Monitoring Bio-available Mercury in San Francisco Estuary Openwater Habitats: Using the Food Web to Assess Interannual and Spatial Trends

Estimated Cost: \$64,000 (composited samples) - \$172,000 (individual samples)

Oversight Group: TRC, possibly a TRC subcommittee

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Target Date
Sampling Report	September 2006
Data and QA Report	February 2007
Journal Publication Submitted	June 2007

OVERVIEW

Mercury contamination is one of the highest-priority water quality issues for the Estuary (Johnson and Looker 2004), and the mercury strategy adopted by CALFED stated that "the primary problem with mercury in aquatic ecosystems can be defined as *biotic exposure to methylmercury*" (p. iv Exec. Summ.; Wiener et al. 2003). Through the mercury TMDL, actions are being initiated to reduce mercury loads to the Estuary. On the other hand, large-scale wetland restoration around the margins of the open-water habitat may exacerbate the problem by causing greater mercury accumulation in the food web. Mercury studies from other parts of the country suggest that small fish are the best indicator of inter-annual and spatial variation in net methylmercury production in aquatic ecosystems. Small fish are useful, because they:

- accumulate the form of mercury (methylmercury) that causes a health risk to biota,
- indicate the net amount of methylmercury production in their home-range area,
- integrate exposure over a defined period of time (e.g., one year), making them a cost-effective and informative monitoring tool,
- indicate spatial patterns over relatively small scales (including near-shore areas) compared to larger sport fish, and
- indicate the health risks for piscivorous wildlife and other predators higher in their food chain, which may include sport fish and eventually humans.

Small fish monitoring can provide information on temporal and spatial trends and wildlife exposure that is crucial to adaptive implementation of the mercury TMDL and that is otherwise unavailable.

BACKGROUND

Mercury contamination is one of the highest-priority water quality issues for the Estuary (Johnson and Looker 2004). Methylmercury is toxic to biota and accumulates to high concentrations in organisms high in the food web, including fish, wildlife, and humans. The greatest health risks are faced by humans and wildlife that consume fish. Significant management actions are underway that are likely to cause changes in mercury concentrations in fish in the Estuary. The mercury TMDL is a major effort designed to reduce mercury accumulation in Estuary fish. On the other hand, major tidal marsh restoration projects are underway that may increase mercury in the food web. Wetlands are sites of methylmercury production, and landscapes with higher percentages of wetlands are associated with higher methylmercury export (Davis et al. 2003). Plans are presently in place to restore 49,000 acres of wetlands in the North and South Bay (SFEI 2004). Adaptive implementation of the mercury TMDL and adaptive management of habitat restoration will depend heavily on appropriate monitoring of impacts on water quality (Mumley and Looker 2004).

Small fish are the best tool available for monitoring inter-annual changes in methylmercury in aquatic ecosystems. The California Bay-Delta Authority, recognizing the potential impacts of habitat restoration on mercury exposure in the Bay-Delta watershed, assembled a team of international mercury experts to develop a "Mercury Strategy for the Bay-Delta Ecosystem: A Unifying Framework for Science, Adaptive Management, and Ecological Restoration" (Wiener et al. 2003). A centerpiece of this Strategy is monitoring mercury in small fish.

Small fish are an essential monitoring tool for mercury contamination for the following reasons.

- 1. Small fish accumulate the form of mercury (methylmercury) that causes the most toxicological effects in biota. Close to 100% of the mercury present in small fish is methylmercury. Methylmercury is the form that biomagnifies in the food web and poses toxicological risks at the top of the food web.
- 2. Small fish mercury concentrations integrate the net amount of methylmercury in the lower levels of their food web in their home-range area. Methylmercury concentrations in water and sediment are highly variable over small temporal and spatial scales. Furthermore, methylmercury has a very complex biogeochemical cycle with many factors affecting methylation and de-methylation rates. Methylmercury concentrations in water and sediment often do not correlate with concentrations in the food web. Small fish are indicators of methylmercury in the food web, and methylmercury in the food web is what truly causes impairment of water quality.
- 3. Small fish integrate exposure over a defined period of time (e.g., one year), making them a cost-effective and informative monitoring tool. Fish accumulate mercury over their entire lifespan. One-year-old fish are an ideal indicator of inter-annual variation because they accumulate their mercury during a well-defined interval. Older fish are

not as valuable for inter-annual trend monitoring because they accumulate over multiple seasons, resulting in a less distinct signal. Fish are integrative indicators because their body burden is a function of all of the temporal and variation in methylmercury that occurs in a habitat. Monitoring with an integrative indicator is much more cost-effective than the intensive water and sediment sampling that would be required to obtain a similar representative index of overall contamination.

