in trophic level three fish; and TL4= estimated threshold concentration in trophic level four fish.

| Species | TL2 (invertebrates) | TL3 (5-15 cm) | TL4 (>15 cm) | Omnivorous Birds |
|---|---|---|---|---|
| Pied-billed Grebe | 0.03 | 0.19 | | |
| Double-crested Cormorant | | 0.06 | | |
| Great Blue Heron | | 0.10 | | ` |
| Great Egret | 0.02 | 0.10 | | |
| Snowy Egret | 0.02 | 0.09 | | |
| Black-crowned Night-Heron* | 0.01 | 0.05 | 0.17 | 0.09 |
| Green Heron | 0.02 | 0.10 | | |
| American Bittern | 0.04 | 0.20 | | |
| **Least Bittern** | 0.01 | 0.07 | | |
| Caspian Tern* | | 0.05 | | |
| Osprey | | 0.09 | 0.30 | |
| Belted Kingfisher* | | 0.05 | | |

**Step 8. Estimated Threshold Methylmercury Concentrations**

The last step in the process is to provide scientific supporting evidence for an estimated methylmercury concentration in prey fish that is likely protective of piscivorous wildlife. This concentration was developed through the calculations of estimates of threshold methylmercury concentrations in total diet (Table 11), and estimated threshold methylmercury concentrations by prey trophic level (Equation 2, Table 12). The goal was to estimate a methylmercury concentration in prey that would most likely be safe for all piscivorous species of birds, based on the currently available toxicity threshold (see Step 5, Reference Dose). **Based on all the assumptions, sources of data, and equations described above the estimated target is 0.05 µg/g (wet) methylmercury for protection of wildlife that consumes trophic level 3 (TL3) fish, 5-15 cm in length** (Table 12). The estimated target calculated for Tomales Bay is protective of the most sensitive species (Kingfisher, Caspian Tern, and Black-crowned Night-Heron), and thus protective of all piscivorous bird species. It was not driven by a threatened or endangered species.

We evaluated other possible targets based on the available information. The lowest TL2 methylmercury concentration, potentially protective of the Black-crowned Night-Heron and the Least Bittern (0.01 µg/g), would likely not protect those species that only consume TL3 fish. The TL3 concentration in the Black-crowned Night-Heron that is equivalent to the TL2 prey concentration was estimated to be 0.05 µg/g, the same as what is estimated to protect two other species of resident birds (Belted Kingfisher and Caspian Tern, Table 12). Similarly, we evaluated a TL4 target. Only two of the 12 species consume TL4 fish, and the equivalent protective TL3 concentration was estimated to be higher than 0.05, so a TL4 target would likely not be protective of all species. Lastly, birds are consumed by only one omnivorous species (Black-crowned Night-Herons). Birds are reported to comprise just 5% of the Black-crowned Night-Heron diet (Post 2008), which seems insufficient rationale for proposing an additional target. Thus, the estimated target methylmercury concentration for TL3 fish is considered likely to protect the 12 selected resident, breeding, piscivorous bird species in Tomales Bay, based on available information and the stated assumptions.

It is important to highlight the limitations of this analysis and the uncertainty associated with the estimated target and threshold concentrations. First, most of the elements that go into the equation to estimate threshold methylmercury concentrations in prey (especially reference dose, food ingestion rate, and diet by trophic level) are estimated based on literature values and other substantial assumptions, and could be significantly improved with more recent, local data. In addition, a study conducted by Heinz (2009) was released after this analysis was completed, and specifically calls into question the reference dose used by USFWS and others to estimate threshold concentrations. Heinz reported that 21 µg methylmercury/kg body weight/day (based on Mallard ducks, Heinz 1979) might be too high for some piscivorous bird species, particularly Caspian Terns, Great Egrets, Osprey, and Snowy Egrets, which are all more sensitive to methylmercury than Mallards (2009). However, without feeding studies for these species, we are left with the Mallard threshold which is likely too high and thus leads to estimated threshold concentrations and targets which may not be fully protective of piscivorous birds. Although it is not possible to quantify the uncertainty associated with the estimated target and threshold concentrations, the point estimates presented should be viewed with the understanding that they have considerable, but un-quantified, confidence intervals associated with them.

### 5.1.3. **Comparison to Other TMDL Targets**

It is instructive to compare the estimated threshold methylmercury concentration developed for Tomales Bay to the targets developed in other TMDLs in order to highlight and explain differences that occur, even though the same methodology was used. Compared to targets proposed through other TMDLs, the estimated threshold concentration for Tomales Bay is higher than the targets developed for San Francisco Bay and the Delta (both 0.03 µg/g for fish smaller than 5 cm in length). The main reason for this is the difference in the presence of piscivorous bird species between the three

watersheds. Tomales Bay does not provide breeding grounds for the California Least Tern, which was the most sensitive species protected by the targets developed for the Delta and San Francisco Bay. There has only been one recorded sighting of Least Terns in Tomales Bay since 1994, presumably because Tomales Bay is north of their typical breeding range (John Kelly, Audubon Canyon Ranch, *pers. comm.*).

The estimated target for TL3 is equal to the TMDL target developed for Walker Creek (0.05 µg/g) for 5-15 cm fish. The Walker Creek TMDL also has a target for 15-35 cm TL3 fish to protect the Osprey, a resident bird that breeds in Tomales Bay. The USFWS proposed that it would be reasonable to assign one threshold concentration that would be protective of all wildlife species in a watershed. Therefore, we evaluated whether the Osprey target is met, and so it can be eliminated for Tomales Bay, as follows.

Local ornithologists report that Tomales Bay Osprey diets consist of almost entirely topsmelt and jacksmelt, with some starry flounder and carp, when available. Data from OEHHA (2004) indicate that jacksmelt in Tomales Bay are, on average 26.5 cm long (in Osprey target range, 15-35 cm) and have a mean mercury concentration of 0.07 µg/g . OEHHA also reported mercury concentrations of smaller TL3 species, shiner perch (average length 11.5 cm, in Belted Kingfisher range, 5-15 cm), to be higher (0.09 µg/g ). Thus, we concluded that despite jacksmelt being larger, their mercury concentrations are similar to those of smaller fish, so the TL3 target proposed in this report will likely still protect birds like Osprey who eat large TL3 fish. We were also able to confirm this with the sampling we conducted in June 2009 (see Results section).

## 5.2. Data collection

In order to evaluate methylmercury concentrations in prey fish relative to the estimated threshold concentration for TL3 fish, and to fill data gaps with regard to methylmercury in Tomales Bay, field sampling was performed, guided by the following questions and hypotheses.

Mercury Processes

**Question 1:** What are the spatial gradients and patterns of total and methylmercury?

**H1:** Mining in the Walker Creek watershed is the major source of mercury to Tomales Bay, thus concentrations of total and methylmercury in sediments are higher in the Walker Creek Delta than other portions of the Bay.

**H2:** Methylation occurs more frequently in tidal salt marsh areas on the eastern edge of the Bay where there is periodic inundation, high organic matter, and substrate dominated by fine sediment.

**H3:** Mercury concentrations are elevated in the fine sediments that occur in the top few centimeters of substrate in the Bay. These sediments originate from upland areas and are transported to the Bay through natural processes and from excessive erosion of fine sediments caused by human actions.

Pathways of Mercury into the Food Chain

**Question 2:** Is mercury from mining sediments entering the food chain of Tomales Bay?

**H4:** Concentrations of MeHg in sediment or water are correlated in time and space with concentrations of THg in fish.
**H5:** Mercury concentrations in prey fish exceed the numeric targets proposed for protection of piscivorous birds, and thus the beneficial uses that provide for the protection of wildlife (among others) are impaired.

In order to try to address these questions and hypotheses (and formulate new hypotheses if necessary), total mercury and methylmercury were analyzed in sediment, water, and small fish.

### 5.2.1. **Sediment Sampling**

**Sampling Objectives**
- Establish spatial gradient of methylmercury concentrations and % methylmercury in sediment.
- Determine where total mercury in sediment is elevated above background concentrations.
- Determine the influence of mercury sources versus sediment properties (grain size and nutrient content) for MeHg in sediments.

**Sediment Methods**

Equipment included glass jars provided by labs, GPS, sampling map, boat, 2 small acrylic cores, long core, water quality meter (WTW Multi340i), 4 stakes, wooden spoon for homogenizing, clean bucket, nitrile gloves, and measuring tape.

All sites were accessed by boat where water depth remains >2 feet, thus sediment samples were representative of subtidal habitat. At sites where water depth is <2 feet, sites were accessed by foot. These samples were representative of intertidal habitat. Sampling for sites on the mudflats of the Walker and Lagunitas Creek deltas occurred as close to a low slack tide as possible, so that sediment was exposed.

Thirty-three samples of surface sediment (<5 cm deep) were collected from selected sites distributed amongst the two large intertidal marsh areas of the Walker and Lagunitas Creek deltas, the eastern shore of Tomales Bay, and at other sites on the western shore (Figure 13). Clean nitrile gloves were worn by field staff during collection for each site though a "clean hands" technique was not employed. At each site in the delta areas (both mudflat and marsh locations) two samples were collected, within 100 meters of each other in order to serve as replicates. All other sites were spaced at least 200 meters apart. At the sites within the Walker and Lagunitas Creek deltas, where large areas of marsh exist, sediment sites were selected so that vegetation was comparable to the extent possible (Canario et al. 2007). In order to compensate for variability within a

site, one shallow core was collected in each of four quadrants within a two meter diameter (Figure 14). The four cores were then placed into a plastic bucket and composited vigorously with a wooden spoon. Three subsamples from this composite were selected randomly by scooping separate clean jars from the bucket (one for mercury and methylmercury, one for grain size, and one for CHN analysis provided to SFEI by analytical labs. For sites that were accessed by boat, a long core (>5 feet) was used and the top 5 cm was cut off of the core to make the sample comparable with those collected by hand. The same compositing methodology was used for those sites accessed by boat. GPS coordinates, depth of core (cm), and narrative description of site and sediment characteristics and sampling issues were recorded to aid in interpretation.

The sample containers for mercury and grain size were placed in a cooler on wet ice for cooling immediately after collection. Samples for CHN analysis were frozen on dry ice as immediately after collection.

Each bulk sediment sample was analyzed for:

- Total mercury (EPA Method 1631)
- Methylmercury (EPA Method 1630)
- Percent total solids (EPA Method SM 2540G)
- Total Nitrogen, Total Carbon, and Total Hydrogen (EPA method 444.0)
- Grain size (sand/silt split; passed through 62.5 μm sieve)

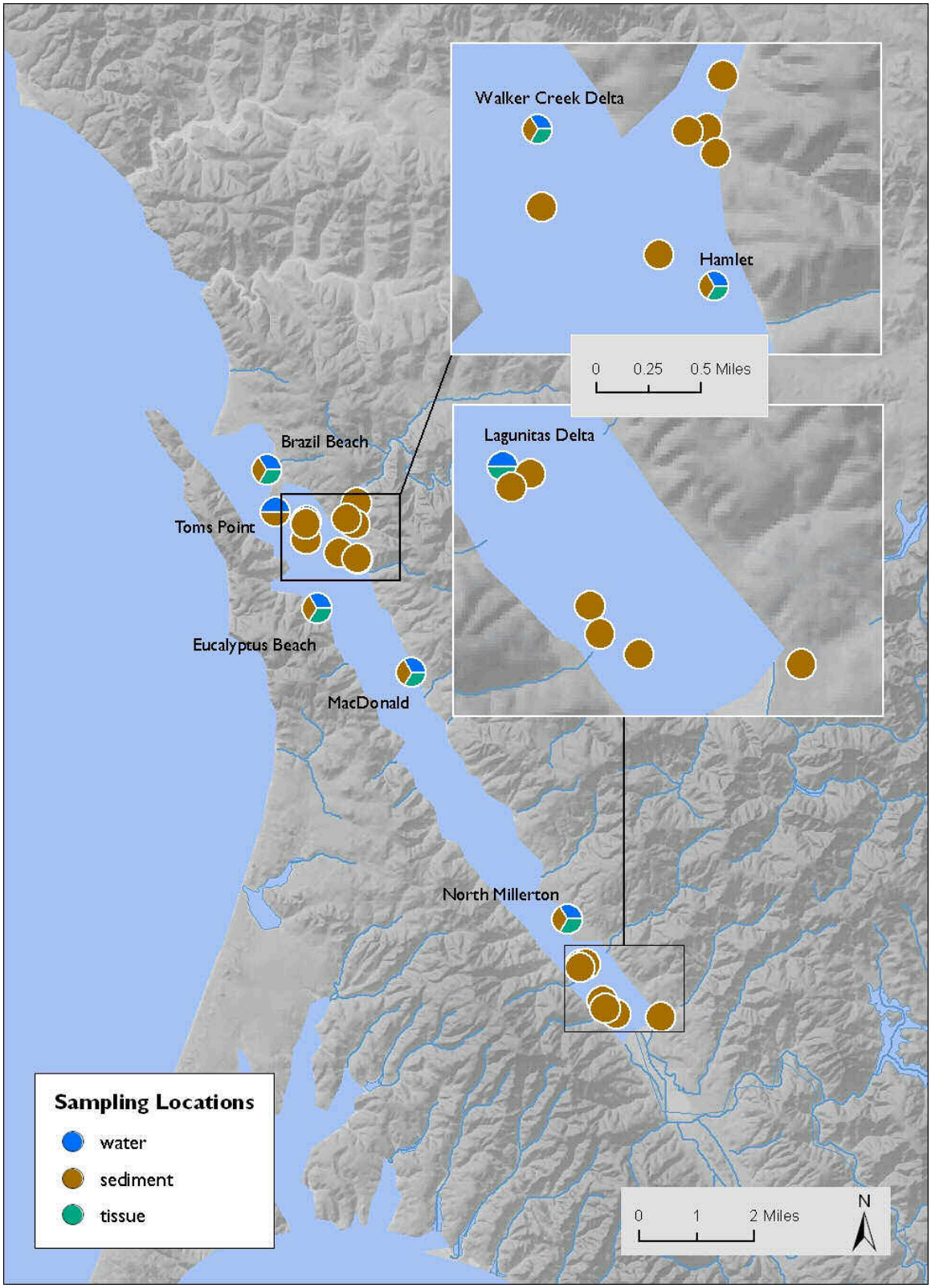



**Figure 13. Sampling locations for three matrices in Tomales Bay, June 2009.**

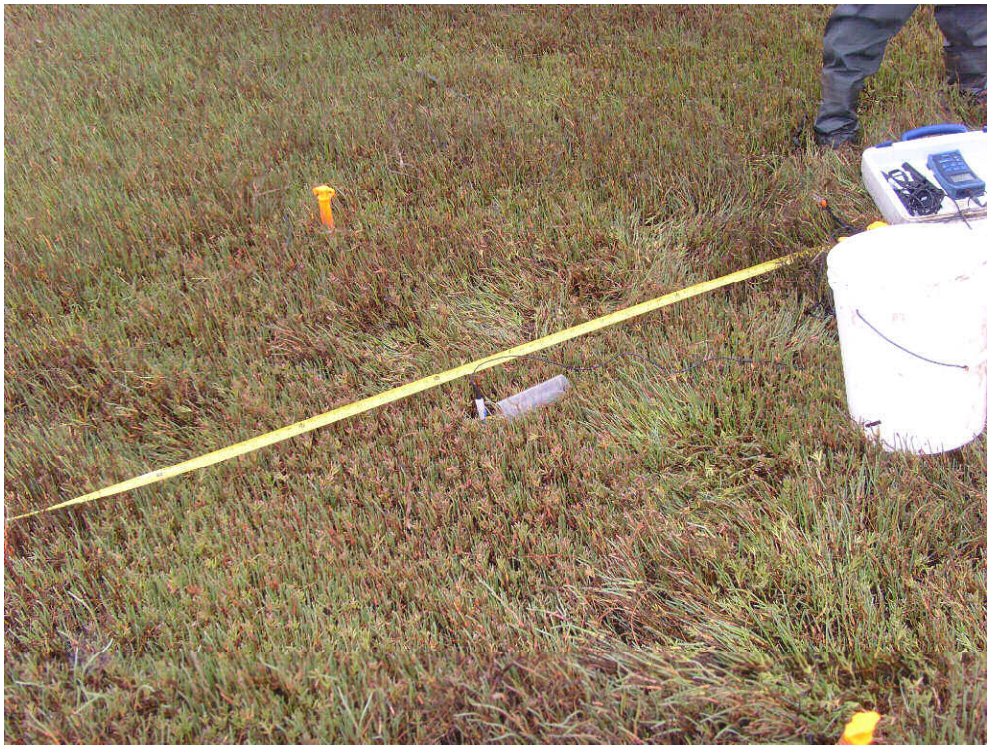


**Figure 14. Sampling sediment at the Walker Creek marsh.** Site was divided into 4 quadrants (marked by orange stakes) in a circle with diameter of 2m (marked by measuring tape).

### 5.2.2. Water Column Sampling

**Water Sampling Objectives**

- Establish spatial gradient of mercury concentrations in water.
- Establish relationships (if any) between water, sediment, and fish concentrations of mercury.

**Water Methods**

Equipment included a daily-calibrated WTW water quality meter with pH, DO, and conductivity probes; 500 mL plastic bottles for DOC, 250 mL acid-cleaned and double bagged plastic bottles for total and methylmercury analysis, and 500 mL acid-cleaned and double bagged plastic bottles for total mercury analysis provided by labs; GPS; sampling map; boat; nitrile gloves for clean hands sampling.

Grab samples of water were collected and handled using the two-person "clean hands, dirty hands" protocol (Bloom and Crecelius 1983) from a boat at eight locations (Figure 13). Sampling occurred as late in an ebbing portion of the tidal cycle as possible, depending on access, availability of water in the intertidal areas, and in order to measure water draining off of areas where sediment was collected. For each sample, water was deep enough to rinse the bottle and cap three times and to fill the bottle and place the cap while under water. Sample bottles provided by analytical labs to SFEI were filled to the top with water and stored in a cooler on wet ice for shipment to labs for analysis as soon

as possible after collection. Samples analyzed for total or methylmercury were double-bagged. Sites were selected based on boat access and proximity to sediment and fish sampling

Measurements of pH (Units), Temperature (°C), Dissolved Oxygen (mg/l), Salinity (%), and GPS coordinates, were recorded at each sampling depth using a daily-calibrated WTW, or refractometer, and GPS. Measurements were taken in site water next to where grab sample was taken, not in sample containers.

Each sample was analyzed for:
- Total mercury (EPA Method 1631)
- Methylmercury (EPA Method 1630)
- Dissolved organic carbon (EPA Method 415.1)

### 5.2.3. **Biosentinel Fish Sampling**

**Fish Sampling Objectives**
- Determine risk to piscivorous wildlife.
- Determine spatial gradients of methylmercury in fish.

