

2010 Data Transmittal for Assessing Impairment in Tomales Bay due to Mercury



**Prepared for the San Francisco Bay Regional Water Quality
Control Board**

By

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1. Purpose

This document is a data transmittal to the San Francisco Bay Regional Water Quality Control Board for samples collected in May-June 2010 from Tomales Bay, California. The data reported include total mercury (Hg) in small fish and sport fish, and methylmercury (MeHg) in shorecrabs. Due to time and budget constraints, the data were not analyzed using statistics. Thus, only qualitative descriptions of data are provided here, summarized in figures and tables. Statistical analysis is required in the future to interpret the data.

The purpose of this data transmittal is to supplement the Tomales Bay Mercury Impairment Assessment (Ridolfi et al. 2010). The dataset summarized in this document provides the baseline from which to assess future trends in Hg bioaccumulation at Walker Creek delta in Tomales Bay. As discussed in the sampling plan, the data reported in this transmittal fill selected data gaps that remained after the first sampling effort in June 2009. The data gaps filled by this baseline and future datasets are summarized below:

- 1) Gather improved and updated information on human exposure by building on datasets of commonly caught sport fish used by California's Office of Environmental Health Hazard Assessment (OEHHA) for the Tomales Bay Fish Consumption Advisory (2004). The Surface Water Ambient Monitoring Program (SWAMP) funded a study of bioaccumulation in sport fish along the California coast, including Tomales Bay (SWAMP, In Press). While several species of sport fish were sampled from Tomales Bay in summer 2009, halibut were not. Since halibut are a preferred species of Tomales anglers, we prioritized this species for future sampling and trend analysis to better characterize risk to humans.
- 2) Provide an updated and statistically robust dataset of invertebrate data from the tidal marsh at Walker Creek delta, to better assess risk from Hg to wildlife that eat invertebrates. Previous studies indicated that MeHg concentrations in clams and shorecrabs (of the sizes and species consumed by wildlife) in this area were elevated above estimated threshold concentrations (Ridolfi et al. 2010). This suggests that risks to wildlife may be greatest in this part of the Bay.
- 3) Better characterize bioaccumulation of MeHg in small fish. A follow-up study to the pilot effort summarized in Ridolfi et al. (2010) was warranted. A more thorough and refined study (in terms of spatial scope), with larger sample sizes, and of fish collected during the piscivorous bird breeding season was needed to provide a more precise assessment of impairment when birds are most at risk of Hg contamination.

The following questions were addressed by this dataset, and will be answered by future long term monitoring to be conducted by the San Francisco Bay Regional Water Quality

Control Board (SFBRWQCB). In addition, we prioritized the questions, and provided hypotheses and information on biota collected in order to inform the long term monitoring effort.

- 1) What is the risk from MeHg over time to wildlife that eat invertebrates from the Walker Creek Delta?

Priority: This is the highest priority for sampling, because the previous dataset (OEHHA 2004) is sparse ($n = 10$ composites), and mean methylmercury (MeHg) concentrations in clams from the Walker Creek Delta ($0.06 \mu\text{g/g}$, wet) were higher than from other sites in Tomales Bay. Invertebrate MeHg concentrations consumed by wildlife in Walker Creek Delta may exceed the trophic-level-2 invertebrate prey Hg threshold of $0.01 \mu\text{g/g}$, wet (Ridolfi et al. 2010).

Hypothesis 1: Methylmercury in shorecrabs will decline over time according to the conceptual model for Hg in Tomales Bay developed by the SFBRWQCB. Mercury load reduction is predicted by the conceptual model due to remediation of the Gambonini mercury mine.

Biota to be collected: *Hemigrapsus oregonensis* or other plentiful and easily-caught intertidal crabs. These shorecrabs are commonly consumed by piscivorous wildlife.

Portion of long-term monitoring program to initiate in this transmittal: Collect data that can be used to quantify risk to wildlife that eat invertebrates, and provide baseline for future trends in invertebrate MeHg concentrations (data gap #2 in list above).

- 2) What is the risk during the breeding season from Hg to piscivorous wildlife?

Priority: Filling this data gap is the second-highest priority for sampling, because Ridolfi et al. (2010) indicated higher potential for risk to piscivorous birds, as compared to risk to humans. Initial data collected in 2009 indicated that Hg concentrations in small prey fish in Tomales Bay were at the trophic-level-3 prey fish Hg threshold of $0.05 \mu\text{g/g}$ wet (Ridolfi et al. 2010) in the middle of the summer, and, thus, further data were required from the bird breeding season (in the spring or early summer).

Hypothesis 2: Methylmercury in small fish is lower in the breeding season than during other times of year. Thus, the times of year when MeHg concentrations and avian sensitivity to MeHg are highest do not coincide.

Biota to be collected: Small fish (5-15 cm); plentiful and easily caught species, e.g., shiner surfperch (*Cymatogaster aggregate*), staghorn sculpin (*Leptocottus armatus*), and threespine stickleback (*Gasterosteus aculeatus*).

Portion of long-term monitoring program to initiate in this transmittal:

Collect data that can be used to quantify breeding season risk to piscivorous wildlife (data gap #3 in list above), and provide baseline for future trends in small fish MeHg concentrations during the breeding season.

3) What is the risk from MeHg in fish to humans?

Priority: This is the lowest-priority data gap, because the existing data set (OEHHA 2004) for preferred fish (halibut) and shellfish (clams) indicates little risk to humans.

