

# South Baylands Mercury Project

## 2007 Year-end Progress Report



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## Executive Summary

The South Baylands Mercury Project was launched in 2006 and continues through the end of 2008. This project is a collaborative effort between the San Francisco Estuary Institute, United States Geological Survey in Menlo Park, and the Santa Clara Valley Water District to characterize mercury (Hg) in the sediment, water, and biota of the Alviso Pond and Slough Complex, as well as across the South Baylands.

This project aims to 1) quantify Hg concentrations in “sentinel” species indicative of different landscape management endpoints and the associated water and sediments, and 2) develop a pre-restoration baseline assessment of Hg concentrations, against which post-restoration conditions could be assessed. Based on these analyses, the potential risks of selected management alternatives related to Hg bioavailability can be assessed. The results from this study are designed to facilitate decision-making regarding management and restoration options for Pond A8.

Field sampling continued for a second year in 2007, with a focus on comparing mercury in the sediment, water, and biota of Pond A8 to that of Alviso Slough and its fringing marsh and tidal channels. Sediment was sampled in summer from four habitat types: Pond A8 borrow ditches and historic channels, Pond A8 mudflats, Alviso Slough main channel, and Alviso Slough marsh plain. Water was sampled approximately every two months from Pond A8, Alviso Slough main channel, and the fringing marsh. Sediment and water measurements included mercury species and ancillary parameters. Habitat-specific biosentinel species (fish, flies, and birds) were sampled in spring and summer from Ponds A8, A7, and A5; Alviso Slough and its fringing marsh; and marshes across South Bay.

All results to date are preliminary and are subject to change pending peer review and project completion. They are presented below as a demonstration of the progress made by this project and should not be circulated without the consent of the scientific institutions controlling that data.

Pond A8 tended to have more methylmercury than Alviso Slough and its fringing marsh, consistently across the three matrices of sediment, water, and biota. Restoration of Pond A8 to tidal marsh will likely reduce methylmercury in the sediment, water, and biota. The restoration of Pond A5 to tidal marsh may result in slightly higher methylmercury in the food web, but this result is based on data from biota only. The result of restoring Pond A7 is not clear and may differ depending on the sentinel species in question.

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## 1. Background on Project

This report describes the progress of the South Baylands Mercury Project during 2007. The purpose of this project is to assess the likely effects of alternative salt pond restoration or management plans and designs in South San Francisco Bay on mercury (Hg) availability to South Bay food webs. In 2007, the project focused on the Alviso Pond and Slough Complex plus reference sites south of Dumbarton Bridge. Project activities in 2007 were funded by the Santa Clara Valley Water District, California State Coastal Conservancy, and San Francisco Foundation on behalf of the South Bay Salt Pond Restoration Project (SBSPRP).

The study design is described in detail in the original project proposal (Collins et al. 2005) and will not be repeated in this progress report. The results presented herein are preliminary and not yet fully interpreted. These results should not be circulated without the consent of the participating agencies.

Forecasting the effects of intertidal landscape management on Hg bioavailability requires understanding of the complex relationship between intertidal physio-chemical processes and plant and animal ecology. To develop the needed understanding, the San Francisco Estuary Institute (SFEI), United States Geological Survey (USGS) of Menlo Park, and the Santa Clara Valley Water District (SCVWD) have collaborated on this project.

This project aims to quantify Hg concentrations in “sentinel” species indicative of different landscape management endpoints and the associated water and sediments and to develop a pre-restoration baseline assessment of Hg concentrations, against which post-restoration conditions could be assessed. Based on these analyses, the potential risks of selected management alternatives related to Hg bioavailability can be assessed.

The USGS studied Hg cycling in sediment to quantify total Hg (THg), methylmercury (MeHg), and reactive inorganic mercury ( $\text{Hg(II)}_R$ ) available for methylation in Pond A8 and Alviso Slough habitats, as well as the factors that control the transformation of inorganic Hg(II) to organic MeHg, and the correlation between Hg speciation in sediment and THg or MeHg concentrations in biota. In 2007, the sediment component of the project focused on sampling of surface sediment (top 0–2 cm) in Pond A8, Alviso Slough, and its fringing marsh in coordination with biota sampling. The field sampling of deep cores in Alviso Slough was previously completed in 2006, with a majority of the data presented in the 2006 Annual Report (Grenier et al. 2007). The remainder of the sample processing and data analysis associated with the 2006 deep-core sampling effort was completed during January thru July of 2007 and ultimately published as a USGS Open File Report in August 2007 (Marvin-DiPasquale and Cox 2007). Thus, only surface sediment sampling conducted during 2007 will be presented and discussed in the remainder of this annual report.

The SCVWD studied THg, MeHg, and other water quality parameters in the water of Alviso Slough, its fringing tidal marsh, and Pond A8. Water samples were analyzed for chemical indicators that correlate with Hg concentrations and bioaccumulation in

associated food webs. Tidal water draining from the fringing marsh was sampled to determine if the marsh plain was a source of MeHg to Alviso Slough and South Bay.

SFEI studied sentinel species indicative of Hg availability in habitats representing alternative tidal restoration or salt pond management plans and designs (Table 1.1). These sentinel species can be used to forecast habitat-specific Hg bioavailability before and after management actions. SFEI has also coordinated the project and provided data and GIS management.

## 2. Mercury Problem Statement

Mercury is a legacy contaminant, mined historically from the California Coast Ranges and transported to the Sierra Nevada for use in gold extraction during the 19th century Gold Rush. Mercury historically entered and continues to enter the Bay from the Sacramento and San Joaquin Rivers and from run-off from mines in local watersheds around the Bay. One of the major local sources of Hg has been the New Almaden Mining District in the watershed that drains through Alviso Slough. Other sources that contribute lesser but potentially significant amounts of Hg to the Bay include atmospheric deposition and urban and industrial runoff.

There is evidence that the transformation from inorganic Hg or Hg(II), which is not significantly bioavailable, to organic methylmercury (MeHg), which is the most toxic form of Hg and most readily enters food webs, can occur at high rates in natural environments subject to frequent wetting and drying. Therefore, the potential exists to increase Hg bioavailability in South Bay through hydrological modification of former salt ponds. Concentrations of total Hg in sediment and water tend to be greater in South Bay than in other parts of San Francisco Bay, and the Alviso Pond and Slough Complex contains more THg than other areas of South Bay (SFEI 2005, Marvin-DiPasquale and Cox 2007).

Higher THg in the Alviso area does not necessarily mean that restoration activities will worsen a mercury problem. The production of MeHg depends on many environmental factors in addition to the total amount of Hg. Also, the uptake of MeHg into food webs varies 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 THg and MeHg data have been collected previously at various locations in South Bay (David et al. 2002, Thomas et al. 2002, Conaway et al. 2003, Topping et al. 2004, Beutel et al. 2004, SFEI 2005), little is known about the regional and habitat-specific processes governing the transport and transformations of different mercury species, including Hg(II)-methylation, Hg(II)<sub>R</sub> concentrations, and MeHg uptake into food webs. Key questions addressed during the 2007 project year included the following:

- How might restoration of managed ponds to tidal wetlands impact the availability of Hg for methylation and uptake into the food web?

- Would conversion of Pond A8 to tidal marsh decrease or increase mercury bioavailability?
- What is the baseline of mercury in the Alviso Pond and Slough Complex prior to restoration or other landscape management actions?
- How does that baseline Hg condition for the Alviso Pond and Slough Complex compare to the ambient condition of comparable habitats in South Bay? This question will be answered more completely in 2008, but the answer begins with the sentinel bird data collected in 2007.

### 3. Approach and Assumptions

The approach to answering these questions was to compare samples collected in the Alviso Salt Ponds (mainly Pond A8) to samples collected in adjacent Alviso Slough and its fringing marsh. This approach was based on the following assumptions.

- The samples in Pond A8 were assumed to represent the current condition of Pond A8 prior to breaching.
- Fringing tidal marsh along Alviso Slough was assumed to be the best available surrogate for the brackish and saline marsh that would eventually develop in place of Pond A8 if it were subjected to fully tidal conditions, given its landscape position, anticipated salinity regime, and sediment sources.
- Ponds A5 and A7 are assumed to be the best available surrogates for the muted tidal lagoon or shallow subtidal and lower intertidal conditions forecasted for Pond A8 during the early stages of conversion to tidal marsh. Ponds A5 and A7 are currently perennial, subtidal ponds with some hydrological connection to Bay waters, and they are adjacent to Pond A8 and Alviso Slough. Following the initial restoration action of the reversible breach, Pond A8 will also be a perennial, subtidal pond with some hydrological connectivity to Bay waters.

### 4. Methods

#### 4.1. Sediment

##### Field Sample Collection

##### *Surface Sediment Sampling*

Surface sediment (0–2 cm) was collected at 20 sites during 2007, which included ten sites from Pond A8, five sites from Alviso Slough main channel, and five sites from Alviso marsh (Table 4.1.1). Sediment was collected using a polycarbonate core ring 2cm deep x 8cm in diameter. The core ring was pressed into the sediment until the top edge was flush with the sediment/water interface. A stiff plastic sheet was inserted under the bottom of the core ring which was then gently lifted out of the sediment. The resulting sediment patty was transferred into an acid-cleaned mason jar. Upon filling the jar with 4–6 patties, sub-samples were taken in the field for Hg speciation (THg, Hg(II)<sub>R</sub> and MeHg), pH, oxidation-reduction potential (ORP), grain size, and organic content as percent weight loss on ignition (%LOI), using a 3-cm<sup>3</sup> cut-off syringe. A final sediment patty was added to the mason jar, so that it was completely filled. The jar was stored on

wet ice until further processing back at the USGS Menlo Park laboratory. The above sub-samples were put in a cooler with dry ice and frozen in the field, then transferred to a freezer back at the laboratory until further processing.

### ***Sediment Pore Water Sub-sampling***

Pore water parameters were sub-sampled in the laboratory under anoxic conditions (in an N<sub>2</sub> flushed glove bag) on the day following the field collection. Sediment was transferred from the mason jars into plastic bags, where it could be more completely homogenized. Plastic centrifuge bottles (250 cm<sup>3</sup>) were filled to the shoulder with the homogenized sediment. The bottles were then centrifuged for 20 min at 3500 rpm, and subsequently were returned to the N<sub>2</sub> flushed glove bag, prior to removing the caps for further sample processing. The marsh plain sites (ASM-WS3, ASM-501, ASM-504, ASM-505, and ASM-506) were too dry to yield enough pore water volume to collect all of the sub-samples required. Therefore, 30 g of sediment and anoxic water (previously N<sub>2</sub> purged) were precisely weighed into the centrifuge bottles, and the exact pore water dilution was subsequently calculated (based on the original sediment porosity and bulk density). The pore water supernatant was decanted into the back end of a plastic syringe (with the plunger initially removed) that was fitted with a 1.6 μm glass fiber prefilter (Whatman 25 mm GF/A syringe filter) and a 0.45 μm nylon filter (Whatman 25 mm GD/X syringe filter). Replacing the plunger, the pore water was pushed through the filters and into the various containers pre-labeled and prepared for the collection of the various pore water constituents (i.e., sulfate and chloride, sulfide and conductivity). Every precaution was taken to minimize changes in redox-sensitive geochemistry between the time of field collection and subsequent sub-sampling and analyte-specific preservation. Precautions included: a) minimal holding times prior to sub-sampling, b) completely filling glass mason jars with sediment, and c) cold storage (on wet ice or refrigerated) during the holding period. Even with these precautions, some changes in redox chemistry may have occurred during the holding period and during the sample processing.

## **Laboratory Analysis**

### ***Sediment***

#### Total Mercury

Sub-samples for THg in sediment were assayed as per an approved USGS method (Olund et al. 2004), with modifications to the sample digestion. Once thawed, sediment samples (approximately 0.25 g wet weight) were initially digested for 24 hours at room temperature in Teflon bombs, using a mixture of 2 mL of concentrated nitric acid and 6 mL of concentrated hydrochloric acid. Subsequently, 22 mL of 5% BrCl was added to each sample. The samples were then heated to 50 °C in an oven overnight. Once the samples had cooled, a 5 ml sub-sample was transferred into a pre-combusted glass container and held until further analysis. The digestate was analyzed on an Automated Mercury Analyzer (Tekran Model 2600, Tekran, Inc., Canada), according to EPA Method 1631, Revision E (USEPA 2002). This standard method is based on the tin reduction of Hg(II) to gaseous Hg<sup>0</sup>, trapping Hg<sup>0</sup> on gold sand, thermal desorption, and quantification of Hg<sup>0</sup> via cold vapor atomic fluorescence spectrometry. Each batch of 10 environmental samples was accompanied by the analysis of the following Quality

Assurance (QA) samples: a) one certified reference material, b) one matrix spike sample, c) one analytical duplicate, and d) one method blank. Calibration standards were prepared from a NIST-certified commercially obtained  $\text{HgCl}_2$  standard. Quality control acceptance criteria for this assay is detailed in the published methods documents (Olund et al. 2004; USEPA 2002).

#### Reactive Mercury

Sediment “reactive” mercury ( $\text{Hg(II)}_R$ ) is methodologically defined as the fraction of THg in a sediment sample, which has NOT been chemically altered (e.g. digested, oxidized or chemically preserved), that is readily reduced to elemental  $\text{Hg}^0$  by an excess of tin chloride ( $\text{SnCl}_2$ ) over a defined (short) exposure time. This operationally defined parameter was developed as a surrogate measure of the fraction of inorganic  $\text{Hg(II)}$  that is most likely available to  $\text{Hg(II)}$ -methylating bacteria responsible for MeHg production. Upon thawing, sub-samples collected and frozen in the field for  $\text{Hg(II)}_R$  were assayed as previously described (Marvin-DiPasquale and Cox 2007).

#### Methylmercury

Upon thawing, sediment samples collected and frozen in the field for MeHg analysis were first sub-sampled (ca. 0.5 g wet weight) into plastic centrifuge tubes and extracted with 2 M sulfuric acid (10 ml) overnight while shaking (200 rpm) at 60 °C. Samples were then centrifuged and a 4 ml sub-sample of the supernatant was transferred into a Teflon distillation vessel containing an aqueous solution (6 ml) of 0.1 M sulfuric acid and 1% KCl. Distillation was conducted at 145 °C until approximately 80% of the solution in the distillation vessel was transferred to a Teflon collection vessel. A 2–5 ml aliquot of the distillate was sub-sampled into a trace-metal clean glass I-Chem vial. The vial was nearly filled with DI water, the pH was adjusted to 4.9 using acetate buffer, and an ethylated agent (sodium tetraethyl borate) was added. The vial was then topped off with DI water, capped with a Teflon septa screw top cap, and shaken well. MeHg was thus converted, within the vial, to volatile methyl-ethyl-mercury, which was subsequently analyzed on an automated MeHg analysis system (Brooks Rand Labs, Seattle, WA) using cold-vapor atomic fluorescence spectrometry (CVAFS) detection. Each batch of 11 environmental samples was accompanied with analysis of the following Quality Assurance (QA) samples: a) one certified reference material, b) one matrix spike sample, c) one analytical duplicate, and d) one method blank. Calibration standards were prepared from a crystalline MeHgCl and compared to a separate, commercially available MeHg standard solution.

#### Sediment pH

Sediment pH was collected and measured in the field. Measurements were made with a pH electrode used in conjunction with a hand held pH/mV multi-meter (Model 59002-00, Cole Parmer®, Vernon Hills, IL). The electrode was calibrated daily with fresh, commercial (pH = 7) phosphate buffer and then rinsed clean with reagent water. The probe was fully inserted into a 20 ml PET plastic vial containing approximately 15 cm<sup>3</sup> of sediment sub-sampled from the sediment composite mason jar for that site. The pH electrode was gently swirled in the sediment matrix until a stable pH reading was achieved.



### Oxidation-Reduction Potential (ORP)

Sediment ORP was collected and measured in the field. Measurements were made with a platinum band ORP electrode (Model EW05990-55, Cole Parmer®, Vernon Hills, IL) used in conjunction with a hand held pH/mV multi-meter (as above). The electrode accuracy was tested daily with freshly made buffer solutions (pH = 7 and pH = 4) saturated with quinhydrone, as per the manufacturer instructions (Cole-Parmer Document #P1937). The ORP potential for each solution was measured and the difference between them calculated. If this value fell within the range of  $173 \pm 4$  mV, the probe was determined to be functioning properly. After cleaning thoroughly with reagent water and drying, the probe was then fully inserted into a 20 ml PET plastic vial containing approximately 15 cm<sup>3</sup> of sediment sub-sampled from the sediment composite mason jar for that site. The ORP electrode was allowed to equilibrate for a minimum of 10 minutes, until a stable reading was achieved, prior to recording the milli-volt (mV) value. The ORP meter values were subsequently converted to E<sub>h</sub> values (which is a standard convention that adjusts the value assuming a normal hydrogen reference electrode), using the following conversion:

$$E_h = \text{ORP (meter value)} + \text{ER}$$

$$\text{ER} = (-0.718 \times T) + 219.97$$

Where: ER = is the standard potential for a normal hydrogen reference electrode and T = temperature (°C)

### Bulk Density, Percent Dry Weight, Porosity and Organic Content

Sediment bulk density, dry weight, porosity and organic content were assayed (in the order listed) from a single sediment sample. An exact 3.0 cm<sup>3</sup> of wet sediment was removed from the sample vial using a 3.0 cm<sup>3</sup> plastic syringe that had the needle end cut off of the syringe barrel. This sub-sample was transferred into a small crucible and weighed. Sediment bulk density (g/cm<sup>3</sup>) was then calculated as the weight:volume ratio.

Sediment dry weight and porosity were measured using standard drying techniques (APHA 1981a). The crucible containing the wet sediment was placed in an oven overnight at 105 °C. The next day, the sample was placed in a desiccator to cool, and then reweighed. The sediment percent dry weight is then calculated as [dry wt/wet wt x 100]. Sediment porosity (mL porewater per cm<sup>3</sup> of wet sediment) was calculated as the volume of water lost upon drying divided by the original sediment wet volume.

Organic content was assessed via the Loss on Ignition (LOI) standard assay (APHA 1981b). The crucible containing the oven-dried sediment is then placed in a combustion oven at 500 °C for four hours. This completely burns off any organic constituents, leaving only mineral material. After cooling and reweighing, the percent weight loss was calculated.

### Grain Size

Grain size, as greater or less than 62 microns (the sand/silt split), was assayed using a standard wet sieve method (Matthes et al. 1992).

### ***Sediment Pore Water***

#### Anions: Sulfate and Chloride

Filtered samples of sediment pore water sulfate and chloride were collected under anaerobic conditions as described above, transferred to 13 cm<sup>3</sup> crimp-sealed serum vials and stored frozen until analysis. Sulfate and chloride were measured on an ion chromatograph (Dionex Model DX-300, Sunnyvale, CA) equipped with an auto-suppressor, an IONPAC AG4A-SC guard column, AS4A-SC analytical column and mobile phase consisting of 1.8 mM Na<sub>2</sub>CO<sub>3</sub> and 1.7 mM NaHCO<sub>3</sub>. Quality assurance included calibration standards, laboratory reagent blanks, filter blanks, and analytical duplicates.

#### Sulfide

Filtered samples of sediment pore water sulfide were collected (3 mL) under anaerobic conditions as described above, preserved with sulfur antioxidant buffer (SAOB, 3 mL), and transferred to 13 cm<sup>3</sup> crimp-sealed serum vials and refrigerated until analysis. Analysis of sulfide was carried out using a sulfide ion-specific electrode, which was calibrated just prior to use. Quality assurance included calibration standards, laboratory reagent blanks, filter blanks, and analytical duplicates.

#### Conductivity

Filtered samples of sediment pore water conductivity were collected under anaerobic conditions as described above into glass scintillation vials and refrigerated until analysis. Conductivity measurements were carried out using a hand held conductivity meter (Cole Parmer® Model 19815-00, Vernon Hills, IL). The meter was calibrated just prior to use by a one-point calibration check using a commercially certified standard (Oakton Instruments, Vernon Hills, IL).