All sites were accessed by boat. All sites were spaced at least one kilometer apart. Sites were chosen based on boat access and local knowledge of fish availability (John Brezina and Associates).

Small fish between 3 and 30 cm in length were captured using an otter trawl at seven locations along the eastern shore of Tomales Bay and at reference sites on the western shore (Figure 12). This size class was the original range for the numeric methylmercury target, however, since sampling was completed, the target size range was refined to 5-15cm (Section 5.1.2). Species were collected opportunistically, depending on availability at each site. The goal was to collect four composites of fish, of two different species at each site (for a total of eight composites per site), within a length range of 3-30 cm. Shiner perch *(Cymatogaster aggregata)* and staghorn sculpin (*Leptocottus armatus)* were found to be the most common fish, and composites of these two species were collected at five of the seven sites. Additional species collected (Table 13) included kelp perch (*Brachyistius frenatus*), threespine stickleback (*Gasterosteus aculeatus*), and speckled sand dabs (*Citharichthys stigmaeus*). Two composites of jacksmelt *(Atherinopsis californiensis)*, one of two major food items of Osprey and the largest of the trophic level three fish consumed by wildlife in the Bay, were also collected. Jacksmelt were caught by hook and line. All fish were separated by species on the boat, and measured for total length (to the nearest millimeter) using a ruler. Composite samples of five or more fish were organized by species and length for analysis. The smallest fish was never smaller than 75% of the length of the largest fish within a composite.

Five composites of fish were analyzed for methylmercury. To pair these composites with the samples that are analyzed for total mercury in order to compare %

methylmercury to total mercury, one double-sized composite (i.e., 10 fish, instead of 5 per composite) was collected for each species to ensure that the five composites analyzed for methylmercury had the same length range, species, and composite weight as those analyzed for total mercury.

**Table 13. Fish species collected for mercury analysis (reported as # composites).**

| Site Name | Shiner perch | Staghorn sculpin | Threespine stickleback | Speckled Sand dabs | Kelp perch | Jacksmelt |
|---|---|---|---|---|---|---|
| Brazil Beach | | 2 | 4 | 4 | 3 | |
| Eucalyptus Beach | 1 | 4 | | 5 | 3 | |
| Hamlet | 4 | 4 | | | | |
| Lagunitas Delta | 4 | 4 | | | | |
| MacDonald | 4 | 4 | | | | |
| N. Millerton | 4 | 2 | | | | |
| Walker Delta | 4 | 2 | 4 | | | |
| Tomales Bay[1] | | | | | | 2 |
| **TOTAL** | **21** | **22** | **8** | **9** | **6** | **2** |

[1]Since jacksmelt move around in large areas, the location of where the fish are caught does not signify where they congregate. Fish were caught at various sites around the by and are considered to be comparable in terms of exposure to mercury.

All fish composites were stored with site water in a zippered plastic bag, placed immediately on wet ice on the boat, and were later transferred to a freezer. Once the samples arrived at Brooks Rand Laboratory (BRL), a sub-sample of homogenized whole body fish was randomly selected for analysis. The remaining sample was archived at BRL.

Each composite fish sample was analyzed for:

- Total mercury (EPA Method 1631, Appendix)
- Methylmercury (for a subset of 5 samples) to estimate % MeHg in tissue (EPA Method 1630)
- Percent total solids (EPA Method SM 2540G)

## 5.3. Statistical Methods

Differences in total mercury concentrations in biosentinel fish tissue were evaluated by one-way analysis of variance (ANOVA). These tests were limited to shiner perch and staghorn sculpin since they were the most frequently sampled species among all sites. The ANOVA tested the null hypothesis that there was no significant difference in mercury concentrations due to 'SITE' (Walker, Lagunitas, or other[2] sites). Analyses were performed on log-transformed data, and the residuals of the analysis tested for normally distributed values using graphical evaluation and the Anderson-Darling and Kolmogorov-Smirnov tests. Significance for all statistical tests was set to alpha = 0.05.

[2] "Other" sites are defined as those sites outside of the Walker and Lagunitas Creek Delta areas. These sites include MacDonald, North Millerton, Eucalyptus Beach, Brazil Beach, and Tom's Point

For sediment we tested statistical differences in total mercury and methylmercury in sediment by two-way ANOVA. The ANOVA tested the null hypothesis that there was no significant difference in concentrations due to either site (Walker, Lagunitas, or reference) or habitat (mud or marsh). Analysis of total mercury was performed on log-transformed data, while methylmercury was evaluated using untransformed data. In each ANOVA, the residuals of the analysis were tested for normally distributed values using graphical evaluations and the Anderson-Darling and Kolmogorov-Smirnov tests.

Third, we employed linear regression analysis to examine relationships across matrices (fish, sediment, and water). The data used for this analysis were average concentrations of total mercury (fish) or methylmercury (sediment and water) for each site. Shiner perch and staghorn sculpin were tested for the correlations in fish as they represented the species most frequently sampled and were found at the majority of sites where the sediment and water samples were collected. Analyses were performed on log-transformed data, and the residuals of the analysis tested for normally distributed values.

# 6. Results

## 6.1. Biosentinel Fish

Fish were collected in accordance with the sampling plan, and full results are available in Appendix, Table 20, as well as several tables and figures throughout this section. Sensitivity was good for this project (no non-detect values reported for all target parameters). Blank contamination was not found in any blanks. Accuracy was reviewed in the certified reference materials (CRMs). Blank Spike, and Matrix Spike (MS) samples were also reviewed for accuracy but were informational only. All accuracy measures were below the measurement qualifying objective (MQO) of 35%. Lab-replicates were analyzed for precision. Average relative standard differences (RSDs) were below the target MQO of 35% for the trace elements. %Solids, mercury, and methyl-mercury RSDs were 0.3, 8 and 5 % respectively. No data were qualified.

**Percent methylmercury in biosentinel fish**

A small number of the fish composites (n = 6) were analyzed for methylmercury to confirm the assumption that total mercury is comprised predominantly of methylmercury in fish tissues (Bloom 1992). The resulting high $R^2$ (0.99) of the regression equation that describes the relationship confirmed this assumption. The proportion of MeHg:THg ranged from 85% (jacksmelt) to > 100% (shiner perch), with an average (± SD) of 97 ± 7%. These results (Appendix, Table 21) clearly support the assumption that methylmercury represents the majority of the total mercury body burden in the fish species sampled for this study, and thus for the results we assume that total mercury concentrations provide good estimates of methylmercury concentrations.

**Biosentinel fish results (June 2009)**

The average mercury concentration of fish in the 5-15 cm size range sampled in June 2009 was equal to the estimated target for protection of wildlife. Mercury concentrations ranged from 0.01-0.10 µg/g wet (Appendix, Table 22). Fish smaller than

5 cm in length had the lowest mercury concentrations (mean=0.02 µg/g wet; Table 14). Fish 5-15 cm were higher in mercury, with a mean concentration of 0.05. Lastly, fish greater than 15 cm in length (the two composites of jacksmelt) had the highest mean concentration (0.08 µg/g wet), though none of these larger fish exceeded the estimated threshold concentration for the size class (0.1 µg/g wet; Table 14).

**Table 14. Fish results by size class. Mercury in fish presented in relation to estimated methylmercury wildlife targets.**

| Size Class | N | Estimated threshold concentration (µg/g wet) | Mean Hg concentration (µg/g wet) | Standard Deviation | Coefficient of Variation |
|---|---|---|---|---|---|
| <5 cm | 40 | NA | 0.02 | 0 | 0.28 |
| 5-15 cm | 46 | 0.05 | 0.05 | 0.02 | 0.50 |
| >15 cm | 2 | 0.17 | 0.08 | 0.01 | 0.16 |

It is important to consider the time of year when piscivorous birds are most sensitive to mercury and seasonal changes in exposure, when evaluating fish results. As stated in section 2.3.2, birds are most sensitive to mercury toxicity during reproduction, mainly through effects on developing embryos and chicks, and also through effects on parental behavior. The critical time period is when birds are bioaccumulating the methylmercury that will be transferred to the egg, which is right before and during the beginning of the breeding season. For most piscivorous birds in Tomales Bay the breeding season lasts from about May through August (Jules Evens, *pers. comm.*). Thus, it is likely that the fish captured in June 2009 were collected during breeding for some species.

It is more difficult to predict if the mercury concentrations in the fish captured would have been higher earlier in the year (prior to breeding, March-April) since we do not have data from other months. Eagles-Smith and Ackerman (2009) performed extensive monitoring of forage fish in San Francisco Bay salt ponds, and demonstrated that concentrations in small fish can double over a one month period. As demonstrated by Whyte and Kirchner (2000) and Johnson et al. (2009), total mercury accumulation in the Walker Creek Delta is episodic in nature, and correlates with storm events. The winter of 2009 was relatively dry, with storms mostly isolated to February and March, based on discharge records for Walker and Lagunitas Creeks (USGS gages 11460750 and 11460600, respectively). We hypothesize that winter storms may transport total mercury downstream into the Bay and associated wetlands, leading to net methylmercury production and bioaccumulation. Depending on methylmercury dynamics, mercury concentrations in the delta areas may be highest in the weeks after such runoff events. Due to reservoirs situated upstream of both of these gages, reservoir releases might also contribute to total and methylmercury loadings outside of rainfall events. A small peak in discharge occurred for both gages in early May, though it was much smaller than those peaks related to storms. Thus it seems possible that fish mercury concentrations in April or May (prior to and the beginning of the breeding season) could have been higher than

those found in fish collected in June. Seasonal sampling of prey fish would help to determine whether this hypothesis is correct.

In addition to time of year, other biases in sample collection that affect data interpretation should be considered. First, fish in this study were collected by otter trawl, which targets slower moving fish along the bottom. The one exception is jacksmelt, which were collected by hook and line. A follow up study using alternative capture methods would determine the amount of bias by using the otter trawl, and could provide a more comprehensive evaluation of wildlife exposure. In addition, fish were collected at various points of the tide cycle and time of day based on daylight, boat access, and sampling schedule. Results may have differed if fish were collected more consistently with regards to tide and time of day.

Mercury concentrations varied by site (Figure 15a), and species (Figure 15b). Staghorn sculpin (all composites 5-15 cm) had an average concentration of 0.06 µg/g wet, the highest concentration of the fish species in this size range. Threespine stickleback in the 5-15 cm size class had an average mercury concentration of 0.05 µg/g. The seven shiner perch composites in the 5-15 cm size range had an average concentration of 0.03 µg/g wet. Two-thirds of the shiner perch composites were under 5 cm and thus not comparable to the sculpin (Table 15). No other species exceeded the estimated target for fish 5-15 cm or estimated threshold concentrations for fish >15 cm (Table 15).

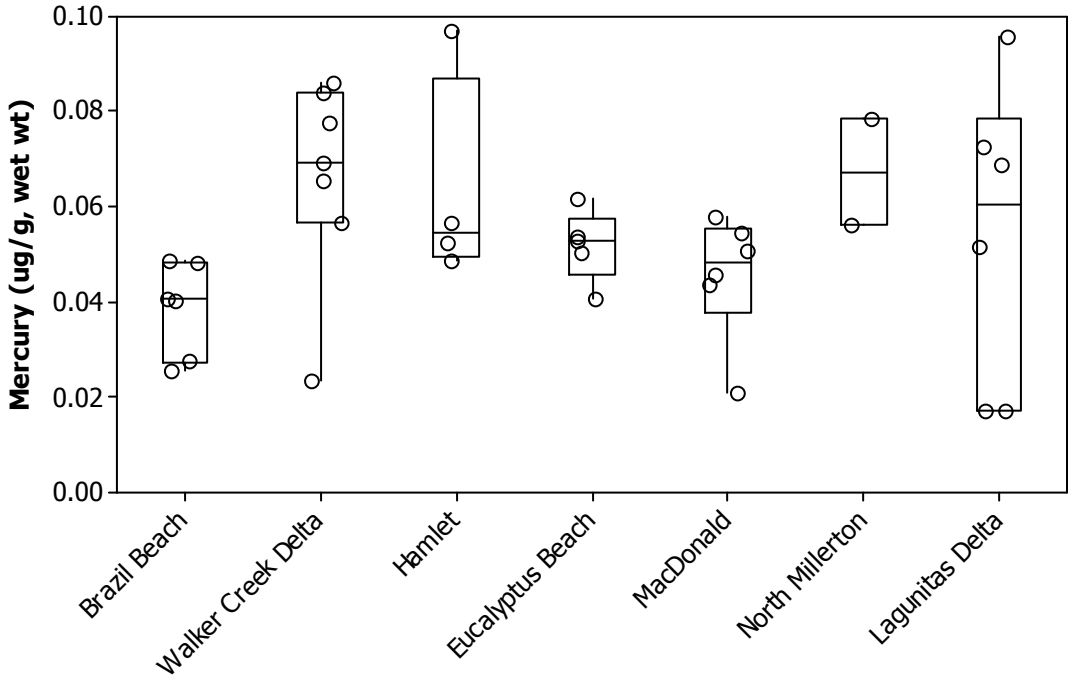



**Figure 15a. Fish (5-15 cm in length) mercury concentrations by site.** Boxplots of three frequently caught species (Shiner perch, Staghorn sculpin, and Threespine stickleback) in target size range (5-15 cm); *n* = 36. Open

circles represent individual composites. The box represents the 25th – 75th percentiles, the midline is median, and whiskers extend through the full data set.

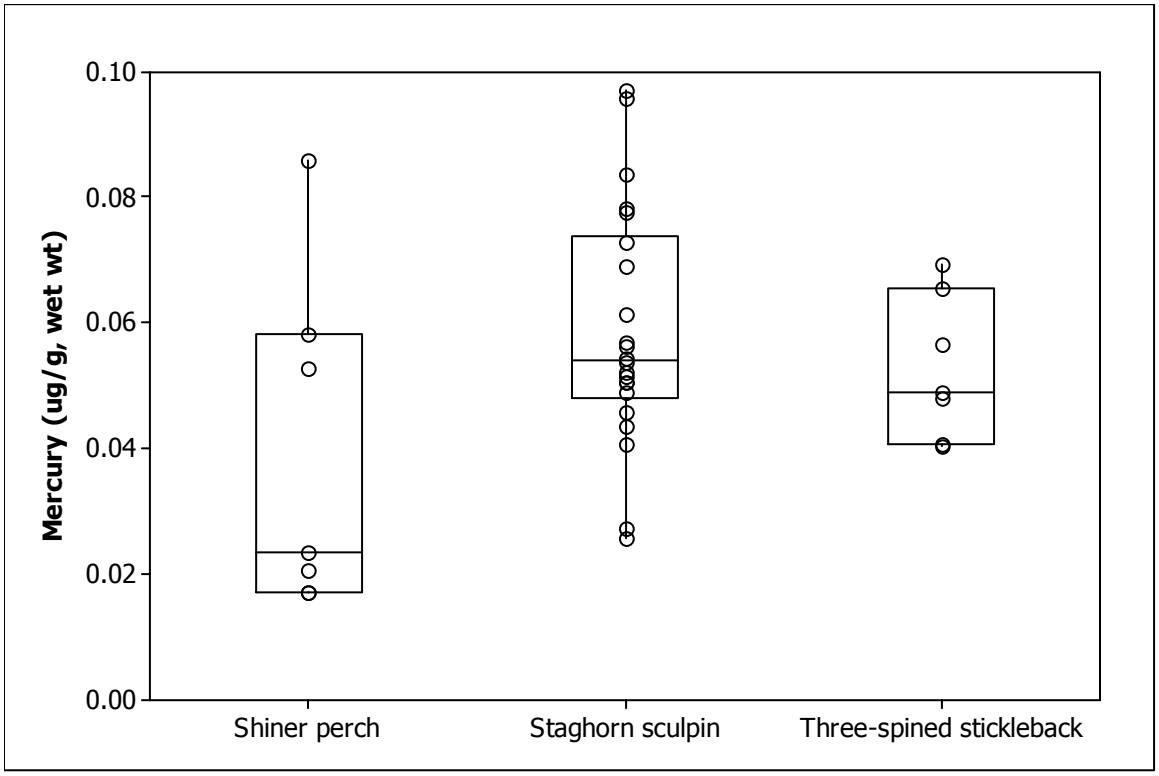



**Figure 15b. Fish (5-15 cm in length) mercury concentrations by species.** Boxplots of three frequently caught species (Shiner perch, Staghorn sculpin, and Threespine stickleback) in target size range (5-15 cm); *n* = 36. The box represents the 25th – 75th percentiles, the midline is median, and whiskers extend through the full data set.

**Table 15. Fish results by species.**

| Species | # Sites | Size Range (mm) | N <5 cm | N 5-15 cm | N >15 cm | Total | Mean THg (µg/g) | Std. Deviation | Coeff. of Variation |
|---|---|---|---|---|---|---|---|---|---|
| Staghorn sculpin | 6 | 70 - 126 | 0 | 22 | 0 | 22 | 0.06 | 0.02 | 0.34 |
| Shiner perch | 5 | 42 - 107 | 14 | 7 | 0 | 21 | 0.02 | 0.02 | 0.83 |
| Kelp perch | 2* | 42 - 57 | 4 | 2 | 0 | 6 | 0.01 | 0 | 0.00 |
| Jacksmelt | 2* | 239 - 267 | 0 | 0 | 2 | 2 | 0.08 | 0.01 | 0.12 |
| Threespine stickleback | 2 | 41 - 77 | 1 | 7 | 0 | 8 | 0.05 | 0.01 | 0.20 |
| Speckled sanddab | 2* | 49 - 92 | 1 | 8 | 0 | 9 | 0.02 | 0 | 0.00 |
| **Total** | | | 20 | 46 | 2 | 68 | | | |
| *Sampled in "other" sites, outside of delta areas only | | | | | | | | | |

Mercury concentrations in fish composites exhibited a weak relationship ($R^2 \leq 0.40$) with length for most species (staghorn sculpin, threespine stickleback, and speckled sand dab; Figure 16). Length: mercury relationships have commonly been found in sport fish species (e.g., Melwani et al. 2009), but can be difficult to detect with narrow size ranges. Only shiner perch exhibited a strong relationship ($R^2=0.87$), though a broad range of lengths was not sampled.

One of the primary goals of this study was to characterize spatial differences in mercury bioaccumulation between Walker Creek Delta, Lagunitas Delta, and other locations in the Bay where previous research has found mercury in biota to be low. The analysis among sites focused on shiner perch and staghorn sculpin since they were the most frequently sampled species. No significant differences were found among the three general areas for either shiner perch ($p = 0.35$) or staghorn sculpin ($p = 0.09$). Average shiner perch concentrations by site ranged from 0.02 µg/g at Lagunitas to 0.05 µg/g at Eucalyptus. Shiner perch at Walker (including Hamlet samples) averaged 0.03 ± 0.02 µg/g. Staghorn sculpin mercury concentrations were higher than shiner perch, which may be explained by three factors: 1) the larger size of prey they consume, 2) association with the benthic food web, and 3) higher site fidelity resulting in higher exposure in methylmercury hot spots as compared with pelagic species that have larger home ranges. Average mercury concentrations in sculpin composites by site ranged from 0.03 µg/g at Brazil to 0.07 µg/g at Lagunitas. Sculpin at Walker (including Hamlet samples) averaged 0.07 ± 0.02 µg/g. Though mercury concentrations in fish tissue did appear to vary among sites in Tomales Bay, none of the differences were statistically significant due to small sample sizes and the resulting low power of the test (Figure 17).

