

The Effects of Wetland Restoration on Mercury Bioaccumulation in the South Bay Salt Pond Restoration Project: Using the Biosentinel Toolbox to Monitor Changes Across Multiple Habitats and Spatial Scales

2010 Annual Report to the
Resources Legacy Fund, State Coastal Conservancy,
and South Bay Salt Ponds Restoration Program

Prepared By:

Josh Ackerman¹, Mark Marvin-DiPasquale², Darell Slotton³, Mark Herzog¹, and Collin Eagles-Smith⁴

¹ USGS, Davis Field Station, One Shields Ave., University of California, Davis, CA 95616

² USGS, Water Resources Division, 345 Middlefield Rd., Menlo Park, CA, 94025

³ UC Davis, Dept. of Environmental Science and Policy, One Shields Ave., Davis, CA 95616

⁴ USGS, Forest and Rangeland Ecosystem Science Center, 3200 SW Jefferson Way,
Corvallis OR, 97331

INTRODUCTION

Two of the most significant anthropogenic changes in the San Francisco Bay (SFB) Estuary over the past 150 years are the loss of over 85% of fringing tidal wetlands and the contamination of the estuarine food web with mercury (Hg). These impacts are particularly pronounced in the South Bay, which was historically fringed with extensive tidal marshes and which receives drainage from New Almaden, the largest historic Hg mining area in North America. Extensive restoration in the South Bay region aims to return much of the important ecosystem function these wetlands provided. However, high rates of methylmercury (MeHg; the most toxic form of Hg) production, export, and bioaccumulation have been associated with wetlands relative to other water bodies (Hurley *et al.* 1995, Krabbenhoft *et al.* 1999, Waldron *et al.* 2000, Yee *et al.* 2008, Ackerman and Eagles-Smith 2010). Thus, the potential exists to increase Hg bioavailability in the South Bay as former salt ponds are restored to tidal marsh. This is a particularly important concern, because Hg concentrations in tissues and eggs of waterbirds in the South Bay currently exceed toxicological thresholds (Eagles-Smith *et al.* 2009, Eagles-Smith and Ackerman 2008), and there is evidence that Hg is impairing nest success, egg hatchability, embryo development, and chick survival (Ackerman and Eagles-Smith 2008, Ackerman *et al.* 2008a). Thus, any increase in MeHg production and subsequent bioaccumulation in waterbirds may have a substantial impact to their reproduction.

One of the first major changes in the restoration process is the recently constructed levee notch (tidal control) structure that will restore muted tidal action to Pond A8, beginning in early 2011. The concerns surrounding this management action include both the scour (due to increased tidal prism) and the redistribution of long-buried sedimentary Hg in adjacent Alviso Slough (which has sediment total mercury (THg) concentrations 3-times higher than in the

greater South Bay), as well as changes in MeHg production and bioaccumulation dynamics within Pond A8 and Alviso Slough (Marvin-DiPasquale and Cox 2007, Grenier et al. 2010).

Within Pond A8 itself, MeHg concentrations in the sediments and biota are among the highest of any measured in the entire South Bay (Miles and Ricca 2010, Ackerman et al. 2007a,b, Ackerman and Eagles-Smith 2008, Grenier et al. 2010). Although, it is unclear how Hg cycling within the pond will change post-breach, other recently breached salt ponds in the region (A19 and A20) showed more than 5-fold increases in sediment MeHg concentrations post-breach (Miles and Ricca 2010). Thus, there is the potential that MeHg concentrations within the pond may increase above the currently high levels following the initial operation of the Pond A8 tidal notch structure, currently due to begin in early 2011. However, a recent study of Pond A8 and Alviso slough concluded that opening up this particular pond to tidal flushing may decrease MeHg production within the pond over the longer term (Grenier et al. 2010). This uncertainty in the ultimate effect of tidal reconnection on Hg cycling with Pond A8 and in Alviso Slough, once the seasonal operation of the A8 notch begins, points to the need to closely monitor the situation in and around Pond A8, before, during, and after the commencement of routine notch operation as planned.