### **Quality Assurance**

The specific QA/QC measures taken for each analyte are noted above in the Laboratory Analysis section. The specific quantified results for each QA metric are given in Table 4.1.2.

## **4.2. Water**

### **Field Sample Collection**

Water Samples were collected by the Santa Clara Valley Water District (as described below) in November 2006 and January, March, May, July, and August 2007, and included three sites each from Alviso marsh, Pond A8, and Alviso Slough main channel. In addition to overlying water samples sent to a commercial laboratory for mercury speciation, a one liter bottle of overlying water from each site/depth was initially stored in a cooler with ice, delivered to the USGS laboratory on the day of collection and stored refrigerated until further processing the next day. Overlying water samples were then filtered (0.45 µm) and analyzed for dissolved organic carbon (DOC), specific UV absorption (SUVA), chloride, sulfate, and total suspended solids (TSS) as described below. These assays were not part of the original contracted work. However, after considering the value of such measurements in understanding the seasonal changes in

plankton versus terrestrial organic matter in each habitat, the project team decided these were worth analyzing.

### ***Alviso Slough***

Station ASW1 was at mid-channel adjacent to freshwater tidal marsh near the proposed breach at the south end of Pond A8. Station ASW2 was at mid-channel adjacent to brackish tidal marsh upstream of ASW3. Station ASW3 was at mid-channel adjacent to saline tidal marsh and near the existing intake at Pond A7. There were two water grabs per station; one at the water surface and one at about 25 cm above the Slough bottom. Surface samples were collected directly into the sample container by submerging the bottle, removing the cap, filling, and replacing the cap. Sample containers were double-bagged and handled using a two-person “clean hands, dirty hands” method. Samples at depth were collected about 25 cm above the Slough bottom using a 2.2-Liter Van Dorn Beta-type (Wildco) sampling device. After retrieval, sample containers were filled directly from the device. Sample containers were double-bagged and handled using a two-person “clean hands dirty hands” method.

All samples were taken during the early part of the ebb phase of an over-bank tide near the end of a spring tide series.

### ***Tidal Marsh***

Stations ASMW1, ASMW2, and ASMW3 were located in small, intertidal channels at least 10 m into the fringing tidal marsh from the Alviso Slough bank in freshwater, brackish, and saline reaches of the Slough, respectively. One depth-integrated water grab was taken at each station.

All samples were taken during the early part of the ebb phase of an over-bank tide near the end of a spring tide series. This assured that the samples represented return water from the adjacent tidal marsh.

Samples were collected into an acid-cleaned glass container by submerging the container into a flowing stream. Each station used a dedicated glass container to avoid cross-contamination. After retrieval, sample containers that could not be filled by submersion were filled directly from the glass container. Sample containers were double-bagged and handled using a two-person “clean hands, dirty hands” method.

### ***Pond A8N***

Station A8WF1 was located in shallow water along the northwest pond shoreline. Station A8WF2 was located in shallow water along the southeast pond shoreline. Station A8WD1 was located in a deeper water area of the interior of the Pond. There was one grab taken near the Pond bottom at stations A8WF1 and A8WF2. Two grabs were taken at station A8WD1, one at the water surface and one about 25 cm above the Pond bottom. All station locations were electronically recorded using Geographic Positioning System (GPS) Garmin GPSmap 76CSx (Table 4.2.1).

All samples were taken within two days of the sampling dates for Alviso Slough and its fringing tidal marsh.

## **Laboratory Analysis**

### Total Mercury (low level)

500-ml acid-cleaned borosilicate glass containers with BrCl preservative or unpreserved sets of four 40-ml glass vials provided by the laboratory were used. Unfiltered samples were analyzed for mercury using EPA Method 1631, with a Reporting Limit of 0.50 nanograms per liter (ng/l).

### Total Methyl Mercury

250-ml acid-cleaned polycarbonate containers with HCl or H<sub>2</sub>SO<sub>4</sub> preservative provided by the laboratory were used. Unfiltered samples were analyzed for mercury using EPA Method 1630 (modified), with a Reporting Limit of 0.05 nanograms per liter (ng/l).

### Total Suspended Solids

Both USGS (Menlo Park, CA) and SCVWD analyzed water samples for total suspended solids. Each method is discussed below.

SCVWD analyzed unfiltered samples for Total Suspended Solids using EPA Method 160.3, with a Reporting Limit of 10 milligram per liter (mg/l).

USGS (Menlo Park, CA) analyzed samples for total suspended solids (TSS) that were collected on pre-weighed combusted 0.7 µm glass-fiber filters used during the DOC filtration, with the exact volume of water filtered recorded. The filters were then placed into plastic petri dishes and were dried in a dessicator for more than 30 days before a final dry weight was recorded.

### Dissolved Organic Carbon & Specific UV Absorption

Overlying water dissolved organic carbon (DOC) and specific ultra-violet absorption (SUVA) analysis were conducted by the USGS (Menlo Park, CA) according to EPA Method 415.3 (USEPA 2005). Within 24 hours of initial field collection, samples for DOC/SUVA were filtered through 0.45 µm membrane filters (and a pre-combusted 0.7 µm glass-fiber filter) on a vacuum filter rig, which was rinsed three times with approximately 100 ml of sample prior to final collection. The resulting filtrate was sub-sampled into acid-cleaned and pre-combusted glass containers. The sub-samples receive a final concentration of 0.1% HCl as a preservative, and to drive off inorganic carbon in solution. Samples were held refrigerated in the dark until further analysis (within 28 days). DOC was assayed using high temperature combustion and IR detection on a Total Organic Carbon Analyzer (Model TOC-VCPH, Shimadzu Scientific Instruments, Columbia, MD). UV-A was measured spectrophotometrically at 254 nm using a Shimadzu Model UV-1601 spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD). Quality assurance measures included calibration standards, laboratory reagent blank, and filter blanks, as detailed in the above EPA method.

### Sulfate and Chloride

Overlying water sulfate and chloride were measured via ion chromatography according to EPA Method 9056A (USEPA 2000), using a Dionex Ion Chromatograph (Model DX-300, Sunnyvale, CA) as described above for pore water. Samples were initially processed

along with those for DOC (as above), but were not preserved with 0.1% HCl. Quality assurance measures included calibration standards, laboratory reagent blank, filter blanks, and analytical duplicate samples, as detailed in the EPA method.

### **Field Analysis**

Measurements of pH (Units), Temperature (°C), Specific Conductivity (ms/cm), Dissolved Oxygen (mg/l), and Turbidity (NTU) were recorded at each sampling depth using a Horiba U-10 Water Quality Checker (Horiba). The Horiba was inserted directly into the water at depth, when possible. Otherwise, samples were collected into a triple-rinsed collection beaker into which the Horiba was inserted.

### **Quality Assurance**

A QA/QC review was performed on all associated QA data. For TSS, at least one laboratory duplicate and one lab blank were run with each analytical batch. For the lab duplicate, the relative percent difference (RPD) was calculated between the parent sample and lab duplicate. The benchmark for acceptable data was a RPD < 20%.

Two batches that included samples collected from the marsh and slough sites on November 16, 2006 had Non-Detectable (ND) concentrations below the Reporting Limit of 10 mg/l. Although the blank and duplicate analyses for these batches met QA criteria, the results were rejected because they were inconsistent with the universe of similar analyses conducted for this study. In the context of the data from these sites, it is illogical that all of these samples would be ND.

The duplicate for two batches that included samples collected from Pond A8 on March 29, 2007 and May 17, 2007, and the duplicate for one batch that included samples collected from Alviso Slough and its fringing marsh on July 12, 2007 were reported to be outside the RPD limits. The results for these batches were included in Figure 5.2.2, because they were similar to the results from other dates. However, they should not be considered reliable.

All unfiltered Total MeHg analyses were conducted by Brooks Rand Laboratories (BRL), which also conducted unfiltered THg analyses for the slough and marsh samples collected on November 16, 2006. At least one sample of certified reference materials (CRM), two matrix spikes, three Continuing Calibration Verification samples and four method blanks were run with each analytical batch. BRL reported that all analyses met QA criteria, and all data are considered usable.

All other THg analyses were conducted by TestAmerica (November 14, 2006 pond samples; January 25, 2007 and January 30, 2007 all sites; March 27, 2007 and March 29, 2007 all sites; May 14, 2007 and May 17, 2007 all sites) or its subsidiary STL (July 12, 2007 and July 16, 2007 all sites; August 27, 2007 and August 29, 2007 all sites). TestAmerica batches included a blank, duplicate and one matrix spike analysis. STL batches included a blank, duplicate and two matrix spike analyses. Matrix spike and matrix spike duplicate analyses did not meet QA criteria for most of the slough and marsh samples collected on January 30, 2007; all of the pond samples and some of the

slough samples collected on March 27, 2007 and March 29, 2007; all of the slough and marsh samples collected on July 12, 2007. Nevertheless, these data were accepted because the results are consistent with the universe of similar analyses conducted for this study.

### **4.3. Biota**

#### **Sampling Design**

The biota sampling was designed to allow comparisons among different habitats and geographic areas (Table 1.1). Sentinel species of brine flies and demersal fish were used to compare the salt ponds (Ponds A8, A5, & A7) to each other and to the adjacent fringing tidal marsh along Alviso Slough. Samples were taken from Ponds A5 and A7 only when the necessary samples could not be obtained from Pond A8. Sentinel birds were used to compare the marshes of Alviso Slough to the ambient condition of marshes across South Bay. The sampling area of Alviso Slough marsh extended from the mouth of the slough to several hundred meters east of the Gold Street Bridge. Reference marshes around South Bay were all south of the Dumbarton Bridge.

Sample sites were selected using the Generalized Random Tessellation Stratified (GRTS) approach (Stevens and Olsen 2004). Randomly selected sites tend to represent conditions that vary in their relative abundance. Sites representing more common conditions are more likely to be selected. GRTS accounts for the different inclusion probabilities of randomly selected sites, and therefore allows the data collected at different sites to be weighted based on the relative abundance of the conditions they represent. GRTS is especially useful for ambient surveys intended to characterize conditions across a variable landscape. To apply GRTS, a map (i.e., a sample frame) is needed of all possible sample sites stratified according to the differences in condition that need to be accounted for in the sample design. For this project, a map developed by SFEI of high (mature) and low (immature) tidal marshlands was used as the sample frame. The sample frame for reference marshes included all marshes south of the Dumbarton Bridge, with the exception of Mowry Marsh.

Samples were collected as near to the randomly selected sites as possible, but access was sometimes limited by logistical issues. At the tidal marsh sites, demersal fish were collected from small channels analogous to those used for water sampling. At the Alviso Slough sites, pelagic fish were collected from the edge of the main channel. There was less Pond habitat than anticipated for sampling brine flies and fish. To meet sample size goals for these sentinel species, they were sampled opportunistically where available, mostly in or near borrow ditches along the Pond perimeters.

#### **Field Sample Collection**

##### ***Demersal and Water-column Fish***

Fish were collected from April through June in Ponds A8, A7 and A5 and in the fringing marsh along Alviso Slough. Few fish remained in Pond A8 at the initiation of sampling, due to high salinity in this seasonal pond after a very dry winter. Therefore, fish samples

were collected mainly from Ponds A5 and A7. These ponds house the source population of fish that enter Pond A8 when water is transferred during pond management events.

In Pond A8, fish were sampled near the culvert connecting Ponds A8 and A7. This was the only area of the Pond where salinities were low enough for the fish to survive by early April 2007. Fish had arrived in the Pond the previous October, when it was filled for duck hunting season. There was initial concern that these fish had recently entered Pond A8 through the culvert and therefore represented conditions in Pond A7. However, the mercury data dispelled this concern; fish in A7 had very different mercury signals than fish in A8. The many fish collected in this small patch of habitat near the culvert in Pond A8 probably congregated there from locations across the Pond as it dried.

Demersal sentinel fish were collected using baited minnow traps in the fringing marsh channels along Alviso Slough and in Ponds A5, A7 and A8. Traps were baited with mackerel or cat food and set for a period of 4 hours to 5 days in the tidal marsh and 1–14 days in the Ponds. Trapped fish could not access the bait, which was contained in metal cans with only very small slits that allowed the scent of food to enter the water. Water-column sentinel fish were collected by beach seine from the main Alviso Slough channel and the Ponds. At tidal marsh sites, the beach seine was walked out into the channel with a person at either end, then extended to the full length of the net and hauled back to shore. In deeper water, the net was set out from a small boat with one person in the water on one end of the net.

All fish were stored in the field in Zip-Lock© freezer bags on ice. After field collection, but before shipment to the analytical lab, fish were weighed, measured for total length, and rinsed with de-ionized water. Water-column fish (Mississippi silverside and threespine stickleback) were grouped into composites by species. Demersal fish (yellowfin goby and longjaw mudsuckers) were not composited. The relationship between fish length and mercury concentration was controlled by restricting the fish sample to individuals within a small size range for each species. Whenever possible, the smallest fish was no smaller than 75% of the length of the largest fish (Table 4.3.1). Fish samples were double-bagged in Ziploc freezer bags at -4 °C until shipment to the analytical lab.

### ***Brine Flies***

Brine flies were collected from Pond A8 and Alviso Slough marsh using sweep nets and pan traps. In the marsh, flies were collected from the main channel or large secondary channel nearest the randomly generated sampling points. No brine flies were found in the fresher reaches of Alviso Slough, where the vegetation was brackish. Flies were observed moving as far as 75m between habitat patches. Therefore, flies collected less than 75m apart in the same habitat type and not separated by a levee or other physical barrier were combined into the same sample.

Sweep nets were used in areas of high fly density, by swinging the net just above the water or sediment surface. In areas of low fly density, pan traps were set out for 1–4 hours. Pan traps were aluminum pans filled with distilled water plus a small amount of

liquid soap to break the surface tension and prevent flies that landed in the pan from escaping. Flies captured in pan traps were rinsed with distilled water immediately after collection to remove any soap residue. Flies were immediately placed in Ziploc freezer bags containing Kimwipes to absorb excess moisture and kept on ice in the field until they could be transferred to a freezer (-4 °C). Before being sent to the analytical lab, flies were rinsed in de-ionized water and sorted by taxa under a dissecting scope. Voucher specimens were sent to Dr. David Herbst at the Sierra Nevada Aquatic Research Laboratory for taxonomic verification. All brine flies analyzed for this project were classified into three taxa: *Ephydra cinerea*, *E. millbrae*, or *Parydra* spp.

### ***Resident Marsh Birds***

Song Sparrow, Common Yellowthroat, Marsh Wren, and other avian species were collected by mist net from the marsh along Alviso Slough and from five reference marshes in South Bay. Birds were collected in May and June, during the height of the breeding season, when these species were territorial. Four to six nets were set at each sampling location. Nets were set in the early morning in areas where birds were active and foraging. Nets were usually set perpendicular to small sloughs in areas of dense *Grindelia* or adjacent to *Scirpus* patches.

After being extracted from the nets, birds were weighed and measured, and their sex and age were determined whenever possible. Blood samples of 10–100 µl were collected by brachial veinipuncture. A small needle was inserted to perforate the brachial vein at the angle of the wing, and then blood was collected in a heparinized microcapillary tube. Capillary tubes were capped with flexible plastic plugs to prevent moisture loss and then placed in larger tubes for transport and storage. Feather samples were also taken, consisting of several body feathers and the distal half of the first primary flight feather (snipped at the coverts) from the right wing. For each bird, body and flight feathers were stored in separate envelopes at ambient temperature, and blood samples were kept on ice in the field until they could be transferred to a freezer (-4 °C) awaiting shipment to the analytical lab. Birds were marked with USFWS metal bands and unique color band combinations for field identification. All birds were released following sample collection.

### **Laboratory Analysis**

All biota samples were sent to the Trace Element Research Laboratory in the College of Veterinary Medicine at Texas A&M University to be analyzed by Dr. Robert Taylor and his staff. This laboratory has extensive experience with analysis of animal samples of very small mass for Hg. Avian blood and whole-body flies and fish were shipped to the analytical lab on dry ice.

### ***Vertebrate Sample Analysis for Total Hg***

Avian blood samples were extracted from capillary tubes and diluted with 2.0 ml of double de-ionized water. Blood was then homogenized and prepared for THg analysis according to TERL SOP-ST16, reducing volumes of reagents to account for small sample volume. Fish samples were freeze-dried using a LabConco Freezone 12L. Fish were dried for three days until all of the moisture was removed. Fish (both individuals and



composites) were then homogenized using a Retsch ZM200 ultra centrifuge mill with titanium parts. Fish samples were then frozen until analysis.

Prior to analysis, whole-body fish and avian blood samples were digested using nitric acid, sulfuric acid, potassium permanganate, and potassium persulfate. Digest solutions were then reduced with hydroxylamine hydrochloride to eliminate excess  $\text{MnO}_2$ . Vertebrate samples were analyzed for total Hg using a Milestone DMA 80. Samples were placed in a nickel boat, combusted in an oxygen-rich atmosphere, passed through a heated catalyst to complete oxidation, and then passed through a gold column which traps Hg. Post combustion, the gold column was heated and trapped Hg was released to quantify by atomic absorption.

#### ***Invertebrate Sample Analysis for MeHg***

Brine fly samples were freeze-dried using a LabConco Freezone 12L. Samples were dried for three days until all of the moisture was removed. Samples were then homogenized using a Retsch ZM200 ultra centrifuge mill with titanium parts and then frozen until analysis. Invertebrate samples were analyzed as composites. MeHg concentrations were determined using a modification of Wagemann et al. (1997). Aliquots of dry, powdered sample were extracted under acidic conditions combining  $\text{CuSO}_4$  and KBr into a mixture of methylene chloride and hexane. Solvent was evaporated, and the extracted MeHg was converted to  $\text{Hg}^{2+}$  via oxidation with BrCl and detected by cold vapor atomic absorption spectroscopy (CVAAS). A Cetac 7500 Quicktrace instrument was used for the CVAAS measurement. Calibration included a blank and five standards. Quality control (QC) samples included a method blank, a certified reference material (NRC DOLT-3), a duplicate sample, and a laboratory control sample (LCS, also referred to as a spiked blank) and spiked sample. The LCS and spiked sample were spiked with a MeHg solution prepared by dissolving MeHgCl (Johnson Mathey Electronics) in ethyl alcohol and then preparing working solutions by diluting further with deionized water. All QC samples were run at a frequency of at least 5% (i.e., at least 1 of each for every twenty samples).

#### **Quality Assurance**

A QA/QC review was performed of all associated QA data. A laboratory duplicate, two certified reference materials (CRM), a matrix spike, and a lab blank were run with each analytical batch. Each analytical batch contained a maximum of twenty field samples. For lab replicates, the relative percent difference (RPD) is calculated between the parent sample and lab duplicate. The benchmark for acceptable data is a  $\text{RPD} < 25\%$ . To date, all duplicate results have been below this benchmark. For CRMs, the percent recovery is calculated between the analytical result and the certified value. The benchmark for acceptable data is recovery in the range of 70–130%. To date, all CRMs have been within this target range. For matrix spikes, the percent recovery is calculated between the parent sample, the spike sample result, and the spike amount. The benchmark for acceptable data is recovery in the range of 70–130%. All recoveries for matrix spikes were within the target range. For blank records, any blank contamination in the analytical process was determined by comparing the quantified blank result against the Method Detection Limit (MDL). If the quantified value was greater than the MDL, then

there was blank contamination. If the field sample quantified value was less than three times the quantified blank value, then the field sample was considered to be blank-contaminated and the result was regarded as unusable. In such a case, the field result concentration was too close to the blank result to differentiate between an actual sample hit and the blank contamination. To date, some blank values have been greater than the MDL of the blank, but none of the field samples have been less than three times the blank result. Therefore, all data have been deemed usable.