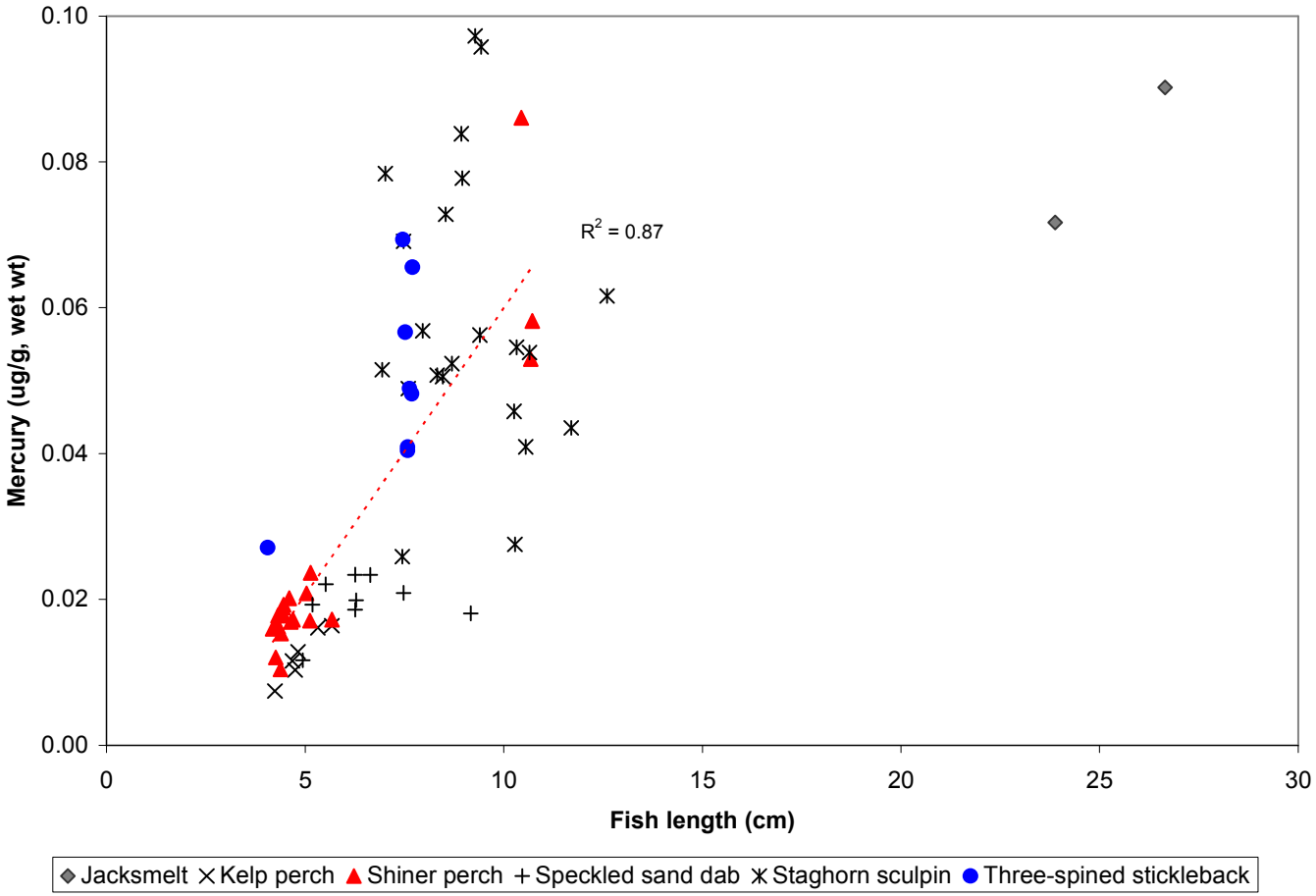



**Figure 16.** **Relationship between fish mercury concentrations (µg/g wet) and fish length (composites)**. Fish length ranged 4–13 cm except jacksmelt, 24–27 cm, $n = 68$. Although a general trend was observed of increased mercury concentration with increased length, the correlation was weak for all species except Shiner perch (regression shown). Note also that mercury concentration did not exceed 0.1 µg/g even in the largest fish. Kelp perch were not included due to small sample size.

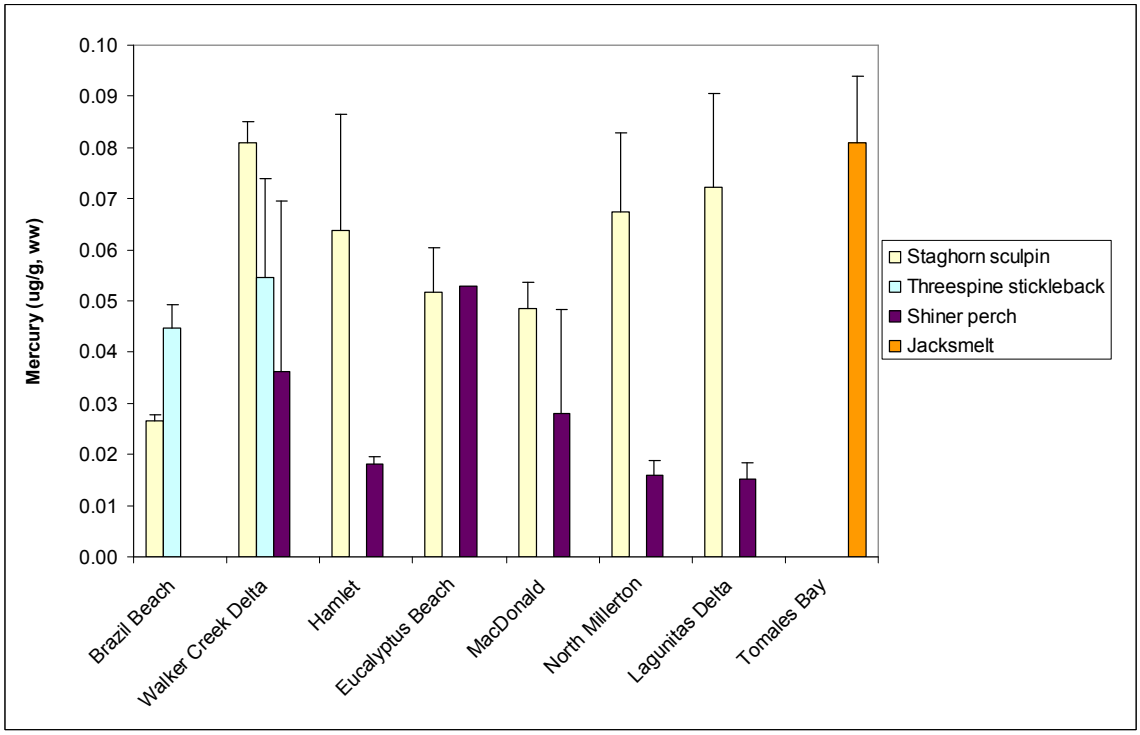



**Figure 17.** **Fish mercury concentrations by species and site (mean).** Fish length ranged from 4–13 cm except jacksmelt, 24–27 cm, *n* = 68. There was no statistical difference in mercury concentrations among sites. Note that kelp perch and speckled sand dab have been removed from this figure. Error bars represent one standard deviation.

**Biosentinel fish results, November 2009**

Four composites of topsmelt *(Atherinopsis affinis)* were collected in the Walker Creek Delta in November 2009 for the RMP, but are noteworthy due to higher mercury concentrations than reported for other fish of similar size in this study. Average mercury concentration for the topsmelt (n=5 per composite in four composites) was 0.12 ± 0.02 µg/g, and average length was 70 ± 0.07 mm (Appendix, Table 23). This length is at the low end of the range of lengths of sculpin collected for mercury analysis in June, but in the middle of the range of shiner perch reported in this study. Using the length:mercury relationship for shiner perch in this study (which was the only significant Hg: length relationship we had in this study), it is predicted that a 70 mm shiner perch would have a mercury concentration of 0.03 µg/g. This is nearly four times lower than what was reported for topsmelt in that size range.

**Comparison to other biosentinel fish data**

Topsmelt collected at 22 sites in San Francisco Bay for the RMP from 2005-2007 had an average mercury concentration about three times lower than the topsmelt collected from the Walker Delta in November (0.04 ±0.015 µg/g, Greenfield and Jahn 2010, Table 16). However the Walker Delta topsmelt are about in the same range as topsmelt

collected for the RMP in the Alviso area of South San Francisco Bay, which is influenced by the New Almaden mercury mining district just upstream along the Guadalupe River (Greenfield and Jahn 2010*)*.

Topsmelt are pelagic fish that frequent estuaries and feed on small invertebrates, similar to shiner perch. However, topsmelt are considered to be bottom-feeding omnivores, based on diet studies from the Navarro River and Anaheim Bay that found detritus, crustacean larvae, and sand grains in stomach contents of juveniles (Moyle 2002).

The large difference in mercury concentrations may be attributed to the difference in season collected. The topsmelt were collected approximately one month following the first major storm of the season in mid-October, which could have eroded mercury-contaminated sediment into the Walker Creek Delta. Topsmelt collected seasonally by the RMP and USFWS tend to have higher mercury concentrations in the winter (SFEI, unpublished data) and other fish also commonly have seasonal fluctuations in mercury (e.g., Eagles-Smith and Ackerman 2009).

Shiner perch have previously been monitored in studies in both Tomales and San Francisco Bays. A 2004 study by OEHHA estimated an average mercury concentration of shiner perch from Tomales Bay of 0.09 ± 0.02 µg/g (n = 7, average length =115 ± 9 mm), more than three times higher than the concentrations measured in this study (average Hg concentration = 0.024± 0.02 µg/g, Table 16). However, the OEHHA-reported fish were about twice the length of the shiner perch reported here (average length=55 mm). Similarly, the Regional Monitoring Program for San Francisco Bay (www.sfei.org/rmp) has monitored shiner perch for mercury bioaccumulation since the 1994 due to their popularity in San Francisco Bay for human consumption. RMP data from 2003 (the most recent year with a complete dataset) had a mean concentration of 0.09 µg/g (n = 14, average length=115 mm), again higher than reported here for larger fish (Table 16).

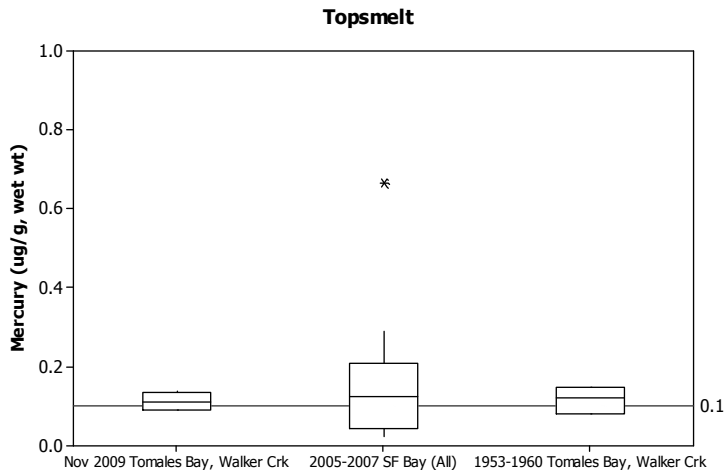
We can also compare data from the present study to previously collected composites of staghorn sculpin and threespine stickleback, collected by the State Water Resources Control Board's Toxic Substances Monitoring Program in Walker Creek in the early 1990s. However, this data set only contains one composite per species, so inferences are difficult without more data. One composite of staghorn sculpin from July 1991 had an average concentration of 0.16 µg/g (n=13, mean length=80 mm). Four years later, fish were collected in October, and the average concentration of one composite was 0.23 µg/g (n=20, mean length=58 mm), despite the much smaller size (Marshall 2006). Concentrations from both of these years were still much higher than concentrations measured in staghorn sculpin collected from Tomales Bay in 2009 (mean concentration=0.06 µg/g, mean length=77 mm). Some of this difference may be explained by collection location (Walker Creek versus Tomales Bay), and timing (pre- and post-remediation of the Gambonini mercury mine). Unexplained spatial and temporal variations are also quite possible given the dynamic and heterogeneous nature of methylmercury cycling. One composite of threespine stickleback collected in Walker

Creek in July 1992 (Marshall 2006) had an average mercury concentration of 0.19 µg/g, much higher than concentrations in fish collected in 2009 (mean concentration=0.05 µg/g, mean length=73mm).

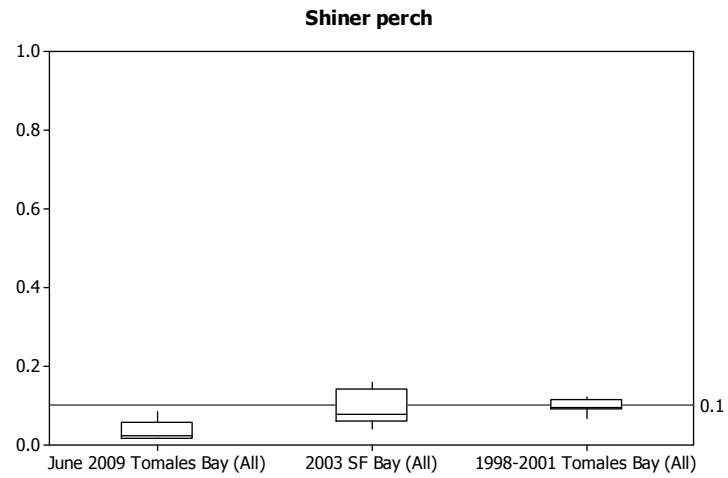
Lastly, we can compare prey fish mercury concentrations collected in Tomales Bay in June 2009, to those collected in the tidal portion of Walker Creek in the 1950s that were archived at the California Academy of Sciences Department of Ichthyology Collection. Archived staghorn sculpin composites (n=6) had an average mercury concentration of 0.15 ±0.05 µg/g (Table 16, Appendix, Table 24). These results are somewhat surprising considering that the fish were collected between 1953 and 1960, before mining activities occurred in the Walker Creek watershed. These concentrations were about twice as high as sculpin collected in this study, even though the average length of the museum specimens was lower (67 mm, compared to 77 mm in this study. The archived mercury concentrations were, however, in about the same range as sculpin collected in Walker Creek in the early 1990s (Marshall 2006). This is surprising given the expectation that mercury concentrations before mining were lower than concentrations post-mining and before remediation of the Gambonini Mine site. Archived topsmelt composites (n=3) had mercury concentrations of 0.12 ±0.03 µg/g, very similar to those collected from Tomales Bay for the RMP in November 2009. It is important to note that both the museum specimens and fish collected for the RMP were analyzed for mercury in a different laboratory than the rest of the fish collected in June 2009.

There are several unknown factors regarding the archived specimens that may account for the differences, especially among staghorn sculpin composites. First, the archived specimens were collected earlier in the year (March-June) when storm-induced erosion of sediments derived from natural mercury deposits was possible. Second, the collection and preservation techniques of the 1950s and 1960s are unknown, including the introduction of materials used for preservation that could have contaminated the samples. Gibbs et al. (1974) demonstrated that preservation tends to increase metals concentrations in fish specimens. Two blank samples of ethyl alcohol, used to preserve most fish at and sent to the mercury lab from the California Academy of Sciences, resulted in non-detects. This alcohol was not used to preserve the fish analyzed and did not come from the preservation bottles; it was simply a blank from the Academy of Sciences' supply of alcohol commonly used to preserve specimens. However, the preservation history of these samples prior to storage in alcohol is unknown. Thus, the comparison is relevant on an order of magnitude basis only, and leaves many unanswered questions regarding changes in mercury concentrations over time. Uncertainty therefore surrounds interpretation of the data for the museum specimens.

**Table 16. Mercury in biosentinel fish 5-15 cm length: comparison to San Francisco Bay.** Midline represents median, whiskers extend to 10th & 90th percentiles, and asterisks indicate points beyond the 90th percentile. *n* = number of composites; L = Mean length (cm) of composite

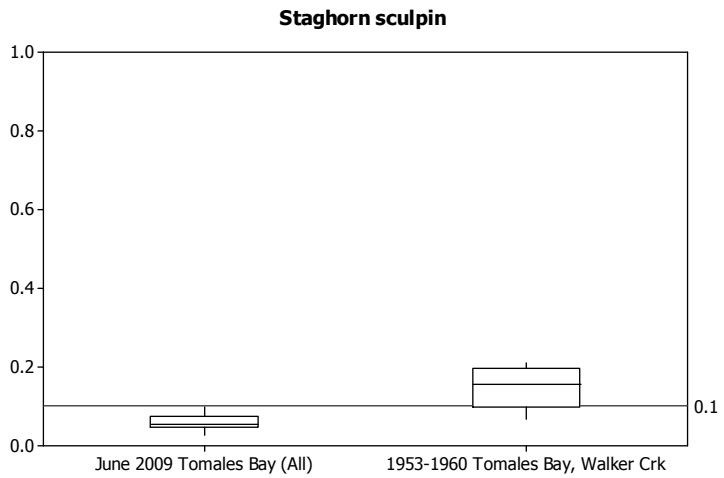



| | Nov 2009 Tomales Bay, Walker Creek | 2005–2007 San Francisco Bay (All) | 1953–1960 Tomales Bay, Walker Creek |
|---|---|---|---|
| *n* | 4 | 50 | 3 |
| L | 7 | 5.1 | 6.3 |

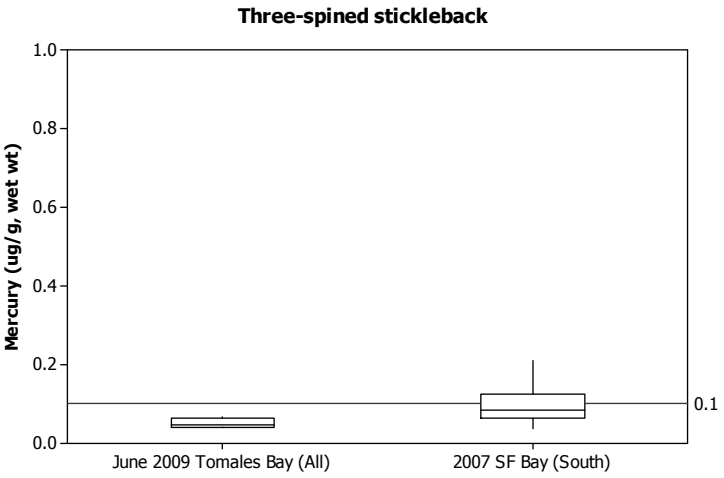



| | June 2009 Tomales Bay (All) | 2003 San Francisco Bay (All) | 1998–2001 Tomales Bay (All) |
|---|---|---|---|
| *n* | 7 | 14 | 7 |
| L | 7.5 | 11.5 | 11.5 |

**Table 17. Mercury in biosentinel fish (continued)**




| | June 2009 Tomales Bay (All) | 1953–1960 Tomales Bay, Walker Creek |
|---|---|---|
| *n* | 22 | 6 |
| L | 9.1 | 6.7 |




| | June 2009 Tomales Bay (All) | 2007 San Francisco Bay (South) |
|---|---|---|
| *n* | 7 | 12 |
| L | 7.6 | 5.3 |

## 6.2. Sediment

Sediment was collected in accordance with the sampling plan; however an error in the field resulted in two samples from the marsh area of Lagunitas Delta to be eliminated from analysis, so that there were an uneven number of samples collected between the two intertidal marsh areas (Lagunitas and Walker Creek Deltas). Sensitivity was good for the mercury dataset (< 50% non-detect values reported for all target parameters). Blank contamination was not found in any blanks. CRM accuracy was within the acceptable range (20-25% of the certified 95% confidence interval) for all target analytes. None of the analytes measured had an RSD greater than the MQO (25%). Lab-replicates from field samples were reviewed for precision. The carbon, hydrogen, nitrogen and grain size data were also acceptable. Minimum detection limits (MDLs) were generally sufficient, only 2 results were non-detects for hydrogen, and one for nitrogen. Carbon (C), hydrogen (H) and nitrogen (N) were not measurable in blanks. Precision on lab replicates was good, with an average RSD within the target range of 5% for C (3%), target 15% for N (6%), and 13% for H (no target but within the N target). Recoveries on lab reference materials were good, with average error <2% for CHN, well within targets. Grain size data had %fines typically around 50%, which was expected.

