Monitoring and Assessment of Environmental Mercury and Mercury Bioaccumulation in South Baylands

"The South Baylands Mercury Project"

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Executive Summary

Problem Statement

The potential exists to inadvertently increase the risk of mercury (Hg) accumulating in South Bay fish and wildlife through hydrological modification of salt ponds as part of the South Bay Salt Pond Restoration Project (SBSPRP). The concern is that management actions will favor conversion of Hg into toxic methylmercury (MeHg) and its uptake into local food webs.

Concerns about possible mercury poisoning exist throughout San Francisco Bay (SFEI 2004, CalFed Bay-Delta Program 2005). Concentrations of Hg in sediment and water tend to be greater in South Bay due to past local mercury mining (Beutel and Abu-Saba 2004). The Alviso Pond and Slough Complex are especially worrisome because they contain more Hg than most other areas of South Bay (SFEI 2005) and because they are slated for early management actions by the SBSPRP.

The mercury problem is complex. The production of MeHg depends on many environmental factors besides the total amount of Hg. The uptake of MeHg into food webs and its bioaccumulation vary within and among species and habitats. Threshold concentrations of MeHg toxicity are not well known for most wildlife species, and habitat designs or management practices that would minimize MeHg bioaccumulation are also unknown.

Although data are being collected about mercury concentrations at various locations within the South Bay (David et al. 2002, Thomas et al. 2002, Conaway et al. 2003, Topping et al. 2004, Beutel et al. 2004, SFEI 2005), very little is known about the associated processes governing Hg physical transport, Hg methylation, and bioacccumulation. Key questions include (a) how much legacy Hg is contained in sediments of different habitats; (b) how readily the available Hg can or will be converted to MeHg; c) how effectively any MeHg will be incorporated into local food webs; and d) how answers to these questions might be influenced by different management actions.

Solution Pathway

Bayland managers need to know how their actions affect the risk of mercury toxicity in wildlife. The risk can be assessed most directly by monitoring Hg in 'biosentinel' wildlife species that represent the baylands. Coupling such a monitoring effort to studies of MeHg production and uptake is essential if we are to understand how the risk of Hg bioaccumulation can be reduced, and thus develop effective management options.

The San Francisco Estuary Institute (SFEI), US Geological Survey (USGS), and Santa Clara Valley Water District (SCVWD) seek \$737,575 for a scientific effort to develop indicators of Hg problems, employ the indicators to survey the magnitude and extent of the problem for South Baylands (beginning with Pond A8 and Alviso Slough), and, where necessary, implement research to understand the problem. The proposed work would be coordinated through SFEI with other mercury studies in the region (e.g., other SBSPRP mercury monitoring efforts, multiple CALFED sponsored Hg studies in San Francisco Bay). The work would be conducted in two phases over two years. The approach is scalable, however, and could be used to monitor any management action at any spatial scale from one local habitat patch to the South Baylands as a whole.

Phase 1 would:

- ✓ Develop sentinel species indicators of Hg exposure;
- ✓ Map the legacy Hg in Alviso Slough that might be mobilized by breaching Pond A8; and
- ✓ Assess the mercury problem for the Pond A8, including assessing existing conditions and the relative risk of restoration to tidal action.
- Establish a baseline for tracking the effects of management actions on the Hg problem into the future.

Phase 2 would:

- ✓ Expand the survey to encompass more of the South Baylands;
- ✓ Continue monitoring the effects of Pond A8 management;
- ✓ Initiate research to understand the Hg problem in selected areas; and
- ✓ Help translate the scientific understanding of the Hg problem into habitat designs and management options that minimize the problem.

Introduction

Mercury (Hg) can become an environmental problem when methylmercury (MeHg), a highly toxic species of mercury, reaches high concentrations in wildlife. For this situation to occur, sufficient MeHg must both exist in the sediment or water and be assimilated by plants or algae and be bio-magnified through the food web to concentrations that endanger wildlife or people.

The total amount of Hg that enters the environment is only one aspect of the Hg problem. The observation that total Hg concentration exhibits little or no correlation with MeHg concentrations is not uncommon in environmental studies. This was the case, for example, in a large set of sediment samples taken within South Bay salt ponds (Beutel and Abu-Saba 2004). Recent evidence suggests that only a small percentage (e.g., 0.1 to 5%) of total Hg is actually available for microbial methylation by sulfate-reducing anaerobic bacteria, in the presence of organic substrates (Marvin-DiPasquale pers. comm). The production of MeHg depends on many microbiological, physical, and geochemical environmental factors operating at different spatial scales (e.g. from cells and organelles to habitats and watersheds) and temporal scales (from seconds to seasons). Furthermore, not all of the MeHg produced in sediments of wetlands or aquatic habitats enters into food webs, due to geochemical and physical limitations of MeHg transfer across the sediment water interface (Gagnon et al. 1996), aqueous-solid phase partitioning in the water column (Babiarz et al. 1998), microbial MeHg degradation (Marvin-DiPasquale et al. 2000), MeHg photodegradation in the water column (Sellers et al. 1996), and possibly other mechanisms. Similarly, the uptake, bioaccumulation, and transfer of MeHg to wildlife also depend on many ecological variables, such as food web structure, composition, length, and base (e.g. benthic vs pelagic vs epiphytic - Wiener et al. 2003). Only a portion of the MeHg produced at any time reaches wildlife or people. A challenging aspect of the Hg problem is the difficulty in understanding the chemical and ecological processes well enough to prescribe preventive or remedial actions. The goal for scientists and managers is to identify the kev factors driving the risk of Hg bioaccumulation, and based on this knowledge to determine if specific management actions can be employed to prevent or minimize this risk.

Mercury that has moved from the land or atmosphere to aquatic systems can be methylated in the water column or in the oxic-anoxic boundary layer of fine benthic sediments. Managing the problem for aquatic systems has largely focused on warning people about the dangers of consuming contaminated fish (e.g., <u>www.oehha.org/fish/nor_cal/int-ha.html</u>), aerating benthic sediments in lakes and reservoirs to prevent MeHg from entering the water column, and identifying terrestrial sources of Hg that can be quarantined or removed.

