South Baylands Mercury Project

Final Report

February 10, 2010

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Suggested Citation:

Grenier, L., Marvin-DiPasquale, M., Drury, D., Hunt, J., Robinson, A., Bezalel, S., Melwani, A., Agee, J., Kakouros, E., Kieu, L., Windham-Myers, L., and Collins, J.. 2010. South Baylands Mercury Project. Final Report prepared for the California State Coastal Conservancy by San Francisco Estuary Institute, U.S. Geological Survey, and Santa Clara Valley Water District, 97 p.

Executive Summary

The South Baylands Mercury Project has been a collaborative effort of the San Francisco Estuary Institute (SFEI), United States Geological Survey (USGS), and the Santa Clara Valley Water District (SCVWD) to compare mercury (Hg) concentrations in habitats and food webs that represent alternative restoration endpoints for Pond A8 of the South Bay Salt Pond Restoration Project (SBSPRP).

Hg becomes a problem when it accumulates in the food web to concentrations that could cause deleterious effects for people and wildlife. An important aspect of the Hg problem is that neither elemental mercury (Hg^0) nor total mercury (THg) are the primary culprits. Rather, methylmercury (MeHg) is the toxic form of Hg that most readily bioaccumulates. The rate of MeHg production and its concentration in sediment, water, and biota typically depend less on THg concentrations and more on multiple environmental processes affecting inorganic mercury (Hg(II)) bioavailability and the activity of bacteria that convert Hg(II) into MeHg. Thus, high THg concentrations do not necessary lead to high MeHg concentrations. The processes that govern MeHg production and its concentration in various matrices are highly variable across a wide range of spatial and temporal scales.

This study answers questions raised by the Project Management Team (PMT) in its effort to prevent Pond A8, which will restore a tidal connection between the pond and Alviso Slough, and other SBSPRP activities from increasing the risk of Hg bioaccumulation in the San Francisco Bay ecosystem:

A. *How should the Hg problem be assessed for Pond A8, Alviso Slough, and the greater SBSPRP?*

   The problem should be assessed by (1) measuring Hg concentrations in wildlife species (Hg biosentinels) indicative of ecosystem and habitat endpoints of the SBSPRP; and (2) comparing these concentrations to known thresholds of deleterious biological or ecological effects and to reference concentrations in biosentinels of the SBSPRP and its surrounding environment.

B. *Would erosion of Alviso Slough related to the contruction of an armored tidal control structure associated with Pond A8 increase the Hg problem?*

   The answer is maybe. There are layers of sediment with relatively high concentrations of THg buried beneath Alviso Slough that could be exhumed by tidal scour resulting from the construction of this (and other) tidal control structure. This scour could increase the amount of Hg(II) that is available for MeHg production and uptake into the food web, at least in the short-term. However, the time period of increased risk and where it would occur is largely unknown. The risk for enhanced MeHg production would initially increase within Alviso Slough and Pond A8. Then the remobilized sediment would mix with other sediment, be dispersed by the tides, and proceed through various fates of deposition, burial or further transport. The likely scour warrants careful monitoring of Pond A8, Alviso Slough and adjacent sediment sinks where the exhumed sediment is likely to be deposited (e.g., Pond A8 and the fringing marsh in Alviso Slough). These sediment sinks can be identified by monitoring erosion and deposition along Alviso

Slough and within adjacent managed ponds after construction of the tidal control structure .

C. *Does the risk of a Hg problem differ between characteristic types of habitat for Pond A8 and Alviso Slough?*

Yes. This study regards Pond A8 and the fringing tidal marsh in Alviso Slough as separate ecosystems with distinctive habitats. Pond A8 consists of habitats – benthic, water-column, and shoreline – that are not subject to tidal action. Tidal marsh consists of the vegetated marsh plain, marsh pannes, and marsh channels that dewater at low tide. The main channel along Alviso Slough is a largely inter-tidal slough that conveys water to and from the fringing marsh. In this study, Pond A8 habitats (as measured in sediment and water) and their biosentinels had higher MeHg concentrations than the tidal habitats and their biosentinels.

D. *Would conversion of Pond A8 to tidal marsh unacceptably worsen the Hg problem in the Pond A8 footprint, Alviso Slough, or South Bay?*

The answer is probably not. All data indicate that the conversion of Pond A8 to fully tidal marsh as exists along Alviso Slough adjacent to Pond A8 would lessen the risk of a Hg problem within the A8 footprint. The restored tidal marsh would likely produce less labile organic matter than what is currently produced in Pond A8, providing less fuel for methylating bacteria, and leading to less MeHg production. Concentrations of THg and MeHg in biosentinels from the current Alviso Slough tidal marshes are the same as concentrations in biosentinels from reference South Bay marshes. Therefore, tidal marsh restoration along Alviso Slough would probably not result in unusually high MeHg concentrations in tidal marsh food webs. The one caveat to this conclusion is the potential for increased MeHg production as a result of significant sediment mobilization within Alviso Slough, as discussed above in B.