Total mercury concentrations in sediment collected from three areas (Walker Creek Delta n=8, Lagunitas Creek Delta n=6, and other sites n=5; Figure 18) ranged from 0.04 – 2.0 µg/g (mean = 0.55 ± 0.53 µg/g ), while methylmercury (Figure 19) ranged from ND – 3.3 µg/kg (mean = 1.0 ± 0.86 µg/kg ). There was a weak overall correlation between total mercury and methylmercury in these samples (Figure 20). Elevated total mercury concentrations appeared to be confined to the Walker Creek Delta, as most other samples had mercury concentrations below the 0.2 µg/g background concentration (Marshall 2006). The sample with the highest total mercury concentration collected in the Lagunitas Creek Delta was mostly composed of fine sediment (<62.5 µm), indicating that this sediment likely traveled south from Walker Creek during a storm event, and does not indicate that there is an elevated source of mercury in the southern portion of the Bay. Higher methylmercury in sediment was also largely present in the Walker Creek Delta (both vegetated marsh and intertidal mudflat sites), though six marsh sites in the Lagunitas Creek Delta had methylmercury concentrations higher than 0.6 µg/kg (the concentration determined as “excess mercury” by Johnson, et al.).

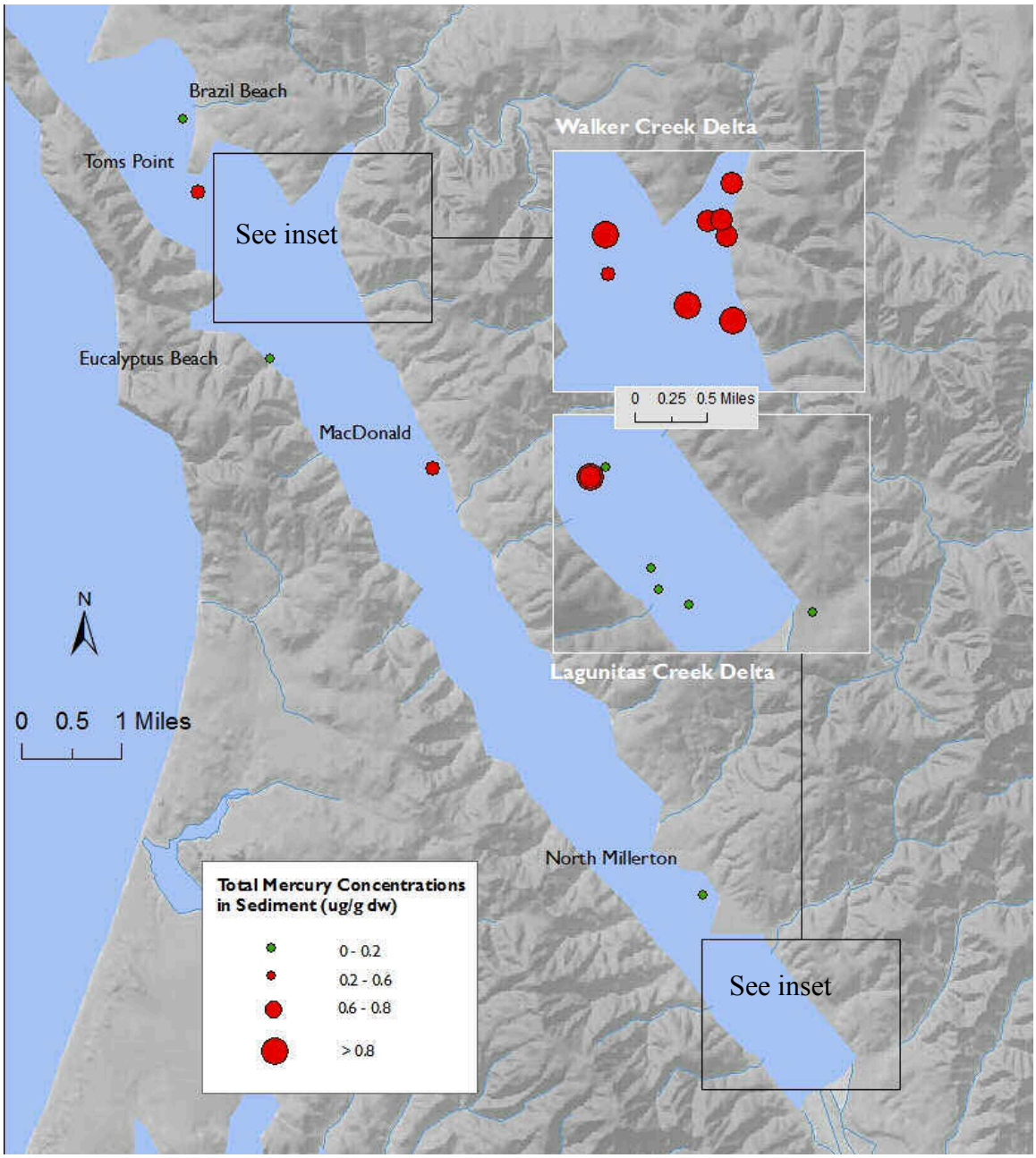



**Figure 18.** **Total mercury in sediment.** Each data point represents the average of two field replicates. Concentrations elevated above background (0.2 µg/g dry; Marshall 2006) are indicated by red, and were mostly isolated in the Walker Creek Delta area.

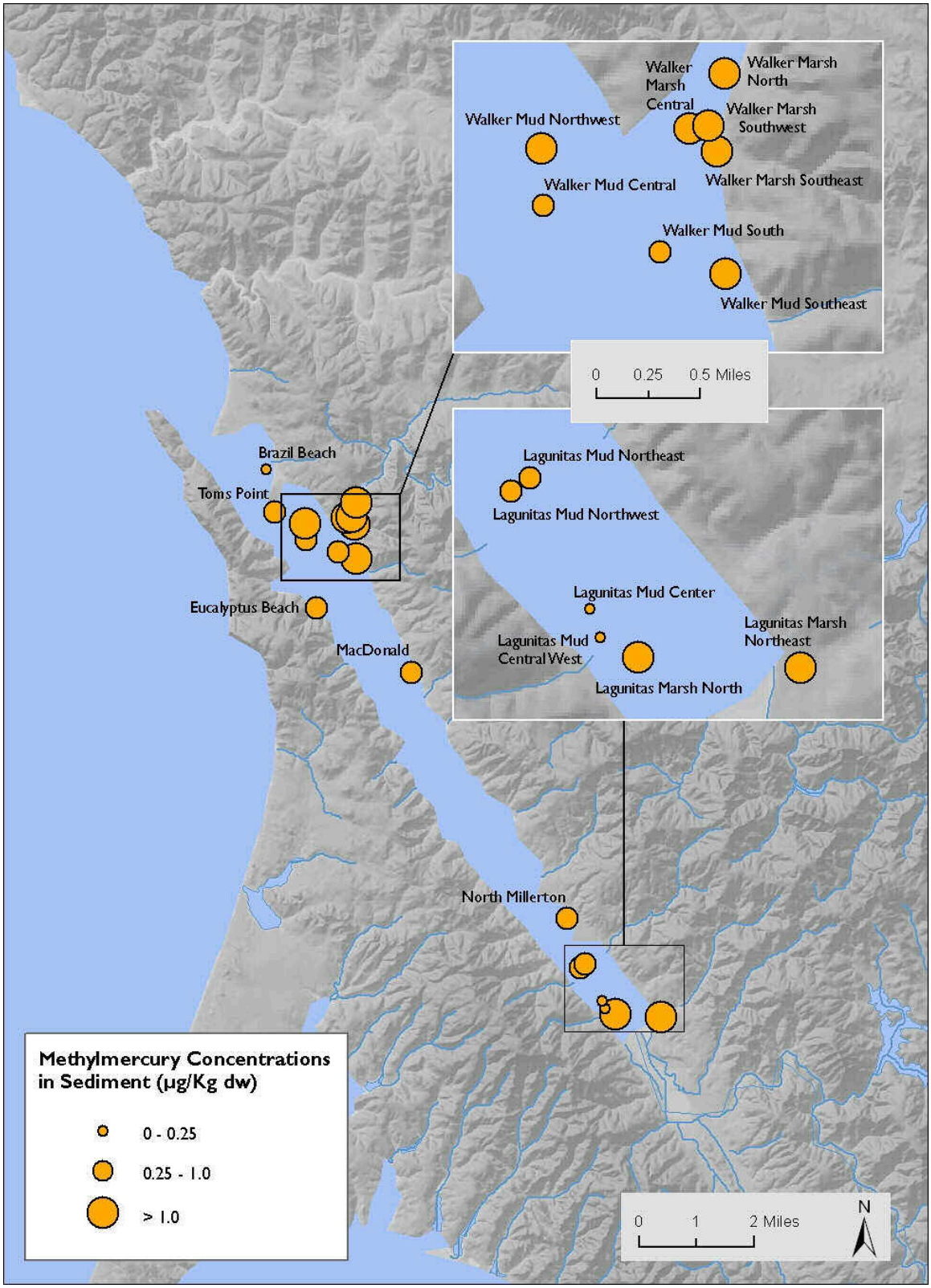



**Figure 19. Methylmercury in sediment.** Each data point represents the average of two field replicates.

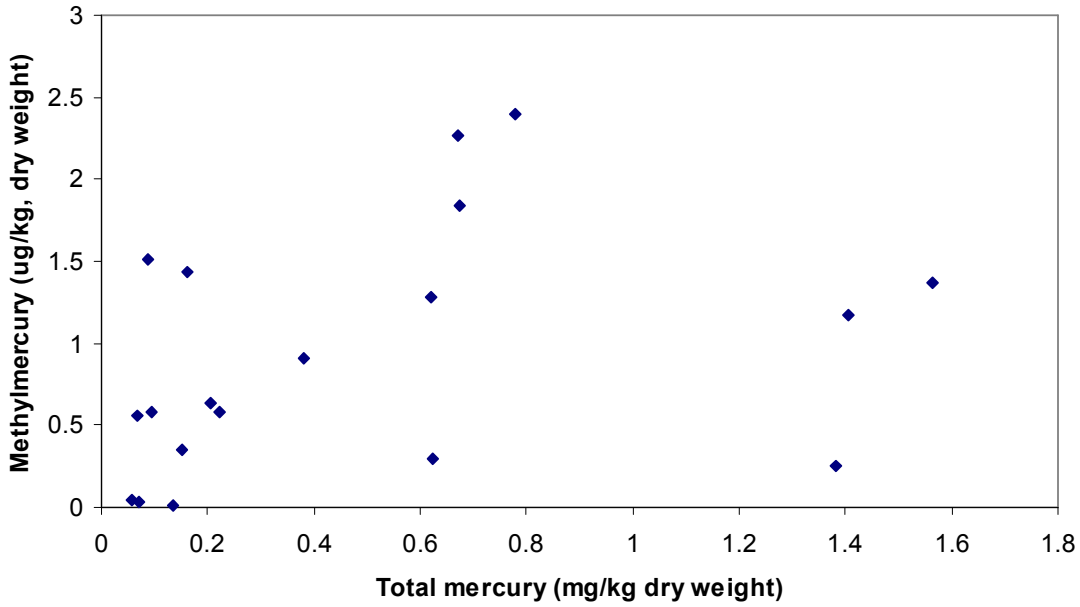



**Figure 20. Relationship between total mercury and methylmercury in sediment.** The correlation was weak (Pearson r=0.34, p>0.05).

Ancillary sediment parameters (grain size, percent carbon, percent hydrogen, and percent nitrogen) were examined for correlation to total mercury and methylmercury to help characterize spatial and habitat patterns. Grain size (as percent fines, <62.5um) did not have a strong relationship with either total mercury or methylmercury concentrations (Table 17). In both cases, the amount of variability explained by the relationships was low (< 22%). Though the relationship of grain size to methylmercury was statistically significant, stronger relationships were observed for percent carbon and percent nitrogen.

**Table 18. Relationships between sediment total mercury, methylmercury, and ancillary variables.** Bold p-values indicate significant relationship.

| Parameter | Ancillary Variable | N | $R^2$ | p-value |
|---|---|---|---|---|
| Sediment Methylmercury | Percent Carbon | 19 | 0.68 | **< 0.0001** |
| Sediment Methylmercury | Percent Nitrogen | 19 | 0.72 | **< 0.0001** |
| Sediment Methylmercury | Percent Fines | 19 | 0.22 | **0.04** |
| Sediment Total Mercury | Percent Carbon | 19 | 0.01 | 0.68 |
| Sediment Total Mercury | Percent Nitrogen | 19 | 0.01 | 0.69 |
| Sediment Total Mercury | Percent Fines | 19 | 0.18 | 0.07 |

Percent carbon and percent nitrogen were both significantly and highly correlated with methylmercury. Between carbon, nitrogen and percent fines, nitrogen content was more strongly correlated with sediment methylmercury, although the regression was influenced by the few marsh sites sampled in Walker Creek Delta that exhibited both higher methylmercury and nitrogen (Figure 21). The carbon data were also significantly

correlated with methylmercury concentrations in sediment, at a similar $R^2$ 0.68 for carbon, 0.72 for nitrogen), and with similar distribution of data into two clumps. Both percent nitrogen and percent carbon are indicators of the organic matter content of sediment. Results from sediment cores collected by Johnson, et al. (2009) for the relationships between methylmercury, carbon, and nitrogen were not nearly as strong ($R^2$ for carbon was 0.23 and for nitrogen, 0.08).

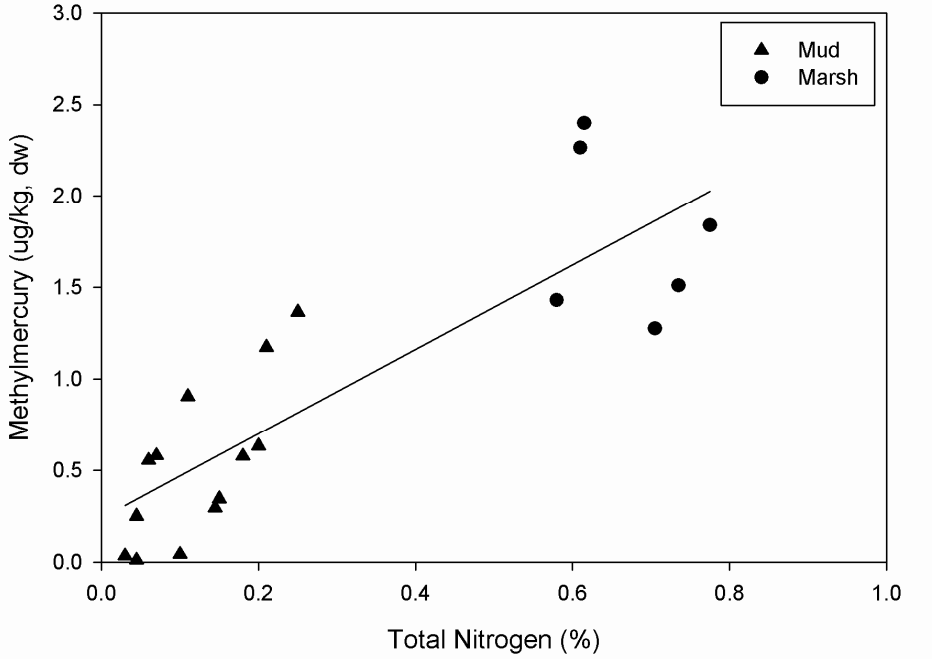



**Figure 21. Relationship between total nitrogen and methylmercury in sediment.** The correlation with nitrogen was stronger than carbon or hydrogen ($R^2$=0.72, p<0.0001).

Similar to the fish sampling, a primary emphasis of the sediment sampling was to characterize spatial differences among the Walker Creek Delta, Lagunitas Delta, and reference sites of the Bay. Overall, there was a significant difference in both total mercury ($p < 0.0001$) and methylmercury ($p < 0.047$) between the three areas of the Bay. In both cases, pair-wise comparisons indicated higher concentrations ($p < 0.05$) in Walker Creek Delta relative to the other areas (Figures 22, 23). However, since the correlation between total and methylmercury in individual samples was weak (Figure 20), these results do not necessarily mean that where there is elevated total mercury, methylmercury will also be elevated. It is also important to note that sediment sampled in the Walker and Lagunitas Creek Delta areas was representative of intertidal habitat, while at other sites the sediment was representative of subtidal habitat since those sites were accessed by boat. Further investigation is needed to determine the conditions in the Walker Delta that allow for higher methylmercury production than in other depositional, tidal marsh areas.

In addition to the overall spatial pattern, differences in sediment mercury, methylmercury, and %methylmercury due to habitat (mudflat, defined as bare soil sampled in the intertidal mudflats of delta areas versus marsh, defined as areas with

emergent vegetation in the tidal marshes; Appendix Figure 31) were examined (Figures 24, 25a, 25b). Methylmercury differed between the marsh and mudflat sites sampled in Tomales Bay ($p < 0.0001$), but total mercury did not ($p = 0.35$). A pair-wise comparison indicated that methylmercury concentrations were significantly higher ($p< 0.05$) in marsh compared to mudflat sediments (Table 19). The lack of a significant difference in total mercury may be due to the larger variability of the mudflat samples.