Most of the Hg sources in the South Bay are well documented but not well quantified. Mercury ore (native mercury, cinnabar, and metacinnabar) was mined in the Guadalupe River Watershed almost continuously from 1845 to 1975. Runoff from the mining operation has carried fine sediment that bears Hg into reservoirs, stream beds, floodplains, the Bay, and the baylands, including the Alviso Pond Complex and Alviso Slough (SFEI 2005). Continuing sources and pathways of Hg, such as atmospheric deposition, urban run-off, and effluent from wastewater treatment plants also contribute to the baylands Hg load. The relative importance of the legacy and continuing Hg sources is unknown, but some of the Hg from all of these sources tends to accumulate in the baylands (Beutel and Abu-Saba 2004).

The Hg load of the South Baylands raises concerns about how they should be managed. Efforts to maintain them as diked wetlands or shallow ponds, or efforts to restore them to full or partial tidal action may increase or decrease their tendency to create a Hg problem, depending on the nature of the baylands and how they are managed. Changes in the risk of Hg ecotoxicity are expected to accompany any major changes in the salinity or hydroperiod (i.e., the frequency and duration of inundation and exposure of the sediments) for the ponds or tidal habitats. In such cases, the specific and relative risk of Hg ecotoxicity will change over time, and may increase or decrease for different wildlife species as their habitats evolve and equilibrate in response to the various management practices.

This proposal addresses the need for a practical program to define, assess, and monitor the mercury problem in South Baylands. We make no assumption that a problem exists at this time, although the risk of a problem warrants the proposed work (Schwarzbach and Adelsbach 2003).

Overall Approach

The regional strategy for solving the mercury problem calls for an integrated program of monitoring plus focused research driven by questions and hypotheses that explicitly reflect the information needs of resource managers (Wiener et al. 2002). The proposed work would start by helping the Project Management Team (PMT) of the South Bay Salt Pond Restoration Project (SBSPRP) define the mercury problem for the South Baylands in practical terms. The work would then proceed to develop cost-effective indicators of the problem, survey its magnitude and extent, test for correlations between the problem and manageable environmental factors, initiate research to understand the primary underlying factors controlling the observed correlations, and translate these findings into recommended actions that would either prevent or correct the problem.

It is anticipated that the approach would be implemented in two phases. Phase 1 would focus on Alviso Slough and Pond A8. This pond is selected for Phase 1 by local interests and members of the PMT. Discussion about breaching the Pond to return tidal action is underway, and adjoining sources of water and sediment for this pond contain legacy Hg. Both muted-tidal and fully tidal breaching scenarios are under discussion for Pond A8 at this time. Phase 2 would continue monitoring Pond A8 and its Slough Complex, and expand the scope of the approach to include other areas of the SBSPRP. The ABAG mercury management project would be provided the Phase 1 and Phase 2 research findings in a timely fashion to help translate them into habitat design and management options.

To meet objectives for data management and sharing, we will compile the survey results into the RMP database, SBSPRP web site, and the Bay Area Wetland Tracker at SFEI. Protocols will be written for sampling the sentinel species. These protocols will be finalized following review through the ST of the SBSPRP and additional outside review as needed during Phase 1. The finalized protocols will be publicly available through the Regional Wetlands Monitoring Program web site (http://www.wrmp.org/documents.html#protocols).

Phase 1 Plan (Year 1)

<u>Assessment Question 1:</u> Will restoration of Pond A8 unacceptably worsen the risk of mercury toxicity for wildlife and people of the South Bay?

A practical definition of the mercury problem for South Baylands has been drafted:

Mercury is a problem when and where methylmercury concentrations in the food web indicate that wildlife or people are being exposed above thresholds for deleterious effects. Elevation of concentrations above the ambient concentration is one indicator of the relative potential for exposure above the effects thresholds.

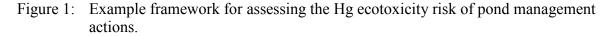
A sentinel population is the individuals of a biological species within a prescribed area, such as Pond A8 or Alviso Slough. The ambient MeHg concentration is defined as the average amount of MeHg in the same or comparable sentinel species across a reference area of the South Baylands, such as the Don Edwards San Francisco Bay National Wildlife Refuge. The ambient reference sites will be chosen within the South Bay. For example, the ambient reference marshes for Alviso Slough marshlands will be selected from South Bay and will cover the same salinity gradient, based on vegetative communities. The fringe marshes along Coyote Creek and/or Mowry Slough are candidate reference areas.

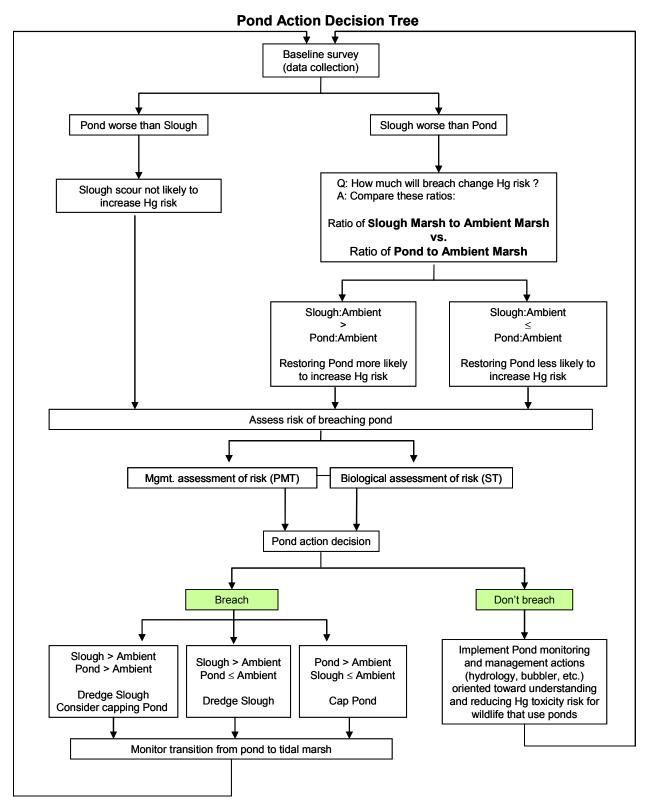
An ecological determination of significance would be ideal but is not possible at this time. While very general guidelines exist to protect wildlife from Hg ecotoxicity (Wolfe et al. 1998), the thresholds of Hg concentration that correspond to harm for most baylands wildlife species are not specifically known. A separate study of Hg biological effects would be required to establish the ecotoxicity thresholds, which is beyond the scope of this proposal.