Hypothesis 3: Methylmercury in migratory California halibut (*Paralichthys californicus*) will decline over time as per the conceptual model for Hg in Tomales Bay developed by the SFBRWQCB. Mercury load reduction is predicted by the conceptual model due to remediation of the Gambonini mercury mine.

Hypothesis 4: Methylmercury in resident species -- red rock crab (*Cancer productus*) or rays -- will decline over time.

Biota to be collected: California halibut and red rock crab of legal size that humans would consume were recommended for long term monitoring. In 2010, the baseline dataset only includes halibut due to budget restrictions.

Portion of long-term monitoring program to initiate in this transmittal:

Sample halibut to track trends in potential human MeHg exposure from fish (data gap #1 in list above) and to supplement the 2009 SWAMP dataset.

2. Methods

2.1. Invertebrates

Equipment: Minnow traps, GPS, sampling map, ruler, stakes, flags, cat food (bait), zippered bags, dry ice.

Access: Sites were accessed by foot.

Sampling design: Sites for trap placement were chosen using the Generalized Random Tessellation Stratified (GRTS) sampling design (Stevens and Olsen 2004). This method was used to provide a random and thorough coverage of the marsh, since this is the first time that the Walker Creek marsh has been sampled systematically for MeHg in shorecrabs. Both target sites and oversample sites were selected using GRTS. If a target site was not within 5 meters of water (along a channel, in a pond, etc.), an oversample site was chosen instead. Minnow traps were set at the closest channel bank or marsh edge location to the selected sites.

Field collection: We collected the shorecrab *Hemigrapsus oregonensis* using minnow traps baited with cat food and set for approximately 48 hours. Traps were set at 25 locations around the Walker Creek marsh (Figure 1) along the creek channel, on the marsh edge, along interior creek channels, or in ponds. One trap was set per site..

Storage: Crabs recovered from each trap were immediately put in zippered freezer bags on dry ice. Each bag was filled with enough site water to generously cover the sample to prevent drying and breakage when stored in a freezer (-4° C) and during transit to the analytical laboratory.

Processing: All crabs were measured for total carapace width using a ruler. Thirty-three samples of up to five crabs each were composited by carapace width for analysis. The smallest crab had a carapace at least 0.75 times the width of the largest carapace within a composite.

Laboratory Analysis: Each composited crab sample was dissected to separate body tissue from the carapace (the priority was leg muscle, but when minimum mass was not reached, other soft tissue was used). The resulting composited sample was homogenized and analyzed by Brooks Rand Laboratory (Seattle, WA) for MeHg (EPA 1631; reported in µg/g, wet) and percent solids.