## **Statistical Analysis**

### ***Demersal and Water-column Fish***

Fish data analyses were conducted using dry-weight concentrations of total mercury. One fish sample (ID 417-012) was excluded, due to concern that the fish may have been collected dead. The mercury data were log-10 transformed, as necessary, to meet assumptions of parametric analyses.

For comparisons among the Pond and Alviso Slough habitats, only fish samples that fell within the size limits (Table 4.3.1) were included. The mercury data clearly indicated that, within a species, each pond represented a different population of mercury values (e.g., mudsucker mercury concentrations from Pond A8 and Pond A5 could not be pooled as if they were drawn from the same population). Therefore, mercury concentrations from each Pond and from Alviso Slough tidal channel habitats were compared to each other, rather than pooling all the pond data and comparing them to the Alviso Slough data. ANOVA and t-tests were used to investigate differences in mercury within a species among habitat types and geographic areas, and Bonferroni corrections were applied to ANOVA post-hoc comparisons. Only mudsucker data were log-transformed for these comparisons.

Two covariates were examined that might have affected mercury concentrations in fish: fish length and date of sampling. To examine the length:mercury relationship, samples of mudsuckers and stickleback outside the target size ranges were analyzed for mercury. These data provided a range of lengths at two sites for each species, one in the Ponds and one in Alviso Slough or the fringing marsh channels. Mercury was regressed on length for each site-species combination using log-transformed mercury data. For each species, one of the sites showed a significant ( $p < 0.05$ ) effect of length on mercury and the other did not. For mudsuckers, the site with a significant regression was in the tidal marsh channels, while for stickleback it was in the Ponds.

These results indicate a slight increase of mercury with increasing length, at least at some sites. Therefore, bias in lengths within the size limits among the different geographic areas was examined for mudsucker and stickleback. No bias in length among geographic areas was found (ANOVA,  $p < 0.05$ ), and there was only very minor variation in the distribution of lengths. Data from yellowfin goby and Mississippi silverside were insufficient to examine length:mercury relationships. Nevertheless, there was no bias in length among the geographic areas for these species.

The data were also explored for trends in mercury over time within each geographic area for each species. Results from the CalFed Bird Mercury Project have indicated that mercury in small fish from the Alviso Pond Complex can change over the short time period of three weeks (C. Eagles-Smith pers. comm.). There was no relationship between mercury and date of sampling, based on visual examination of scatter plots of mudsucker and stickleback data. Yellowfin goby and silverside had too few data to adequately assess this relationship, yet the goby data suggested an increase in mercury over time. The gobies from Alviso Slough were collected nine days later, on average, than those from Pond A5. This slight difference in the timing of sampling may have contributed slightly to the result that gobies from the Slough had higher mercury than gobies from the Pond. However, even gobies collected during the same week tended to have higher mercury in the Slough than in the Pond.

### ***Brine Flies***

Methylmercury concentrations in composite *Ephydra* samples from Alviso Slough and Pond A8 locations were compared using dry weight concentrations. Two samples from Pond A8 with very low percent moisture were not included in the analysis, due to concern that the flies may have been collected dead. Methylmercury concentrations from both the Pond and marsh sample populations were normally distributed. The variance was unequally distributed, however. Therefore, a Kruskal-Wallis one-way ANOVA was used, rather than parametric statistics. The mercury analysis for *Parydra* brine flies is pending.

### ***Resident Marsh Birds***

A more complex statistical analysis method was used for the avian data, because they were collected across a broader range of habitat conditions and geographic areas. This broader scope afforded the opportunity to examine the possible effects of marsh salinity (as evidenced by dominant plants) and elevation (as evidenced by USGS data on subsidence) on mercury concentrations in birds.

The birds were the biosentinels for which the GRTS sampling design could be followed most precisely in the field. Therefore, site was used as a random variable during statistical analysis, and the assumption was made that the sampling locations were representative of South Bay marshes as a population. A general linear mixed model (PROC MIXED in SAS v. 9.1; Littell et al. 1996) was used to examine spatial variation in mercury concentrations for Song Sparrow, Common Yellowthroat, and Marsh Wren. Model structure in PROC MIXED is similar to a traditional general linear model (ANOVA) approach, except that PROC MIXED allows for the rigorous modeling of random effects. A mixed model procedure was used to treat sampling site as a random effect. Thus, the findings can be more confidently extrapolated to geographic areas, rather than just to the particular sampling locations.

Spatial differences in mercury concentrations were examined in the sentinel bird data. Sites with two or fewer samples of a given species were excluded. Geographic area was treated as a fixed effect in the model and represented either Alviso Slough or the other marshes across South Bay, which gave a reference for ambient condition. In addition to the influence of site and geographic area, habitat variables (subsidence and salinity) were

examined for their influence on mercury concentrations in Song Sparrows. This species was chosen for more detailed analysis, as it represented the largest dataset of the three target species.

Deviations from the assumption of normally distributed values and equal variances were examined using the residuals of the mixed model analysis for each species. Raw mercury values were used in the analysis of Common Yellowthroat. For Marsh Wren, a log-10 transformation was necessary to meet assumptions, while a square-root transformation was necessary for the Song Sparrow data.

The mixed model procedure employed dummy variables to determine differences in mercury concentration among geographic areas and locations, and, in sparrows, due to subsidence and salinity. Significant interactions among model effects were tested for each species. Only for Song Sparrows was an interaction suggested (Site x Salinity;  $p = 0.06$ ). For this analysis, site was selected in lieu of salinity, since salinity was not significant ( $p = 0.38$ ).

#### **4.4. Data Management**

The data for the South Baylands Mercury Project were stored in an Access 2003 relational database. Field data and lab results for all three matrices (sediment, water, and biota) were initially submitted as Excel spreadsheets. These spreadsheets were reviewed for accuracy and completeness by a data manager at SFEI and revised as needed before being imported into the Access database. Overall, data management activities for this project were shaped by an objective to create a consistent and standardized format for representing both field and lab results across all three matrices.

A connection from the Project database to a GIS was established to display the results of queries returning unique sampling locations and mercury concentrations per species. The map figures were designed using a combination of ESRI ArcInfo 9.1 and Google Earth 4.2 software, and are in California Teale Albers NAD 83 and Simple Cylindrical WGS84 projections, respectively.

### **5. Results and Discussion**

All results to date are preliminary and are subject to change pending peer review and project completion. They are presented below as a demonstration of progress during 2007 and should not be circulated without the consent of the scientific institution controlling that data. Results are presented with little or no interpretation, as many samples already collected remain to be analyzed, many samples have not yet been collected, and not enough time has passed to allow the research team to thoroughly synthesize the data in hand, particularly synthesis among the individual datasets collected by each of the cooperating research groups.

Sediment and water collection sites are shown in Figure 5.1, and maps showing the many biota sampling locations appear later in this document. The sediment and water locations are shown separately to facilitate tracking the descriptions below with their labeled locations on the map.

## 5.1. Sediment

The sediment data collected to date were grouped into four habitat categories for the purposes of statistical and graphical analysis, a) Pond A8 mudflats [A8-MF], b) Pond A8 historic channels and borrow ditches [A8-CH] (Figure 5.1), c) Alviso Slough main channel [AS-MC], and d) Alviso slough vegetated marsh plain [AS-MP]. Each category represents five samples. The following section uses these designations to present and discuss the sediment data collected during 2007.

### Mercury Speciation

The sediment mercury speciation is presented in Figure 5.1.1. Median values of sediment THg (Figure 5.1.1a; expressed as dry weight) ranged from 370 ng/g (AS-MP) to 722 ng/g (A8-MF) among habitats, with a mean ( $\pm$  standard deviation) of  $603 \pm 408$  ng/g for the complete data set ( $N = 20$ ). As such, all habitats were elevated in THg compared to the values typically seen on surface sediments of south San Francisco Bay (i.e. 200-300 ng/g dry wt.). Median values of sediment Hg(II)<sub>R</sub> (Figure 5.1.1b) ranged from 0.24 ng/g (for both AS-MC and A8-CH) to 1.26 ng/g (A8-MF), although samples from AS-MP are not included in this analysis. These samples are scheduled to be rerun in January 2008, because they were much higher than our typical standard curve when they were first analyzed. Expressed as a percentage of THg, median values of %Hg(II)<sub>R</sub> (Figure 5.1.1c) ranged from 0.05% (AS-MC) to 0.17% (A8-MF), again excluding the AS-MP samples that need to be rerun. Thus, concentrations of Hg(II)<sub>R</sub> are a very small percentage of THg, as was seen in the Alviso slough deep core study (Marvin-DiPasquale and Cox 2007). Median sediment MeHg concentrations (Figure 5.1.1d) ranged from 0.5 ng/g (AS-MP) to 8.6 ng/g (AS-MF), with a mean ( $\pm$  standard deviation) of  $6.8 \pm 12.5$  ng/g for the complete data set ( $N = 20$ ). Expressed as a percentage of THg, median values of %MeHg (Figure 5.1.1e) ranged from 0.1% (AS-MP) to 1.7% (A8-MF), with a mean ( $\pm$  standard deviation) of  $1.0\% \pm 1.5\%$  for the complete data set ( $N = 20$ ). The %MeHg metric is often used as a proxy measure for Hg(II)-methylation efficiency and, as such, would suggest that the trend across habitats is [A8-MF > A8-CH  $\approx$  AS-MC  $\gg$  AS-MP]. One implication of this observed trend for the salt pond restoration project is that, ultimately, emergent tidal marsh habitats may have lower benthic MeHg levels (per m<sup>2</sup>) than managed ponds.

The correlation between sediment THg and MeHg was modest among all sites (Figure 5.1.2a), as was the correlation between sediment THg and Hg(II)<sub>R</sub> (Figure 5.1.2b), indicating that factors other than the concentration of THg play a significant role in mediating both the pool size of Hg(II)<sub>R</sub> and of MeHg. In particular, it is generally accepted that the concentration of MeHg is a function both of the pool size of Hg(II) available to Hg(II)-methylating bacteria (i.e., Hg(II)<sub>R</sub>) and the activity of those bacteria in a given setting, which in turn is a function of suitable organic matter and the availability of suitable electron acceptors (i.e., sulfate). Further, the habitat-specific trend in MeHg concentration is ultimately driven by relative organic inputs and sediment redox conditions (controlled by SR rates, elevation and hydrology), as described below.

### Additional Sediment Characterization

Sediment organic content (expressed as percent loss on ignition) had median values ranging from 6.3% (AS-MC) to 18.9% (A8-CH), and indicated that all sites within Pond A8 are high in organic matter compared to the Alviso Slough and marsh habitats (Figure 5.1.3a). Similarly, the Pond A8 sites were comparatively reducing (negative  $E_h$ , as assessed by sediment oxidation-reduction potential measurements), relative to the Alviso Slough and marsh sites (positive  $E_h$ ), which were comparatively oxidized (Figure 5.1.3b). Not surprisingly, the hypersaline Pond A8 environment had pore water chloride ( $Cl^-$ ) concentrations (1.3 to 3.0 mol/liter;  $N = 10$  sites) that were high compared to the Alviso Slough and marsh sites (0.05 to 0.71 mol/liter;  $N = 10$  sites) (not shown).

Correspondingly, pore water  $SO_4^{2-}$  concentrations (Figure 5.1.3c) exhibited a higher range in Pond A8 (67 to 132 mmol/liter;  $N = 10$ ) compared to the Alviso Slough and marsh sites (4 to 76 mmol/liter;  $N = 10$ ). Pore water sulfide (Figure 5.1.3d) ranged over three orders of magnitude among habitats, with the highest median value in the A8-CH (1125  $\mu\text{mol/liter}$ ) to the lowest measured median value in the AS-MC habitat (0.7  $\mu\text{mol/liter}$ ). Pore water sulfide was not assayed in the AS-MP habitat, because the very oxic conditions (e.g.,  $> 100$  mV) indicated that no sulfide was present. Sediment pH varied over a comparatively narrow range among habitat types, with median values from 6.8 pH units (AS-MP) to 7.3 pH units (AS-MC), data not shown. Sediment grain size (as %  $< 63$   $\mu\text{m}$ ; sand/silt split) did range significantly among habitats, with the AS-MP habitat exhibiting a very high percentage of particles  $< 63$   $\mu\text{m}$  (median = 94%), compared to the three other habitats where median values ranged from 67% (A8-MF) to 78% (AS-MC) (not shown).

### Controls on Inorganic Reactive Mercury Concentration

The two key question regarding what ultimately controls MeHg production among these habitat types are: a) What controls the activity of the Hg(II)-methylating microbial community? and b) What controls the pool size of  $Hg(II)_R$  which is available to those Hg(II)-methylating microbes? In Phase 1B of this project, we did not employ isotope tracer experiments typically used to address the first question, so the answer to that is still somewhat unresolved. However, the comparatively high organic content, the negative redox conditions ( $< 0$  mV), and the elevated levels of pore water sulfide observed in the Pond A8 sites suggest that microbial sulfate reduction is generally higher in this salt pond, as compared with either the Alviso Slough or marsh habitats.

We did assess the  $Hg(II)_R$  pool and how it varied among the sites, and thus can begin to examine the second question posed above. The X-Y plot of pore water sulfide versus the sediment  $Hg(II)_R$  concentration (Figure 5.1.4) reveals some important trends. First, there is a sharp increase in  $Hg(II)_R$  concentration with increasing sulfide concentrations for the AS-MC sites. This may reflect previous assertions that at the low end of the sulfide gradient (e.g.  $< 10$   $\mu\text{mol/liter}$ ), small increases in sulfide facilitate the partitioning of Hg(II) off of sediment particles and into the pore water fraction, thus making it more available for methylation. Second, there is an exponential decrease in sediment  $Hg(II)_R$  concentration with increasing pore water sulfide concentration in the Pond A8 sites. This parallels previous findings that suggest at high sulfide concentrations Hg(II) becomes less available as it is incorporated into precipitating sulfide minerals. These two trends

illustrate the dual effect of sulfide on Hg(II) availability. Third, at modest levels of sulfide (e.g. 1–10  $\mu\text{mol/liter}$ ), as were observed in the A8-MF sites, the pool size of Hg(II)<sub>R</sub> was greatest, and this corresponds to the habitat type with the highest MeHg concentration. One potential implication of the above findings is that MeHg concentrations within Pond A8 will ‘eventually’ be lower than they are today, if tidal connection is restored, due to both decreased organic loadings to the benthos and increase in the sediment redox status (more oxidized surface sediments).

### **Conclusions from Sediment Sampling**

Based on the surface sediment sampling to date, the following tentative conclusions were reached: MeHg production and concentrations are higher in Pond A8 than in Alviso Slough and the adjacent marsh. This is driven by both high concentrations of Hg(II)<sub>R</sub> associated with mudflat areas of Pond A8 and by much higher rates of microbial activity in Pond A8 generally, which is in turn driven by high loading rates of readily degraded phytoplankton. Sulfate concentrations do not limit rates of microbial sulfate reduction (or MeHg production) in any of the habitats investigated. Restoring muted tidal action to Pond A8 will likely decrease MeHg concentrations within Pond A8. As the restoration moves towards full implementation, emergent tidal marsh habitats may have lower benthic MeHg levels (per  $\text{m}^2$ ) than will managed ponds. However, these conclusions are based on comparing mercury speciation and associated sediment geochemistry of Pond A8 (specifically) to Alviso Slough and marsh, and the strong habitat differences observed thus far might not hold true if other existing salt ponds were considered. Biota data (discussed below) indicate that Pond A8 may be a particularly active zone for MeHg production and bioaccumulation, as compared to Ponds A5 and A7. Thus, similar detailed sediment sampling of other pond units would be needed to test and verify the above conclusions.

### **5.2. Water**

There are no historical or other data collected from Pond A8 for comparison to the data collected for this project. The results from this effort are presented in Tables 5.2.1–5.2.6. The applicable water quality criterion for total mercury in water is found in the California Toxics Rule (CTR). For the Lower South Bay, the CTR criterion of 0.051  $\mu\text{g/l}$  (51  $\text{ng/l}$ ) applies for both fresh and saline waters. Samples collected from Pond A8 frequently exceeded the criterion, particularly as the summer season progressed. A few samples from the slough and marsh exceeded the criterion.

The Regional Monitoring Program (RMP) collects water samples from several locations in the Lower South Bay. In 2006 the RMP samples contained less than 0.13  $\text{ng/l}$  of total methylmercury (SFEI 2007). This was the range of concentrations observed in the Alviso slough samples during the November and January excursions. However, samples collected from later events were significantly higher by as much as a factor of 10. Methylmercury concentrations in samples from the marsh locations were generally similar to the adjacent slough locations. On most events, a gradient was evident where methylmercury concentrations were higher near Pond A8 (ASW1 and ASMW1) and decreased with distance toward the Bay.

Mercury and methylmercury concentrations in samples collected from Pond A8 were typically an order of magnitude higher than samples collected from the Slough and its fringing marsh. There was some seasonality to the data for the northern end of the Pond (A8WF2) and in the middle of the Pond (A8WD1), with higher concentrations observed at these sites for the March, May and July samples compared to the November and August samples. The concentrations were also similar between samples collected at these sites for most of the sampling events. Samples collected from the southern portion of the Pond (A8WF1) contained higher concentrations on all sampling events than did the other sampling sites in the Pond.

### **Alviso Slough**

Methylmercury concentrations ranged from 0.111 to 0.833 ng/l in surface water samples collected at ASW1 (furthest upstream from the bay) and from 0.126 to 1.260 ng/l in samples collected from 0.25 meters off the bottom (Figure 5.2.1). Highest concentrations were observed during the August 27, 2007 sampling event, and lowest concentrations were observed during the November 16, 2006 (deep sample) and January 30, 2007 (surface sample) sampling events.

Methylmercury concentrations ranged from 0.084 to 0.300 ng/l in surface water samples collected at ASW2 (mid-way to bay) and from 0.122 to 0.310 ng/l in samples collected from 0.25 meters off the bottom. Highest concentrations were observed during the May 14, 2007 sampling event, and lowest concentrations were observed during the January 30, 2007 sampling event.

Methylmercury concentrations ranged from 0.084 to 0.240 ng/l in surface water samples collected at ASW3 (furthest downstream at bay end) and from 0.101 to 0.377 ng/l in samples collected from 0.25 meters off the bottom. Highest concentrations were observed during the May 14, 2007 (surface sample) and August 27, 2007 (deep sample) sampling events, and lowest concentrations were observed during the November 16, 2006 (surface sample) and January 30, 2007 (deep sample) sampling events.

Total mercury concentrations ranged from 1.2 to 33.000 ng/l in surface samples collected at ASW1 (furthest upstream from bay) and from “not detected above reporting limit (of 0.50 ng/l)” to 52.7 ng/l in samples collected from 0.25 meters off the bottom at this location [Note: variations in significant figures are the result of different laboratories conducting the analyses]. Highest concentrations were observed during the November 16, 2006 (surface sample) and August 27, 2007 (deep sample) sampling events, and lowest concentrations were observed during the March 29, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to Total Suspended Solids (TSS) concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC) was 0.31 ng/mg (parts per million) for surface water samples and 0.38 ng/mg for deep samples (Figure 5.2.2).

Total mercury concentrations ranged from 3.8 to 20.1 ng/l in surface samples collected at ASW2 (mid-way to bay) and from 3.9 to 31.2 ng/l in samples collected from 0.25 meters



off the bottom at this location. Highest concentrations were observed during the May 14, 2007 sampling event, and lowest concentrations were observed during the March 29, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to TSS concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC), was 0.20 ng/mg for surface samples, and 0.21 ng/mg for deep samples (Figure 5.2.2).

Total mercury concentrations ranged from 13.100 to 23.3 ng/l in surface water samples collected at ASW3 (furthest downstream at bay end) and from 21 to 83.4 ng/l in samples collected from 0.25 meters off the bottom at this location. Highest concentrations were observed during the May 14, 2007 sampling event, and lowest concentrations were observed during the March 29, 2007 (deep sample) and August 27, 2007 (surface sample) sampling events. The average concentration ratio of Mercury (ng/l) to TSS concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC), was 0.23 ng/mg for surface samples, and 0.26 ng/mg for deep samples (Figure 5.2.2).