This project presents an opportunity to conduct an adaptive management experiment that will improve our understanding of the impacts of baylands habitat restoration on mercury exposure to wildlife and humans, and the mechanisms underlying the response. The proposed work would yield multiple benefits, including:

- 1. supporting a decision framework that can be used to determine whether management actions to reduce mercury risks should be implemented during the course of restoration;
- 2. developing a predictive capacity for evaluating similar restoration actions (i.e., opening ponds with nearby deposits of legacy mercury contamination to tidal action); and
- 3. improving understanding of mercury cycling in the Bay and baylands and thereby enhancing our predictive capacity for restoration projects in a more general sense.

At this time, we suggest that the baylands managers use a decision framework supported by empirical field data to evaluate potential risks of alternative Pond A8 management scenarios (Fig. 1). The mercury problem is both political and scientific in definition. Therefore, based on the results of the first year of monitoring, the baylands managers will have to weigh-in on whether the monitoring results indicate a need for actions to reduce mercury exposure or that the project should proceed under an adaptive management approach. Actions that might be considered along the way to potentially reduce mercury exposure include dredging of sediment from Alviso Slough if very high concentrations of mercury are found there, or capping sediment in the Pond if high mercury concentrations are observed.





Task 1: Finalize the problem definition

The draft definition of the mercury problem and its assessment framework (see Fig. 1) will need to be reviewed by resource managers and other stakeholders concerned with the South Baylands. We propose to submit the draft definition and framework to the PMT and the Science Team (ST) of the SBSPRP for review. The definition, as refined by the PMT and ST, could then be provided through the PMT to the Stakeholder Groups of the SBSPRP.

Assessment Question No. 2: How is the problem assessed?

A variety of practical questions are embedded in the assessment of the problem. How do we know if the problem originates in the South Baylands, rather than somewhere else? Not all baylands are the same; can the types be ranked based on their contribution to the problem? What about saline, brackish, tidal, non-tidal, old or young baylands? Each type of bayland is actually a complex of different habitats or features, such as channels, vegetated plains, pannes, and so forth. Can these habitats be ranked according to their contribution to the problem?

We propose to develop and implement protocols for using sentinel species of MeHg accumulation in wetlands and shallow aquatic habitats of the South Baylands. The major habitats we will address are:

- ✓ Vegetated tidal marsh plain;
- ✓ Tidal marsh pannes;
- ✓ Benthic intertidal channel and benthic managed pond;
- ✓ Pelagic subtidal habitat in large tidal channels; and
- ✓ Pelagic habitat of managed ponds.

By definition, the problem is assessed by measuring MeHg concentrations in sentinel populations. To link their MeHg loads to each habitat, the sentinel populations should have the following characteristics (adopted from Darell Slotton, UC Davis):

- ✓ Locally resident within South Baylands;
- ✓ Small home range;
- ✓ Non-migratory;
- ✓ Important component of local food web;
- ✓ Accumulate enough MeHg to differentiate subtle variability;
- ✓ Relatively short-lived or sensitive to annual changes in MeHg accumulation;
- ✓ At least seasonally abundant;
- ✓ Easily sampled;
- ✓ Well-studied.

These criteria assure that any assessment of a problem relates to recent local conditions within the South Baylands. Based on these criteria, a variety of candidate sentinel species have been identified. When these are cross-referenced to the habitat types of most interest, a small set of candidate species emerge (Table 1).

| | Location of Habitat Type in the Geographic Areas to be Sampled | | | |
|---|---|---------|-----------------------------|--|
| Habitat Type | Ambient Marshes | Pond A8 | Alviso Slough Marshes | Candidate Sentinel Species |
| Vegetated marsh plain | X | | X | Alameda song sparrow (<i>Melospiza melodia pusillula</i>) |
| Marsh pannes and managed pond margins | X | X | X | Brine fly (Ephydra spp.) |
| Benthic zone of channels and managed ponds | X | X | X | Longjaw mudsucker (Gillichthys mirabilis) |
| Pelagic zone of channels and managed ponds | X | X | X | Topsmelt (Atherinopsis affinis) |

Task 2: Finalize the Choice of Sentinel Species

We propose to revise the draft list of sentinel species based on reviews by the PMT and the ST of the SBSPRP and any further data available on the presence and abundance of candidate species.

Assessment Question No. 3: What is the sampling design to get the data that are needed?

The purpose of the Phase 1 sampling plan is to investigate the mercury problem for the Alviso Pond and Slough Complex, and to provide a scientific basis for adjusting the restoration design, operations, or restoration actions for Pond A8.

Task 3: Finalize the Phase 1 (Alviso Pond and Slough Complex) Sampling Design

We propose to revise this sampling plan based on reviews by the PMT and the ST of the SMSPRP. The steps in the draft plan are identified below as subtasks for this Task 3.

Task 3A: Assess the distribution and abundance of mercury in sediment that may threaten the success of management actions for the Pond A8 complex.

Legacy loads of mercury are distributed in sediments that have accumulated in Alviso Slough adjacent to Pond A8. The PMT is concerned that breaching this Pond will cause Alviso Slough to scour, making legacy loads of Hg available for methylation and thus increasing uptake of toxic MeHg into the local food web. The few data that exist suggest that the highest mercury concentrations occur at varying depths below the present surface of the sediments, and perhaps below the depth zone that supports the greatest rate of MeHg production. Erosion of surface sediments may bring the zone of MeHg production into contact with the peak concentrations of mercury, thus increasing the pool of MeHg that is available for biological uptake. Furthermore, erosion would cause the mercury-laden sediments to be re-suspended and moved by the tide downstream into the Bay or upstream into breached ponds. While it won't be possible to confidently predict what would happen next in either the Bay or the ponds, knowing whether or not Slough erosion might significantly increase the pool of available MeHg would be useful to understanding the mechanisms behind changes in mercury accumulation as a result of the

project. Understanding these mechanisms will hopefully lead to an improved capacity to predict the consequences of future restoration actions.

We propose to take 1-m deep cores of existing sediments at five cross-sections evenly spaced along the portion of Alviso Slough that is likely to erode following a breach of Pond A8. The geographic scope of the coring effort will be determined by comparing the existing width and depth of the Slough to that which is predicted due to the breach (PWA 2005). This is made possible by existing empirical models that relate channel geometry to tidal prism, and by knowing how much tidal prism will be added by the breach. At each cross-section, one core will be taken from each bank and from the Slough centerline. These cores will be used in two ways: (i) to predict if Slough erosion will increase the in situ pool of available MeHg in the Slough (i.e., whether erosion will cause the zone of highest methylation to contact higher concentrations of total Hg that are currently buried); and (ii) to profile the distribution of total Hg (HgT) in the Slough that might be eroded away.