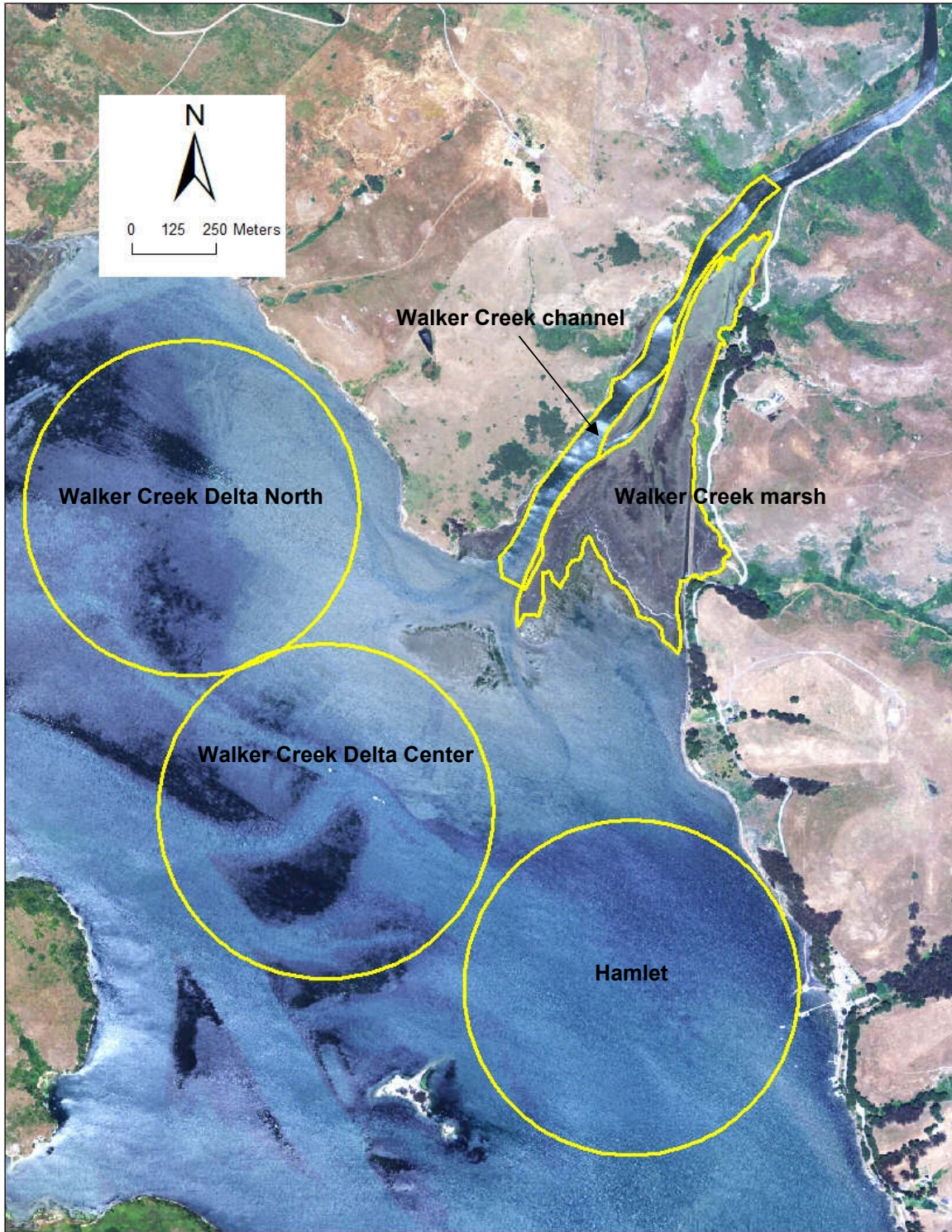


Figure 1. Locations of biota collection. Shorecrabs were collected from Walker Creek marsh, while small fish were collected from four named sites above.

2.2. *Small Prey Fish*

Equipment: Zippered bags, GPS, sampling map, boat, scale, ruler, small dip net, dry ice.

Access: Four sites (all except for the Walker Creek marsh) were accessed by boat launched from Nick's Cove. Some fish were collected from traps set throughout the Walker Creek marsh, which was accessed by foot.

Sampling design: We divided the area around the Walker Creek Delta into three, 1 km diameter sampling sites to ensure thorough coverage of the area, based on an assumption of 1 km diameter home range size for small fish. We added the Walker Creek channel site to attempt to re-sample topsmelt from the area where they were collected in November 2009 with high MeHg concentrations (Ridolfi et al. 2010). Last, we recovered several fish in the traps set for crabs, and kept them for analysis to get a sense of relative MeHg bioaccumulation between open water and the marsh. Since fish were plentiful at each of these four sites, we hypothesized that piscivorous wildlife would consume them from any one of the four sites, and potentially be at risk.

Field collection: Small fish between 5 and 15 cm in length were captured using an otter trawl at four locations around the Walker Creek Delta and by minnow traps set throughout the Walker Creek marsh (Figure 1). We kept the most abundant species, including staghorn sculpin, threespine stickleback, and longjaw mudsucker (*Gillichthys mirabilis*).

Processing: All fish were measured for total length using a ruler. Composites of threespine stickleback and staghorn sculpin with up to six fish each were grouped by species and length for analysis. The smallest fish was at least 0.75 times the length of the largest fish within a composite. Longjaw mudsucker were analyzed as individuals, since there were fewer of them recovered in traps.

Preservation: Immediately following collection, fish were placed in a zippered freezer bag on dry ice. Each bag was filled with enough site water to generously cover the sample to prevent drying and breakage when stored in a freezer (-4° C) and during transit to the analytical laboratory.

Laboratory Analysis Parameters: Each composited fish sample was homogenized (whole-body), and analyzed at Brooks Rand Laboratory (Seattle, WA) for total mercury (EPA 1630; reported in µg/g, wet) and percent solids.

2.3. *Sport fish*

Equipment: Zippered bags, boat, scale, ruler, fishing pole, dry ice, plastic cutting board, clean knife

Access: All sites were accessed by boat launched from Lawson's Landing.

Sampling design: The sampling design for halibut was opportunistic. Since halibut move around Tomales Bay and out to the Pacific Ocean, it was not important to sample them at a particular site within the Bay. The number of samples was limited by time available to spend fishing.

Field collection: Halibut were caught by hook and line wherever they were available for capture within Tomales Bay (most from near Hog Island and closer to the mouth of the Bay). All halibut collected were legal length (> 22 in).

Processing: Each fish was measured for total length. Fish were rinsed with site water. Dissection of samples (from skinless filets) was performed following U.S. EPA (2000). 20 g of fillet was dissected from each fish for analysis, and each fish was analyzed as an individual.

Preservation: Each sample was placed in a zippered freezer bag on dry ice immediately following dissection. Frozen samples were shipped overnight to the analytical laboratory.

Laboratory Analysis Parameters: Each composite fish sample was analyzed at Brooks Rand Laboratory (Seattle, WA) for total mercury (EPA 1630; reported in $\mu\text{g/g}$, wet) and percent solids.

3. Results

3.1. *Invertebrates*

Mean shorecrab MeHg concentrations varied by nearly an order of magnitude across the sampling sites. No obvious spatial pattern was apparent (Figure 2). Overall, mean MeHg in shorecrabs ($0.06 \mu\text{g/g}$ wet, Figure 3) exceeded the threshold concentration for trophic-level-2 prey ($0.01 \mu\text{g/g}$ wet, Ridolfi et al. 2010). Statistical tests are required to understand if there was a relationship between carapace width and MeHg, although it appears to be likely (Figure 4).