Salinity values ranged from 0.07 percent (%) to 1.01% in the surface samples collected from the slough at ASW1 (furthest upstream from the bay) and from 0.12% to 1.61% in the samples collected from 0.25 meters off the bottom at this location.

Salinity values ranged from 1.02% to 2.22% in the surface samples collected from the slough at ASW2 (mid-way to bay) and from 1.84% to 2.35% in the samples collected from 0.25 meters off the bottom at this location.

Salinity values ranged from 1.87% to 2.51% in the surface samples collected from the slough at ASW3 (furthest downstream at bay end) and from 2.05% to 3.37% in the samples collected from 0.25 meters off the bottom at this location.

#### **Alviso Slough Marsh**

Methylmercury concentrations ranged from 0.137 to 0.584 ng/l in surface samples collected at ASMW1 (Figure 5.2.3). Highest concentration was observed during the August 27, 2007 sampling event, and lowest concentration was observed during the January 30, 2007 sampling event.

Methylmercury concentrations ranged from 0.062 to 0.350 ng/l in surface samples collected at ASMW2 (across from ASW2). Highest concentration was observed during the May 14, 2007 sampling event, and lowest concentration was observed during the November 16, 2006 sampling event.

Methylmercury concentrations ranged from 0.147 to 0.847 ng/l in surface samples collected at ASMW3 (across from ASW3). Highest concentration was observed during the May 14, 2007 sampling event, and lowest concentration was observed during the January 30, 2007 sampling event.

Total mercury concentrations ranged from 4.4 to 81.500 ng/l in surface samples collected at ASMW1 (across from ASW1). Highest concentration was observed during the November 16, 2006 sampling event, and lowest concentration was observed during the January 30, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to TSS concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC), was 0.39 ng/mg.

Total mercury concentrations ranged from 15.000 to 19.8 ng/l in surface samples collected at ASMW2 (across from ASW2). Highest concentration was observed during the August 27, 2007 sampling event, and lowest concentration was observed during the November 16, 2006 sampling event. The average concentration ratio of Mercury (ng/l) to TSS concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC), was 0.25 ng/mg.

Total mercury concentrations ranged from 11.2 to 22.2 ng/l in surface samples collected at ASMW3 (across from ASW3). Highest concentration was observed during the May 14, 2007 sampling event, and lowest concentration was observed during the August 27, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to TSS concentrations (mg/l; excluding the November 16, 2007 event due to TSS analyses failing QA/QC), was 0.21 ng/mg.

Salinity values ranged from 0.16% to 0.68% in samples collected from the marsh at ASMW1 (across from ASW1).

Salinity values ranged from 1.66% to 2.00% in samples collected from the marsh at ASMW2 (across from ASW2).

Salinity values ranged from 1.95% to 2.63% in samples collected from the marsh at ASMW3 (across from ASW3).

#### **Pond A8**

Methylmercury concentrations ranged from 1.460 to 10.200 ng/l in surface samples collected at A8WF1 (across levee from ASW1) (Figure 5.2.4). Highest concentration was observed during the May 17, 2007 sampling event, and lowest concentration was observed during the August 29, 2007 sampling event.

Methylmercury concentrations ranged from 0.378 to 3.970 ng/l in surface samples collected at A8WF2 (near pump station at levee corner across from Pond A7). Highest concentration was observed during the May 17, 2007 sampling event, and lowest concentration was observed during the August 29, 2007 sampling event.

Methylmercury concentrations ranged from 0.265 to 3.530 ng/l in surface samples collected at A8WD1 (middle of the pond), and from 0.249 to 3.270 ng/l in samples collected from 0.25 meters off the bottom at this location. Highest concentrations were observed during the March 27, 2007 sampling event, and lowest concentrations were observed during the August 29, 2007 sampling event.

Total mercury concentrations ranged from 47 to 230 ng/l in surface samples collected at ASWF1 (across from ASW1). Highest concentration was observed during the August 29, 2007 sampling event, and lowest concentration was observed during the January 25, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to TSS (mg/l) was 0.31 ng/mg (Figure 5.2.2).

Total mercury concentrations ranged from 32 to 89.0 ng/l in surface samples collected at ASWF2 (near pump station at levee corner across from Pond A7). Highest concentration was observed during the July 16, 2007 sampling event, and lowest concentration was observed during the November 14, 2006 sampling event. The average concentration ratio of Mercury (ng/l) to TSS (mg/l) was 0.18 ng/mg (Figure 5.2.2).

Total mercury concentrations ranged from 6.6 to 65.9 in surface samples collected at A8WD1 (middle of the pond), and from 7.2 to 68.8 ng/l in samples collected from 0.25 meters off the bottom at this location. Highest concentrations were observed during the July 16, 2007 (surface sample) and August 29, 2007 (deep sample) sampling events, and lowest concentrations were observed during the March 27, 2007 sampling event. The average concentration ratio of Mercury (ng/l) to TSS (mg/l) was 0.13 ng/mg (surface) and 0.15 (deep) ng/mg (Figure 5.2.2).

Salinity values exceeded the range of the equipment at all sampling locations in Pond A8 on November 14, 2006 and January 25, 2007, and at all but one location on March 27, 2007. Salinity values ranged from 11.0% to 27.9% in samples collected from Pond A8 at A8WF1 (March through August, 2007), and from 15.6% to 24.7% at A8WF2 (May through August, 2007). Salinity values ranged from 14.7% to 24.9% in surface samples collected at A8WD1, and from 19.7% to 25.4% in the samples collected from 0.25 meters off the bottom at this location.

### **Dissolved Oxygen**

Dissolved oxygen concentrations were measured to be slightly lower than air saturation (> 5 mg/l) at all marsh and slough locations for all sampling events, and for all sampling locations in Pond A8 for the November 14, 2006 and January 25, 2007 sampling events. Low oxygen concentrations (< 3 mg/l) were observed at all Pond A8 locations during the March 27, 2007 sampling event. Anoxic conditions (< 1 mg/l) were observed at A8WF1 on July 16, 2007 and August 29, 2007, at A8WF2 and the deep samples at A8WD1 on May 14, 2007, July 16, 2007 and August 29, 2007, and in the surface samples at A8WD1 on May 17, 2007 and July 16, 2007.

### **Sulfate, TSS, DOC and SUVA**

The overlying water constituent data measured by the USGS (sulfate, TSS, DOC and SUVA) were pooled into three spatial categories for the purposes of statistical analysis and graphical representation (Fig 5.2.5), and are Alviso Marsh (N = 18), Alviso Slough (N = 36, includes both depths), and Pond A8 (N = 24, includes both depths). The comparatively high sulfate concentrations in Pond A8 (Figure 5.2.5a) parallel the results found in sediment pore water, as described above. The comparatively high TSS and DOC

concentrations in Pond A8 (Figs 5.2.5b and 5.2.5c, respectively) also confirm the previous assertion that the salt pond is enriched in organic material compared to both Alviso Slough and the fringing marsh. The comparatively low SUVA values in Pond A8 indicate that the nature of this organic material is autochthonous in nature (i.e., phytoplankton) as compared to Alviso Slough and marsh, where the organic matter appears to be of more terrestrial origin (higher SUVA = more lignin / aromatic organics = higher order plants). The time series plots of DOC and SUVA (Figure 5.2.6) indicate that the peak of the phytoplankton bloom in Pond A8 occurred during July of 2007.

### **Conclusions from Water Sampling**

The data indicate there is generally a gentle downstream decrease in methylmercury concentrations in Slough and fringing marsh water (Figure 5.2.3). An opposite gradient is evident for water salinity. No other physical parameter was positively or negatively correlated with mercury. The Slough data also indicate that Slough water contained higher concentrations with each successive sampling period, but this trend was not as evident in the tidal marsh data.

The Pond A8 data indicate that concentrations of methylmercury in water observed at all Pond sampling locations are significantly higher (generally more than an order of magnitude) than at the Slough and tidal marsh locations. Samples from A8WF1 were consistently higher in methylmercury than all other Pond samples.

Normalized concentrations of total mercury in suspended sediment in the Slough and tidal marsh indicate a gradient with higher concentrations in the upstream samples. Normalized concentrations for A8WF2 and A8WD1 (surface and deep) were lower than all of the Slough and marsh normalized concentrations. The normalized concentration for A8WF1 was similar to the normalized concentrations for ASMW1 and ASW1.

These observations suggest that tidal water flooding and draining tidal marshland has much lower concentrations of methylmercury than Pond A8 water. This is evident even though similar normalized concentrations of total mercury in suspended solids were observed between the Pond, the Slough, and the tidal marsh, suggesting that the same relative amount of mercury is available for methylation in all three of these habitat types.

The proposed project alternative to convert Pond A8 into a tidal or muted tidal system with fringing tidal marsh will probably result in lower concentrations of total methylmercury in the restored Pond complex. The dilution of the water in Pond A8 by the elevation change that will occur following equilibrium with Pond A7 (after the opening of the tidal gates) will probably provide a near-term reduction in methylmercury concentrations as well as total mercury concentrations in Pond A8. Increased salinity near ASW1 should result in reduced methylmercury concentrations in the Slough and fringing marsh at that location and downstream. The anticipated result is that equilibrium concentrations of methylmercury and total mercury are likely to be lower in the Pond, Slough and existing tidal marsh following the proposed change to Pond A8.

### 5.3. Biota

Despite the challenge of having to collect biota samples earlier than expected, after a very dry winter, the project was able to meet and sometimes exceed the sample size goals (Tables 1.1 and 5.3.1). Enough fish were sampled to better understand the length:mercury relationship and how it might affect project findings (Table 5.3.2; see Methods). Biosentinels were sampled across a wider spatial scope, at more sites, and earlier in the year than in the 2006 field season, with valuable results (Figures 5.3.1–5.3.4). The analytical lab was able to provide THg and MeHg measurements with excellent QAQC, despite the challenge of extremely small sample masses in some cases.

The ability to collect data strictly according to the GRTS model varied among habitat types. The model was easiest to follow in Alviso Slough, the tidal marsh plain, and the tidal marsh channels. Early desiccation of Pond A8 precluded sampling many of the sites selected for the Pond using GRTS. Fish collections in Ponds A5 and A7 were mainly limited to the borrow ditches around the Pond perimeters and the historic channels in the Pond interiors (Figures 5.3.1 and 5.3.2); access to the other more isolated areas of remaining water was extremely difficult. Fly collections were limited to the accessible areas of Pond A8, outside the Snowy Plover breeding areas, where flies occurred at the margins of the water. Given these constraints, only 18 independent samples of flies were collected in Pond A8 (Figure 5.3.3). Bird sampling locations were generally located at the probabilistic sampling sites (Figure 5.3.4).

#### Demersal and Water-column Fish

Significant differences in fish mercury concentrations among the habitat types were found for every species. For the longjaw mudsucker, Ponds A5 and A7 had the lowest mercury, followed (in increasing order) by the tidal channels of Alviso Slough fringing marsh, and then Pond A8 ( $n = 55$ ,  $df = 3, 51$ ,  $F = 22.95$ ,  $p < 0.001$ ; Figure 5.3.5). For the yellowfin goby, Pond A5 and the marsh tidal channels had the lowest mercury, followed by Pond A7 ( $n = 20$ ,  $df = 18$ ,  $t = 3.99$ ,  $p = 0.001$ ). For threespine stickleback, Pond A5 had the lowest mercury, followed by Alviso Slough, then by Pond A7 ( $n = 43$ ,  $df = 2, 40$ ,  $F = 18.73$ ,  $p < 0.001$ ; Figure 5.3.6). For Mississippi silverside, Pond A5 had the lowest mercury, followed by Alviso Slough ( $n = 18$ ,  $df = 2, 15$ ,  $F = 27.93$ ,  $p < 0.001$ ).

These comparisons of habitat types and geographic areas using sentinel fish were quite consistent across species, as summarized in the table below. Pond A5 always had the lowest mercury concentrations; Alviso Slough and its fringing tidal marsh nearly always had the next highest mercury concentrations, and Pond A8 always had the highest mercury (although Pond A8 was only sampled for mudsuckers).

Summary table of relative mercury rankings based on biosentinel fish data.

Habitat	Species	Mercury Ranking by Geographic Area		
		Least	Mid	Highest
Demersal/Benthic	LOMU	Pond A5, Pond A7	tidal channels	Pond A8
	YFGO	Pond A5, tidal channels	Pond A7	
Water-column	TSSB	Pond A5	tidal channels	Pond A7
	MISI	Pond A5	tidal channels	

Only Pond A7 varied in relative Hg exposure ranking according to species. The reasons for Pond A7 having potentially higher food-web mercury than Pond A5 are not known. One reasonable hypothesis is that the greater food-web Hg in Pond A7 may relate to a greater tendency to desiccate.

### **Brine Flies**

Brine flies had significantly higher mercury concentrations in Pond A8 than in the tidal channels of Alviso Slough (Mann-Whitney  $U = 126.0$ ,  $n = 25$ ,  $p < 0.001$ ; Figure 5.3.7). Seven Alviso Slough samples were compared to 18 samples from Pond A8. Mean MeHg concentrations were  $0.31 \pm 0.02$  ( $\pm 1$  Std. Dev.)  $\mu\text{g/g}$  dry weight in the tidal channels and double that value,  $0.67 \pm 0.14$   $\mu\text{g/g}$  dry weight, in the Pond.

Comparisons of mercury concentrations between flies in the Pond and the Slough were complicated by differences in the species present in the two habitats. Flies taken from Pond A8 were identified as *Ephydra gracilis*, while flies from Alviso Slough were found to be a mix of *E. millbrae* and *Parydra* spp. In this report, the two *Ephydra* are compared to each other. Although the species were segregated by habitat, we believe they fill similar roles in the food web. Brine flies eat blue green algae and associated bacteria on the water and sediment surface at the margins of saline water bodies. Brine flies are consumed in the larval, pupal, and adult life stages by many animals, particularly shorebirds.

Mercury data from the *Parydra* collected have not yet been received from the analytical lab. These *Parydra* data will be used to test whether different brine fly species in the same habitat have similar mercury concentrations. Mercury concentrations will be compared between *Parydra* and *E. millbrae*, both of which were collected from Alviso Slough and fringing tidal marsh channels. This information will help to evaluate whether the differences between the flies in the Pond and the Slough were more related to habitat type (the hypothesis we believe is correct) or species type (to be tested).

The comparison of Pond and Slough habitats based on brine flies also was complicated by differences in brine-fly phenology. Brine flies bloomed later in the Slough than in the Pond. This difference is not surprising, given the higher temperatures and early development of saline conditions in the Pond. Brine flies were collected from mid-April to mid-May in the Pond and from early to mid June along the tidal marsh channels and Slough. No obvious trends in methylmercury over time were evident for flies in either the Pond or Slough.

### **Resident Marsh Birds**

Spatial and habitat variation in mercury concentrations was suggested by the analysis of bird blood data (Table 5.3.3, Figures 5.3.8 and 5.3.9). All three sentinel bird species showed a significant site effect. However, broader differences between Alviso Slough and South Bay were only evident for Song Sparrows. There is a possibility that the larger sample size achieved for Song Sparrows was needed to reveal this large-scale spatial

variability. Furthermore, the Song Sparrow dataset supported an analysis of the effect of marsh elevation, as represented on maps of marsh subsidence, which helped explain spatial variation in mercury concentration for this species.

Song sparrows residing in the tidal marshes fringing Alviso Slough had lower mercury concentrations than song sparrows in other tidal marshes in South Bay. This result may seem surprising, given that the Slough is downstream of the New Almaden Mining District. Relative to South Bay marshes as a whole, the Alviso Slough marshes are generally lower in elevation (due to subsidence) and therefore wetter (less subject to desiccation), fresher (closer to local runoff), and less organic (the sediments of lower-elevation marshes tend to have more inorganic silts and clays). These characteristics of the placement of Alviso Slough in the landscape likely explain why the Alviso marsh group had significantly lower mercury in sparrows (CalFed Petaluma River Mercury Study and our SBMP results from 2006).

The bird data may indicate that higher-elevation marshes are correlated with higher mercury in biota that feed on tidal marsh plains. However, salinity and subsidence (i.e., elevation) were confounded in this data set. As salinity decreased, subsidence increased, except for the Coyote Creek Lagoon site (RefM-095), which was the only unsubsided freshwater marsh site. The data from RefM-095 suggest that lower salinity may be correlated with lower mercury in biota (Figures 5.3.8 and 5.3.9), as this freshwater unsubsided site had lower sparrow mercury than the unsubsided saltmarsh site near Dumbarton bridge (RefM-071). Differences in food-web mercury related to salinity may be plant-mediated. Results from the Petaluma study and recent work in the Alviso area by L. Windham-Myers suggest that higher root volume of pickleweed in saline marshes, relative to that of *Scirpus* in fresher areas, may provide more methylation sites. The larger data set to be collected in 2008 across marshes south of San Mateo Bridge should help to resolve the confounding of salinity and subsidence.

Older marshes tend to be higher in elevation than younger marshes, because they have accreted more sediment and peat over time. Higher-elevation marshes tend to have higher salinity than lower-elevation marshes, because they are flushed by the tide less frequently. Therefore, if elevation and salinity are drivers of food web mercury, we may expect to see low mercury in newly restored marshes and a slow increase over years or decades as the marsh increases in elevation and salinity. Sea-level rise will counteract the tendency of marshes to rise in elevation, but encroachment of the tide into fresher areas may increase the salinity of brackish and freshwater marshes.

A surprising proportion of the biosentinel birds sampled were above the threshold of concern for songbirds of 0.96 ug/g ww (Table 5.3.4, Figure 5.3.8; Evers et al. 2005). This proportion varied with site, according to subsidence and salinity, as discussed in the previous paragraph. This limited dataset suggests that in relatively unsubsided salt marshes of lower South Bay (e.g., RefM-071) a large proportion of sparrows (four of seven in this sample) are likely to be over the threshold of concern. Comparing Hg concentrations in sentinel species to thresholds of concern is useful in getting a general idea of the potential for effects from Hg exposure. Species-specific thresholds are needed

to fully quantify the risk, however. The results from this project should not be interpreted as a risk assessment.

During the 2007 field sampling, song sparrows with crossed bills or that had an upper mandible much longer than the lower were observed at two sites (ASM-506 and RefM-095). Similarly, Carl's Marsh in San Pablo Bay was documented by the Point Reyes Bird Observatory as having sparrows with crossed bills in 2007. Further study is required to understand the causes of these deformities. In the literature, "crossed-bill syndrome" is correlated with dioxin-like PCBs, but other causes are also possible.

### **Conclusions from Biota Sampling**

Across the different biosentinel species and the habitats they represent, Pond A8 was consistently higher in food-web mercury than Alviso Slough marsh and tidal channels, as well as higher than the other Ponds (Figures 5.3.5–5.3.7). Alviso Slough marsh and tidal channels tended to have higher food-web mercury than Pond A5, however. Pond A7 varied among biosentinels in terms of having higher, lower, or similar mercury as the Alviso Slough habitats. Therefore, the biota results suggest that, after the interim breach, as conditions in Pond A8 become more like those in Ponds A5 and A7, food-web mercury is likely to decrease. After a full breach, as Pond A8 becomes a tidal marsh, food-web mercury might increase somewhat but would likely still be lower than in the original seasonal Pond A8.

This result requires a revisiting of the decision tree that was included in the original study proposal. Figure 5.3.10 is an updated version that includes decision pathways related to the reversible breach. Comparison of Pond A8 biosentinel mercury to Alviso Slough biosentinel mercury selects for the left side of the first branch at the top of the figure, because the Pond is worse than the Slough. However, comparison of Alviso Slough habitats to Pond A5 selects for the right side of the first branch, because the Slough is generally worse than the Pond. These results from midway through the Project suggest that whether restoration of salt ponds to tidal marsh will increase or decrease mercury in the food web will probably depend on the specific characteristics of the ponds and marshes in question. Ongoing monitoring and adaptive management will be necessary to track and respond to changes in food-web mercury.