The majority of inorganic Hg is not available for conversion to MeHg, as it is largely complexed or bound to solid-phase organic and inorganic matrices in sediment. However, recent advances have been made in assessing the pool size of the small fraction of inorganic Hg that is likely available for methylation. The pool is operationally defined as the amount of inorganic Hg(II) in sediment that is readily converted to gaseous Hg^0 by tin chloride under anoxic conditions. Ecosystem Hg process studies currently being conducted in the San Francisco Bay Delta, the Lake Pontchartrain Drainage Basin (LA), and a suite of 7 streams in FL, WI and OR (sampled as part of the USGS NAWOA program) all indicate that assessment of this pool of reactive mercury $(Hg(II)_R)$, in conjunction with radiotracer studies of Hg-methylation, is a better predictor of insitu Hg-methylation rates than are radiotracer studies alone. Furthermore, results from these ecosystem studies indicate a significant negative relationship between the Hg(II)_R pool size and in situ rates of microbial sulfate reduction, the very bacteria that are responsible for Hg methylation. Thus, there is a negative feedback between sulfate-reducing bacterial activity that tends to increase the potential for Hg-methylation, and the amount of reduced sulfate that is produced. This suggests that there exists an optimal point for Hg-methylation in the interaction between these two primary controls. This is akin to observations reported for a transect of sites in the Florida Everglades, where the balance of low sulfide and moderate sulfate reduction rates were associated with the region of maximal Hg-methylation (Gilmour et al 1998), and similar observations reported for the San Francisco Bay Delta (Marvin-DiPasquale and Agee 2003). Given these results to date, we hypothesize that $Hg(II)_R$ is an important inorganic indicator of methylmercury production rates. The linkage of measurement of methylmercury production rates in sediment with food web monitoring in this project will provide an effective tool for understanding conditions that lead to increased biotic methylmercury exposure. This linkage will be perhaps even more valuable for identifying cases where methylmercury production is high, but food web accumulation is low – these cases may provide insights on what type of conditions in restored wetlands tend to minimize methylmercury exposure.

It is expected that the zone of maximum concentration of reactive inorganic mercury $(Hg(II)_R)$ and MeHg production will exist somewhere within the upper 25 cm of the sediment pile (i.e., within the major portion of the root zone of the marsh plain, or near the anoxic boundary of the subtidal sediments). The zone of maximum MeHg production in not likely to be below 25 cm in depth. It is also expected that salinity affects the rate of MeHg production. We will therefore survey total mercury, $Hg(II)_R$, and MeHg for the upstream (least saline), downstream (most saline) and middle cross-sections at the following depths (in cm) below the substrate surface: 2.5, 5, 10, 15, 20, 30, 40, 50. Correlations between these measurements and mercury accumulation in the food web will be examined.

Each core from all five cross-sections will be profiled for HgT at 10-cm intervals of depth. These profiles will be used to construct a 3-D schematic of the total amount of mercury existing along the channel through the reach represented by the cross-sections. This schematic will be compared to the expected erosion in 3-D to estimate how much Hg might be mobilized by the erosion. This approach would also suggest which part of the sediment pile would have to be removed (i.e., dredged) to reduce the risk of increased mercury exposure.

Dredging could remove contaminated sediment that is likely to scour and end up in the Pond following breaching. However, dredging would not guarantee that the sediments that accumulate in the Pond during restoration are uncontaminated; other contaminated sediments from the watershed or the Bay could enter with the tides. Capping the Pond with clean sediment or other studies of sediment transport might be required (see Figure 1).

| Analytes | Number of Cross-sections | Cores per X-section | Sample Units per Core | Sampling Periods per Year | Samples per Year |
|--|-----------------------------|------------------------|--|---------------------------------|---------------------|
| Total Hg | 2 | 3 | 10 (every 10 cm for 1- m core) | 1 | 60 |
| Total Hg, Hg(II) _R , MeHg | 3 | 3 | 8 (at 2.5, 5, 10, 15, 20, 30, 40, 50 cm) | 1 | 72 |

 Table 2. General sampling scheme to profile total mercury and maximum MeHg zone over depth and distance in Alviso Slough.

Task 3B: Develop the sentinel species indicators

The two main objectives of this task are (i) confirm the presence of the candidate species within the selected habitat types and locations in South Bay and finalize capture methods, or select alternative candidates, if necessary; and (ii) estimate the optimal sample size for each sentinel species in each habitat.

This task will be accomplished during preliminary field visits. Permits for destructive sampling should be obtainable for all the candidate species except the Alameda song sparrow. Feathers can be taken from sparrows to test for MeHg bio-magnification without harming the birds. Feather mercury has been demonstrated to be a good indicator of mercury exposure in birds (Monteiro and Furness 1995, Spalding et al. 2000).

If, for example, the mercury problem were defined as the threshold of bioaccumulated Hg that harms a sentinel species, and if the desired certainty in detecting the threshold were known, and

if a sample of the Hg concentrations were available for analysis, then the variability of the sample could be used to estimate the number of sample replicates needed to detect differences from the threshold with the desired certainty. There is no sample to analyze at this time, however, and neither the critical threshold of Hg concentration nor the desired confidence level is known. Instead, we have proposed using Hg concentrations in sentinel species and their habitats to compare selected locations to ambient conditions, and to support the baylands managers' deliberation about whether or not the differences indicate a problem. In the context of determining sample size, the relevant question is about the degree of difference between locations that can be determined for any sample size. To address this question in Phase I, we propose to take a large sample (n = 30) of each sentinel species in each habitat in each geographic area and use these data to relate sample size to detectable differences for a range of Type I and Type II error rates. Sample replicates will be processed in batches, and the effect of each additional batch on power will be analyzed. In this way, the total cost of sample analysis can be minimized.

For each sentinel species population, sample size (i.e., the number of sample replicates) will depend on the variability in Hg concentration within the population, as well as the desired level of certainty in determining a mercury problem. Larger samples provide more certainty, but also cost more. The need for certainty will therefore have to be balanced against the sampling costs.

Each sample replicate will consist of material from individual organisms for fish and sparrows and from a number of individuals (composites) for brine flies, which are too small to sample as individuals. Individual analysis will allow characterization of the variance in Hg concentration within each species in each geographic area. This analysis will provide the foundation for conducting power analyses to determine sample sizes and compositing regimes in future years. Composites will be comprised of organisms from a limited spatial area (e.g., 0.1 ha).