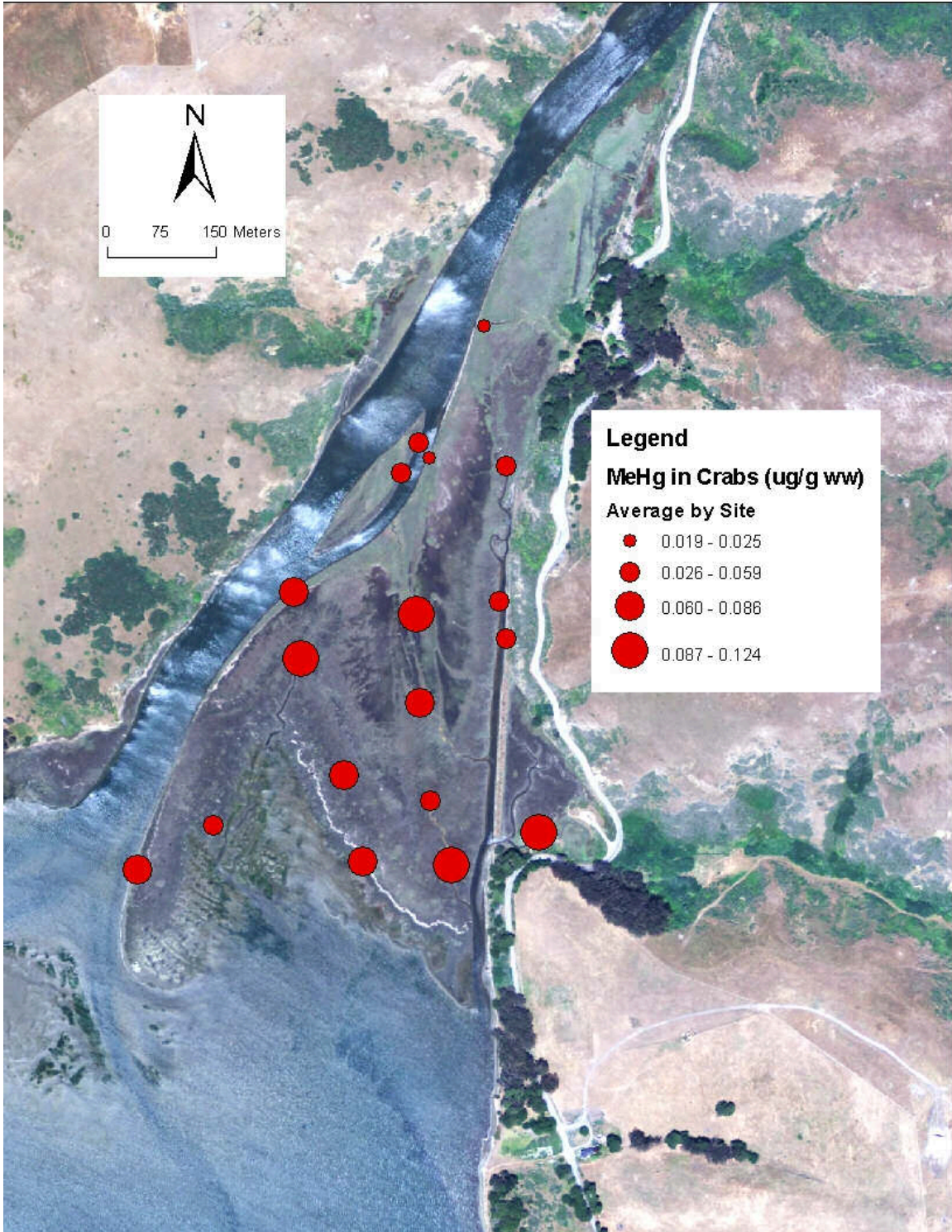


Figure 2. MeHg concentrations in shorecrabs. Some sites had multiple composites of crabs, and in that case, the concentrations were averaged for the site.