- 4. Small fish can indicate spatial patterns over relatively small scales (including near-shore areas). Small fish with relatively small home ranges indicate food-web mercury over small spatial scales. Larger sport fish generally move throughout the Estuary and, thus, are not useful for regional spatial comparisons. Furthermore, small fish are present in near shore areas and tidal marshes where methylmercury production is hypothesized to be greatest. Transplanted bivalve sampling in the RMP serves this purpose for organic contaminants, but transplanted bivalves are not an effective tool for mercury monitoring.
- 5. Small fish are indicators of health risks faced by piscivorous wildlife. The sport fish sampled by the RMP are generally too large to be consumed by seals and birds. Small fish, such as gobies, anchovies, and smelt, comprise the bulk of piscivore diets in the Estuary. Published thresholds exist for contaminant concentrations in prey that pose health risks to piscivorous wildlife.

For these reasons, small fish are an essential indicator to include in a program of adaptive management for mercury contamination in the Estuary. They are an excellent tool for evaluating long-term trends, spatial patterns, and wildlife health risks. They provide a valuable complement to other methylmercury monitoring tools being employed in the RMP: sport fish, avian eggs, water chemistry, and sediment chemistry. While this proposal focuses on mercury, the same arguments can be made for the value of small fish in monitoring other bioaccumulative contaminants of concern, such as PCBs and PBDEs. Samples taken for the proposed mercury study could be archived for future analysis of other contaminants. Small fish sampling is crucial to tracking whether mercury concentrations are increasing or decreasing in response to management actions and to determining the local and regional impacts of load reductions and restoration projects. Small fish monitoring should begin soon, because the TMDL process and wetland restoration projects are already well underway.

APPLICABLE RMP OBJECTIVES AND MANAGEMENT QUESTIONS Not yet completedxx

APPROACH

Small fish from two habitat types, demersal (benthic) and pelagic, will be sampled. The food webs in these habitats may have different mercury uptake due to variation in environmental conditions where the primary producers (benthic and pelagic marine algae) are located. Also, the benthic species chosen are less mobile and have

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smaller home ranges than the pelagic species. Therefore, this sampling design will provide both fine-scale and sub-embayment-level information on spatial variation. Two species will be sampled in each habitat type in order to provide coverage across the entire salinity gradient from Suisun Bay to South San Francisco Bay. The suggested species are as follows.

- Benthic habitat bay goby (saline) and Shimofuri goby (brackish). These species overlap in range in the fresher parts of San Pablo Bay and the more saline parts of Suisun Bay. CDFG data indicate that both are sufficiently abundant to be feasibly collected. There is a strong potential for collaborating with the CDFG San Francisco Bay Study to reduce duplication of effort in collecting these species.
- 2) Pelagic habitat Topsmelt (saline) and inland silversides (brackish). These species overlap in range and are abundant in the Estuary. A collection program separate from the CDFG sampling may be necessary to capture sufficient numbers. These species are better captured in shallow water using beach seines than in the deeper trawls of the CDFG study.

Small fish would be collected in late summer or fall, allowing capture of as much of the summer increase in growth, consumption, and consequent mercury uptake as possible. Fish would be captured in a large number of sites (30) to evaluate the spatial variation that exists throughout the Bay. Sampling locations will ideally be chosen to coincide with RMP methylmercury sampling sites to develop quantitative sediment-biota accumulation factors for subsequent food-web modeling. This design would provide a random sample stratified across the Estuary to provide comprehensive spatial coverage with data useable to make statistical inferences about non-sampled areas. Alternatively, if interest is greater in choosing sites based on specific restoration projects or other sediment or biota sampling programs (e.g., CBDA restoration sites or USGS sediment sampling), then sampling could be non-random.

The range in cost per year depends on whether the fish are analyzed as composites or as individuals: \$64,000 (composite samples) - \$172,000 (individual samples). Ideally, the fish would be analyzed as individuals. The size:mercury relationship would be characterized for each location, and analysis of covariance would be used to make statistically rigorous comparisons among locations. This approach would be especially valuable in a pilot study, with the possibility of scaling back after the size:mercury relationships are characterized. If available funds are not sufficient for this approach, another option would be controlling for fish size by compositing samples of fish from narrow size ranges. This approach is less powerful but far better than no data of any kind.

This project would be coordinated with other fish sampling projects in the Bay to avoid duplication of effort and reduce costs. In particular, the estimated field costs of around \$30,000 per year (included in the previous cost estimates) could be reduced through coordination and collaboration. Important efforts to collaborate with include the DFG Bay Study previously mentioned, the CALFED-funded USGS study of mercury in birds and their prey, the Port of Oakland fish studies, and any future mercury monitoring in biota by the South Bay Salt Pond Restoration Project.

To minimize the budget, this proposal focuses only on mercury. Small fish would also be a valuable indicator for other food-web contaminants, such as PCBs, PBDEs, and legacy pesticides. Tissue from this pilot study could be archived to enable future analysis of other contaminants.

The ultimate product will be a manuscript submitted for publication in a peerreviewed scientific journal. The manuscript will describe spatial patterns in food-web mercury in open-water habitats of the Estuary for 2005. The relationship between fish mercury concentrations and other factors (e.g., salinity, distance to Hg inputs, sediment concentrations) will be explored. This work will provide standard protocols and initial data that will form a foundation upon which a future small-fish monitoring program can be built.

LITERATURE CITED

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