Since Hg accumulates in organisms over time, Hg concentrations can vary among organisms of the same species with different ages. Concentrations can also vary due to phenology (e.g., sexual maturation, breeding, molt, etc.), as well as diet and environmental conditions. The sample variability of a sentinel population can therefore be reduced by restricting the sample to individuals of similar age, phenology, and location. Such standardization greatly improves the ability to separate the differences between sample sites from the differences between individuals in the sample population. The feasibility of such standardization differs among the candidate sentinel species, however, and will be maximized for each species as much as possible. Sparrows will be sampled by taking feathers from adults. All adults molt in the fall, so the samples will reflect deposition of Hg in the feathers during the same time period from the same age class. Standardization for fish will be achieved by constructing MeHg:length relationships within each geographic area, which will enable normalization of Hg concentrations for fish of all lengths. In future years, certain size classes of fish may be targeted for sampling based on this analysis of Phase I data. Brine fly samples will be standardized by collecting adults in the summer .

In fish and birds, most mercury (>90%) exists as MeHg, so only total mercury needs to be measured. The proportion of total mercury that is MeHg varies in invertebrates, so MeHg must be measured in the brine flies.

Task 3C: Assess the extent and magnitude of the mercury problem for the Pond A8

3Ci: Sentinel species survey

We propose to sample sentinel species in the habitats of Alviso Slough and Pond A8 to meet the following three objectives:

- Assess the possible effects of converting Pond A8 to tidal flat or tidal marsh (and thus transferring sediment from the Slough into the Pond);
- Compare the habitats based on their relative risks of having a Hg problem; and
- Establish a baseline for long-term, cost-effective monitoring of the Hg problem at the Alviso Pond and Slough Complex.

The approach is to compare Hg levels in the same species across different geographic areas – Pond A8, Alviso Slough, and ambient SBSPRP marshes – to compare the MeHg concentrations in biota from each of these areas. This approach will enable the following assessments.

- The difference between Pond A8 and the habitats within Alviso Slough.
 - If Pond A8 is breached, sediments from the Slough are likely to scour and be transferred to the Pond. Therefore the MeHg concentrations of biota in the Slough habitats give an indication of likely concentrations in biota of a restored marsh inside Pond A8.
- The importance of the difference between the Pond and the Slough relative to the extent that they each differ from ambient habitats in the SBSPRP.
 - It is important to understand how much worse or better a restored Pond might be relative to ambient conditions. For example, the Slough may be worse than the Pond, but that difference could be insignificant if both the Slough and the Pond are much worse than the ambient conditions. In such a case, the restored marsh scenario is not very different than the current Pond scenario.

In general, one candidate sentinel species will be selected per habitat, and sampled just once during Phase 1. The approximate sampling scheme is outlined in Table 3 below.

| Habitats | Species per Habitat | Geographic Areas to Compare | Sample Replicates per Geographic Area | Sampling Periods per Year | Samples per Year |
|----------|---------------------------|-----------------------------------|---|---------------------------------|------------------------|
| 4 | 1 | 3 | 30 | 1 | 360 |

Table 3. General sampling scheme for sentinel populations during Phase 1.

3Cii: Pond A8 and Alviso Slough Water Quality

This task will focus on the temporal and spatial variation of aquatic mercury species in Pond A8 relative to potential changes to water quality following conversion of the Pond from its existing hydraulically isolated status to a muted or fully tidal condition. The information gained by this study will provide the basis for routine monitoring and be used to understand the seasonal variations and correlations of parameters such as salinity, temperature, dissolved oxygen, dissolved organic carbon, and biota (phytoplankton and zooplankton) to HgT, dissolved mercury, and MeHg in the water column and the pelagic and benthic sentinel fish species.

Little is known about the water column chemistry and productivity in Pond A8, how it relates to sediment concentrations of mercury and methylmercury, and whether or not methylation of mercury occurs in the water column and if so, whether or not the rate is significant. This lack of understanding is not limited to Pond A8, and intensive investigation at this juncture will serve to inform restoration and management efforts for other ponds. A thorough evaluation of the mechanisms of mercury methylation and entry into the food web is warranted as adaptive management of the SBSPRP begins.

The data collection regime (Table 4) is designed to allow comparison of environmental conditions following a change in operation of Pond A8 and Alviso Slough through time, including the following:

- The quantity of mercury (and in what form; i.e., particulate, dissolved, methylated) transported inland and outward via tidal and riverine inflows;
- Sources of mercury to the pond;
- Seasonal load and flow variations of mercury as well as its characteristics; and
- Seasonal variation of aqueous MeHg and factors that may influence aqueous MeHg.

Table 4. Sampling plan for Pond A8, Alviso Slough, and ambient marshes. Sampling would be conducted monthly, with additional sampling in response to important events.

| Environment | Chemical Factor | Pond Benthic | Slough |
|-------------|-----------------|--------------|--------|
| Water | Unfiltered MeHg | Х | Х |
| | Unfiltered HgT | | Х |
| | Salinity | Х | Х |
| | Temperature | Х | Х |
| | DO | Х | Х |
| | DOC | Х | Х |
| | TOC | Х | Х |
| | SSC | Х | Х |
| | Sulfate | Х | Х |
| | Sulfide | Х | Х |
| | Nutrients* | Х | Х |
| | PH | Х | Х |
| | | | |

| Sediment | HgT | Х | Х |
|-------------|---------|---|---|
| | MeHg | Х | Х |
| | Hg(II)R | Х | Х |
| | Sulfate | Х | Х |
| | Sulfide | Х | Х |
| | | | |
| | | | |
| Zooplankton | MeHg | Х | Х |
| | | | |

* Nutrients include chlorophyll-a and –b, nitrate, nitrite, ammonia, total kjeldahl nitrogen, and total phosphorus.

Water quality sampling would be conducted monthly, with additional sampling in response to important events. Zooplankton sampling would occur seasonally (3 times per year). We propose to sample water and zooplankton in Pond A8 and Alviso Slough during Phase 1 to meet the following objectives.

- To determine optimal sample sizes;
- To identify correlations between MeHg in the water column and other water quality parameters;
- To develop water quality data for Alviso Slough as a function of flow and season; and
- To provide sufficient data to evaluate the potential effects on water quality of different Pond A8 operational changes.

The questions to be addressed by this task are as follows.