### **5.4. Integration across Sediment, Water and Biota**

The result that Pond A8 tended to have more methylmercury than Alviso Slough marsh and tidal channels was consistent across the three matrices of sediment, water, and biota. The principal investigators from the three collaborating agencies on this project agree that restoration of Pond A8 to tidal marsh will likely reduce methylmercury in the sediment, water, and biota. The restoration of Pond A5 to tidal marsh may result in slightly higher methylmercury in the food web, but this result is based on data from biota only. The result of restoring Pond A7 is not clear, and it may differ depending on the sentinel species in question.



The seasonal changes in water methylmercury could not be compared to seasonal changes in biota or sediment. Biota were sampled only once during the year, and the second sediment sampling season has not yet occurred.

The strong increase in sparrow mercury from the town of Alviso to the mouth of Alviso Slough (Figure 5.3.8 and 5.3.9) stood in contrast to a slight tendency for the more upstream marsh water site (ASM-W1) to have higher methylmercury than the more downstream marsh water site (ASM-W3). This difference in pattern could result from the water trend not occurring during the spring and summer (Figure 5.2.3), or not being a statistically significant difference. Sediment in the main Alviso Slough channel from the three downstream sites had a higher MeHg content (2.1 to 2.9 ng/g) than the two upstream sites (0.7 to 1.0 ng/g). However, no trend was apparent in the marsh plain sediment samples. Thus, the trend in marsh plain biota was not present in the abiotic samples from the marsh and its tidal channels. More study would be needed to understand if this lack of concordance is related to the trend in biota being food-web mediated (rather than related to net MeHg production) or if the lack of concordance is related to the biota integrating over a larger space and a longer time than the sediment and water samples.

We have built a working conceptual model to facilitate development of hypotheses relating to patterns of methylmercury in the Alviso Baylands (Figure 5.4.1). This model includes ideas stemming from research by Lisa Windham-Myers at USGS, Menlo Park. The hypotheses represented are under development by the PIs and should not be used for decision-making.

## **6. Phase 2 Sampling in 2008**

### **6.1. Sediment and Water**

A second sampling (completion of Phase 1 sediment sampling) of the twenty surface sediment sites presented in this report is tentatively scheduled for January 2008. This will fulfill the original vision of sampling these habitats during two different hydroperiods (i.e., dry and wet periods), and complete Phase 1B for the sediment component of the project.

The original proposal called for a hiatus in sediment and water studies during Phase 2 of the project, which will occur in 2008, followed by in-depth sediment and water process studies in Phase 3, during 2009. Based on changes in the timing of Phase 1 and the progress that has been made during the first two years of the project, the principal investigators are now considering coupling the sediment and water Phase 3 studies with the sentinel species Phase 2 survey in 2008. If the overall project goals warrant it, this change in scope will need to be addressed with the funding agencies.

### **6.2. Biota**

A general survey of biosentinel species across the marshes and salt ponds south of the San Mateo Bridge is planned for 2008. This survey will place the Alviso Pond and Slough Complex data gathered to date in the context of the South Bay and as a whole,

enabling comparison of how the Hg contamination of the Alviso food web compares to that in other marshes and salt ponds. The 2008 survey will also provide baseline data from the biosentinels prior to other SBSRP actions.

The 2008 survey will be similar to the biosentinel work from 2007 in that a probabilistic (GRTS) set of sampling locations will be used. The work plan calls for 15 samples to be collected for each sentinel species group from salt ponds and 15 from marshes. Water-column fish will not be targeted in 2008 with beach seining. This choice was made to reduce costs and because these fish have a larger spatial footprint and are less habitat-specific than the other biosentinels, which makes data from them more difficult to interpret. Threespine stickleback, which is a water-column biosentinel, will be sampled opportunistically when they are captured in minnow traps set for longjaw mudsucker. The 2008 biosentinel sampling effort will be coordinated with the RMP Small Fish project to accomplish beach seining at some SBMP sites, which will likely provide data on Mississippi silversides.

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**9. Tables**

**Table 1.1.** Sampling design for biosentinels. The design allows for direct comparison of mercury concentrations in biota of the same species between salt pond and marsh habitats.

Biosentinel Group	Common and Scientific Names	Habitats	Ponds	Slough	Reference Marshes
Demersal Fish	Longjaw mudsucker ( <i>Gillichthys mirabilis</i> ) Yellowfin goby ( <i>Acanthogobius flavimanus</i> )	Pond and Slough Benthos	20	20	
Water-column Fish	Mississippi silverside ( <i>Menidia audens</i> ) Threespine stickleback ( <i>Gasterosteus aculeatus</i> )	Pond and Slough Water Column	20	20	
Brine Flies	Brine fly ( <i>Ephydra millbrae</i> and <i>E. gracilis</i> )	Pond Margins, Tidal Channels	20	20	
Marsh Birds*	Alameda song sparrow ( <i>Melospiza melodia</i> ) Marsh wren ( <i>Cistothorus palustris</i> ) Common Yellowthroat ( <i>Geothlypis trichas</i> )	Vegetated Marsh Plain		20	20

\*Bird samples were collected in clusters.

**Table 4.1.1.** Pond A8 and Alviso Slough sediment station descriptions.

Station Code	Sampling Date	Latitude <sup>1</sup>	Longitude <sup>1</sup>	Datum	Location	Feature Type
A8SEBD1	5/08/07	37 25.373	121 1.198	NAD27	Pond A8	Borrow Ditch
RA8N-200	5/08/07	37 25.537	121 1.225	NAD27	Pond A8	Borrow Ditch
A8NPH	5/08/07	37 26.323	121 0.176	NAD27	Pond A8	Borrow Ditch
A8NRS4	5/08/07	37 25.908	121 59.804	NAD27	Pond A8	Historic Slough Channel
A8NRS5	5/08/07	37 25.856	121 59.751	NAD27	Pond A8	Historic Slough Channel
A8NMF1	5/08/07	37 25.460	121 58.814	NAD27	Pond A8	Historic Marsh Plain
A8NMF2	5/08/07	37 25.860	121 59.765	NAD27	Pond A8	Historic Marsh Plain
A8NMF3	5/08/07	37 25.968	121 59.820	NAD27	Pond A8	Historic Marsh Plain
A8NMF4	5/08/07	37 25.987	121 59.818	NAD27	Pond A8	Historic Marsh Plain
A8NMF5	5/08/07	37 26.016	121 59.804	NAD27	Pond A8	Historic Marsh Plain
ASW3	5/22/07	37 27.507	122 1.237	WGS84	Alviso Slough	Main Channel
ASW2	5/22/07	37 26.816	122 0.742	WGS84	Alviso Slough	Main Channel
AS-T2B	5/22/07	37 26.316	121 59.588	WGS84	Alviso Slough	Main Channel
AS-T1B	5/22/07	37 25.912	121 59.313	WGS84	Alviso Slough	Main Channel
ASW1	5/22/07	37 25.499	121 58.746	WGS84	Alviso Slough	Main Channel
ASM-WS3	7/05/07	37 27.496	122 01.310	WGS84	Alviso Slough	Marsh Plain
ASM-501	7/05/07	37 25.711	122 58.897	WGS84	Alviso Slough	Marsh Plain
ASM-505	7/05/07	37 25.856	121 58.765	WGS84	Alviso Slough	Marsh Plain
ASM-506	7/05/07	37 26.359	121 59.516	WGS84	Alviso Slough	Marsh Plain
ASM-504	7/05/07	37 26.779	122 00.715	WGS84	Alviso Slough	Marsh Plain

<sup>1</sup>All latitude/longitude coordinates are given in degrees and decimal minutes (e.g. DDD MM.MMM)

**Table 4.1.2.** Quality Assurance metrics for USGS (Menlo Park, CA) analyses. The values listed represent the mean ( $\pm$  standard error) in each case. The number of observations (N) is given in parentheses. Cells that are blank indicate that particular QA metric was not appropriate or not run for that particular analyte. Average Daily Detection Limit (DDL) is given in cases where method blanks are below the DDL.

Analysis	Method Blanks (count)	Analytical Duplicate % Dev (count)	Certified Reference Material % Recovery (count)	Matrix Spike % Recovery (count)
Sediment Total Mercury	0.006 $\pm$ 0.003 $\mu$ g/g dw (4)	11.5 $\pm$ 1.4 (4)	97.2 $\pm$ 4.7 (5)	91.7 $\pm$ 4.2 (4)
Sediment Methylmercury	0.07 $\pm$ 0.02 ng/g dw (5)	10.0 $\pm$ 5.6 (4)	105.3 $\pm$ 4.1 (8)	95.8 $\pm$ 5.1 (7)
Sediment Reactive Mercury	0.03 $\pm$ 0.01 ng, absolute (8)	3.9 $\pm$ 0.9 (3)		
Sediment Dry Weight		1.7 $\pm$ 0.5 (20)		
Sediment Bulk Density		0.6 $\pm$ 0.1 (20)		
Sediment Loss on Ignition		4.3 $\pm$ 1.6 (20)		
Sediment Porosity		1.2 $\pm$ 0.4 (20)		
Pore Water Sulfate	< 0.6 $\mu$ mol/L DDL (8)	8.1 $\pm$ 2.6 (18)		
Pore Water Chloride	< 1.7 $\mu$ mol/L DDL (8)	4.5 $\pm$ 0.9 (18)		
Pore Water Sulfide	< 0.2 $\mu$ mol/L DDL (2)	7.3 $\pm$ 2.2 (13)		
Pore Water Conductivity		1.5 $\pm$ 0.5 (25)		
Overlying Water Dissolved Organic Carbon	< 0.5 mg/L DDL (2)	1.6 $\pm$ 1.5 (13)		
Overlying Water Sulfate	< 0.6 $\mu$ mol/L DDL (8)	1.6 $\pm$ 0.4 (5)		
Overlying Water Chloride	< 1.7 $\mu$ mol/L DDL (8)	0.6 (1)		
Overlying Water Total Suspended Solids		11.1 $\pm$ 5.1 (35)		

**Table 4.2.1.** Pond A8 and Alviso Slough water station descriptions.

Station Code	Latitude <sup>1</sup>	Longitude <sup>1</sup>	Datum	Location	Feature Type
A8WD1Surface and Deep	37.4331	121.99577	WGS84	Pond A8	Historic Slough Channel
A8WF1	37.4254	121.98087	WGS84	Pond A8	Borrow Ditch
A8WF2	37 26.323	121 0.1760	WGS84	Pond A8	Borrow Ditch
ASW1Surface and Deep	37.42503	121.97909	WGS84	Pond A8	Slough Channel
ASW2Surface and Deep	37.44705	122.01232	WGS84	Pond A8	Slough Channel
ASW3Surface and Deep	37.45827	122.02056	WGS84	Pond A8	Slough Channel
ASMW1	37.42477	121.97920	WGS84	Pond A8	Marsh Plain
ASMW2	37.44636	122.01189	WGS84	Pond A8	Marsh Plain
ASMW3	37.45807	122.02126	WGS84	Pond A8	Marsh Plain

<sup>1</sup>All latitude/longitude coordinates are given in decimal degrees (e.g., ddd.ddddd).

**Table 4.3.1.** Size limits for fish applied to control for the length:mercury relationship in comparisons among salt ponds and Alviso Slough habitats.

Species	Min. Length (mm)	Max. Length (mm)
longjaw mudsucker	92	123
yellowfin goby	54	74
threespine stickleback	28	37
Mississippi silverside	56	71



**Table 5.2.1.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. November 14–16, 2006 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results November 14, 2006</b>										
A8WF1	54 <sup>1</sup>	3.480	52	*	6.91	14.6	8.78	173	83.5	Surface
A8WF2	32 <sup>1</sup>	2.460	34	*	6.51	14.9	8.68	145	77.8	Surface
A8WD1Surface	49 <sup>1</sup>	2.770	27	*	7.12	15.7	8.68	150	77.2	Surface
A8WD1Deep	28 <sup>1</sup>	0.532	120	*	1.73	16.2	7.43	*	*	1.25 meters
<b>Alviso Slough Results November 16, 2006 (Tide = 9.1 ft above MLLW)</b>										
ASW1Surface	33.000	0.131	*	0.12	5.90	16.2	7.87	89	2.52	Surface
ASW1Deep	36.600	0.126	*	0.12	6.90	16.2	7.91	90	2.49	2.75 meters
ASW2Surface	13.700	0.172	*	1.19	5.70	16.0	7.83	48	20.1	Surface
ASW2Deep	17.200	0.132	*	2.09	7.00	15.5	7.74	73	33.5	2.5 meters
ASW3Surface	13.100	0.084	*	2.22	5.86	14.9	7.87	40	35.2	Surface
ASW3Deep	26.300	0.116	*	2.39	6.08	14.9	7.85	72	37.8	1.75 meters
<b>Marsh Results November 16, 2006</b>										
ASMW1	81.500	0.312	*	0.16	12.3	15.0	7.97	69	3.19	Surface
ASMW2	15.000	0.062	*	1.26	6.83	15.5	7.95	56	21.2	Surface
ASMW3	16.300	0.188	*	2.00	6.70	13.5	7.96	77	32.3	Surface

<sup>1</sup> QA criteria not met. Results usable for the purpose of this project.

\* Results determined unusable due to field and/or lab error.

**Table 5.2.2.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. January 25–30, 2007 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results January 25, 2007</b>										
A8WF1	47	5.270	170	*	6.76	10.7	8.14	370	86.0	Surface
A8WF2	49	0.572	180	*	6.62	9.5	8.26	360	87.0	Surface
A8WD1Surface	12	0.811	200	*	9.73	10.1	8.31	370	88.0	Surface
A8WD1Deep	45	1.240	170	*	10.06	9.0	8.28	370	88.0	1.0 meters
<b>Alviso Slough Results January 30, 2007 (Tide = 10.9 ft above MLLW)</b>										
ASW1Surface	13	0.111	20	0.77	5.01	13.2	7.71	38	13.6	Surface
ASW1Deep	3.2	0.162	52	1.35	5.03	12.8	7.58	52	22.6	4.75 meters
ASW2Surface	11	0.084 <sup>1</sup>	63	2.22	4.95	11.4	7.78	59	35.6	Surface
ASW2Deep	30	0.122 <sup>1</sup>	61	2.27	5.00	11.1	7.77	98	36.5	2.75 meters
ASW3Surface	16	0.104 <sup>1</sup>	60	2.25	4.65	11.1	7.72	56	36.1	Surface
ASW3Deep	24	0.101 <sup>1</sup>	94	3.37	4.64	10.8	7.78	110	37.9	3.5 meters
<b>Marsh Results January 30, 2007</b>										
ASMW1	4.4 <sup>1</sup>	0.137	27	0.36	5.66	11.5	7.81	65	6.92	Surface
ASMW2	19 <sup>1</sup>	0.195	71	1.66	5.04	12.1	7.81	56	27.5	Surface
ASMW3	20 <sup>1</sup>	0.147	68	1.95	5.93	11.2	7.89	25	31.8	Surface

<sup>1</sup> QA criteria not met. Results usable for the purpose of this project.

\* Results determined unusable due to field and/or lab error.

**Table 5.2.3.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. March 27–29, 2007 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results March 27, 2007</b>										
A8WF1	110 <sup>1</sup>	5.130	200 <sup>1</sup>	11.0	2.82	13.8	8.48	230	99.0	Surface
A8WF2	65 <sup>1</sup>	3.780	210 <sup>1</sup>	*	3.02	12.7	8.64	360	94.0	Surface
A8WD1Surface	6.6 <sup>1</sup>	3.530	200 <sup>1</sup>	*	3.18	13.4	8.56	361	97.0	Surface
A8WD1Deep	7.2 <sup>1</sup>	3.270	190 <sup>1</sup>	*	2.74	13.3	8.55	364	63.0	1.25 meters
<b>Alviso Slough Results March 29, 2007 (Tide = 8.7 ft above MLLW)</b>										
ASW1Surface	1.2 <sup>1</sup>	0.223	29	0.07	4.95	15.7	7.95	55	1.55	Surface
ASW1Deep	<0.50 <sup>1</sup>	0.275	31	0.24	4.89	15.6	8.17	77	4.73	3.75 meters
ASW2Surface	3.8 <sup>1</sup>	0.278	41	1.02	5.04	16.2	7.86	34	7.40	Surface
ASW2Deep	3.9 <sup>1</sup>	0.128	170	1.84	4.93	14.8	7.73	112	29.9	2.0 meters
ASW3Surface	15 <sup>1</sup>	0.180	71	1.87	5.35	15.3	7.75	33	29.3	Surface
ASW3Deep	21 <sup>1</sup>	0.192	120	2.05	5.13	14.8	7.90	106	32.9	1.3 meters

<sup>1</sup> QA criteria not met. Results usable for the purpose of this project.

\* Results determined unusable due to field and/or lab error.

**Table 5.2.4.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. May 14–17, 2007 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results May 17, 2007</b>										
A8WF1	84.9	10.200	310 <sup>1</sup>	14.8	4.54	20.9	8.62	101	222	Surface
A8WF2	41.5	3.970	340 <sup>1</sup>	15.6	0.00	19.3	8.50	32	236	Surface
A8WD1Surface	39.1	2.830	350 <sup>1</sup>	14.7	0.17	19.1	8.51	38	221	Surface
A8WD1Deep	42.2	3.230	220 <sup>1</sup>	19.7	0.00	16.9	8.50	21	265	1.0 meters
<b>Alviso Slough Results May 14, 2007 (Tide = 7.5 ft above MLLW)</b>										
ASW1Surface	20.9	0.600	41	0.68	6.79	19.0	8.50	58	12.4	Surface
ASW1Deep	36.8	0.460	59	0.87	4.86	19.1	8.62	57	15.1	3.0 meters
ASW2Surface	20.1	0.300	67	2.01	5.42	20.3	8.48	29	32.5	Surface
ASW2Deep	31.2	0.310	84	2.25	4.36	18.9	8.49	81	35.6	2.0 meters
ASW3Surface	23.3	0.240	96	2.51	6.60	20.0	8.20	30	39.2	Surface
ASW3Deep	83.4	0.300	270	2.85	5.07	18.5	8.35	185	43.9	2.25 meters
<b>Marsh Results May 14, 2007</b>										
ASMW1	22.1	0.290	40	0.65	7.14	18.9	8.47	38	11.5	Surface
ASMW2	17.9	0.350	70	1.76	8.00	21.1	8.65	48	28.6	Surface
ASMW3	22.2	0.200	82	2.63	6.52	20.4	8.50	76	40.6	Surface

<sup>1</sup> QA criteria not met. Results usable for the purpose of this project.

**Table 5.2.5.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. July 12–16, 2007 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results July 16, 2007</b>										
A8WF1	149	5.230	510	19.9	0.95	25.1	7.94	240	290.0	Surface
A8WF2	89.0	2.340	580	21.9	0.5	22.2	7.75	43	314.8	Surface
A8WD1Surface	65.9	1.840	480	18.6	0.44	25.5	7.78	29	274.4	Surface
A8WD1Deep	65.4	3.040	480	21.0	0.34	23.1	7.78	32	284.8	0.75 meters
<b>Alviso Slough Results July 12, 2007 (Tide = 7.7 ft above MLLW)</b>										
ASW1Surface	19.2	0.397	92 <sup>1</sup>	0.80	6.18	23.1	8.00	26	13.9	Surface
ASW1Deep	33.0	0.554	46 <sup>1</sup>	1.05	4.83	22.3	8.24	42	17.8	2.5 meters
ASW2Surface	16.8 <sup>1</sup>	0.258	86 <sup>1</sup>	2.02	4.54	23.8	7.87	25	32.1	Surface
ASW2Deep	30.3 <sup>1</sup>	0.296	140 <sup>1</sup>	2.14	3.72	22.8	7.88	74	33.9	2.5 meters
ASW3Surface	19.0 <sup>1</sup>	0.208	90 <sup>1</sup>	2.35	5.33	24.3	7.71	68	37.0	Surface
ASW3Deep	38.4 <sup>1</sup>	0.254	150 <sup>1</sup>	2.53	4.14	22.3	7.84	90	39.5	2.5 meters
<b>Marsh Results July 12, 2007</b>										
ASMW1	14.6 <sup>1</sup>	0.334	36 <sup>1</sup>	0.52	5.61	21.2	7.49	13	9.36	Surface
ASMW2	19.4 <sup>1</sup>	0.172	71 <sup>1</sup>	1.82	5.63	25.0	7.95	67	29.3	Surface
ASMW3	18.0 <sup>1</sup>	0.280	95 <sup>1</sup>	2.38	5.81	25.2	7.88	82	37.4	Surface

<sup>1</sup> QA criteria not met. Results usable for the purpose of this project.