This finding with respect to methylmercury and habitat follows findings of Johnson et al. (2009) that reported that sediments underneath algal mats in the Walker Creek marsh had higher methylmercury concentrations than sediments in barren sediment. This also follows the line of evidence of the current dataset that indicate presence of organic material (represented by higher nitrogen) correlate with methylmercury in sediment.

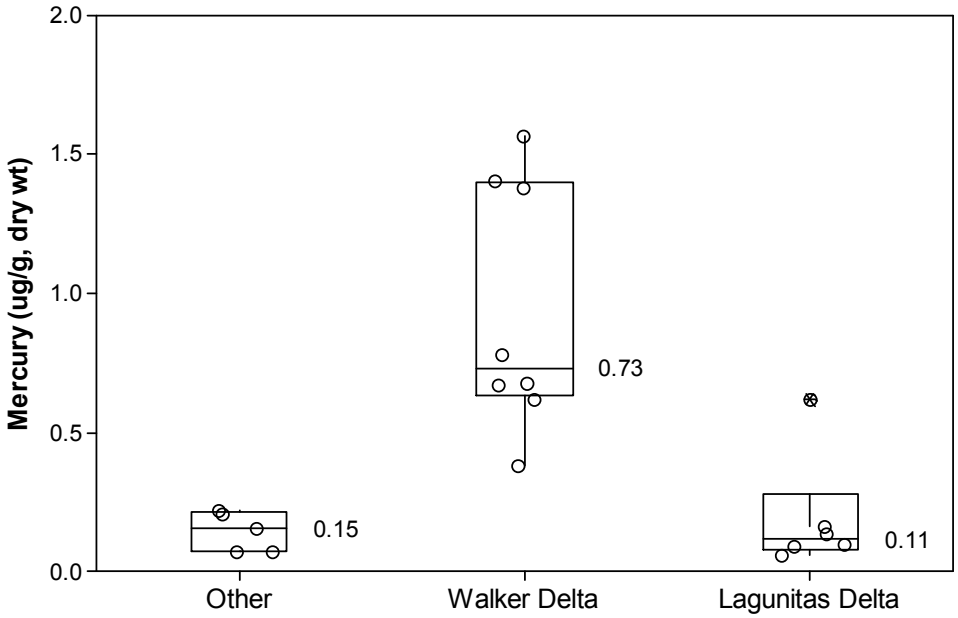



**Figure 22.** **Boxplot of total mercury in sediment by area.** Mercury concentrations (µg/g, dry) and variability were much higher in the Walker Delta area, than other sites and Lagunitas Delta. Open circles represent individual samples. The box represents the $25^{th}$ –$75^{th}$ percentiles, the midline is the median (value is displayed), and whiskers extend through the full data set. Asterisk over highest results at Lagunitas Delta indicates exceeds $90^{th}$ percentile.

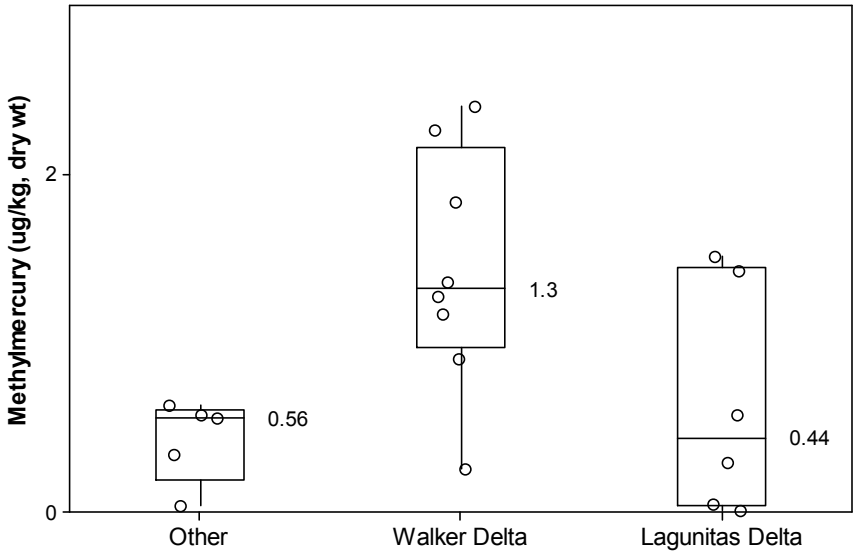



**Figure 23.** **Boxplot of methylmercury in sediment by area.** Methylmercury (µg/kg, dry) was higher in the Walker Delta samples. Open circles represent individual samples. The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median (value is displayed), and whiskers extend through the full data set.

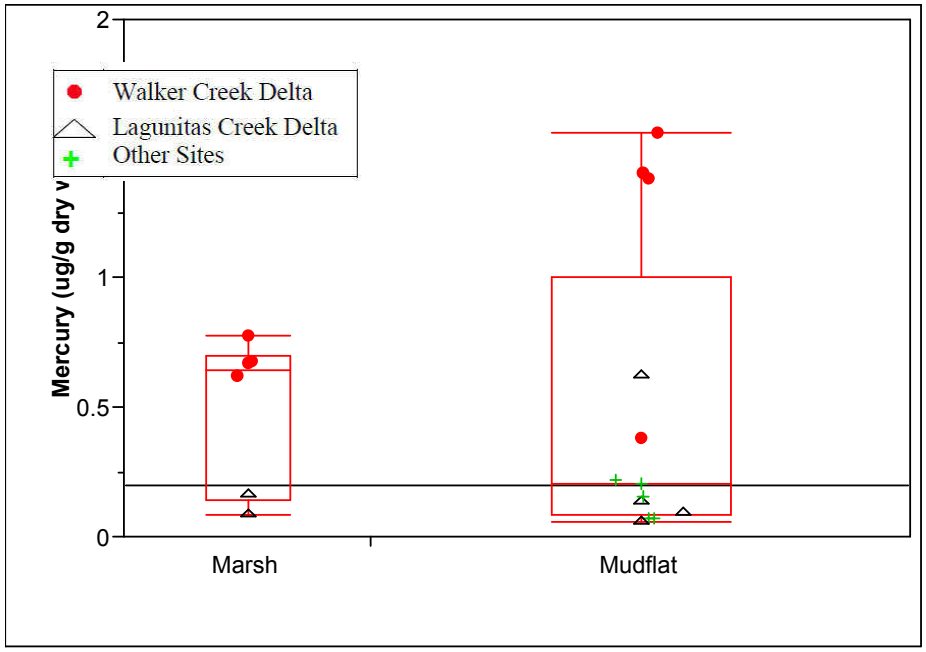



**Figure 24.** **Boxplot of total mercury in sediment by habitat.** Though variability in mudflat ($n$ = 13) sites was higher, the median marsh ($n$ = 6) total mercury concentration was higher than mudflat sites and exceeded the background concentration (0.2 µg/g dry, black line). The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median, and whiskers extend through the full data set.

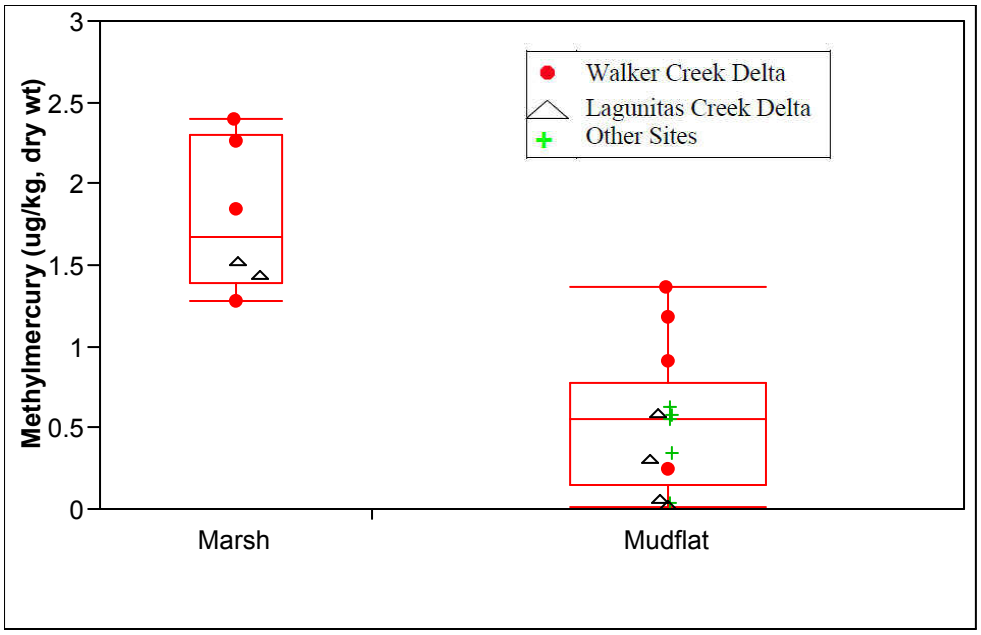



**Figure 25a. Boxplot of methylmercury in sediment by habitat.** Methylmercury concentrations (µg/kg, dry) were higher in marsh sites ($n$ = 6), than in mudflat sites ($n$ = 13). The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median, and whiskers extend through the full data set.

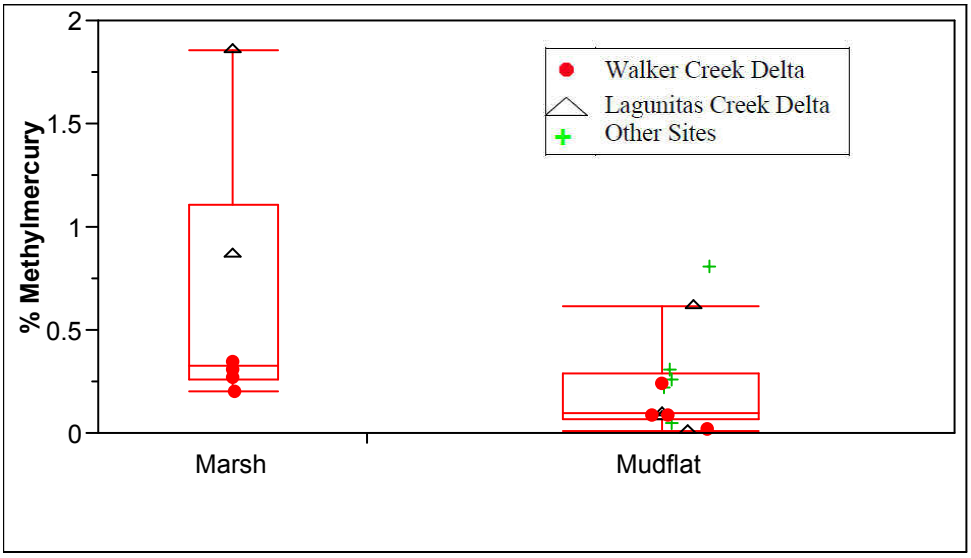



**Figure 25b. Boxplot of %methylmercury in sediment by habitat.** Variability in %methylmercury was higher in marsh sites ($n$ = 6), than in mudflat sites ($n$ = 13), but medians were similar. Open circles represent individual samples. The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median, and whiskers extend through the full data set.

**Table 19. Results of ANOVA to evaluate differences due to habitat, area of Tomales Bay (Walker Creek Delta, Lagunitas Creek Delta, or other sites), and a) total mercury (log transformed); or b) methylmercury in sediment samples.** There was no significant difference for total mercury concentrations in sediment between mudflat and marsh sites, but there was a significant difference between the three areas of Tomales Bay ($p<0.05$, indicated by bold text). Methylmercury concentrations in sediment between mudflat and marsh, and between areas of Tomales Bay all also showed a significant difference ($p<0.05$, indicated by bold text).

a)

| **Response Variable: Total mercury** | Model $R^2 = 0.70$ | | | | |
|---|---|---|---|---|---|
| **Factors** | **Sum of Squares** | **DF** | **Mean Squares** | **F** | **p** |
| Habitat (Mud or Marsh) | 0.077 | 1 | 0.077 | 0.914 | 0.35 |
| Area (Walker,Lagunitas, Reference) | 5.572 | 2 | 2.786 | 32.98 | **< 0.0001** |

b)

| **Response Variable: Methylmercury** | Model $R^2 = 0.59$ | | | | |
|---|---|---|---|---|---|
| **Factors** | **Sum of Squares** | **DF** | **Mean Squares** | **F** | **p** |
| Habitat (Mud or Marsh) | 7.82 | 1 | 7.82 | 23.19 | **< 0.001** |
| Area (Walker,Lagunitas, Reference) | 2.308 | 2 | 1.154 | 3.423 | **0.047** |

**Walker Creek Delta sediment mercury 2000-2009**

Previous sediment data, compared to the present study, suggest a declining trend in both total and methylmercury concentrations in the top five centimeters of sediment collected from Walker Creek from 2000-2009. Whyte and Ganguli (2000) sampled 10 stations in Walker Creek, as well as Hamlet. Total mercury concentrations (Figure 26) frequently exceeded the 0.2 µg/g background concentration for Walker Creek (Marshall 2006) and had a median concentration of 1.9 µg/g (Whyte and Ganguli 2000). The median concentration of total mercury in sediment at 8 sites within the Walker Creek Delta from this study (2009) was almost three times lower (0.73 µg/g dry). The median methylmercury concentration reported by Whyte and Ganguli was 2.3 µg/kg, higher than the mean 1.3 µg/kg reported in this study (2009, Figure 27).

As indicated by Johnson, et al. (2009), it is possible that after 9 years of erosion between Whyte and Ganguli (2000) and this study, cleaner sediment has buried more contaminated sediment, or re-working of the sediment by biota and tides has resulted in the lower total mercury concentrations found in this study. The results could also differ due to location. Whyte and Ganguli collected samples in the spring (March-May) of 2000, which was shortly after remediation of the Gambonini Mine when contaminated sediment could have been close to the surface. Three of Whyte and Ganguli's ten sampling sites were along the Walker Creek channel (closer to the mine source), whereas this study focused on the marsh and the intertidal mudflats (which could experience more mixing due to tides, wind, and biological activity).

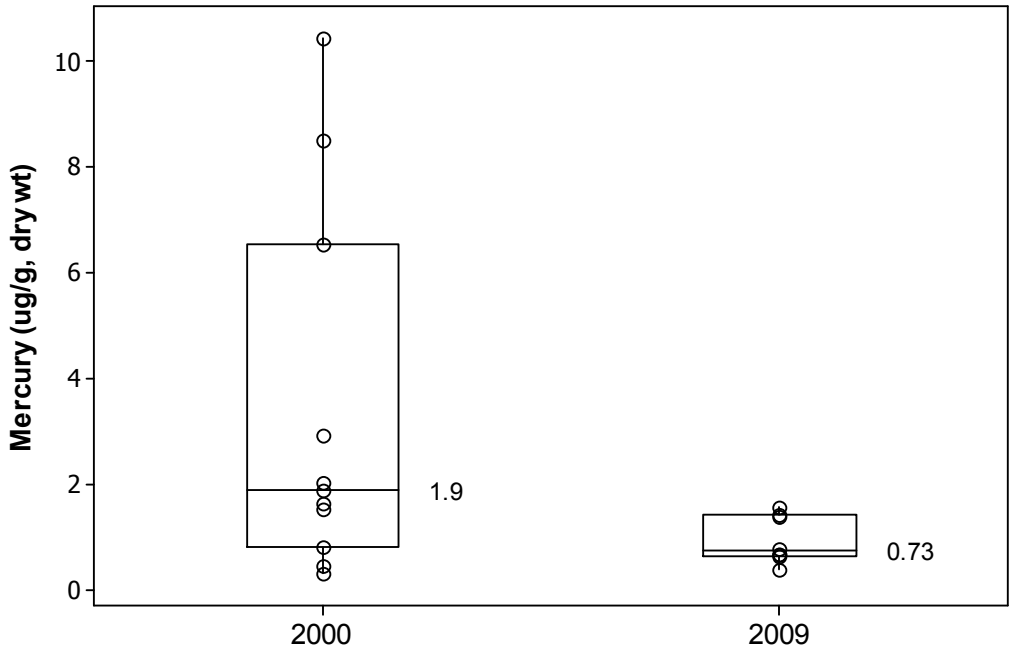



**Figure 26. Boxplot of total mercury concentrations in sediment at Walker Creek Delta over time**. Mercury concentrations (µg/g, dry wt) and variance were higher in 2000 ($n$ = 11) than in 2009 ($n$ = 8). Open circles represent individual samples. The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median (value is displayed), and whiskers extend through the full data set.

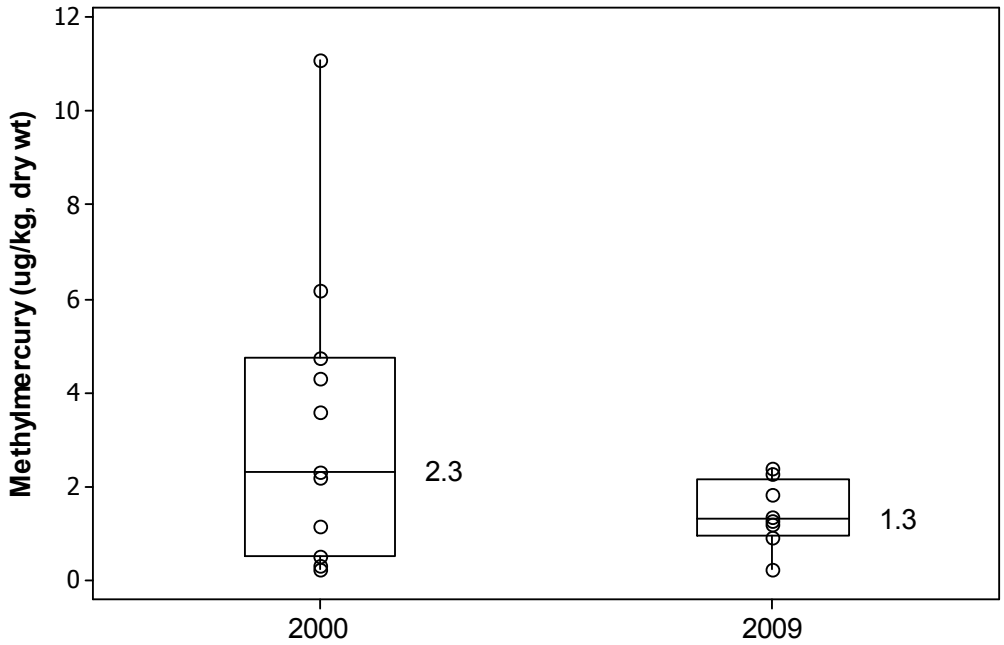



**Figure 27. Boxplot of methylmercury in sediment over time**. Methylmercury concentrations (µg/g, dry wt) and variance were higher in 2000 ($n$ = 11) than in 2009 ($n$ = 8). Open circles represent individual samples. The box represents the 25$^{th}$ –75$^{th}$ percentiles, the midline is the median (value is displayed), and whiskers extend through the full data set.