- 1. What is the mercury load associated with the ebb and flow tides in Alviso Slough?
 - a. Measurement of total, dissolved, and methyl mercury concentrations in spring ebb tides in the Slough provides information to estimate the load of each mercury species that would enter Pond A8 if it were opened to muted or fully tidal exchange.
 - b. Measurement of total, dissolved and methyl mercury concentrations in spring ebb and flow tides provides baseline data for comparison following operational change, estimation of the net loading of mercury in this section of the slough, and evaluation of methyl mercury production rates in the bay, the river and the slough.
- 2. What are spatial and temporal water quality characteristics of Pond A8 and Alviso Slough?
 - a. Measurements of methylmercury concentrations in the Pond and Slough over time will provide data that can be compared to other water quality parameters to identify correlations between water column chemistry, methylmercury production, and accumulation in the food web.
 - b. Measurements of HgT in the Pond and Slough over time will provide an indication of the sources of mercury to the water column of these ecosystems.

- c. Measurements of water quality chemistry in the Pond and Slough provide information regarding the ecological status and health of the water bodies, identification of factors controlling phytoplankton and zooplankton abundance and diversity (e.g. nutrient limitations, salinity), and identification of factors associated with methylmercury production (e.g., dissolved oxygen, temperature, salinity).
- 3. What are the spatial and temporal assemblages of phytoplankton and zooplankton, and what is the mercury content of zooplankton?

Measurements of mercury in zooplankton will provide information for estimating the existing exposure of the sentinel fish species, and the potential exposure following an operational change.

Limnological characterization of Pond A8 and Alviso Slough is necessary to understand the trophic status of the water bodies, the abundance and diversity of planktonic biota, the cycling of nutrients, and to identify factors controlling growth of phytoplankton. Under the existing operation, Pond A8 likely undergoes a significant change in salinity over the course of one year. Salinity will be at a minimum at the end of the wet season, when the volume of water in the pond has reached its maximum for that year, and salinity will be at a minimum at the end of the pond has reached its minimum for that year. Conversion of the pond to muted tidal or fully tidal would damp this effect, narrowing the range of seasonal fluctuation of salinity in the pond. It is hypothesized that the biota in Pond A8 will react to these fluctuations in salinity, and that it is possible to predict what the species mix would be following a change of operation.

Seasonal sampling (spring, summer, and fall) of the water in Pond A8 and Alviso Slough is necessary to understand how water quality varies due mainly to climatically driven changes in dissolved oxygen (DO). Changes in DO will results in the redistribution of chemicals in the surface sediments at the bottom of the pond, changes in chemical exchange rates between the sediments and the water column, and changes in the kinds and rates of chemical inputs from surrounding soils and vegetation. It is hypothesized that MeHg concentrations in the water column will increase under anoxic conditions. However, as discussed above, the increase in salinity or reduced sulfate may decrease the rate of net MeHg production. Therefore, the study includes a component for sampling in response to changes in water quality chemistry, in addition to sampling at specified intervals.

Since the pond is shallow, it may not exhibit stratification as a whole, but may have localized areas of anoxia. In order to obtain representative data, water samples will be collected from four locations, two in the littoral or shallow zone at the perimeter of the pond, and two in the deeper middle areas of the pond. Field measurements at each station include water column profiles of dissolved oxygen, temperature, salinity, conductivity, pH, oxidation-reduction potential, turbidity, total dissolved solids, total depth, and Secchi depth.

Biological uptake of MeHg will be evaluated seasonally by measuring concentrations of MeHg in zooplankton. This will allow for correlation of mercury in biota to water column chemistry on a seasonal and event-driven basis. These lower trophic level measurements will also provide a

link between methylmercury in water and sediment and methylmercury in higher trophic level biosentinel fish.

The monitoring plan for each element described above is summarized as follows.

- Water quality sampling will be conducted monthly and at significant back-to-back changes in field measurements of temperature, salinity, and dissolved oxygen.
- Zooplankton collection will be conducted seasonally for a minimum of three events. Additional events may be conducted in response to visual blooms or to significant changes in back-to-back or month-to-month salinity measurements.

In addition, measurements made on ebb and flood tides will provide information to estimate mercury loading and salinity changes to Pond A8 following conversion of the pond to muted tidal or fully tidal status. Water samples will be collected during ebb and flood tide in one 12-hour tidal cycle each month. Zooplankton collection in Alviso Slough will be conducted seasonally (spring, summer, fall), in conjunction with the water sampling in Pond A8. Additional sampling in the Slough may be conducted in response to visual algal blooms or significant changes in salinity.

3Ciii: Pond A8 sediment sampling

This task will focus on elucidating the spatial distribution of mercury species in sediment in Pond A8. The resulting detailed characterization of sediment in the pond will provide a baseline for assessing the effects of future hydrological changes, including tidal restoration or fluvial flooding that overtops the peripheral levee of the pond. The results of this Task 3Ciii and Task 3A can be used to compare the sediments of Pond A8, Alviso Slough, and ambient marshes, as needed to help explain projected effects of Pond A8 restoration based on sentinel species.

The sampling plan for Pond A8 is shown in Tables 5 and 6. Two alternative approaches of comparable cost to stratify Pond A8 as a sampling universe are being considered at this time. One approach is to create a grid of about 40 roughly equal-sized areas of about 500 feet per side, and to take one composited sample unit of surface sediment (0-5 cm deep) from each grid node. The other approach is to assume that, if the Pond is restored to tidal action, then the historical tidal marsh channel system will be exhumed by channel scour, thus mobilizing the channel sediments and deposited them on the neighboring pond plain. Based on this assumption, we would focus sampling on the larger historical channels that might be exhumed. SFEI has prepared a detailed map of historical channels that could be used as the sample frame. In either case, the sediment samples will be analyzed for total mercury and other ancillary parameters listed in Table 6.

| Species | Habitat Types | (nominal) Sites per habitat type | Total Sites (adjusted) | Replicates per site | Sampling Periods per year | Base samples per Year | QA Duplicates at 10% | Total Samples |
|---------|------------------|---|------------------------------|------------------------|---------------------------------|-----------------------------|----------------------------|------------------|
| HgT | 2 | 4 | 8 | 3 | 1 | 24 | 8 | 32 |
| Hg(II)R | 2 | 4 | 8 | 3 | 1 | 24 | 8 | 32 |
| MeHg | 2 | 4 | 8 | 3 | 1 | 24 | 8 | 32 |

Table 5. Sampling plan for Pond A8 sediments.

| | | Pond Benthic | Slough | Ambient Marshes Phase 1 |
|----------|---------|--------------|--------|----------------------------|
| Sediment | HgT | Х | Х | Х |
| | MeHg | Х | Х | Х |
| | Hg(II)R | Х | Х | Х |
| | Sulfate | Х | Х | Х |
| | Sulfide | Х | Х | Х |

Table 6. Proposed Laboratory Analyses for Sediment Samples

Task 4: Manage Data

Data management for this effort would include the following:

- Developing and testing a project-specific tabular database for storing and sharing data for all sampling plans, raw data, QA/QC conduct and outcomes, data analyses, draft and final findings;
- Linking the tabular database of spatial data to a GIS for map-based data retrieval and display;
- Posting data summaries, reports, maps and related products to the South Bay Salt Pond Restoration Project website and the Wetland Tracker.