**Table 5.2.6.** Surface water field measurements, total mercury, total methylmercury, and total suspended solids. August 27–29, 2007 sampling events.

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
<b>Pond A8N Results August 29, 2007</b>										
A8WF1	230	1.460	910	27.9	0.31	27.5	7.61	277	422	Surface
A8WF2	67.8	0.378	540	24.7	0.52	24.4	7.68	22	378	Surface
A8WD1Surface	62.3	0.265	580	24.9	2.05	27.5	7.70	51	379	Surface
A8WD1Deep	68.8	0.249	520	25.4	0.98	23.9	7.68	15	387	0.5 meters
<b>Alviso Slough Results August 27, 2007 (Tide = 8.5 ft above MLLW)</b>										
ASW1Surface	21.7	0.833	62	1.01	5.28	22.8	8.03	2	17.3	Surface
ASW1Deep	52.7	1.260	140	1.61	3.38	22.2	8.09	61	26.1	3.75 meters
ASW2Surface	13.7	0.277	76	2.17	5.79	24.1	8.03	18	34.2	Surface
ASW2Deep	28.8	0.278	150	2.35	4.46	22.2	8.01	102	37.0	2.75 meters
ASW3Surface	14.2	0.196	66	2.37	5.43	24.8	7.89	8	36.8	Surface
ASW3Deep	46.7	0.377	180	2.67	4.22	22.6	7.95	73	41.5	1.75 meters
<b>Marsh Results August 27, 2007</b>										
ASMW1	24.0	0.584	62	0.68	3.73	21.1	8.09	185	12.2	Surface
ASMW2	19.8	0.320	96	2.00	4.58	24.0	8.00	61	31.7	Surface
ASMW3	11.2	0.167	99	2.53	5.67	24.0	7.98	29	39.4	Surface

**Table 5.3.1.** Number of samples analyzed for total mercury (vertebrates) and methylmercury (brine flies) from 2007 field collections. Numbers for fish indicate samples that fell within size-limit criteria, which were applied to control for any length:mercury relationship.

<i>Species</i>	<i>Pond A5</i>	<i>Pond A7</i>	<i>Pond A8</i>	<i>Pond Total</i>	<i>Reference Marsh</i>	<i>Alviso Slough &amp; Marsh</i>	<i>Grand Total</i>
<i>Demersal Fish</i>							
longjaw mudsucker	5	6	12	23		32	55
yellowfin goby	12			12		8	20
<i>Water-column Fish</i>							
threespine stickleback	19	8		27		16	43
Mississippi silverside	6	4		10		8	18
<i>Brine Flies</i>							
<i>Ephydra</i> spp.			18	18		7	25
<i>Resident Marsh Birds</i>							
Song Sparrow					29	30	59
Marsh Wren					10	16	26
Common Yellowthroat					8	14	22

**Table 5.3.2.** Number of additional fish samples analyzed for total mercury to investigate length:mercury relationships.

<i>Species</i>	<i>Pond A5</i>	<i>Pond A7</i>	<i>Pond A8</i>	<i>Pond Total</i>	<i>Reference Marsh</i>	<i>Alviso Slough &amp; Marsh</i>	<i>Grand Total</i>
<i>Demersal Fish</i>							
Longjaw mudsucker	3	2	12	17		8	25
<i>Water-column Fish</i>							
threespine stickleback	25	1	1	27		20	47



**Table 5.3.3.** Results of analysis of spatial variation in mercury concentrations in bird blood. Each table shows the results of a mixed model ANOVA for a given species. Site was significant for all species. Song Sparrows, which had the largest sample size, also showed significant variation by geographic area (Alviso Slough marshes versus ambient reference marshes in lower South Bay) and by degree of subsidence.

A. Common Yellowthroat

Source	SS	MS	F value	DF	P
GeoArea	4.73	2.36	6.98	2	0.13
Site(GeoArea)	0.68	0.34	12.38	2	< 0.01
Residual	0.27	0.03	-	10	-

B. Marsh Wren

Source	SS	MS	F value	DF	P
GeoArea	1.77	0.88	3.27	2	0.14
Site(GeoArea)	1.07	0.27	7.49	4	< 0.01
Residual	0.64	0.04	-	18	-

C. Song Sparrow

Source	SS	MS	F value	DF	P
GeoArea	6.88	3.44	25.02	2	< 0.01
Subsidence	0.58	0.58	23.34	1	< 0.0001
Site(GeoArea)	1.02	0.20	8.18	5	< 0.0001
Residual	1.14	0.03	-	46	-

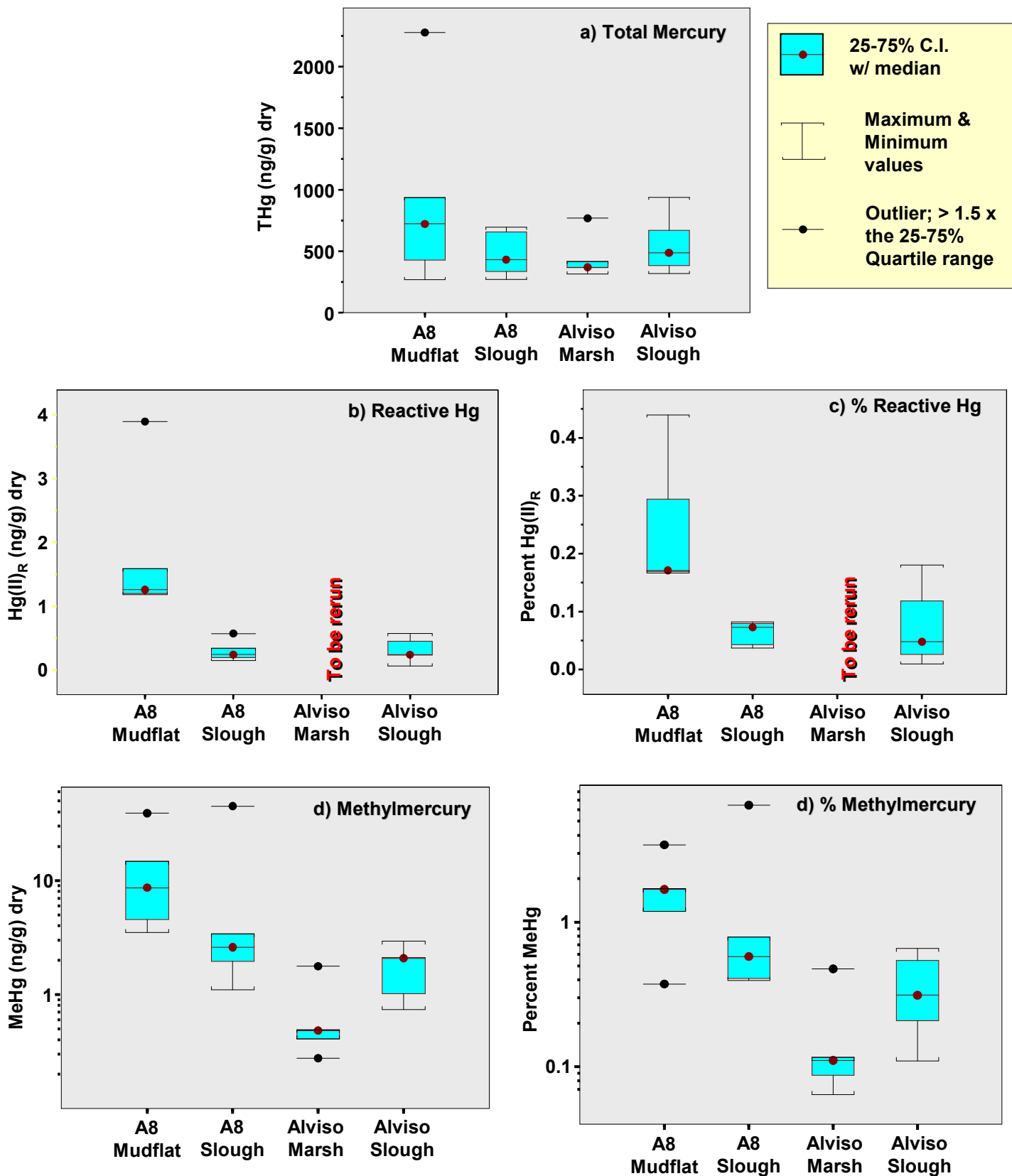
**Table 5.3.4.** Blood mercury concentration-of-concern thresholds extrapolated from Tree Swallows and Common Loons and applied to songbirds (as per Evers et al. 2005).

Mercury (ug/g ww)	Effects Risk
< 0.96	None to Low
0.96–1.38	Likely
> 1.38	High

10. Figures

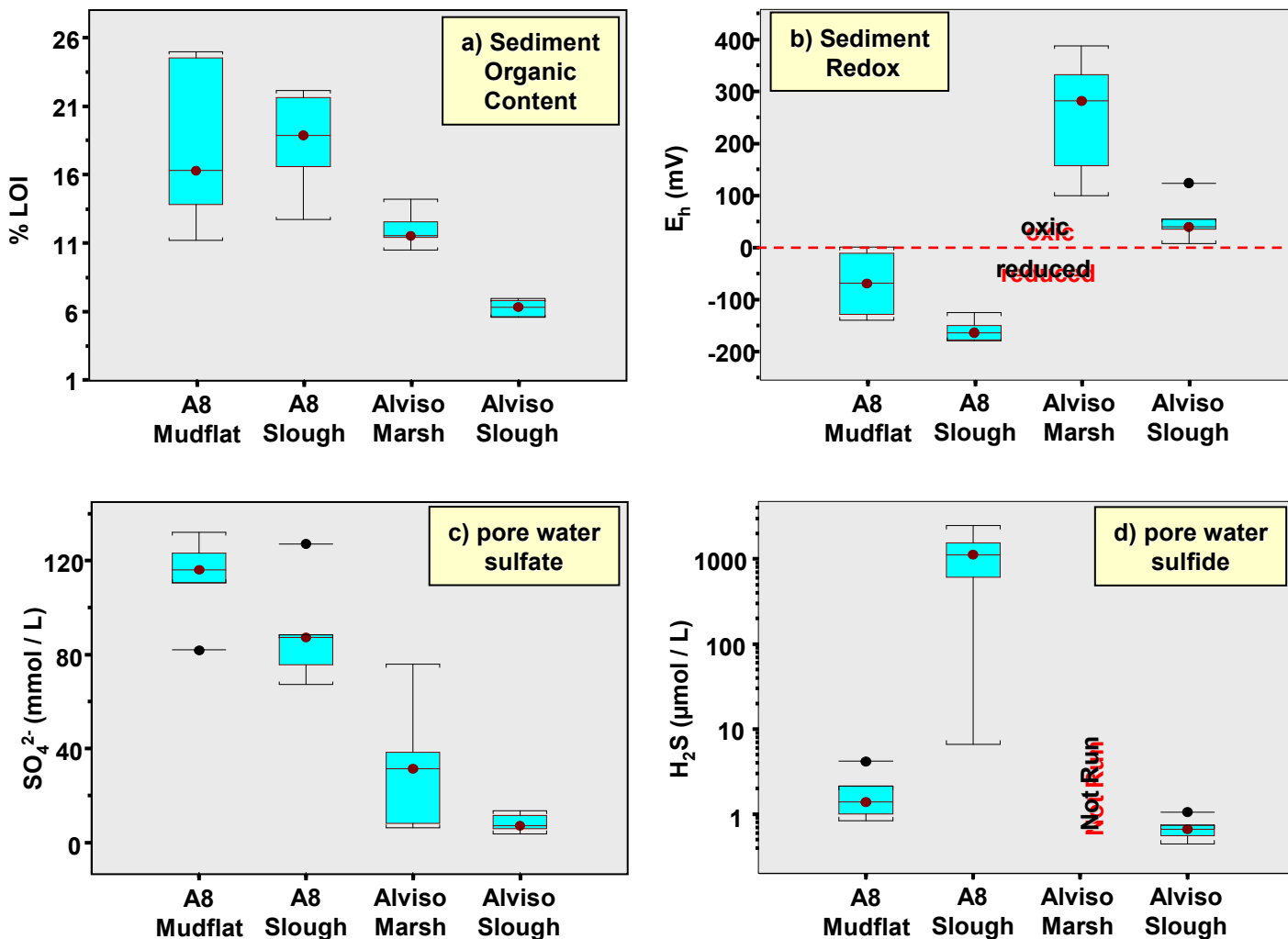


Figure 5.1. Sampling locations in 2007 for sediment and water.

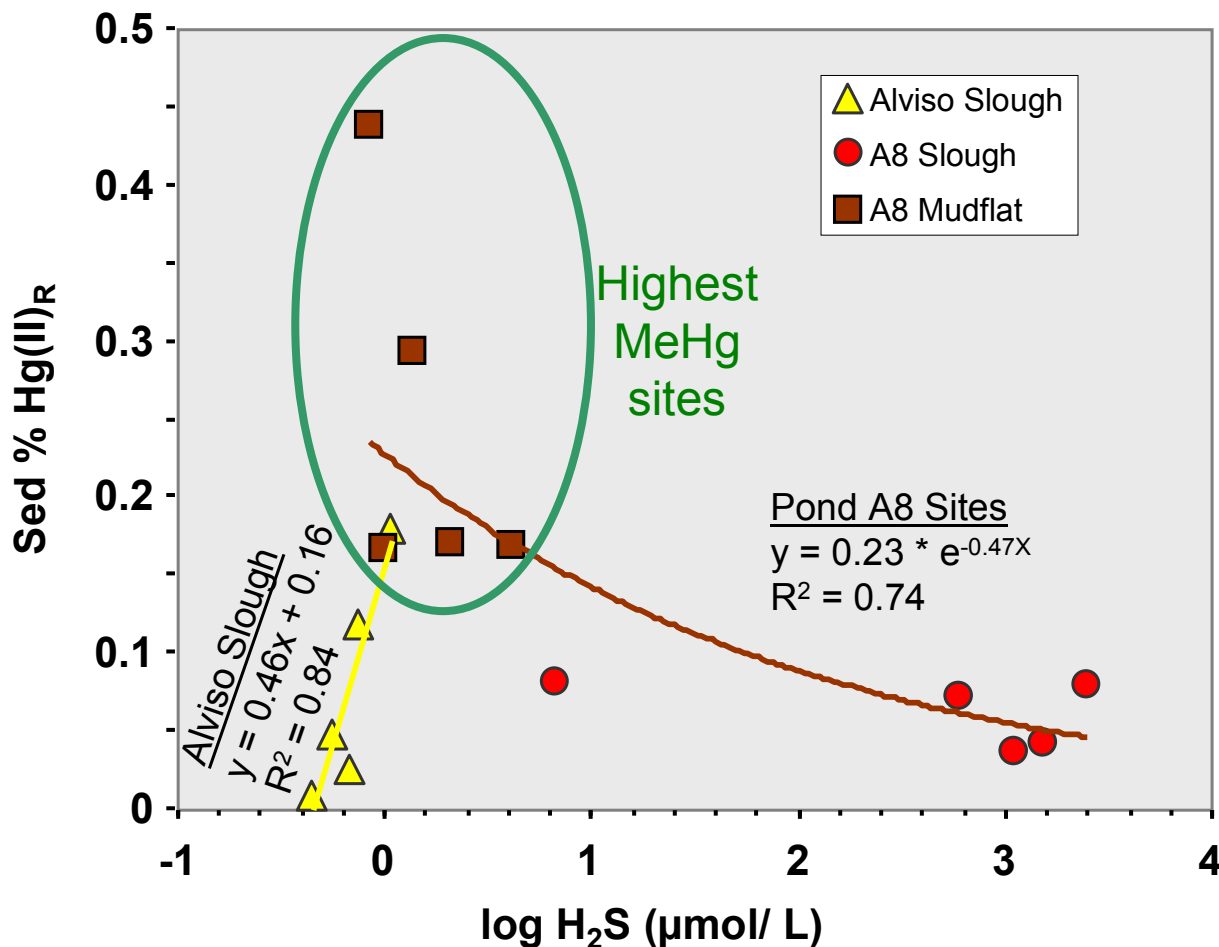


**Figure 5.1.1.** Box and whisker plots of sediment Mercury species (total mercury (THg), methylmercury (MeHg) and reactive mercury (Hg(II)<sub>R</sub>) in Pond A8 and Alviso Slough and marsh, sampled between May and July 2007. Each habitat represents N = 5 individual sites.





**Figure 5.1.3.** Box and whisker plots of sediment organic content as %LOI (a), sediment redox (b), pore water sulfate (c) and pore water sulfide (d) in Pond A8 and Alviso Slough and marsh, sampled between May and July 2007. Each habitat represents N = 5 individual sites. Box and whisker legend, as per Figure 5.1.1.



**Figure 5.1.4.** X-Y Plot of pore water sulfide (logarithmic scale) versus the percentage of sediment total mercury that exists as reactive mercury (% Hg(II)<sub>R</sub>), for sediments collected from Alviso Slough main channel and Pond A8 (slough and mudflat) sites. A positive linear regression was used to fit the Alviso Slough main channel data, while a negative non-linear regression was used to fit the Pond A8 data. The green circle surrounding the A8 Mudflat sites is a reminder that these are the same sites that exhibited the highest sediment MeHg concentrations.

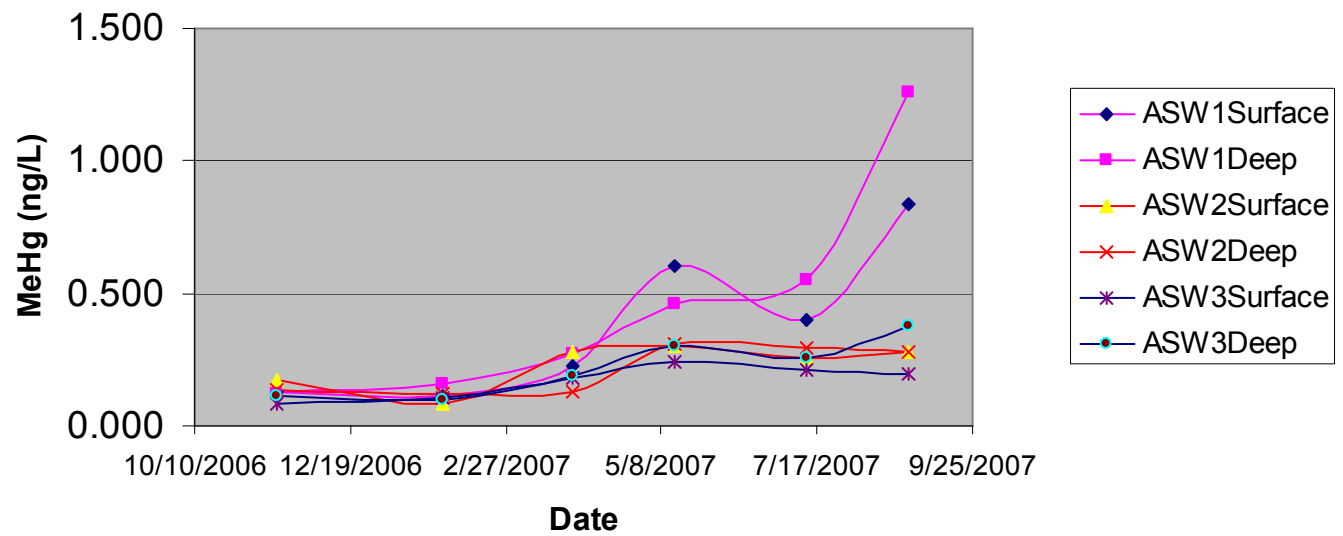


Figure 5.2.1. Methylmercury in slough samples.