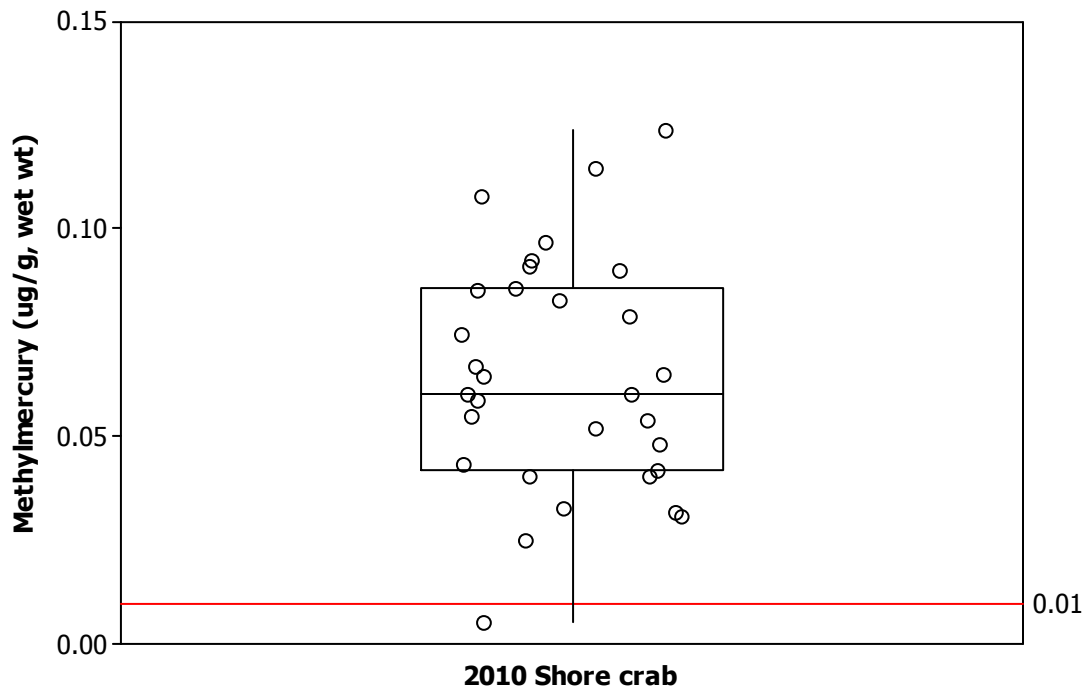


Figure 3. Methylmercury in leg muscle and other soft tissue from shorecrabs from Walker Creek delta, June 2010 ($n = 31$). Red line represents the threshold mercury concentration for wildlife that consume trophic level 2 prey ($0.01 \mu\text{g/g}$ wet). The box represents the 25th – 75th percentiles (interquartile range, IQR), the midline is median, and whiskers extend to 1.5 times IQR.

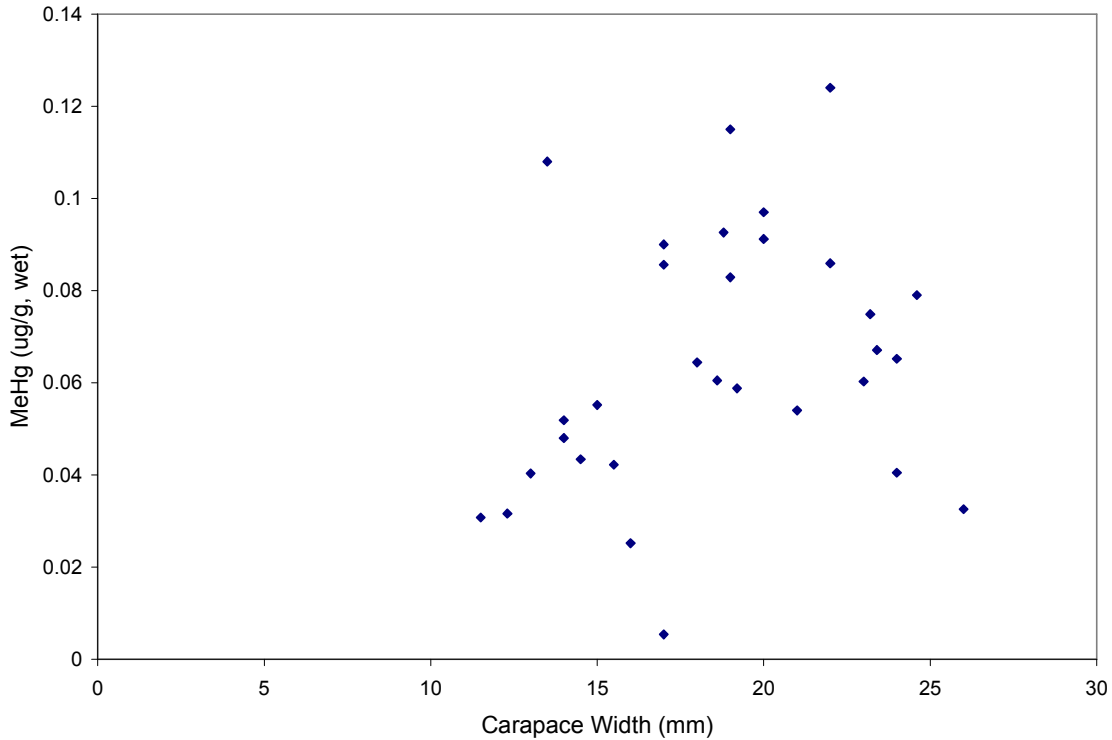


Figure 4. Shorecrab MeHg concentrations and mean carapace width, $n = 31$ composites.

3.2. Prey Fish

Generally an analysis of these data would control for fish species and length, because both are known to relate to Hg concentration. In this data transmittal, we report the data in a more aggregated manner, because resource limitations preclude more in-depth analysis. One difficulty in describing these data is that species and location of capture (habitat) are confounded. Therefore, if one species or location has higher Hg bioaccumulation than another, we cannot say if that difference was due to the species or to the location.

Mercury concentration appeared to vary by species (Figure 5) and/or location (Figure 6). Longjaw mudsucker had the highest mean Hg concentration ($0.18 \mu\text{g/g}$ wet) of the prey fish species. One possible explanation for this result is the larger size of longjaw mudsuckers collected, as compared to other species. Larger individual fish often have higher Hg concentration. Another possible explanation is habitat; mudsucker live in small channels in tidal marsh, a wetland habitat that has been hypothesized to have high MeHg production. Mercury in staghorn sculpin was second highest after mudsucker, with a mean concentration of $0.09 \mu\text{g/g}$ wet, followed by threespine stickleback ($0.07 \mu\text{g/g}$ wet, Table 1).