All of these tasks will build on existing capacity at SFEI for multi-partner data management and sharing. Since this is part of an adaptive science and management project, it is likely that the database will need to evolve over time. A large aspect of this task could be accommodating adjustments in study objectives and sampling design. This aspect of the task has been considered in the budget for data management and sharing.

Task 5: Project Management

SFEI will manage the project including subcontracts and reporting. These tasks will be divided between the three SFEI co-PIs and the SFEI contracts officer. Project management will include regular meetings of the PIs, plus at least three meetings with the PMT and ST of the SBSPRP to discuss interim and final results of field and laboratory work. SFEI will follow the reporting schedule and means decided by the sponsors.

Phase 2 Plan (Year 2)

The monitoring and assessment approach outlined above for Phase 1 is scalable. Habitats can be added or omitted from the approach, and the geographic scope of the monitoring can also be adjusted.

At this time, Phase 2 is intended to expand the survey of the extent and magnitude of the problem to encompass all of the SBSPRP. Any problem areas identified in Phase 1 would be investigated in detail to discover their likely causes. Additional problem areas identified during the Phase 2 survey could be investigated in subsequent phases, if required.

Task 6: Survey the extent and magnitude of the mercury problem for the SBSPRP.

The expanded survey in Phase 2 will focus on sentinel species, using the same sentinel species and protocols as the initial survey conducted for the Alviso Pond and Slough Complex during Phase 1 (see Task 3C), and based on sample size analyses conducted using Phase 1 data (see below). The updated NWI will serve as the sample frame for either a stratified-random sampling design, or a non-random design that fits the particular needs of the baylands managers.

| Habitats | Species per Habitat | Geographic Areas (Spatial populations to sample) | Sample Sites per Habitat (really TBD based on year 1 analyses) | Sample Replicates per Site (composites) | Sampling Periods per Year | Samples per year |
|----------|---------------------------|--|--|--|---------------------------------|---------------------|
| 4 | 1 | 2 | 3 | 3 | 1 | 72 |

Table 7. General sampling scheme for sentinel populations during Phase 2.

Sample sizes for Phase 2 will be assessed using power analyses based on Phase 1 data, with statistical assistance on a subcontract basis from the USEPA Monitoring Program Design Team at Corvalis, Oregon, Compositing schemes will also be designed with the help of this team.

Task 7: Explaining Mercury Accumulation Patterns

For those sites that are classified as relatively high risk during Phase 1, the processes of MeHg production and uptake into the sentinel species will be studied in detail to investigate the driving factors controlling the problem. The intent is to "drill down" into the problem through the food webs of the sentinel species to the methylation and transport processes in the sediment or water. The findings will be provided to the Monitoring Options Project of ABAG to help develop restoration designs and project operational practices that can minimize the mercury problem.

The key aspect of this approach is that all studies of the problem, including studies of sediment chemistry, water chemistry, and food webs of the sentinel species will co-occur at the sites where the sentinel populations have indicated a problem exists, and at control or ambient sites for which no comparable problem has been identified. These ambient sites will be chosen from the surveys conducted in Tasks 3C and 5 above. It is essential to keep all chemical and ecological sampling within the time-space coordinates of the sentinel populations.

Each problem site and chosen ambient site will be characterized in terms of plant species cover and density, soil and water salinity and other chemical parameters, land use history, and hydroperiod including water management regimes if applicable. These data will be used to classify the problem sites with regard to conditions that can be managed, and to help account for the variability in MeHg bioaccumulation between sites.

There will be considerable variability in structure and form within each site that cannot be known at this time but that must also be accounted for. This can be done through within-site stratification and allocation of the sampling effort among the strata. While this approach might provide insights about components of a site that promote MeHg production or uptake, it can also

greatly increase sampling costs. We will restrict within-site stratification to the most obvious strata, and to the extent reasonable, we will composite sample units across the within-site variability.

Chemical sampling will focus on measurements of methylation processes in sediment or water, depending the sentinel species of concern. Water is assumed to be the primary source of bioaccumulated MeHg in the topsmelt, since it is a pelagic feeder. For all other sentinel species, the primary source is assumed to be the wetland or benthic sediments. Total mercury, reactive mercury (HgII_R), and MeHg will be sampled as three composited replicates within each problem site (if the problem is focused on water, then only total mercury and MeHg will be sampled). A suite of ancillary parameters that have been shown in other studies to often correlate with MeHg will also be measured to better understand what controls increased exposure and accumulation in the sentinel species. If the focus of a problem site is on a pelagic sentinel species, then collected water samples will be composited spatially and replicated temporally (i.e. at different stages of a tidal cycle or at the same stage for different days) to capture the range of conditions to which the biota are exposed (see Tasks 3Cii and 3Ciii above).

We will select biota of the food webs of the sentinel population of each problem site based on the same criteria used to select the sentinel species (see Assessment Question No. 2 above). One primary producer , one primary consumer, and the sentinel species will be sampled at each problem site. The timing of their sampling will depend on their natural history and that of the sentinel species, but a single sample period is anticipated. The biota will be composited as three or more replicate sample units within each problem site. The approximate sampling scheme is outlined in Table 8 below.