Although the Alviso Pond/Slough Complex contains more THg than other areas of the South Bay (SFEI 2005, Marvin-DiPasquale and Cox 2007), wetland restoration may not necessarily increase MeHg in the local food web because MeHg production depends on many environmental factors in addition to THg concentration. Recent studies indicate significant spatial variation in Hg bioaccumulation are related to differences in habitat type (Eagles-Smith et al. 2008, Stewart et al. 2008). Even within a single type of wetland, Hg bioaccumulation within the same biosentinel species can vary greatly among wetlands with different characteristics (Grenier et al. 2010). Further, Hg concentrations in several waterbird species vary greatly even among adjacent wetlands (Ackerman et al. 2007a,b, 2008a,b,c), indicating the importance of processes governing MeHg production, transport and partitioning (among solid and dissolved phases) that occur within wetlands. In order to understand how management actions influence MeHg production and bioaccumulation into the food web, an integrated monitoring program that incorporates abiotic and process studies with biological indicators of exposure has been initiated. The focus of the project is to assess changes in Hg cycling and bioaccumulation in Pond A8 and Alviso Slough, before and after the initial operation of the newly constructed tidal notch structure. Since no single biosentinel species can provide the information needed across all habitats, spatial scales, and components of the food web, the current project involves a multiple biosentinel approach to determine how management actions will affect MeHg in the food web, and ultimately risk to sensitive wildlife.

The project was initiated in April 2010, and to date has included four sampling events of surface water (April, May, June/July, and August 2010) and five sampling events of biota (April, May, June/July, August, and September 2010) and three sampling events for surface sediment (May, June/July, and August 2010). This 2010 sampling period represents the 'pre-condition' relative to the initial operation of the A8 notch tidal structure (reinstating muted tidal exchange between Pond A8 to Alviso Slough), which is due to commence in Spring 2011. This annual report briefly summarizes our progress to date.

STUDY OBJECTIVES

Wetland restoration and management practices that would minimize MeHg bioaccumulation are not well known. Therefore, this project aims to monitor changes in Hg bioaccumulation that may occur after the planned breach of Pond A8, which will return it to muted tidal action. Biosentinel monitoring is being coupled with water and sediment chemistry to understand the processes that cause changes in Hg bioaccumulation and to determine if and how the operation of the A8 Notch causes a direct change in MeHg production in Pond A8 or in Alviso Slough. An increase in the bioavailability of MeHg could negatively impact breeding waterbirds, a result opposite to the management goal of restoring waterbird habitat for the Don Edwards San Francisco Bay National Wildlife Refuge and the SBSP Restoration Project. An increase in MeHg export to surrounding waters, habitats, and the wider Bay also could have important regulatory ramifications. By monitoring across multiple habitats and spatial scales, we will increase the information that managers can draw upon as they attempt to minimize Hg risk while moving forward with restoration. As such, the primary objectives of this project are to:

- Assess the impact of the A8 notch on Hg cycling within Pond A8 and Alviso Slough main-channel and adjacent marshes using an integrated biosentinel approach coupled with a stable isotope food web assessment, and process-level water-column and sediment studies.
- Determine the extent of the effect of the A8 notch implementation over time and with distance from the restoration site, and the relative effect among the different habitats and biosentinel species.
- Use water column and sediment mercury concentration and speciation data to link the underlying processes of MeHg production to bioaccumulation, and to investigate whether MeHg production potential changes as a function of changes in a) phytoplankton production, and/or b) Hg remobilization associated with Alviso Slough sediment scour.

The objectives described above are further divided into the following specific tasks as defined within the final scope of work:

- *Task 1a – Biosentinel Monitoring of Mercury in Waterbird Eggs*
- *Task 1b – Biosentinel Monitoring of Mercury in Fish within Ponds*
- *Task 1c – Biosentinel Monitoring of Mercury in Fish within Sloughs*
- *Task 2 – Stable Isotope/Trophic Relationship Assessment*
- *Task 3 – Sediment Mercury Dynamics*
- *Task 4 – Water Column Mercury Dynamics*
- *Task 5 – Reporting*

PROJECT SUMMARY TO DATE (BY TASK)

Task 1a – Biosentinel Monitoring of Mercury in Waterbird Eggs

USGS-BRD completed, finalized, and obtained approval from EPA for the QAPP for this project; a 26 page document entitled “Quality Assurance Project Plan for Monitoring Mercury in Waterbird Eggs in Association with the South Bay Salt Pond Restoration Project.”