**Comparison of Walker Creek Delta sediment mercury to other sites in Tomales Bay**

Lastly, we compare sediment results from sites outside of the Walker Creek Delta to earlier work. Whyte and Ganguli (2000) reported data from one site outside the Walker Creek Delta (McDonald) that had similar total and methylmercury concentrations to those observed at 11 stations for the present study (2009). The total mercury concentration in the top five centimeters of sediment for McDonald (2000 data) was 0.23, about the same as the total mercury measured at McDonald for this study (0.22 µg/g dry), and at the lower end of the range (0.06-0.62 µg/g dry) for other sites from this study (2009). The methylmercury concentration at the same site in 2000 was 0.85 ng/g dry, higher than the methylmercury measured at McDonald in 2009 (0.58 µg/g dry), but in the same range as other sites in this study (0.012-1.5 ng/g dry). Thus, while mercury concentrations are decreasing over time at the Walker Creek Delta, concentrations at other sites are relatively similar.

## 6.3. Water

Water sampling followed the sampling plan closely and all the mercury data were acceptable. Sensitivity was good (no non-detect values reported for all target parameters). Blank contamination was not found in any blanks. Accuracy was reviewed in the CRM, Blank Spike, and Matrix Spike samples and all were below the MQO of 35%. No lab-replicates were analyzed in these whole water grab samples as expected (only one sample can be analyzed per grab sample). Two matrix spike lab-replicates were evaluated for the precision review, and they showed good precision (5 and 1 % relative percent difference for mercury and methyl-mercury respectively). The dissolved organic carbon dataset was qualified with a 'generous' non-censoring precision qualifier based on dropping one of two lab-replicates that seemed to be unusually different from the parent sample. However, sensitivity was fine (no non-detects). Accuracy was good (RSD of matrix spikes was 2, well below the MQO of 5). Precision was evaluated based on the average RSD of one lab-rep, a field-rep, and LCS samples (avg RSD of 7) resulting in a non-censoring 'VIL' qualifier. It should be noted that the analytical lab seemed to have difficulty meeting the desired MQO of 5% for the analyses of DOC in water. Their reported MQO is 33%.

Based on sampling at eight locations, total mercury in water ranged from 1.3 to 4.6 ng/L (average = 3.0 ± 0.2 ng/L). Total mercury was lowest (< 2.0 ng/L) at Brazil, Eucalyptus Beach, and Lagunitas (Figure 28). The highest concentrations (> 3.5 ng/L) were at Tom's Point, Hamlet, and MacDonald. Walker Creek exhibited a relatively moderate concentration (n = 1) of 3.0 ng/L. Methylmercury ranged from 0.05 to 0.16 ng/L (average = 0.09 ± 0.03 ng/L). Methylmercury was relatively low (< 0.08 ng/L) at North Millerton and Lagunitas, the two southernmost locations sampled. Concentrations greater than 0.15 ng/L were only measured at McDonald, with the remainder of sites having relatively moderate concentrations (0.08-0.15 ng/L). The limited sample size precluded statistical evaluation of spatial differences in these data. However, the highest total mercury concentration (6.0 ng/L at Hamlet) was well below the WQO of 51 ng/L (U.S. EPA 2000) and Basin Plan Objective of 210 ng/L (SFRWQCB 2007). Dissolved

organic carbon ranged from 2600 – 5200 ug/L, however, these data suggested a lack of correlation between DOC and either total mercury or methylmercury in the Bay.

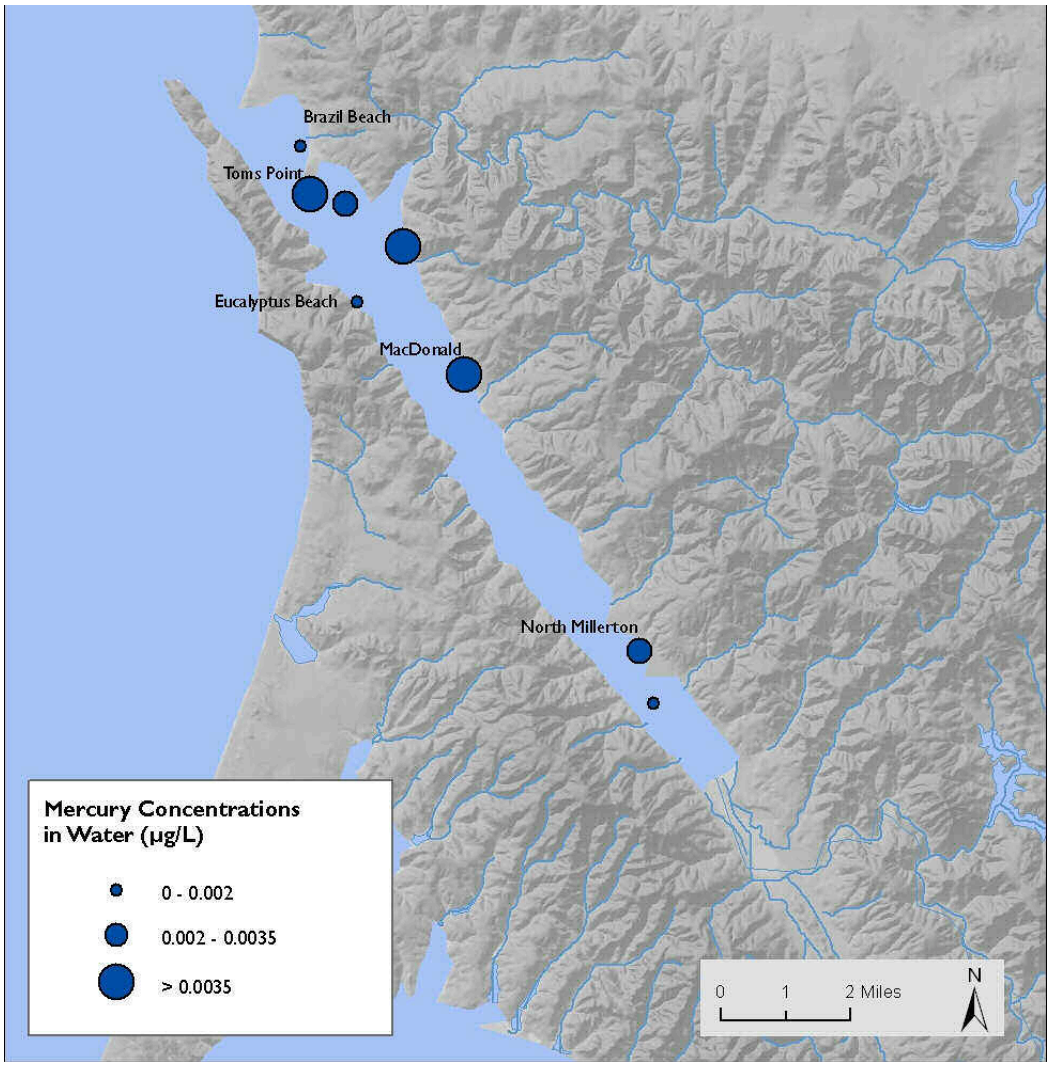



**Figure 28.** **Mercury concentrations in water.** None of these concentrations exceed the federal (51 ng/L; USEPA 2000) or state (210 ng/L; SFBRWQCB 2007) water quality objectives.

**Comparison among matrices**

Linear regression was employed to examine relationships across matrices. Results indicated that staghorn sculpin had a significant relationship to sediment methylmercury ($R^2 = 0.81$, $p = 0.015$), but shiner perch did not ($p > 0.05$). This may be due to a closer association of staghorn sculpin with the sediments in both life history and diet. Adult shiner perch are known to consume benthic invertebrates, but feed on plankton at younger life stages (Gobas and Arnot 2005). Relationships between fish mercury and water methylmercury and between sediment and water were also examined, but no correlations were apparent.

# 7. Source Analysis

## 7.1. Mining legacy

### 7.1.1. Gambonini mine activity

As mentioned earlier in this report (section 2.4.1), several small mining operations operated in the Walker Creek watershed in the 1960s and 1970s, and are the major point source of mercury to Tomales Bay. The largest mine, and processing facility for the smaller mines, was the Gambonini Mine. The waste pile of mercury-contaminated soil was located on the slopes of a small channel which drains to Salmon Creek, a tributary to Walker Creek (Figure 29). Release of mercury-contaminated sediments was mostly a product of intense bursts of rain and resulting erosion (Whyte and Kirchner, 2000).

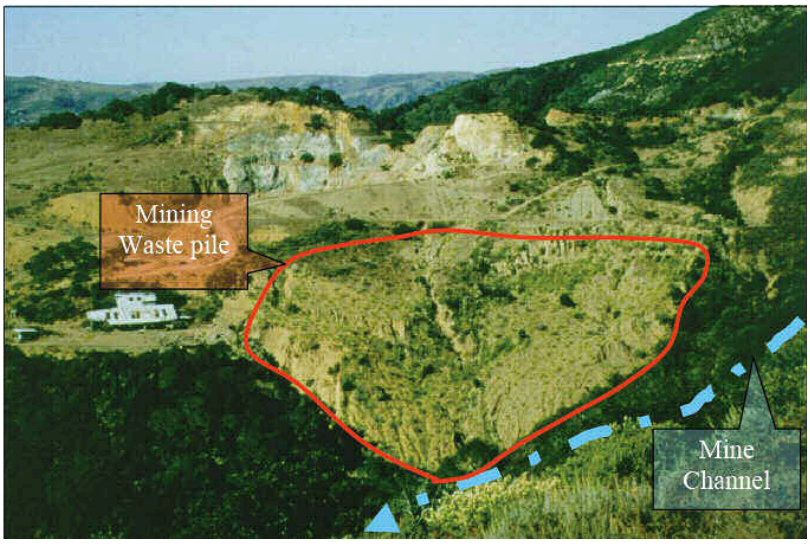



**Figure 29. Gambonini mine waste pile (Marshall 2006).**

### 7.1.2. Mercury accumulation in the Walker Creek Delta

Johnson et al. (2009) collected eighteen 1-2 m sediment cores from the Walker Creek Delta in October 2003 to evaluate historic accumulation of total mercury in sediments. The samples were sliced into 2 cm segments and dated using gamma-counting $^{137}Cs$. Excess mercury was defined as 0.6 µg/g, or three times the background concentration in non-mining areas. Subsequently, Johnson, et al. (2009) reported that peak mercury loadings to the Walker Creek Delta occurred between 1975 and 1985, and a second small peak in the late 1990s. These peaks most likely coincide with particularly wet years when storm-induced erosive forces sent mining waste into Walker Creek. In addition, delayed transport of mining waste due to storage in floodplains or sediment mixing processes could account for the peak of mercury accumulation in the 1990s (Johnson et al. 2009).

Using the coring data, Johnson et al. (2009) estimated the total inventory of mercury that accumulated at the Walker Creek Delta between 1940 and 2003 to be 2,500 ± 500 kg, with a majority (80%) associated with fine (<63 µm) sediments (Figure 30). At

the peak of accumulation (late 1970s to early 1980s), approximately 60-70 kg/yr of mercury was deposited in the Walker Creek Delta. This period includes two consecutive large storm years, 1982-3, and the failure of the tailings dam at the Gambonini Mine in 1982. However, mercury releases may have been greater than 70 kg/yr in wet years. Accumulation prior to 1964, when the Gambonini Mine began production, was estimated to be 20 kg/yr. The accumulation estimated in Figure 30 probably includes some influence from smaller mining operations in the watershed. Prior to all mining activity, the estimated accumulation rate was ≤5 kg/yr, based on the background concentration of 0.1 µg/g, found at the bottom of the sediment cores (Johnson et al. 2009). Overall mercury accumulation into Tomales Bay from the Gambonini Mine site and other mercury mines in the Walker Creek watershed have fluctuated significantly from less than 5 kg/yr (pre-mining) to over 80 kg/yr (winter 1998), and tend to be episodic in nature with storm events (Whyte and Kirchner 2000).

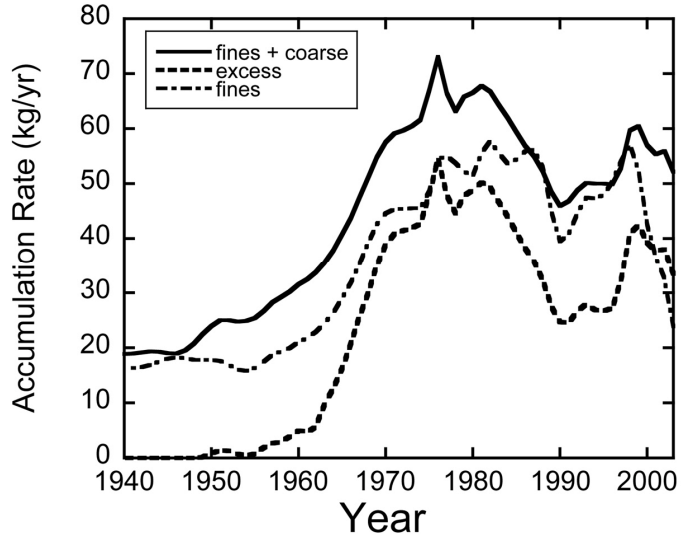



**Figure 30. Estimated accumulation rate of mercury in the Walker Creek Delta (Johnson et al. 2009).** Fines are defined as sediment <63 µm, coarse sediments are >63 µm, and excess mercury is defined as concentrations greater than 0.6 µg/g.

## 7.2. Loading from watersheds and atmospheric deposition

With the exception of mercury runoff from the Gambonini mercury mine measured in a tributary to Walker Creek watershed (Whyte and Kirchner 2000), there are no previously published estimates of mercury loads entering Tomales Bay from its watershed.

We used USGS-measured suspended sediment loads in two locations in the Tomales Bay Watershed during three water years (2004-2006) to estimate mercury loads from the watershed. Two gages, Lagunitas Creek at Samuel P. Taylor State Park (11460400) and Walker Creek near Marshall (11460750), measured water and suspended sediment discharge from an area of 34.3 $mi^2$ (89 $km^2$) and 31.1 $mi^2$ (80.5 $km^2$), respectively. We used this data to develop a regression relationship between monthly discharge and monthly suspended sediment loads for each USGS gage. In addition, we

assumed that discharge over the period of record (water year 1984-2009) was representative of the full range of flow conditions and that the sediment data collected over just three water years is representative (understanding that this is a large assumption). Using the regression and two assumptions, we calculated the average annual suspended sediment load per watershed to be 4,354 metric tons (49 metric t/$km^2$) in Lagunitas Creek and 18,297 metric tons (227 metric t/$km^2$) in Walker Creek.

Stream flow and suspended sediment yield were also measured by a continuous monitoring gage installed by Questa Engineering Corp. over three water years beginning October 1986 and ending September 1989 from Olema Creek (a tributary to Lagunitas Creek which joins Lagunitas Creek below the USGS gage at Samuel P. Taylor Park). Olema Creek (at Bear Valley bridge) was studied in relation to erosion problems after the 1983-86 series of storms (Questa Engineering Corp 1990). Using the data on stream flow, and suspended and bed load sediment collected from their gage, Questa Engineering Corp estimated an annual long term average total sediment yield of 20,473 tons of which 80% was suspended load. The watershed of Olema Creek at the Bear Valley Bridge is 32.6 $km^2$. Thus the annual average suspended sediment yield is estimated to be 502 metric t/$km^2$.

Assuming these three data sets are representative of the entire Tomales Bay watershed, these results were summed and scaled up by area to estimate an average watershed load of 102,778 metric t over the Tomales Bay watershed (minus the area of the Bay itself). Since we only had suspended sediment data for the areas captured by USGS gages, we had to estimate suspended sediment load from the entire watershed (by multiplying suspended sediment loads by a ratio of area captured by gages to total watershed). To estimate background total mercury load, this estimate of annual average suspended sediment load was multiplied by 0.2 µg/g (the measured concentration in bed sediments upstream from mining influence [Marshall 2006]). The resulting load calculated in this manner is 21 kg per year (Table 19).

A literature review by McKee et al. (2004) provided another estimate for total mercury watershed contribution that was lower than the estimate based on suspended sediment loads from gages. McKee et al. (2004) presented a hypothesis that mixed land use watersheds (including urban, agricultural, and open space lands) like Tomales Bay tend to have an average aqueous mercury concentration of 8-90 ng/L. Combining this concentration range with annual watershed runoff (479 mm per unit area) calculated by Fischer et al. (1996), it is estimated that Lagunitas Creek supplies about 0.7-7.6 kg/yr, Walker Creek supplies 0.2-2.1 kg/yr, and the other small tributaries (including Inverness Ridge and the east side of the Bay) contribute between less than 0.1-0.4 kg/yr for a total of about 1-10 kg/yr of mercury. In comparison to San Francisco Bay, input to Tomales Bay from local small tributaries are estimated to be about 2.5 times lower per unit area, which is consistent with the less urbanized setting in the Tomales Bay watershed. For this source analysis, we will use the estimate of watershed load calculated from the USGS suspended sediment data and known background mercury concentration, since they are local datasets.

Atmospheric deposition is another source of mercury that can contribute to the annual mercury load of the Tomales Bay watershed. Using a combined dry and wet deposition rate of 15.1-17.7 $\mu g/m^2/yr$ estimated from deposition measured at three sites in the San Francisco Bay Area (Tsai and Hoenicke 2001), and a Tomales Bay surface area of 29 $km^2$, about 0.4-0.5 kg/yr of atmospheric mercury is deposited onto Tomales Bay's surface each year (Table 19).

The annual load of methylmercury was also estimated, since methylmercury is of greater concern from a toxicological standpoint. Rytuba (2003) established a relationship between total and methylmercury in mining drainage from mercury mines around the world, and reported that in silica-carbonate type mercury deposits (found in the Coast Range), about 1% of total mercury is methylmercury. Based on this finding, an estimated 0.2-0.8 kg per year of methylmercury is transported from mining areas into Tomales Bay. Yee et al. (2008) estimated that atmospheric deposition contributes 0.1 g/day of methylmercury to San Francisco Bay. Scaling this down to the size of Tomales Bay, an estimated annual methylmercury load from atmospheric deposition to Tomales Bay is $9.62x10^{-4}$ kg. Lastly, watershed contributions of methylmercury in the Tomales Bay watershed were estimated using a range of the percentage of total mercury load that is methylmercury based on a literature review of mixed land use watersheds that contain open space and agriculture, like Tomales Bay (McKee et. al 2006). This resulted in an estimate of 0.14-2.4 kg/year contributed to Tomales Bay from the watershed (based on a range of 0.7-11.4% of total mercury load comprised of methylmercury, McKee, et. al 2006). Combining all three sources of methylmercury, the estimated total methylmercury load to Tomales Bay is 0.35-3.2 kg/yr (Table 19).