The results of Task 7 will be provided to the ABAG Proposition 13 project to help develop habitat designs and management options that minimize the risk of mercury poisoning for wildlife associated with the baylands of South Bay.

| Geographic Areas (problem, ambient) | Sample Sites per Geographic Area (nominal) | Species per Sample Site | Replicates Per Sample Site (minimum) | Sampling Periods per Year | Samples per year |
|--|--|----------------------------|--|---------------------------------|---------------------|
| 2 | 2 | 3 biota | 3 | 1 | 36 biota |
| 2 | 3 | 3 chemical | 3 | 1 | 54 chemical |

Table 8. General sampling plan to explain problem sites for 1 habitat identified during Phase 1

Budget and Timeline

The proposed approach can be scaled. The scope of Phase 1 is based on the assumption that the survey of mercury problems for Pond A8 should include all of the major habitat types that are likely to be affected by hydrological modification of Pond A8. Further discussion with the PMT or ST might conclude that one or more of these habitat types does not need to be examined. The Phase 1 budget also assumes that the limnological comparison of Pond A8 and Alviso Slough can proceed while Pond A8 is being actively managed. This will have to be confirmed in discussions with the PMT and ST. The work plan for Phase 2 might be adjusted by adding or omitting habitats to be surveyed, or by adjusting the geographic scope of the survey. For example, the PMT might decide to focus on the effects of new management practices, such as pond aeration or the breaching of the Island Ponds. The approach can be adjusted to accommodate the evolving needs of the PMT.

The budget is based on the plans for both Phases of the work as proposed. It is assumed that personnel for field work will be provided by the principal partners, but additional sources of labor can be explored through state and community colleges, the PMT member agencies, etc. Costs for labor are similar for the principal partners and therefore their separate costs have not been itemized. The budget focuses on the costs per task, given that the partners can organize themselves to accomplish the tasks for the budget provided. SFEI plans to take the administrative lead, and subcontract to the partners. However, direct awards to all three principals may also be appropriate.

| Phase | Task | Cost | Completion Date |
|---------|--|---------|------------------------|
| Phase 1 | 1: Finalize problem definition | 5,250 | Month 1 |
| | 2: Finalize sentinel species selection | 10,500 | Month 3 |
| | 3A: Assess risk of slough scour | 75,250 | Month 12 |
| | 3B: Develop sentinel species indicators | 14,650 | Month 9 |
| | 3Ci: Pond A8, Alviso Slough and reference site sentinel species survey | 137,300 | Month 12 |
| | 3Cii: Pond A8 and Alviso Slough Water Sampling | 310,000 | Month 12 |
| | 3Ciii: Pond A8 sediment sampling | 20,000 | Month 12 |
| | 4: Manage data | 30,000 | Ongoing |
| | 5: Project management | 15,000 | Ongoing |
| | Phase 1 subtotal | | 617,950 |
| Phase 2 | 6: Survey Hg problem for SPRP | 47,900 | Month 24 |
| | 7: Explain HG accumulation patterns | 71,725 | Month 24 |
| | Phase 2 subtotal | | 119,625 |
| | Grand Total | | 737,575 |

References

- Babiarz, C.L., J.P. Hurley, J.M. Benoit., M.M. Shafer, A.W. Andren, and D.A. Webb. 1998. Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds. Biogeochemistry 41:237-257.
- Beutel, M., and K. Abu-Saba. South Bay Salt Ponds Restoration Project: Mercury Technical Memorandum. Brown and Caldwell / Larry Walker and Associates. Report prepared for the South Bay Salt Ponds Restoration Project Management Team. 47 pp.
- CalFed 2005. Mercury in every mix. Science in Action, CalFed Bay-Delta Program, Sacramento CA.
- Conaway, C.H., S. Squire, R.P. Mason, A.R. and Flegal. 2003. Mercury speciation in the San Francisco Bay estuary. Marine Chemistry 80:199-225.
- David, C.P.C., S.N. Luoma, C.L. Brown, D.J. Cain, M.I. Hornberger, and I.R. Lavigne. 2002. Near Field Receiving Water Monitoring of Trace Metals in Clams (*Macoma balthica*) and Sediments Near the Palo Alto Water Quality Control Plant in South San Francisco Bay, California: 1999-2001. U.S. Geological Survey Open File Report 02-453.
- Gagnon, C., E. Pelletier, A. Mucci, and W.F. Fitzgerald. 1996. Diagenetic behavior of methylmercury in organic-rich coastal sediments. Limnology and Oceanography 41:428-434.
- Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill, and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 40:327-345.
- Marvin-DiPasquale, M., and J.L. Agee. 2003. Microbial mercury cycling in sediments of the San Francisco Bay-Delta. Estuaries 26:1517-1528.
- Marvin-DiPasquale, M., J. Agee, C. McGowan, R.S. Oremland, M. Thomas, D. Krabbenhoft, and C. Gilmour. 2000. Methyl-mercury degradation pathways: a comparison among three mercury-impacted ecosystems. Environmental Science and Technology 34:4908-4916.
- Monteiro, L. R., and R. W. Furness. 1995. Seabirds as monitors of mercury in the marine environment. Water, Air, & Soil Pollution 80:851-870.
- PWA. 2005. Draft landscape assessment for the South Bay Salt Pond Restoration Project. Philip Williams ands Associates, San Francisco CA.
- Schwarzbach, S. and T. Adelsbach. 2003. CALFED Bay-Delta Mercury Project Subtask 3B: Field Assessment of avian mercury exposure in the Bay-Delta ecosystem.
- Sellers, P., C.A. Kelly, J.W.M. Rudd, and A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. Nature 380:694-696.

SFEI. 2004. The Pulse of the Estuary 2004. San Francisco Estuary Institute, Oakland, California.

- SFEI. 2005. The Pulse of the Estuary 2005. San Francisco Estuary Institute, Oakland, California.
- Spalding, M., P. Frederick, H. McGill, S. Bouton, and L. McDowell. 2000. Methylmercury accumulation in tissues and its effects on growth and appetite in captive great egrets. Journal of Wildlife Disease 36:411-422.
- Thomas, M.A., C.H. Conaway, D.J. Steding, M. Marvin-DiPasquale, K.E. Abu-Saba, and A.R. Flegal. 2002. Mercury contamination from historic mining in water and sediment, Guadalupe River and San Francisco Bay, California. Geochemistry: Exploration, Environment, Analysis 2:211-217.
- Topping, B.R., J.S. Kuwabara, M.C. Marvin-Dipasquale, J.L. Agee, L.H. Kieu, F. Parchaso, S.W. Hager, C.B. Lopez, and D.P. Krabbenhoft. 2004. Sediment Remobilization of Mercury in South San Francisco Bay, California: U.S. Geological Survey Scientific Investigations Report 2004-5196.
- Wiener, J.G., D.P. Krabbenhoft, G.H. Heinz, and A.M. Scheuhammer. 2003. Ecotoxicology of mercury. *In* Handbook of Ecotoxicology, 2nd edition. D.J. Hoffman, B.A. Rattner, G.A. Burton, and J. Cairns, eds. Boca Raton, CRC Press, pp. 409-463.