USGS-BRD is currently performing mercury analysis for 15 eggs from 2 species (Forster's Terns and American Avocets) from four colonies sampled in 2010. USGS-BRD also has collected eggs from several additional colonies. Analysis of mercury at these locations is beyond the scope of work, so eggs will be archived until additional funds can be found.

Task 1b – Biosentinel Monitoring of Mercury in Fish within Ponds

USGS-BRD is tasked with collecting and analyzing fish within A8, A16 (recently breached 'control' pond), and A3N (non-breached 'control' pond) during a minimum of three sampling periods from April to August in 2010 and three sampling periods in 2011 bounding the breaching of A8 with Alviso Slough.

During 2010 USGS-BRD made extensive efforts to capture and collect fish at 3 sites within A8, 2 sites within A16, and 2 sites within A3N. The second sampling sites in both Ponds A16 and A3N are beyond the originally funded scope of work. Subsequently, fish collected from the 2nd site in Ponds A16 and A3N will be archived for later mercury analysis if additional funds are found.

Despite continued intensive fish sampling in Pond A8, we collected very few fish in A8 until the week of July 12-16, 2010 when the pipe from A7 to A8 was opened. Consequently, fish moved into A8 and during the July sampling event we were able to collect a number of fish from several species at the northern-most site in A8. However, it is important to note that these are likely A7 fish that had just recently moved into A8 and therefore will have a mercury signature representative of Pond A7 and not A8.

Since there were extremely low densities of fish in Pond A8 throughout the April-September sampling periods, USGS-BRD initiated a back-up plan and has continued to sample fish in salt ponds A5 and A7 which are adjacent to A8 (see map below). Together with A8, these two additional salt ponds will ultimately form the larger restored pond complex of A5/A7/A8. We will continue to collect fish in Ponds A5, A7, and A8, which is beyond the scope of the originally funded study. As such, fish will be archived and it will be subsequently determined which fish can be analyzed for mercury. Additional funds will be necessary to assess mercury concentrations in fish from the extra ponds and sites.

In addition to the added sampling sites in 2010, USGS-BRD also completed additional fish sampling on more dates so as to ensure a more robust time series of sampling around the timing of the A8 breach. This increased the sampling effort to 5 sampling sessions from April to September 2010, rather than the 3 originally funded sampling sessions. Fish from these additional time periods are beyond the scope of work originally funded, and will be archived for later mercury analysis if additional funds are found.

Currently, all fish sampled in 2010 have been identified, measured, weighed, and otherwise processed and are now ready for total mercury analysis. The next steps will be to dry and homogenize the fish samples, and then analyze them for total mercury. We anticipate the first year's mercury data analysis to be completed by the summer 2011.



Figure 1. Sampling locations (in orange) for biosentinel fish within ponds A8, A16 ('breached' control), A3N ('non-breached' control), A5 (back-up plan for A8), and A7 (back-up plan for A8).

Task 1C – Biosentinel Monitoring of Mercury in Fish within Sloughs

UC Davis is tasked with collecting and analyzing appropriate small fish biosentinels from a series of four sites along Alviso Slough and from a single control location on Mallard Slough, five sites in total. Alviso Slough sites include an upstream location near Highway 237 above the A8 notch, a site directly at the A8 notch, a site approximately midway down the slough below the notch, and a downstream site near the confluence with Coyote Creek. The work scope includes small fish collections from these 5 sites on 3-4 sampling periods per year between April and August of both 2010 and 2011 in relation to the opening of the A8 notch. Primary target biosentinel fish are threespine stickleback (*Gasterosteus aculeatus*) and Mississippi silverside (*Menidia audens*). The scope of work includes the collection and analysis, as available, of 10 individual stickleback to be analyzed individually and up to 48 silverside to be analyzed as 6 multi-individual composites for each site-sampling, with stickleback targeted at all 5 of the sites and silversides generally present at 4 of the 5 sites (all but the uppermost Alviso Slough location). The stickleback links directly to corresponding fish collections from the ponds by USGS-BRD, while the silverside composites link to the Bay-wide small fish mercury monitoring program conducted by UC Davis for the Regional Monitoring Program.