Statistical analysis is required to analyze differences in Hg concentrations among the years of this study (Figure 4). Staghorn sculpin collected in 2009 had a mean Hg concentration of $0.06 \mu\text{g/g}$ wet, while in 2010 the mean was $0.09 \mu\text{g/g}$ wet. Threespine stickleback had a mean in 2009 of $0.05 \mu\text{g/g}$ wet, while in 2010 it was $0.07 \mu\text{g/g}$ wet. Staghorn sculpin collected in 2009 were slightly larger (7–12.6 cm total length), and

included more adults (> 10 cm) than those from 2010, which probably contained more young-of-year fish. However, 2009 sculpin appeared to have lower Hg, despite their larger size. Possible explanations for any difference between Hg bioaccumulation in 2009 and 2010 include the time of year (June 2009 vs. May 2010) or the fact that winter 2009-2010 was particularly wet with large storms that could have eroded Hg-laden sediment into the Delta area. Threespine stickleback had approximately the same size range in 2009 and 2010.

Table 1. Fish results by species.

Species	Size Range (mm)	N 5-15 cm	Mean THg ($\mu\text{g/g}$)	Std. Deviation	Coefficient of Variation
Staghorn sculpin	54-103	22	0.09	0.03	0.33
Threespine stickleback	50-77	18	0.07	0.11	1.62
Longjaw mudsucker	57-138	10	0.18	0.16	0.89

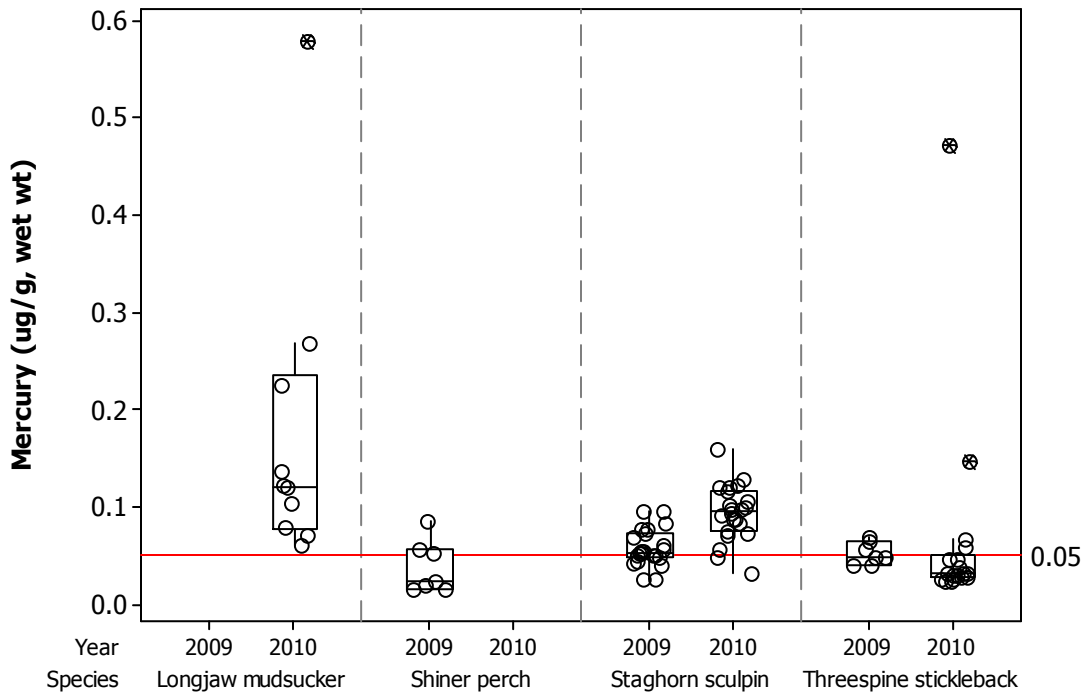


Figure 5. Fish (5-15 cm in length) mercury concentrations by species. Boxplots of four abundant prey fish species; $n = 86$ samples. Red line represents the threshold mercury concentration for wildlife that consume trophic level 3 prey ($0.05 \mu\text{g/g}$ wet). The box represents the 25th – 75th percentiles

(interquartile range, IQR), the midline is the median, and circles with asterisks indicate data beyond 1.5 times IQR.

Spatial relationships are important to examine, to determine where in the Walker Creek Delta wildlife may be most at risk, and to inform future sampling. These relationships are confounded by differences in fish size and species, as previously discussed. Small fish caught in the marsh appeared to have the most variable Hg concentrations, followed by fish caught in the three Delta sites, and, finally, fish from the Walker Creek channel (Figure 5). The greater variability in Hg concentrations in fish from the marsh may be due to a larger size range of longjaw mudsucker being sampled, relative to the other species. It is important to note that the species captured varied by site, and all species of small fish (5 - 15cm in length) were aggregated for Figure 6. Species caught in the marsh were longjaw mudsucker (n = 10) and threespine stickleback (n = 3, Figure 6). Fish caught in the Delta were threespine stickleback (n = 15) and staghorn sculpin (n = 10), and in the channel only staghorn sculpin were caught (n = 12). The apparent spatial differences in fish Hg concentrations may be driven by differences in species. Thus, statistical analysis is needed to explore these patterns.