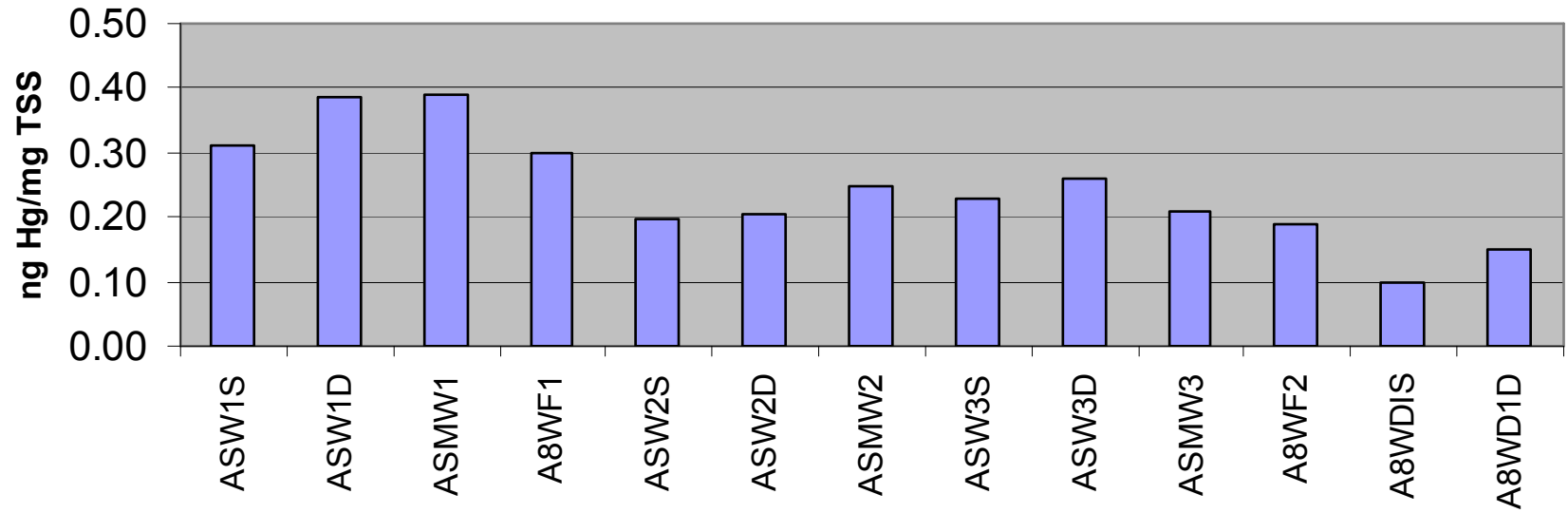


Figure 5.2.2. Total Hg/TSS (average concentration ratios).

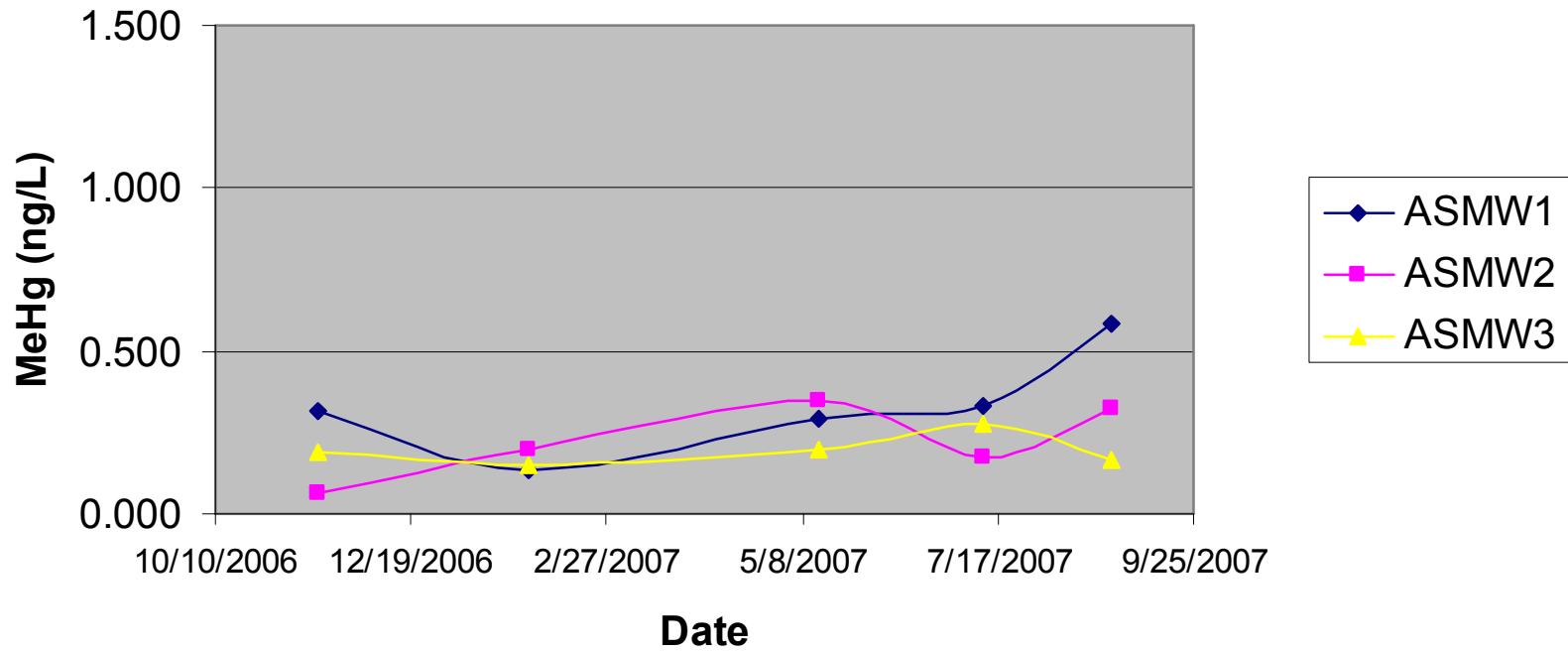


Figure 5.2.3. Methylmercury in marsh samples.

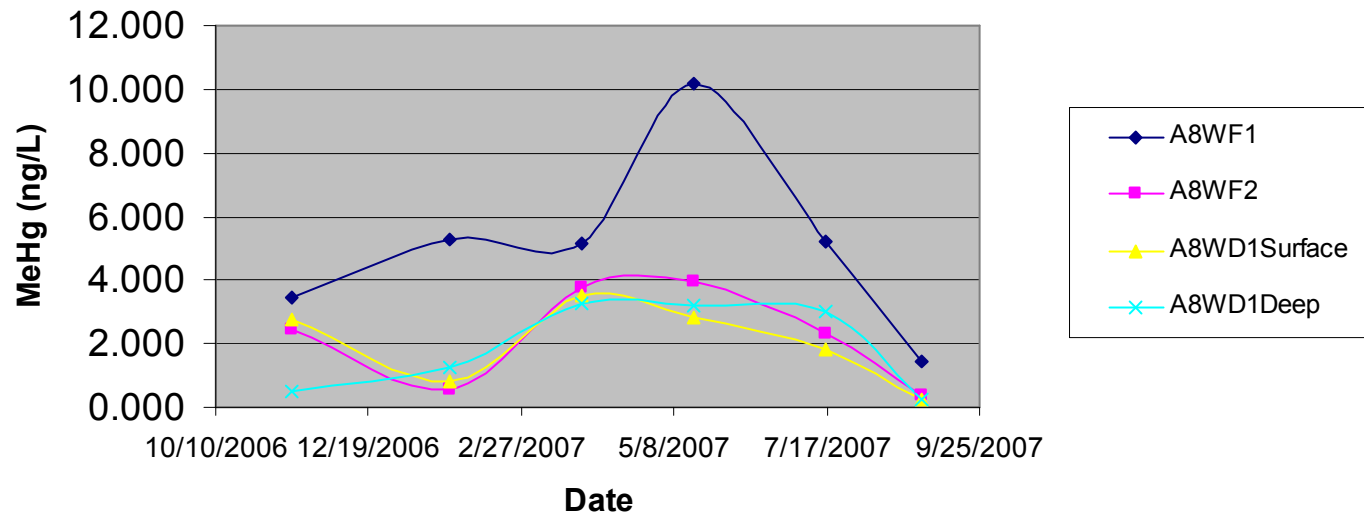
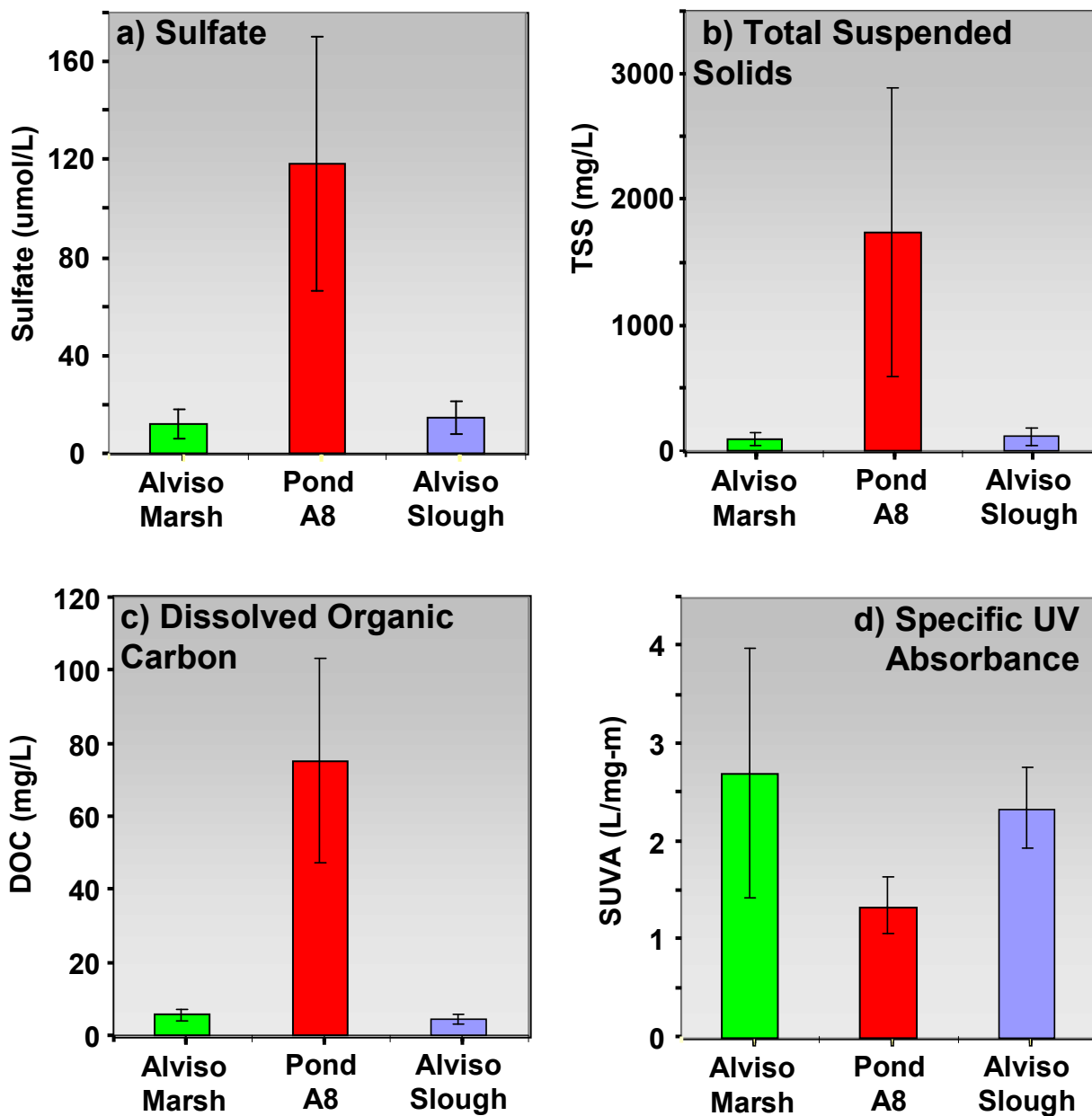
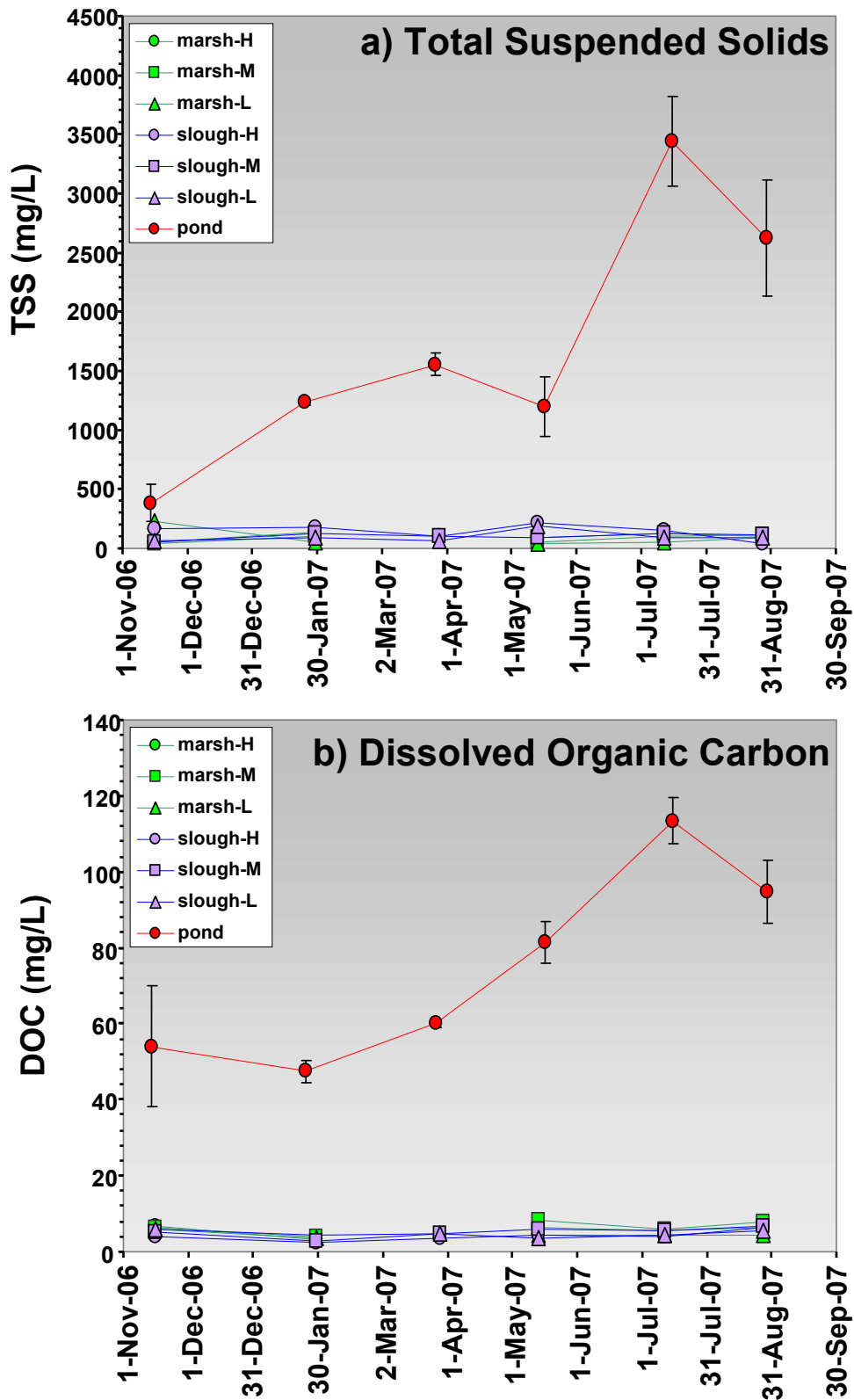


Figure 5.2.4. Methylmercury in Pond A8 samples.



**Figure 5.2.5.** Bar graphs of overlying water concentrations of sulfate (a), total suspended solids (b), dissolved organic carbon (c), and specific ultra-violet absorption (d), in waters collected from Alviso Marsh, Alviso Slough (main channel), and Pond A8. Each bar represents the average of six sampling events (November 2006 through August 2007) and multiple sampling sites within each habitat type, where N = 18, 24 and 36 for Alviso Marsh, Pond A8 and Alviso Slough, respectively. Error bars represent ± 1 standard deviation of the mean.



**Figure 5.2.6.** Time series graphs of overlying water concentrations of total suspended solids (a) and dissolved organic carbon (b), in waters collected from Alviso Marsh and Slough (high [H], mid [M] and low [L] along the salinity gradient), and Pond A8. Alviso Slough and Marsh symbols represent the average of N = 2 and N = 1 site(s), respectively. Pond A8 symbol represents the average of N = 7 sampling sites, and error bars represent  $\pm 1$  standard error of the mean.



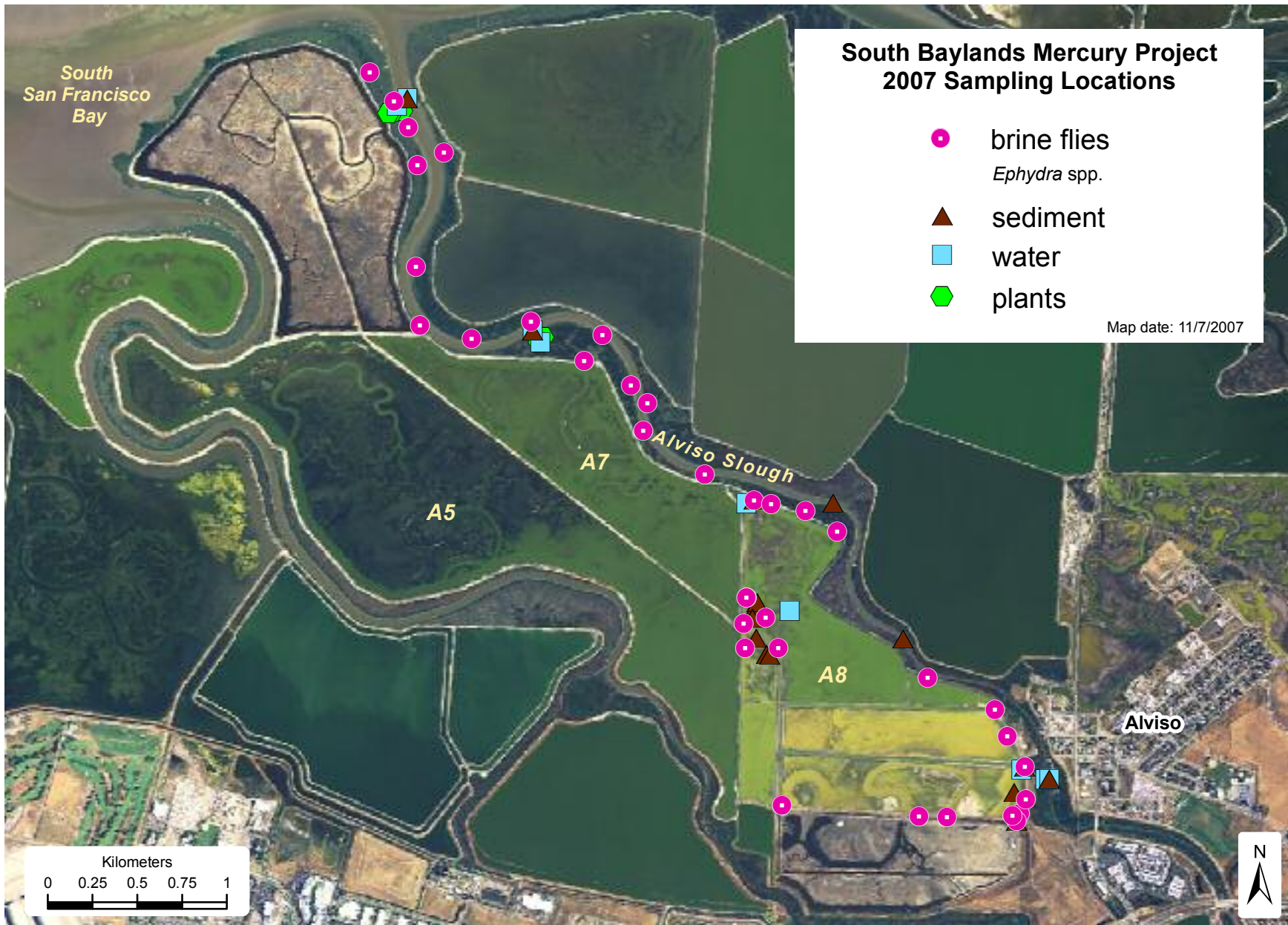
**Figure 5.3.1.** Sampling locations in 2007 for demersal/benthic biosentinel fish: longjaw mudsucker and yellowfin goby. Plant sites are from a separate, but coordinated, USGS study.