In 2010, slough fish work was conducted during April, June, July, and August, in conjunction with pond biota and water/sediment work by the two USGS teams. UC Davis provided water collections in the sloughs for USGS during 3 of the 4 sampling periods. A mid-sized research boat with a variety of large seines is required for the slough work. Some of the

chosen sites present substantial logistical challenges and there were a series of setbacks, including engine damage, destruction of nets by underwater hazards, and puncturing of our heavy-duty boat hull by submerged metal beneath one of the upstream bridges. Additionally, the uppermost site was found to contain very sparse resident fish populations, several of the sites require extreme low tides for effective sampling, and the life histories of some of the target species were found to move them away from some of the target locations in some seasons. Most of these complications have been dealt with throughout the year with multiple return trips and revised sampling approaches. It has been possible to obtain nearly ideal samples from most of the sites and dates. On some occasions and at some sites, it was necessary to shift to alternate biosentinel species.

UC Davis collections in 2010 were supplemented by a fifth full set of collections in September, corresponding with the extra work performed in the ponds by USGS-BRD. Rather than preparing and analyzing 10 stickleback per site-sampling as per the UC Davis work scope, this was increased to 12 stickleback analyses per sample. Additionally, in leveraged monitoring work for the RMP to be shared with this project, the base site of Alviso Slough was sampled in both November 2010 and January 2011 (in addition to fall sampling in each of the prior 5 years), with the Mallard Slough control site also sampled in January 2011. Numerous nearby comparison sites were sampled in the South Bay, in addition to dozens of other sites across the entire Bay.

At this time (January 2011) we are completing the processing and mercury analysis of 353 stickleback and silverside samples from the April, June, July, August, and September collections. This is in comparison to the originally planned and funded analysis of 296 total samples per year. We also have retained a good number of samples of additional potentially useful indicator species that might supplement and bolster trends detected in the primary species, particularly rainwater killifish (*Lucania parva*), topsmelt (*Atherinops affinis*), and northern anchovy (*Engraulis mordax*), but may need to secure additional sources of funding to be able to process and analyze these.

Sampling in Year 2 should benefit from the techniques and strategies developed in Year 1.

Task 2 – Stable Isotope/Trophic Relationship Assessment

USGS-BRD and USGS-FRESC have collected snails to base-line correct for nitrogen stable isotopes. Fish and waterbird eggs were also collected for stable isotope analysis as described above for mercury analysis, and are currently in the queue to be processed and then analyzed; first for total mercury concentrations and then for stable isotope levels. Isotope analyses are planned for after the 2011 field season (Fall 2011/Winter 2012) when both years of samples are able to be sent to the stable isotope laboratory for testing.

Task 3 – Sediment Mercury Dynamics

The USGS Water Resources Discipline (WRD) team is responsible for the collection and analysis of surface sediment (0-2 cm) samples at all locations sampled for biota as detailed above (three sites in Pond A8, one site in Pond A16, one site in Pond A3N, four sites along Alviso Slough, and one site in Mallard Slough). In support of our USGS-BRD colleagues 'back-up plan' for biota sampling due to the absence of fish in Pond A8, we also adapted our originally

funded sampling schedule to include single sites in Ponds A5 and A7, should the number of fish collected in Pond A8 be not sufficient. Sediment was collected at these 12 sites during May, June/July, and August of 2010, representing the 'pre-condition' relative to the operational initiation of the Pond A8 notch.

Sediment field samples were processed (sub-sampled and preserved for specific analytes) the day after field collection, and incubated for MeHg production potential (MPP) rates ($^{200}\text{Hg(II)}$ stable isotope incubations) and microbial sulfate reduction rates (^{35}S -sulfate radiotracer incubations) two days after field collection. Whole sediment also was sub-sampled and preserved for the following analytes: organic content (via Loss on Ignition), pH, oxidation-reduction potential, water content, bulk density, iron speciation (Fe(II) and Fe(III)), total reduced sulfur, grain-size, and Hg speciation (THg, MeHg, and Hg(II)_{R}). Sediment pore water was sub-sampled for: sulfate, sulfide, chloride, acetate, Fe(II), dissolved organic carbon (DOC), and specific-UV absorbance (SUVA). To date, all assays have been completed for sediment and porewater samples collected in 2010 except for those incubated with $^{200}\text{Hg(II)}$ to assess MeHg production potential rates. Problems with our ICP-MS had suspended the analysis of these samples, but those problems have now been solved and final analysis of samples for MPP rates should be completed by the end of February 2011. All sediment and porewater data collected to date has been summarized in an Excel database, and analysis of spatial and temporal trends for all sediment analytes has begun. Some highlights of these results will be presented at the upcoming SBSRP Science Symposium, scheduled for February 3rd, 2011, at the USGS facility in Menlo Park, CA.