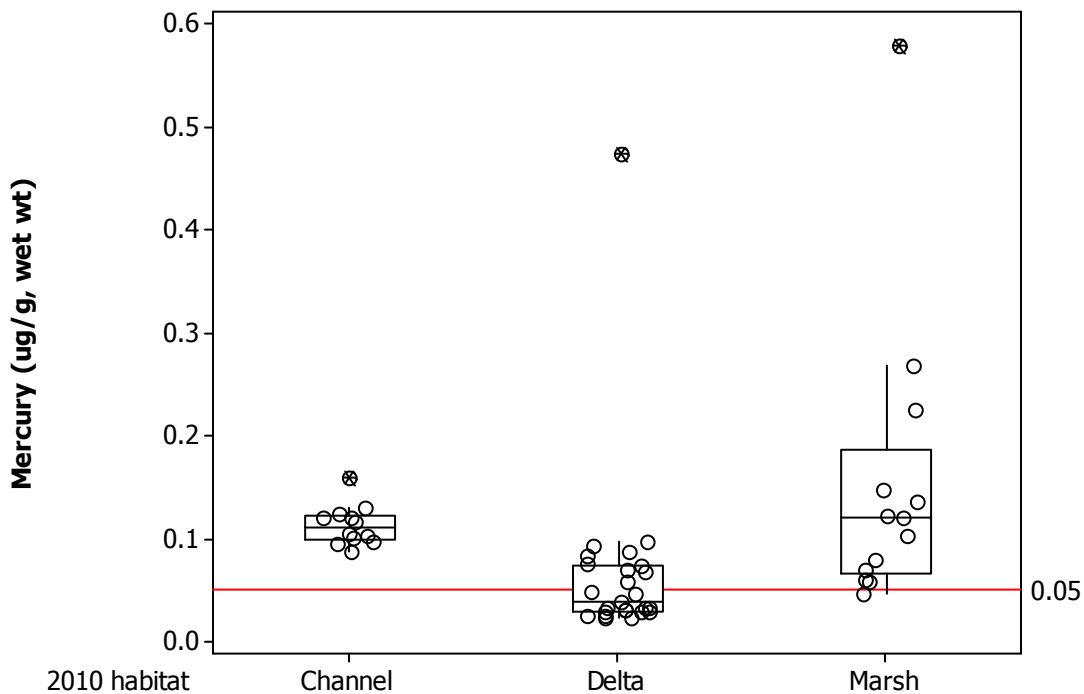


Figure 6. Boxplot of 2010 prey fish (5 – 15 cm staghorn sculpin, threespine stickleback, longjaw mudsucker) by sampling area (channel, delta, marsh); $n = 50$ samples. Red line represents the threshold mercury concentration for wildlife that consume trophic level 3 prey (0.05 $\mu\text{g/g}$ wet). The box represents the 25th – 75th percentiles (interquartile range, IQR), the midline is the median, and circles with asterisks indicate data beyond 1.5 times IQR.



Figure 7. Locations in the Walker Creek marsh where fish were caught by minnow trap (7 of 25 traps). Species captured were threespine stickleback and longjaw mudsucker.

The relationship between fish length and Hg concentration may have varied among the species of small fish (Figure 8). However, the size ranges also varied among the species, with mudsucker being sampled over a much larger size range. Therefore, the ability to detect a length-mercury relationship with this data set is greater in mudsucker. Statistical analysis is warranted to further explore this relationship, including controlling for size in the analyses of spatial patterns, species differences, temporal differences, etc.

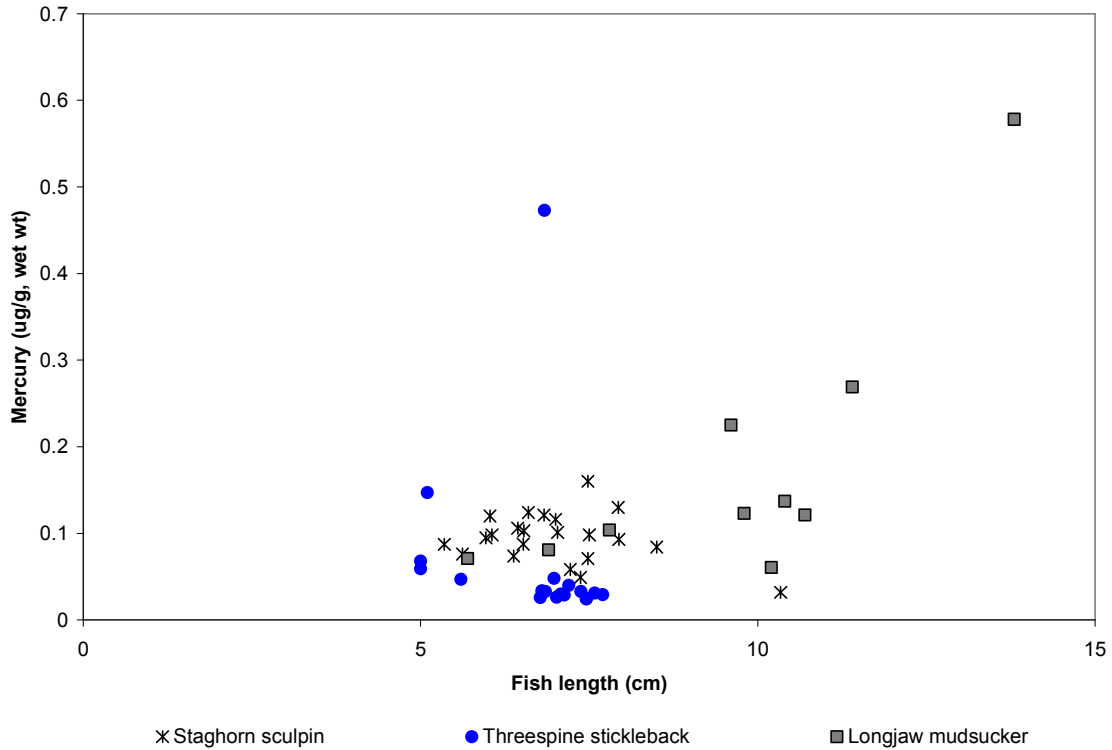


Figure 8. Relationship between 2010 small fish mercury concentrations (ug/g) and fish length (composites), $n = 50$ samples.