**Figure 5.3.2.** Sampling locations in 2007 for water-column biosentinel fish: threespine stickleback and Mississippi silverside. Plant sites are from a separate, but coordinated, USGS study.



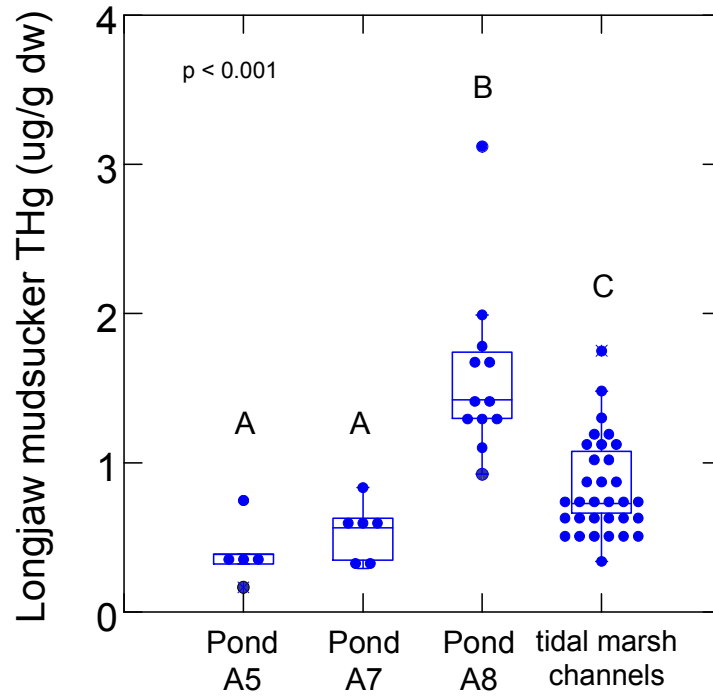


**Figure 5.3.3.** Sampling locations in 2007 for brine flies (*Ephydra* spp.). *Ephydra gracilis* was collected in Pond A8, and *E. millbrae* was collected in Alviso Slough and the tidal channels of the fringing marsh. Plant sites are from a separate, but coordinated, USGS study.

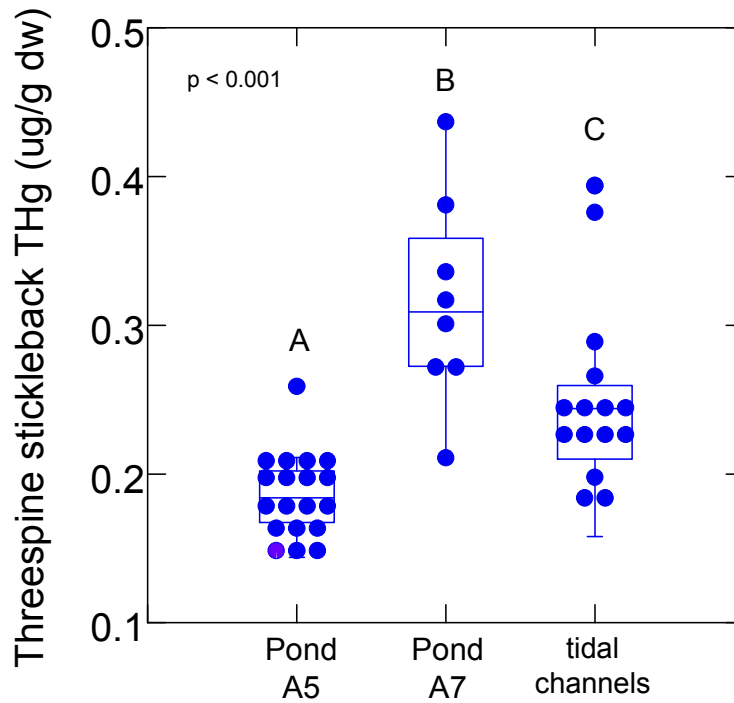




**Figure 5.3.4.** Sampling locations in 2007 for resident marsh birds: Song Sparrow, Marsh Wren, and Common Yellowthroat. Plant sites are from a separate, but coordinated, USGS, study.

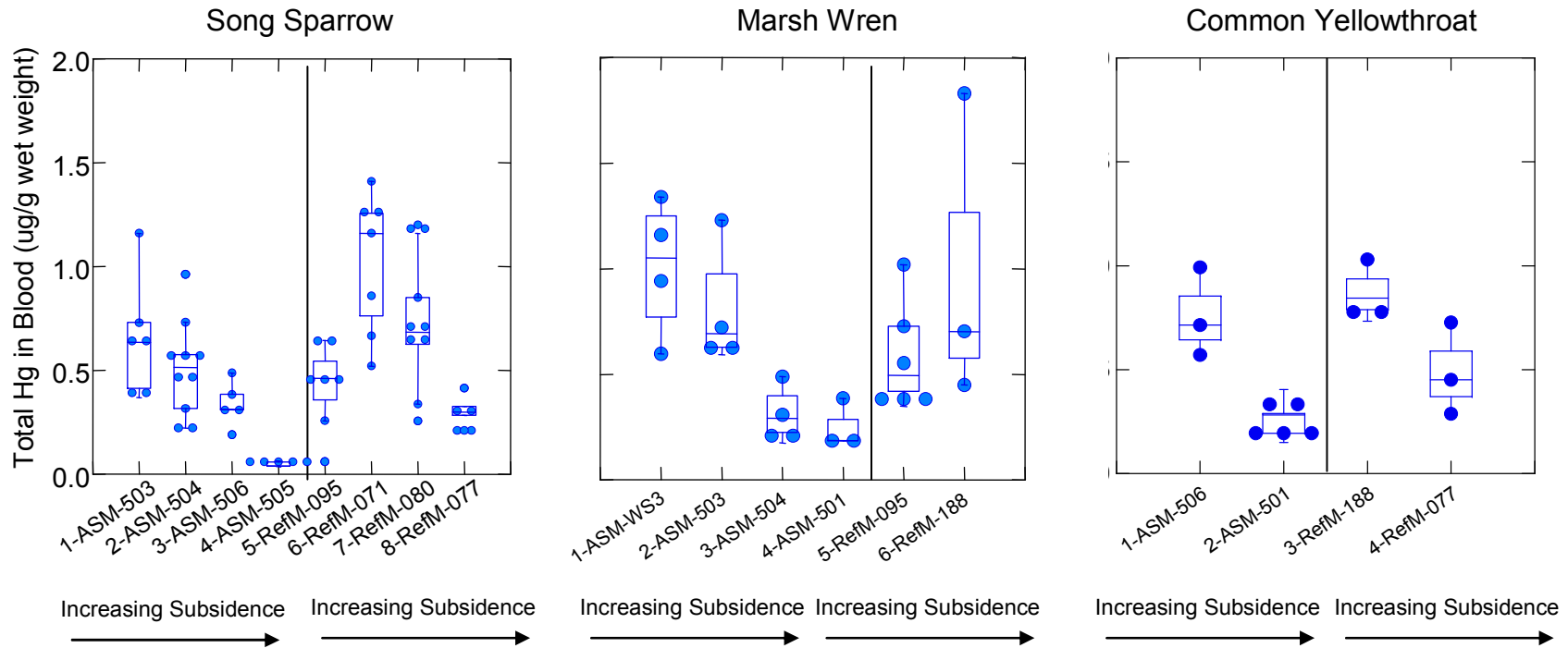


**Figure 5.3.5.** Mercury concentrations in whole-body longjaw mudsuckers (*Gillichthys mirabilis*) were highest in Pond A8 and lowest in Ponds A5 and A7, with tidal channels falling in between the pond groups. Letters above each box plot indicate significantly different groups. The lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median value for the site, and the lines extending above and below the box represent those values that fall within  $\pm 1.5$  times the inter-quartile range. The individual data points for each site are represented by solid blue dots.



**Figure 5.3.6.** Mercury concentrations in whole-body threespine stickleback (*Gasterosteus aculeatus*) were highest in Pond A7 and lowest in Pond A5, with tidal channels falling in between the two ponds. Letters above each box plot indicate significantly different groups. The lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median value for the site, and the lines extending above and below the box represent those values that fall within  $\pm 1.5$  times the inter-quartile range. The individual data points for each site are represented by solid blue dots.





**Figure 5.3.8.** Concentrations of total Hg in blood from A) Song Sparrows, B) Marsh Wrens, and C) Common Yellowthroat from Alviso Slough marshes (ASM) and ambient reference marshes (RefM) South of Dumbarton Bridge. The x-axis represents different sites ordered from least subsided to most subsided within each geographic area. Note that increasing subsidence is correlated with decreasing salinity, except for RefM-095. RefM-095 is the only fresh to brackish marsh site that has little subsidence. Data are plotted as box plots where the lower and upper ends of the box represent the 25<sup>th</sup> and 75<sup>th</sup> percentiles, the horizontal line within each box represents the median value for the site, and the lines extending above and below the box represent those values that fall within  $\pm 1.5$  times the interquartile range. The individual data points for each site are represented by solid blue dots.





Figure 5.3.9. Song sparrow mercury concentrations across South Bay marshes generally varied according to a gradient of subsidence, which was somewhat confounded with the salinity gradient. Marshes that experienced less subsidence and were in saltier areas of South Bay tended to have higher mercury in sparrows. For example, the marsh with the highest mercury concentrations (far left), where four of seven sparrows captured were above the level of concern for effects in songbirds (0.96  $\mu\text{g/g ww}$ ; Evers et al. 2005), was both the most saline and in the least-subsided category. The freshwater marsh with the least subsidence (top right) had lower mercury than the unsubsided saltmarsh previously mentioned (far left) but higher mercury than the freshwater subsided marsh near the town of Alviso (lower right). Subsidence is indicated by the brightly colored lines: pink = 1ft, blue = 2ft, green = 4ft, yellow = 6ft (Poland and Ireland 1988). Height and color of symbol indicate mercury concentration of whole blood in wet weight (see legend above).

### Pond Action Decision Tree

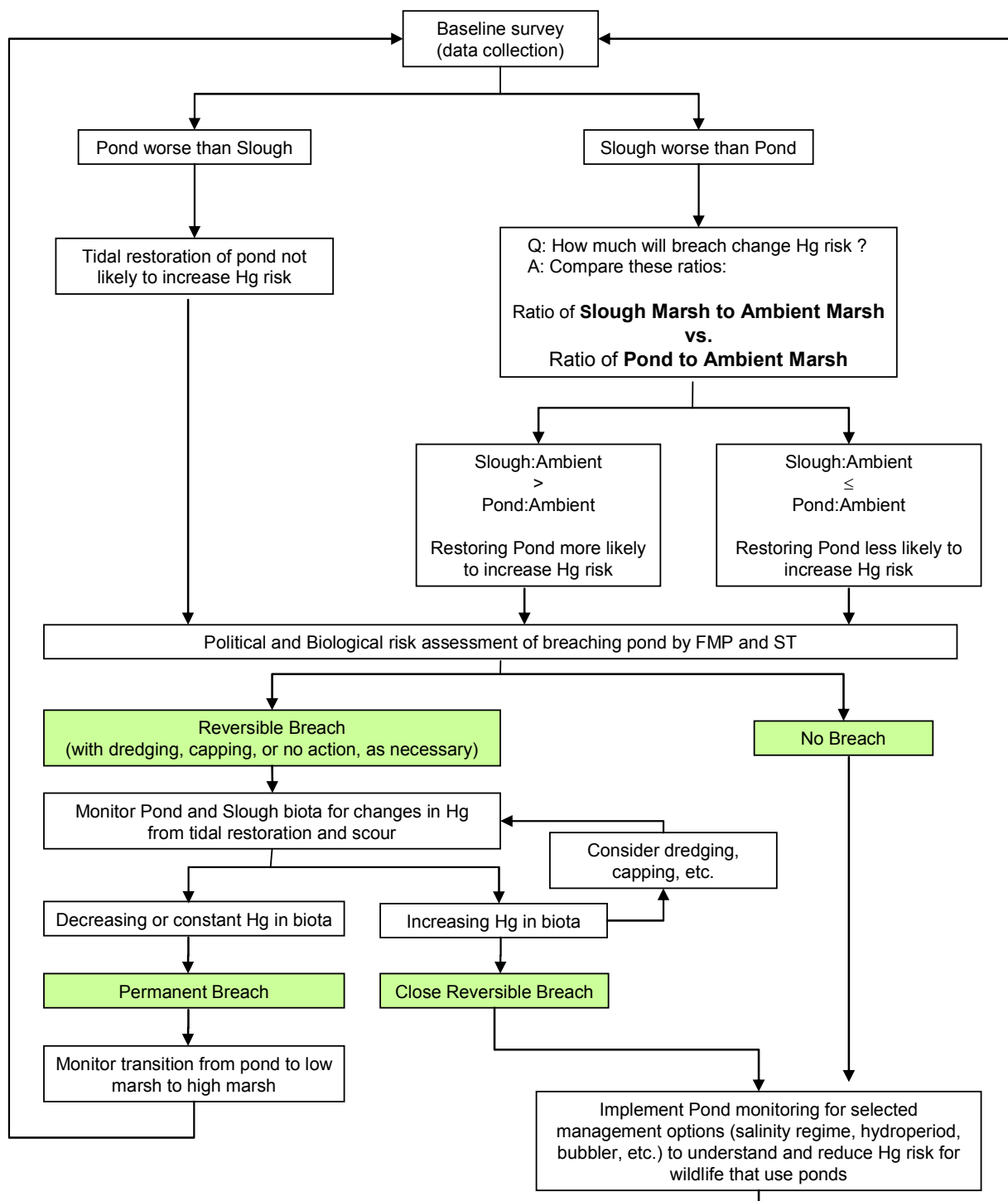
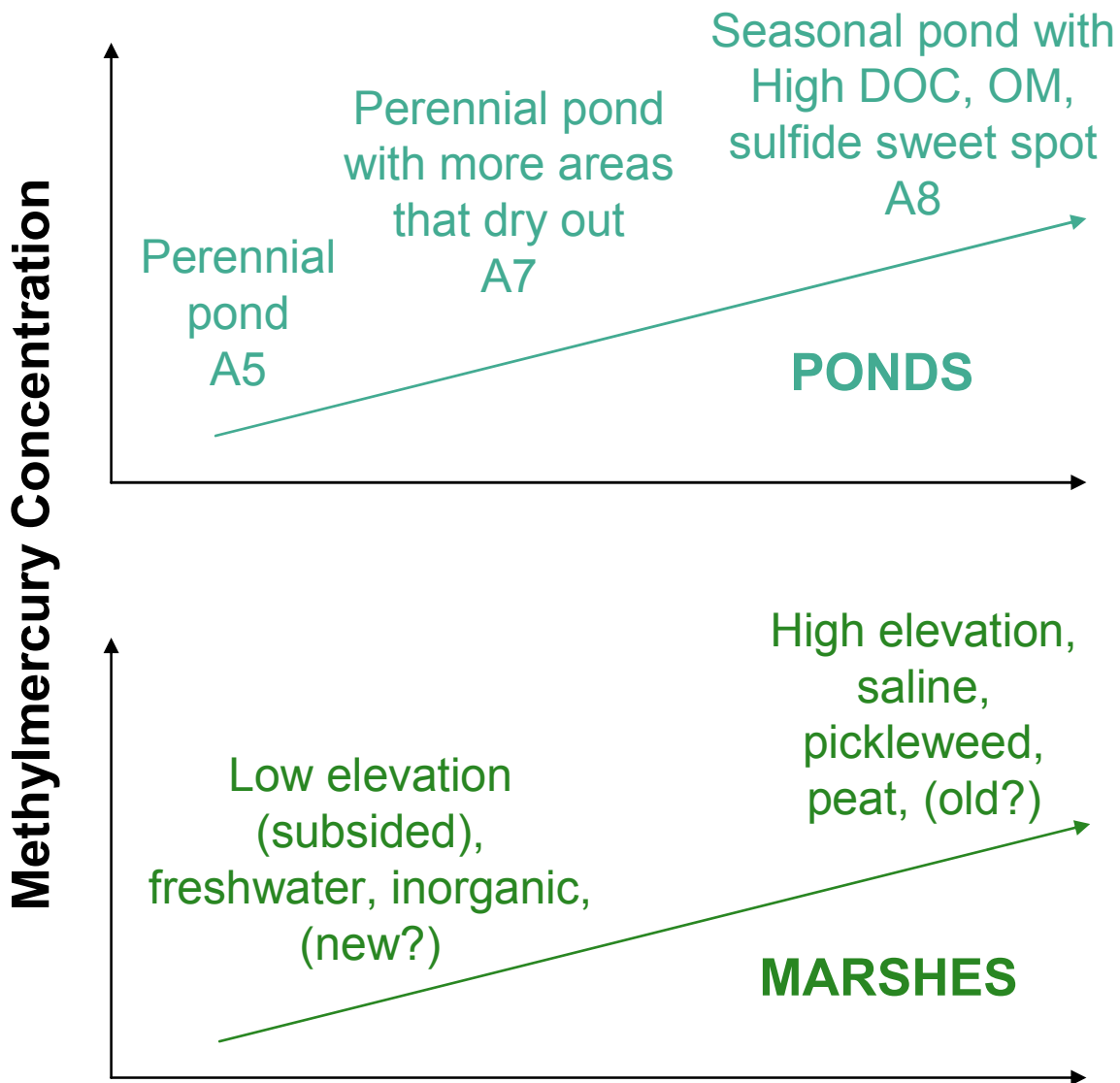


Figure 5.3.10. Decision framework for using SBMP biota results. This decision framework is based on using mercury data from biota. Data from other sources, such as concentrations of contaminants in sediment at depth, should also impact decision making.



<b>Hydroperiod</b>	Always Wet	➔	Wet/Dry Cycles
<b>Elevation</b>	Low, closer to MHHW		Higher relative to MHHW
<b>Salinity</b>	Brackish plants		Pickleweed
<b>Sediment</b>	Inorganic		Peat
<b>Plant Effects</b>	Low root volume & acids		High root volume & acids

Figure 5.4.1 Working conceptual model of patterns of methylmercury in the Alviso Baylands. This model represents ongoing hypothesis development by the PIs and should not be used for decision-making.