There are three types of external mercury sources to Tomales Bay discussed in this report: loads from historic mercury mining, watershed loading, and atmospheric deposition. When combined, these sources contribute approximately 41-102 kg/yr to the Bay (Table 19). Mining is by far the largest contributor, and can fluctuate depending on the frequency and magnitude of storms, and associated erosion of contaminated sediments. Since the Gambonini Mine has been remediated, and cleaner sediments have accumulated on top of contaminated sediment in the Walker Creek Delta, it is likely that the annual load from mine sources would be on the low end of that range (20-30 kg/yr). In a relatively dry year, loading could be less than 1 kg. Following mining, the other two sources in decreasing order of magnitude are watershed loadings and atmospheric deposition. Other sources of mercury including urban stormwater and industrial inputs are not included in this analysis because they are considered likely to be insignificant. In addition, any internal production of mercury that may occur is beyond the current scope.

**Table 20. Estimated mercury loadings from mining, watershed, and atmospheric sources.** This source analysis only includes external inputs, and omits any internal production of mercury that may occur.

| Source | Range of annual Hg load (kg) | Range of annual MeHg load (kg) | Area ($km^2$) |
|---|---|---|---|
| Mining | 20-80 | 0.2-0.8 | |
| Watershed contribution | 21 | 0.14-2.4 | 561 |
| Atmospheric deposition | 0.4-0.5 | $9.62x10^{-4}$ | 29 |
| **TOTAL** | **41-102** | **0.35-3.2** | |

# 8. Methylmercury in Tomales Bay

Since methylmercury is the most bioavailable and toxic form of mercury, understanding methylmercury cycling in Tomales Bay is an integral part of assessing potential risks. Previous data (collected in 2003) on methylmercury in sediments at the Walker Creek Delta indicated that methylmercury production was elevated in this area compared to reference sites, and was greater in intertidal areas than in vegetated marsh. Johnson et al. (2009) reported methylmercury concentrations in intertidal sediments of 0.3-11.4 ng/g, and in vegetated marsh areas of 0.2-5.0 ng/g. These were greater than in a reference site 4 km south of the Delta (McDonald, 0.2-0.7 ng/g). Sediment samples collected in the present study in June 2009 had relatively low average methylmercury concentrations, but indicate the opposite effect of methylmercury production in intertidal versus marsh areas. Methylmercury concentrations in sediment from 2009 were higher in vegetated marsh (1.3-2.4 ng/g) compared to intertidal mudflat sites of Walker Creek (0.3-1.4 ng/g; see Figure 25, section 6.2). Bay-wide, marsh sites were also significantly higher than mudflat sites ($p<0.001$, Table 17b, section 6.2). Methylmercury in sediments from 2009 from McDonald was lower than Walker Creek area sites, and within the range of previous results (0.6 ng/g). Given the dynamic nature of methylmercury production and degradation, these apparently contradictory results are not necessarily surprising.

Limited data available for methylmercury in invertebrates from Johnson et al. (2009) were similar to the sediment data, indicating higher methylmercury concentrations in biota from the Walker Creek Delta than at reference sites south of Walker Creek. Resident bivalves from Walker Creek had methylmercury concentrations of 0.07µg/g (wet), while similar bivalves at Millerton had methylmercury concentrations of 0.02-0.04µg/g. The difference in shorecrab methylmercury concentrations was even more pronounced: 360 ng/g at Walker Creek, compared to 64 ng/g at McDonald.

The Lagunitas Delta appears to be another zone of net methylmercury production in the Bay, but there is far less information regarding mercury dynamics in this large marsh system than for the Walker Delta. Though Lagunitas marsh sites exhibited higher methylmercury concentrations (1.4-1.5 ng/g) than mudflat sites, as in the Walker Delta, Lagunitas mudflat sites were in the same range as other reference sites (0.1-0.6 ng/g), though there were only two marsh sites for Lagunitas, compared to four in the Walker Creek marsh. Considering that the Lagunitas marsh is nearly twice the size (215 ha) of

the Walker marsh (110 ha), the Lagunitas marsh may be a large contributor to methylmercury contamination of the Tomales Bay food web. The contribution of the Lagunitas marsh to the Bay methylmercury budget is therefore an important data gap. This is particularly relevant considering the recently completed restoration of tidal action to some sections of the Lagunitas marsh which will increase seasonal fluctuations in water level, a phenomenon that is conducive to methylmercury production (Wiener et al. 2003).

## 8.1. Effects on beneficial uses

The following section will review each beneficial use potentially impaired by methylmercury (section 2.1), based on the data presented in this report and the framework provided in section 1. In most cases, beneficial uses are grouped for interpretation.

### 8.1.1. Human health beneficial uses: ocean, commercial, and sport fishing; shellfish harvesting

Based on data from OEHHA (2004), some species of sport fish have tissue concentrations of methylmercury that could adversely affect humans who consume those fish (Figure 3). Brown smoothhound shark, leopard shark, bat ray, and Pacific angel shark all had average methylmercury concentrations that exceeded the 0.3 µg/g USEPA tissue criterion. A health advisory was issued in 2004 by OEHHA that provided guidelines for safe consumption of these and other sport fish species. It will be important to periodically re-sample commonly-caught sport fish in order to determine trends in risks to human health and to adjust the advisory if necessary. Sport fish sampling conducted as part of the Surface Water Ambient Monitoring Program in 2009 will provide useful information. The existing consumption advisory for sport fish indicates that the beneficial use is impaired by mercury. In contrast to sport fish, OEHHA (2004) reported that commercial shellfish contained relatively low concentrations of mercury and did not present a human health risk from mercury.

Commercial fishing in Tomales Bay is almost entirely comprised of herring. As stated in section 3.1.7, the past few years have seen minimal catch, due to a variety of factors including low international demand for roe and the high cost of fuel and boat operation. Herring are small, migratory fish that do not spend their whole life in Tomales Bay, so as discussed in section 4.3, they are presumed to not have high methylmercury concentrations. We were unable to find any studies describing the toxicity of methylmercury to herring. Based on the life history of herring in Tomales Bay and the moderate degree of contamination of the Tomales Bay food web, it is unlikely that this fishery is impaired by methylmercury.

Methylmercury concentrations in Tomales Bay commercial shellfish appear to be below thresholds for concern, and thus the beneficial use is not impaired. OEHHA (2004) reported that the average methylmercury concentration in commercial clams (0.04 µg/g) was safe for humans to consume. Johnson et al. (2009) reported similar

methylmercury concentrations in commercial clams (0.06 µg/g at Walker Creek Delta, which had the highest methylmercury concentration measured).

### 8.1.2. **Wildlife beneficial uses: estuarine, marine, and wildlife habitat**

The very limited dataset available for tidal marsh biota in Tomales Bay suggest that risks to wildlife may be greatest in this part of the ecosystem, though a more recent dataset would help to answer this question. Previous studies have shown that invertebrates (including clams, oysters, shorecrabs, and mussels) had higher total and methylmercury concentrations in the Walker Creek Delta, as compared to other parts of Tomales Bay (Whyte and Ganguli 2000, Johnson et al. 2009). Methylmercury concentrations reported for shorecrabs (mean concentration=0.26 µg/g at Walker Creek, RWQCB unpublished data) and wild clams (0.02-0.1 µg/g wet, OEHHA, unpublished data) are high enough to suggest the possibility of problematic methylmercury exposure in some specific Tomales Bay habitats, particularly tidal marsh. Most of these data exceed the estimated threshold methylmercury concentration in trophic level two prey in order to protect predators ( 0.01-0.04 µg/g wet, section 5.1.2). In San Francisco Bay, California Clapper Rails are at risk from methylmercury exposure (Schwarzbach et al. 2006) in spite of their low trophic level invertebrate diet, apparently due to their dependence on habitat with high methylmercury concentrations.

Piscivorous wildlife are generally a larger concern with regard to mercury impairment, due to their higher trophic position and the biomagnification of mercury in aquatic food webs, as described in 4.3. Prey fish were therefore sampled in 2009 to determine risk to wildlife species that consume prey fish. Of the fish composites with a mean length between 5-15 cm, the mean mercury concentration of mercury was 0.05 µg/g wet (section 6.1). This estimated mean concentration (0.05 µg/g wet) is equivalent to the estimated target methylmercury concentration in this size class to protect wildlife (section 5.1.2). In larger fish (>15 cm), the estimated threshold concentration was 0.17, which was not exceeded by any of the samples in this study. The prey fish data therefore indicate that average concentrations in the Tomales Bay food web are at a level that appears to be safe for piscivorous birds, but that any increase in concentration would cause them to exceed the threshold for risks to these birds.

Since the 5-15 cm size class wildlife estimated target is theoretically protective of the Belted Kingfisher, it is important to consider the prey species that are actually consumed by this piscivore and whether the estimated target would be protective of this species in reality. Based on diet studies reported in the literature and local biologists, Belted Kingfishers typically consume fish less than 10 cm, including staghorn sculpin and gobies (Jules Evens, *pers. comm.*). The average mercury concentration of fish in this size class collected in June 2009 from Tomales Bay (0.034 µg/g) was lower than the 0.05 µg/g estimated target. Thus, it is likely, based on our limited data, that if the Belted Kingfisher were to consume the species analyzed in this study, at the time of year this study was conducted, they would be safe from methylmercury toxicity. However, two other species of piscivores, the Black-crowned Night-Heron and Caspian Tern, have similar estimated threshold concentrations as the Belted Kingfisher but eat fish throughout the size class (up to 15 cm). For these birds, averaging all fish 5-15 cm in

length is a more appropriate measure of methylmercury exposure, and the data reported indicate that the methylmercury concentrations in trophic level three prey necessary to protect these species are also met.

It is likely that wildlife consume prey from a variety of locations around the Bay, and choose their prey opportunistically, so it is unlikely that staghorn sculpin or other species that exceeded the mercury target would comprise the entire diet of any species of wildlife. However, little is known about the food web of Tomales Bay, including the specific diets of breeding, piscivorous wildlife, so it is difficult to determine the methylmercury exposure of Tomales Bay piscivores based on this fish dataset alone.

Due to budget and time limitations, it was not possible to collect samples of predator tissue for this study. This is an important data gap. Direct measurement of predator exposure would be valuable to reduce uncertainty regarding risks to predators from methylmercury.

#### 8.1.3. **Wildlife beneficial use: rare and endangered species**

Tomales Bay is home to numerous rare and endangered species, including 48 plant species, ten invertebrates species, four fish species, one amphibian species, one reptile species, eight mammal species, and ten bird species (CNDDB database). It is possible that the tidewater goby (*Eucyclogobius newberryi*) was extirpated from the watershed. The last sighting of the species was in 1953, followed by five individuals preliminarily identified as tidewater gobies in 2005 (CSLC 2007). However, the extirpation, if the recently found individuals are not tidewater gobies, is likely due to loss of habitat by sedimentation in marshes (CSLC 2007), and there is no evidence to suggest that this was related to methylmercury. At present there is no evidence to suggest that rare and endangered species are impaired by methylmercury because we have not sampled any directly.

# 9. Conclusion

## 9.1. Summary of findings based on sampling plan hypotheses

Mining of naturally occurring mercury deposits in the Walker Creek watershed in the 1960s and 1970s has resulted in mercury-contaminated sediment eroding into creek channels during storms, and eventually discharging into Tomales Bay. Methylmercury, the most toxic and bioavailable form of mercury, is of great concern due to its potential toxic effects on fish, wildlife, and humans. Methylmercury concentrations in certain species of sport fish exceeded the USEPA tissue criterion for human health and have prompted a fish consumption advisory for Tomales Bay. This study provided a comprehensive quantification of potential risk to wildlife and greatly enhanced the available dataset, allowing for a robust conceptual model of mercury contamination in Tomales Bay.

Samples of small fish, sediment, and water were collected throughout Tomales Bay to evaluate the spatial distribution of mercury and methylmercury and whether prey

fish exceeded estimated threshold concentrations for wildlife consumption. The results of the study support the following answers to the original questions and hypotheses of interest.

***Question 1:*** *What are the spatial gradients and patterns of total and methylmercury?*

***H1:*** *Mining in the Walker Creek watershed is the major source of mercury to Tomales Bay, thus concentrations of total and methylmercury in sediments are higher in the Walker Creek Delta than other portions of the Bay.*

The results of this study supported this hypothesis. The source analysis indicated that mining sources were of equal or greater mass than other total mercury sources to Tomales Bay. Elevated total mercury in sediment was largely confined to the Walker Creek Delta. Methylmercury in sediment also was highest in the Walker Creek Delta, although there were elevated concentrations from the Lagunitas Delta as well.

***H2:*** *Methylation occurs more frequently in tidal salt marsh areas on the eastern edge of the Bay where there is periodic inundation, high organic matter, and substrate dominated by fine sediment.*

This hypothesis was supported in that methylmercury concentrations in tidal marsh sediment (mean=1.79 ng/g) were nearly 3.5 times higher than those collected in the mudflat sediment (mean=0.52 ng/g). In addition mean %methylmercury in tidal marsh sediments was four times higher (4%) than in mudflat sediments (1%). There was a significant, positive correlation between both percent carbon and percent nitrogen with methylmercury concentration in sediment in this study and in the sediment cores collected by Johnson, et al (2009). However there was no significant correlation between %fine sediments and methylmercury.

***H3:*** *Mercury concentrations are elevated in the fine sediments that occur in the top few centimeters of substrate in the Bay. These sediments originate from upland areas and are transported to the Bay through natural processes and from excessive erosion of fine sediments caused by human actions.*

This hypothesis is supported for the Walker Creek Delta area, but only partially supported elsewhere. Total mercury concentrations in the top 5 cm of sediment in the Walker Creek Delta were elevated above the 0.2 µg/g dry concentration measured in areas upstream of mining operation. This indicates that mercury-contaminated sediment continues to erode from the mine, or from floodplain storage areas along Walker Creek, into Tomales Bay.

***Question 2:*** *Is mercury from mining sediments entering the food chain of Tomales Bay?*

***H4:*** *Concentrations of MeHg in sediment or water are correlated in time and space with concentrations of THg in fish*

This hypothesis was weakly supported by the available data. Methylmercury bioaccumulation in small fish and bivalves appeared to correlate with the spatial pattern observed in sediment methylmercury or sediment total mercury, however the low statistical power of the small fish design precluded detection of statistically significant differences in the small fish. Spatial patterns in water and temporal patterns in any of these matrices could not be analyzed due to insufficient data.

***H5:*** *Mercury concentrations in prey fish exceed the estimated threshold concentrations for protection of piscivorous birds, and thus the beneficial uses that provide for the protection of wildlife are impaired.*

The estimated target methylmercury concentration is 0.05 µg/g wet for fish 5-15 cm in length. The available data do not support this hypothesis for prey fish. In this study, fish 5-15 cm in length had a mean mercury concentration of 0.05 µg/g wet, which is equivalent to the suggested wildlife target for that size class (meaning, on average, piscivorous wildlife that consume these fish are protected). However, estimated average concentrations in prey fish are equal to the threshold for risks to predators. If the estimated average is not truly representative of average prey concentrations and predator exposure, then it is possible that the threshold may actually be exceeded in Tomales Bay. In addition it should be noted that any increase in food web methylmercury could raise concentrations above the estimated target.

A very sparse data set (2 composites) for the larger size class of fish does not support this hypothesis. Fish greater than 15 cm in length (the two composites of jacksmelt) had a mean concentration of 0.08 µg/g wet. Neither of these composites of larger fish exceeded the suggested wildlife target for this size class (0.17 µg/g wet).

The data available indicate that certain beneficial uses may be impaired by methylmercury. These beneficial uses include sport fishing, and wildlife habitat in some cases. Further study of methylmercury bioaccumulation in Tomales Bay may help regulators to more accurately assess impairment and tailor management actions to reduce methylmercury contamination in Tomales Bay.

## 9.2. Information gaps

The information gaps related to understanding impairment of Tomales Bay by methylmercury should be filled in a hierarchical manner, such that each new gain in knowledge informs which information gaps to tackle next. A list of initial information gaps to be filled is provided below, along with where these gaps were identified in the body of the report (in parentheses).

The approach taken in San Francisco Bay by the Mercury Strategy of the Regional Monitoring Program for Water Quality is a useful model for prioritizing knowledge gaps. That strategy takes the following steps:

1) characterize spatial and temporal patterns in food web uptake,
2) identify the high leverage pathways,
3) identify opportunities for management intervention, and
4) monitor to evaluate effectiveness of interventions.

Based on this approach, knowledge is still lacking about patterns in food web uptake (RMP Mercury strategy step 1). Therefore, some high priority knowledge gaps to fill are as follows:

- Directly sample the tissues of wildlife suspected of facing greatest risks (section 8.1.2).
  - Kingfisher eggs could be sampled to determine mercury concentrations directly in the life stage of greatest sensitivity.
  - Wildlife species around the margin of Tomales Bay may be experiencing high bioaccumulation of mercury, and few data are available to assess their risk. The finding that methylmercury in sediment is higher in tidal marsh than in mudflat, the relatively high methylmercury concentrations in intertidal invertebrates, and the medium to high mercury sensitivity of egret and heron species that feed around the margin of the Bay all combine to point toward the wetland margins of the Bay as a potential area of maximum methylmercury risk for birds.
- Provide an updated dataset to compare to existing invertebrate data from the tidal marsh areas of Tomales Bay. Previous studies indicated that methylmercury concentrations in clams and shorecrabs exceeded the estimated threshold concentration in trophic level two prey to protect piscivorous wildlife. This suggests that risks to wildlife may be greatest in this part of the Bay, and a time trend analysis would improve assessment of this risk (sections 2.4.2, 8.1.2).
- Better characterize bioaccumulation in small fish. A follow-up study to the pilot effort presented here would be valuable. A more thorough and refined study, with larger sample sizes, better representation of the 10-15 cm size group, and fish collected during the piscivorous bird breeding season, would allow a more definitive assessment of impairment (sections 6.1, 8.1.2).
- Better characterize methylmercury production and bioaccumulation in the Lagunitas Creek marsh. The Lagunitas marsh is nearly twice the size (215 ha) of the Walker marsh (110 ha), but had fewer sediment samples (6) than Walker marsh (8) due to an error made in the field, and the total number of samples was not allocated proportional to area in the sampling plan. Due to its size, the marsh may be a large contributor to methylmercury contamination of the Tomales Bay food web. This is particularly relevant considering the recently completed restoration of tidal action to some sections of the Lagunitas marsh which will increase seasonal fluctuations in water level, a

phenomenon that is conducive to methylmercury production (sections 6.2, and 8).

- Develop more accurate, local data for estimating targets and threshold concentrations of methylmercury to protect wildlife. Reference doses, feeding ingestion rate, and distribution of diet across trophic levels are three factors in this analysis where better information is needed (section 5.1.2).
- Gather improved and updated information on human exposure by filling the data gaps identified by OEHHA (2004) (sections 2.4.2, 8.1.1).