3.3. Sport Fish

Halibut were sampled to better assess risk to humans. Four fish were collected and analyzed as individuals, with a mean Hg concentration of 0.2 $\mu\text{g/g}$ wet (Figure 10), which is equal to the target for Hg concentrations in sport fish tissue established for the San Francisco Bay Mercury TMDL to protect human health (Austin and Looker 2006), and less than the U.S. EPA criterion of 0.3 $\mu\text{g/g}$ wet (USEPA 2001) for consumption of sport fish.

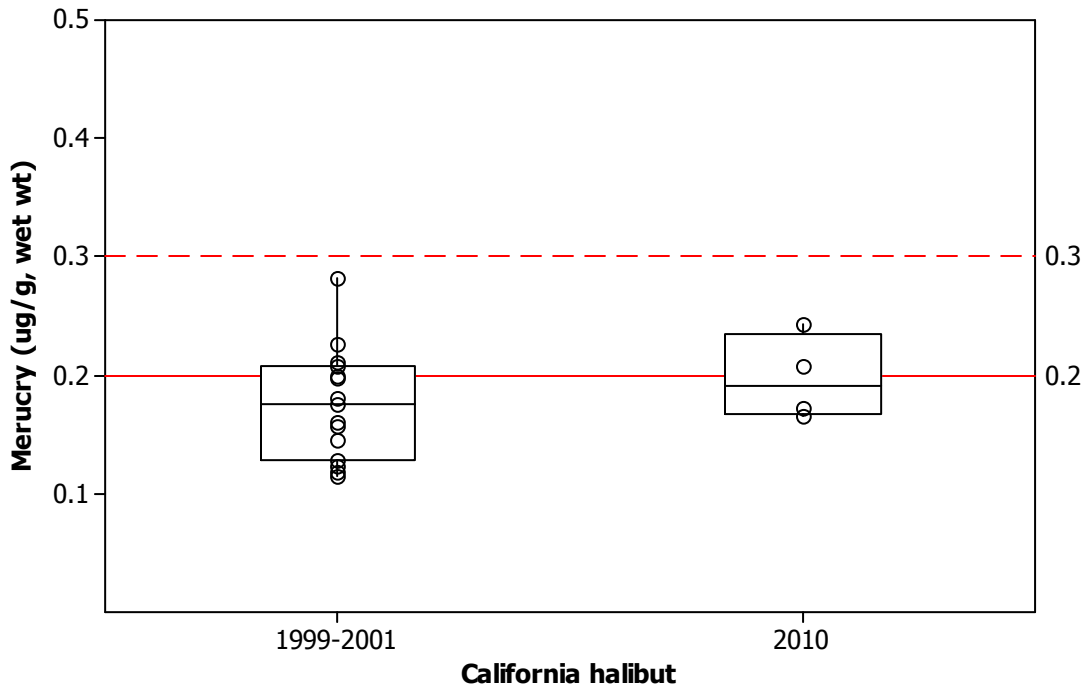


Figure 9. Mercury concentrations in California halibut from Tomales Bay, fish from 2010 ($n = 4$) compared to fish from 1991-2001 ($n = 15$). The box represents the 25th – 75th percentiles (interquartile range, IQR), the midline is the median, and solid circles indicate data beyond 1.5 times IQR. The solid line (0.2 $\mu\text{g/g}$ wet) represents the target established for the San Francisco Bay mercury TMDL. The dotted line (0.3 $\mu\text{g/g}$ wet) represents the U.S. EPA MeHg criterion.

4. Conclusions and Recommendations

This data transmittal summarizes Hg concentrations for three types of biota collected in Tomales Bay from May-June 2010. These data suggest that some wildlife may be at risk from consumption of prey from Tomales Bay, based on MeHg concentrations from Walker Creek Delta biota. Although this dataset indicates that halibut meet the San Francisco Bay TMDL target, the Office of Environmental Health Hazard Assessment recommends that women under 45 years and children limit their consumption of halibut to one meal per week (OEHHA 2009). A long-term dataset and statistical analysis are needed to further explore the risk and future trends of MeHg in biota in Tomales Bay.

For future sampling efforts, we offer three recommendations:

- If resources for sampling are limited, focus sample collection on the Walker Creek Delta, where total Hg in sediment is higher (Ridolfi et al. 2010) and some biota have elevated tissue Hg. Within the Delta, it appears as though the highest risk of MeHg to vertebrate wildlife (from comparing both invertebrate and small fish prey

concentrations to threshold Hg concentrations) is in the marsh. However, further analysis is needed to test this qualitative observation.

- We also recommend ongoing monitoring of shorecrab and small fish, as they are excellent biosentinels for wetland and aquatic wildlife exposure to Hg. A power analysis should be conducted to determine the intensity of sampling of these biota that would be needed to track future trends.
- When setting crab traps, it would be most efficient to have three people: two people with GPS units to find sites, and one person to set the traps.

5. References

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