Task 4 – Water Column Mercury Dynamics

With the assistance of USGS-BRD and UC-Davis colleagues for field sampling, the USGS-WRD team is responsible for the analysis of surface water samples at all locations sampled for biota as detailed above (three sites in Pond A8, one site in Pond A16, one site in Pond A3N, four sites along Alviso Slough, and one site in Mallard Slough). In support of our USGS-BRD colleagues 'back-up plan' for biota sampling, we also adapted our originally funded sampling schedule to include single sites in Ponds A5 and A7, should the number of fish collected in Pond A8 be not sufficient. Surface water was collected at these locations during April, May, June/July, and August 2010, representing the 'pre-condition' relative to the operational initiation of the Pond A8 notch. In addition, water samples were collected at a 2nd site in 'control' Ponds A3N and A16 during April 2010 (only). The USGS-BRD group conducted field collections of surface water in pond sites on all sampling occasions. The UC-Davis group conducted field collections of surface water for all slough sites on all sampling occasions, except during August 2010, when field collection was done by the USGS-WRD group.

Surface water samples were processed (filtered as appropriate and preserved for specific analytes) within hours of field collection. Analyses included: **particulate water parameters** – total-Hg, methyl-Hg, total suspended solids, chlorophyll-A, % Organic Carbon, % total nitrogen, ^{13}C stable isotope, and ^{15}N stable isotope; **dissolved (filter-passing) water parameters** – total-Hg, methyl-Hg, dissolved organic carbon, specific UV absorbance, reactive phosphorous (organic-P plus orthophosphate), and oxidized nitrogen (NO_3^- plus NO_2^-). To date, all assays have been completed for surface water samples collected in 2010. All surface water data collected to date has been summarized in an Excel database, and analysis of spatial and

temporal trends has begun. Some highlights of these results will be presented at the upcoming SBSRP Science Symposium, scheduled for February 3rd, 2011, at the USGS facility in Menlo Park, CA.

Task 5 – Reporting

We have completed all Quarterly Reports (submitted April, July and October 2010), as well as this Annual Report, on schedule as detailed in the Scope of Work grant document.

INTERIM MANAGEMENT RECOMMENDATIONS

- Find funds for total mercury analyses of the archived fish samples (A5, A7, A16, and A3N) to make conclusions more robust and find funds for total and methylmercury analyses of the archived sediment samples collected before the breaching of salt pond A6.
- Initiate a long-term mercury monitoring program for water, sediment, waterbird eggs, and fish at several fixed sampling sites that are sampled annually to assess the long-term impact of the South Bay Salt Pond Restoration Project on the mercury contamination of biota within the project area.

COMPLIANCE WITH TERMS AND CONDITIONS IN GRANT

- At this time, no extenuating circumstances exist, and we have not adjusted our research in any way that would substantially affect the final products.

BUDGET

Listed below is the original funded budget by task, the expenses used to date, and the remaining funds available on this project. All costs include benefits and administrative costs. This budget table summarizes the 3 separate Statement of Works and associated budgets arranged by the Resources Legacy Fund, and the requested re-characterization of our task list by the South Bay Salt Pond Restoration Project.

Task	Original Budget (Total)	Expenses to Date (1/28/2010)	Remaining Funds
(1A) Biosentinel Waterbird Eggs	49,528	18,884	30,644
(1B) Biosentinel monitoring of Mercury in Fish within Ponds	113,471	37,826	75,645
(1C) Biosentinel monitoring of Mercury in Fish within Sloughs	57,946	29,475	28,471
(2) Stable Isotope/Trophic Relationship Assessment	13,270	2,250	11,020
(3) Sediment Mercury Dynamics	48,412	22,666	25,746
(4) Water Column Mercury Dynamics	54,678	25,600	29,078

(5) Reporting	28004	12623	15,381
Operating Expenses: USGS-WERC	57,292	31,864	25,428
Operating Expenses: USGS-WRD	85,356	39,964	45,392
Operating Expenses: UC Davis	11,755	4,937	6,818
Total	519,712	226,089	293,623

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