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# Appendix

Tables 21a-g. provide detailed data on a variety of fish methylmercury concentrations collected throughout California, compared to specimens collected in Tomales Bay.

**Table 21a. Brown smoothhound shark (Trophic level 4) methylmercury concentrations, Tomales Bay compared to other sites.**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales Bay | 1.34 | 878.00 | 12 | 1998, 2001 | OEHHA 2004 |
| Mission Bay | 0.18 | 870.67 | 9 | 2002 | OEHHA unpublished |
| San Francisco Bay | 0.68 | 720.00 | 9 | 2003 | RMP 2003 |

**Table 21b. Leopard shark (Trophic level 4) methylmercury concentrations, Tomales Bay compared to other sites.**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales Bay | 1.00 | 1010.22 | 21 | 1999, 2001 | OEHHA 2004 |
| San Francisco Bay | 0.90 | 1057.00 | 15 | 2003 | RMP 2003 |
| Elkhorn Slough | 0.93 | 1204.69 | 13 | 2001, 20002 | OEHHA, unpublished |
| Newport Bay | 0.07 | 609.00 | 1 | 2003 | OEHHA, unpublished |
| San Diego Bay | 0.77 | 950.60 | 5 | 2002 | OEHHA, unpublished |

**Table 21c. Jacksmelt (Trophic level 3) methylmercury concentrations, Tomales Bay compared to other sites**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales (this study) | 0.08 | 252.65 | 2 | 2009 | This study |
| Tomales Bay | 0.07 | 260.77 | 7 | 1998, 1999 | OEHHA 2004 |
| White's Point | 0.02 | 235.40 | 1 | 2001 | OEHHA unpublished |
| San Francisco Bay | 0.05 | 250.5 | 4 | 2003 | RMP 2003 |

**Table 21d. Topsmelt (Trophic level 3) methylmercury concentrations, Tomales Bay compared to other sites**

| Location | Mean MeHg (µg/g) | Mean Size | N | Years | Source |
|---|---|---|---|---|---|
| Tomales (this study) | 0.12 | 70 | 4 | 2009 | RMP, unpublished data |
| RMP sites | 0.23 | 46.78 | 93 | 2005-2007 | Greenfield and Jahn 2010 |

**Table 21e. Threespine stickleback (Trophic level 3) methylmercury concentrations, Tomales Bay compared to other sites**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales (this study) | 0.05 | 70.73 | 8 | 2009 | This study |
| SF Bay (south) | 0.08 | 78.17 | 134 | 2006-2007 | Grenier, et. al 2010 |

**Table 21f. Staghorn sculpin (Trophic level 3) methylmercury concentrations, Tomales Bay compared to other sites**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales (this study) | 0.06 | 91.29 | 22 | 2009 | This study |
| SF Bay (south) | 0.08 | 65.49 | 19 | 2007 | Grenier, et. al 2010 |

**Table 21g. Shiner perch (Trophic level 3) methylmercury concentrations, Tomales Bay compared to other sites**

| Location | Mean MeHg (µg/g) | Mean Size (mm) | N | Years | Source |
|---|---|---|---|---|---|
| Tomales (This study) | 0.02 | 54.54 | 21 | 2009 | This Study |
| Tomales Bay | 0.10 | 114.81 | 7 | 1998-2001 | OEHHA 2004 |
| Anaheim Bay | 0.01 | 123.88 | 3 | 2001-2002 | OEHHA unpublished |
| San Francisco Bay | 0.10 | 114.75 | 9 | 2003 | RMP 2003 |
| Bodega Harbor | 0.07 | 114.88 | 2 | 1999, 2001 | OEHHA unpublished |
| Catalina Island | 0.07 | 126.55 | 1 | 2005 | OEHHA unpublished |
| Channel Islands Harbor | 0.03 | 124.90 | 2 | 1999, 2003 | OEHHA unpublished |
| Elkhorn Slough | 0.05 | 116.72 | 5 | 2000-2002 | OEHHA unpublished |
| Hollywood Beach | 0.07 | 136.80 | 1 | 1999 | OEHHA unpublished |
| Humboldt Bay | 0.11 | 133.85 | 5 | 1999-2003 | OEHHA unpublished |
| Mission Bay | 0.04 | 116.83 | 6 | 2001-2002 | OEHHA unpublished |
| Newport Bay | 0.04 | 103.60 | 1 | 1999 | OEHHA unpublished |
| Noyo Harbor | 0.17 | 105.75 | 2 | 2003 | OEHHA unpublished |
| Princeton Harbor Jetty | 0.09 | 99.78 | 1 | 2001 | OEHHA unpublished |
| Samoa Pennisula | 0.07 | 109.87 | 1 | 2001 | OEHHA unpublished |
| San Diego Bay | 0.05 | 120.83 | 5 | 2000-2002 | OEHHA unpublished |
| Ventura Marina Jetty | 0.04 | 132.80 | 1 | 1999 | OEHHA unpublished |

**Table 22. Fish tissue results. All results are reported as composites.**

| StationName | Species | Average length (mm) | Solids (%) | THg_dw (µg/g ) | THg_ww (µg/g ) |
|---|---|---|---|---|---|
| Brazil Beach | Jacksmelt | 266.5 | 24.25 | 0.372 | 0.090 |
| Brazil Beach | Kelp Perch | 53.2 | 16.47 | 0.098 | 0.016 |
| Brazil Beach | Kelp Perch | 56.7 | 16.06 | 0.102 | 0.016 |
| Brazil Beach | Kelp Perch | 48.2 | 15.25 | 0.084 | 0.013 |
| Brazil Beach | Speckled Sanddab | 91.7 | 19.26 | 0.094 | 0.018 |
| Brazil Beach | Speckled Sanddab | 74.8 | 18 | 0.116 | 0.021 |
| Brazil Beach | Speckled Sanddab | 49.4 | 13.32 | 0.087 | 0.012 |
| Brazil Beach | Speckled Sanddab | 62.8 | 15.9 | 0.125 | 0.020 |
| Brazil Beach | Staghorn Sculpin | 102.8 | 17.43 | 0.158 | 0.028 |
| Brazil Beach | Staghorn Sculpin | 74.5 | 15.95 | 0.162 | 0.026 |
| Brazil Beach | Threespine stickleback | 76.8 | 24.22 | 0.199 | 0.048 |
| Brazil Beach | Threespine stickleback | 75.8 | 25.27 | 0.160 | 0.040 |
| Brazil Beach | Threespine stickleback | 76.3 | 27.96 | 0.175 | 0.049 |
| Brazil Beach | Threespine stickleback | 75.8 | 25.08 | 0.163 | 0.041 |
| Eucalyptus Beach | Jacksmelt | 238.8 | 20.25 | 0.354 | 0.072 |
| Eucalyptus Beach | Kelp Perch | 42.4 | 15.95 | 0.047 | 0.007 |
| Eucalyptus Beach | Kelp Perch | 46.8 | 18.36 | 0.063 | 0.012 |
| Eucalyptus Beach | Kelp Perch | 47.5 | 17.1 | 0.060 | 0.010 |
| Eucalyptus Beach | Shiner perch | 106.8 | 22.93 | 0.231 | 0.053 |
| Eucalyptus Beach | Speckled Sanddab | 62.6 | 16.59 | 0.112 | 0.019 |
| Eucalyptus Beach | Speckled Sanddab | 66.4 | 17.82 | 0.131 | 0.023 |
| Eucalyptus Beach | Speckled Sanddab | 55.2 | 17.38 | 0.127 | 0.022 |
| Eucalyptus Beach | Speckled Sanddab | 51.8 | 18.53 | 0.104 | 0.019 |
| Eucalyptus Beach | Speckled Sanddab | 62.6 | 18 | 0.130 | 0.023 |
| Eucalyptus Beach | Staghorn Sculpin | 105.5 | 18.51 | 0.221 | 0.041 |
| Eucalyptus Beach | Staghorn Sculpin | 84.6 | 18.39 | 0.275 | 0.051 |
| Eucalyptus Beach | Staghorn Sculpin | 106.5 | 18.38 | 0.293 | 0.054 |
| Eucalyptus Beach | Staghorn Sculpin | 126 | 18.5 | 0.333 | 0.062 |
| Hamlet | Shiner perch | 46 | 17.24 | 0.117 | 0.020 |
| Hamlet | Shiner perch | 43.2 | 16.96 | 0.105 | 0.018 |
| Hamlet | Shiner perch | 46.4 | 16.92 | 0.100 | 0.017 |
| Hamlet | Shiner perch | 46.9 | 15.81 | 0.109 | 0.017 |
| Hamlet | Staghorn Sculpin | 79.6 | 16.92 | 0.336 | 0.057 |
| Hamlet | Staghorn Sculpin | 87 | 16.25 | 0.322 | 0.052 |
| Hamlet | Staghorn Sculpin | 76 | 16.53 | 0.296 | 0.049 |
| Hamlet | Staghorn Sculpin | 92.8 | 18.18 | 0.535 | 0.097 |
| Lagunitas Delta | Shiner perch | 41.8 | 14 | 0.114 | 0.016 |
| Lagunitas Delta | Shiner perch | 56.8 | 13.89 | 0.124 | 0.017 |

| StationName | Species | Average length (mm) | Solids (%) | THg_dw (µg/g ) | THg_ww (µg/g ) |
|---|---|---|---|---|---|
| Lagunitas Delta | Shiner perch | 51.2 | 14.72 | 0.116 | 0.017 |
| Lagunitas Delta | Shiner perch | 43.8 | 13.77 | 0.076 | 0.010 |
| Lagunitas Delta | Staghorn Sculpin | 74.8 | 14.83 | 0.466 | 0.069 |
| Lagunitas Delta | Staghorn Sculpin | 85.4 | 17.33 | 0.420 | 0.073 |
| Lagunitas Delta | Staghorn Sculpin | 69.4 | 14.67 | 0.351 | 0.051 |
| Lagunitas Delta | Staghorn Sculpin | 94.3 | 17.04 | 0.562 | 0.096 |
| MacDonald | Shiner perch | 44.6 | 13.4 | 0.133 | 0.018 |
| MacDonald | Shiner perch | 107.2 | 20.78 | 0.280 | 0.058 |
| MacDonald | Shiner perch | 44 | 12.99 | 0.118 | 0.015 |
| MacDonald | Shiner perch | 50.4 | 15.2 | 0.137 | 0.021 |
| MacDonald | Staghorn Sculpin | 102.6 | 17.48 | 0.262 | 0.046 |
| MacDonald | Staghorn Sculpin | 117 | 16.55 | 0.263 | 0.044 |
| MacDonald | Staghorn Sculpin | 103.2 | 17 | 0.321 | 0.055 |
| MacDonald | Staghorn Sculpin | 83.2 | 15.57 | 0.326 | 0.051 |
| North Millerton | Shiner perch | 43.2 | 15.18 | 0.107 | 0.016 |
| North Millerton | Shiner perch | 42.6 | 12.86 | 0.094 | 0.012 |
| North Millerton | Shiner perch | 42.8 | 14.91 | 0.112 | 0.017 |
| North Millerton | Shiner perch | 44.4 | 15.49 | 0.122 | 0.019 |
| North Millerton | Staghorn Sculpin | 70.2 | 16.82 | 0.466 | 0.078 |
| North Millerton | Staghorn Sculpin | 94 | 16.59 | 0.339 | 0.056 |
| Walker Creek Delta | Shiner perch | 44.6 | 15.81 | 0.122 | 0.019 |
| Walker Creek Delta | Shiner perch | 42.8 | 14.89 | 0.109 | 0.016 |
| Walker Creek Delta | Shiner perch | 51.4 | 17.53 | 0.135 | 0.024 |
| Walker Creek Delta | Shiner perch | 104.4 | 21.41 | 0.402 | 0.086 |
| Walker Creek Delta | Staghorn Sculpin | 89.6 | 17.24 | 0.451 | 0.078 |
| Walker Creek Delta | Staghorn Sculpin | 89.3 | 15.85 | 0.529 | 0.084 |
| Walker Creek Delta | Threespine stickleback | 75.2 | 22.13 | 0.256 | 0.057 |
| Walker Creek Delta | Threespine stickleback | 40.6 | 19.64 | 0.138 | 0.027 |
| Walker Creek Delta | Threespine stickleback | 77 | 22.38 | 0.293 | 0.066 |
| Walker Creek Delta | Threespine stickleback | 74.6 | 23.27 | 0.298 | 0.069 |

**Table 23. Fish tissue results for those composites analyzed for methylmercury. The relationship between total and methylmercury in fish was strong ($R^2$=0.99), and the equation is MeHg=0.85(THg)+0.003**

| Station Name | Species | Average length (mm) | Solids (%) | THg_ww (µg/g ) | MeHg_ww (µg/g ) |
|---|---|---|---|---|---|
| Lagunitas Delta | Shiner perch | 43.8 | 13.77 | 0.010 | 0.010 |
| Hamlet | Shiner perch | 46.9 | 15.81 | 0.017 | 0.018 |
| Eucalyptus Beach | Speckled Sanddab | 62.6 | 18 | 0.023 | 0.024 |
| MacDonald | Staghorn Sculpin | 102.6 | 17.48 | 0.046 | 0.043 |
| Hamlet | Staghorn Sculpin | 76 | 16.53 | 0.049 | 0.048 |
| Eucalyptus Beach | Jacksmelt | 238.8 | 20.25 | 0.072 | 0.061 |

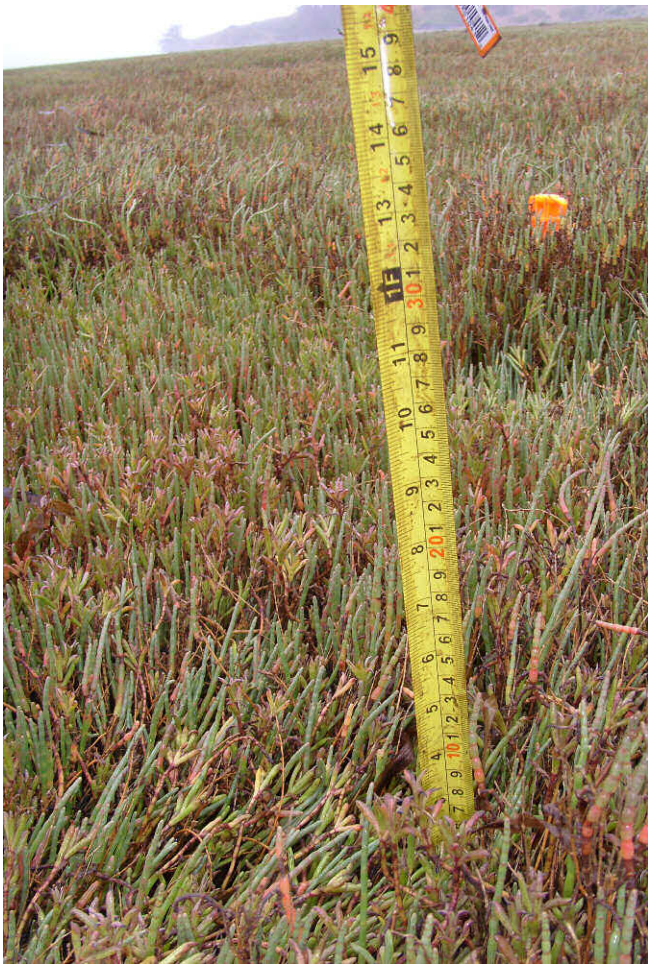
**Table 24. Fish tissue results for topsmelt collected in November 2009.**

| Sample Date | Location | N | Avg. Length (mm) | Avg. Solids (%) | Mecury concentration (ug/g, wet) |
|---|---|---|---|---|---|
| 11/12/09 | Tomales Bay base of Walker Cr. | 5 | 62.4 | 23.79 | 0.09 |
| 11/12/09 | Tomales Bay base of Walker Cr. | 5 | 66.4 | 24.49 | 0.12 |
| 11/12/09 | Tomales Bay base of Walker Cr. | 5 | 71.8 | 24.67 | 0.1 |
| 11/12/09 | Tomales Bay base of Walker Cr. | 5 | 79.6 | 25.44 | 0.14 |
| Mean | | | 70.05 | | 0.12 |
| Standard deviation | | | 7.44 | | 0.02 |

**Table 25. Fish tissue mercury concentrations for museum specimens. All fish were received from the California Academy of Sciences, preserved in ethyl alcohol, and composited prior to analysis by the lab.**

| Date collected | Location collected | Species | N | Avg Length (mm) | THg_ww (µg/g ) |
|---|---|---|---|---|---|
| 5/10/53 | Walker Creek Tomales Bay, Sta 3, Hwy 1 bridge, 2.1 miles upstream from mouth of Walker Cr. | Staghorn Sculpin | 2 | 63.5 | 0.193 |
| 5/10/54 | Walker Creek Tomales Bay, Sta 3, Hwy 1 bridge, 2.1 miles upstream from mouth of Walker Cr. | Staghorn Sculpin | 2 | 72 | 0.160 |
| 4/27/53 | Walker Creek Tomales Bay, Sta. 4, abandoned RR bridge, 1.0 mile upstream from mouth of Walker Cr. | Staghorn Sculpin | 2 | 64.5 | 0.155 |
| 6/8/53 | Walker Creek Tomales Bay, Sta. 4, abandoned RR bridge, 1.0 mile upstream from mouth of Walker Cr. | Staghorn Sculpin | 2 | 83.5 | 0.210 |
| 3/15/54 | Walker Creek Tomales Bay, Sta. 4, abandoned RR bridge, 1.0 mile upstream from mouth of Walker Cr. | Staghorn Sculpin | 2 | 54 | 0.109 |
| 4/25/60 | Tomales Bay unnamed creek near Tomales Bay, CA | Staghorn Sculpin | 2 | 67 | 0.068 |
| | | | **Mean** | **67.4** | **0.149** |
| | | | **SD** | | **0.052** |
| 7/17/54 | Walker Creek Tomales Bay, Sta 3, Hwy 1 bridge, 2.1 miles upstream from mouth of Walker Cr. | Topsmelt | 2 | 61.5 | 0.149 |
| 8/16/54 | Walker Creek Tomales Bay, Sta 5, 0.5 miles upstream from the mouth of Walker Cr. | Topsmelt | 2 | 56.5 | 0.120 |
| 6/24/55 | Walker Creek Tomales Bay, Sta. 6, 0.5 miles S of Blake's Landing | Topsmelt | 2 | 71.5 | 0.081 |
| | | | **Mean** | **63.2** | **0.117** |
| | | | **SD** | | **0.035** |
| | | ETOH Blank 2 ml | | | 0 |
| | | ETOH Blank 2 ml | | | 0 |

a)



b)

**Figure 31. Typical vegetation height for sediment sampling sites defined as "marsh" at a) Lagunitas Marsh and b) Walker Marsh**