The answer to this question might be different for other managed ponds. Pond A8 had the worst Hg condition in the biosentinels of any of the SBSPRP ponds studied. Therefore, whether the conversion to tidal marsh of other ponds that have less MeHg in the food web might improve or worsen a Hg problem within their existing footprint or within the greater South Bay will depend on the particulars of those ponds. However, as a general conclusion, ponds that currently experience very high rates of primary production would likely benefit (in terms of lowering current MeHg concentrations) from being opened up to tidal flushing.

Other key findings were as follows:

- There was a decoupling between MeHg bioaccumulation in different parts of the marsh ecosystem (e.g., if the marsh plain had high MeHg in the food web of sparrows, then the tidal channels in the same marsh did not necessarily have high MeHg in resident small fish). This difference in spatial patterns of MeHg may indicate that marsh plain sediment is not the MeHg source for all marsh food webs.

- There was a strong correlation between % MeHg in the marsh plain sediment and THg in Song Sparrow blood. A novel conclusion of this study is that Song Sparrows appear to be especially useful for assessing Hg bioaccumulation in tidal marsh plains.
- The large pool of easily degraded organic matter (from algal production) in Pond A8 is most likely the driving force that leads to higher MeHg concentrations in Pond A8 sediment, water, and biota. This organic matter fuels the bacteria that methylate Hg(II). In contrast, the organic matter associated with Alviso Slough and the fringing marsh is largely terrestrial in nature, and much less easily degraded by bacteria, presumably leading to overall lower rates of microbial activity and MeHg production.
- Reactive inorganic mercury ($Hg(II)_R$), the fraction most readily available for Hg(II)-methylation, was significantly higher in the marsh plain compared to Pond A8. However, this did not lead to higher MeHg concentrations in the vegetated marsh, as the microbial activity fueled by the extensive algal production within Pond A8 (noted above) was a more dominant driver of MeHg concentration. This conclusion is a critical step towards understanding the relative importance of microbial activity versus the availability of Hg(II) for methylation in the MeHg production process, as the SBSPRP moves forward with management actions that will ultimately affect the distribution of ponds and vegetated marsh in South San Francisco Bay.

This study raises three cautions.

- First, monitoring data can reveal *what* is happening, but not necessarily *why*. Correlations between monitoring results and SBSPRP activities can guide the activities to reduce their risk of exacerbating the Hg problem. However, if an increase in MeHg in biota occurs, the solution and future prevention will require further 'process' studies as to its causes. Answering the '*why*' question will depend on explicit investigation of processes governing the factors driving MeHg production and its uptake into the food web.
- Second, sentinel species must be carefully selected for the particular ecosystems and habitats that are to be assessed. Individual habitats, such as tidal marsh plains or the benthic habitat of a managed pond, are best assessed using sentinel species that are restricted to those habitats and therefore cannot "import the problem" from somewhere else.
- Third, the findings of this study are not without uncertainty. While they are certain enough to inform Pond A8 restoration objectives and designs, they do not eliminate the need for future monitoring and assessment of the effects of Pond A8 management actions on Hg concentrations.

The risk of Hg accumulation in the food webs of wildlife and people of South Bay warrants a program of Hg monitoring that measures risk to wildlife based on available Hg thresholds established from local and national research. This study provides the baseline measures of condition that could serve as a foundation for the monitoring program that is needed.

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Acronyms, Abbreviations, and Chemical Notation

Acronyms

CA DFG, California Department of Fish and Game

CDF, Cumulative Distribution Function

CRM, certified reference material

CVAFS, cold vapor atomic-fluorescence spectrometry

DI, deionized (water)

DO, dissolved oxygen

DOC, dissolved organic carbon

EDTA, ethylenediamine tetra-acetic acid

LOI, loss on ignition

ND, non-detectable

ORP, oxidation-reduction potential

PET, polyethylene terephthalate

QA, quality assurance

QC, quality control

RPD, relative percent difference

SBSPRP, South Bay Salt Pond Restoration Project

SCVWD, Santa Clara Valley Water District

SFEI, San Francisco Estuary Institute

$SUVA_{254}$, specific (dissolved organic carbon normalized) ultraviolet absorbance measured at 254 nanometer wavelength

TSS, total suspended solids

USEPA, United States Environmental Protection Agency

USFWS, United States Fish and Wildlife Service

USGS, United States Geological Survey

UVA_{254}, optical ultraviolet absorbance measured at 254 nanometer wavelength

Abbreviations

cm, centimeter

E_h, electrochemical redox corrected for the hydrogen half-cell reaction

g, gram

g/l, grams per liter

kg, kilogram

l, liter

mM, millimolar

mg, milligram

ml, milliliter

mol/l, moles per liter

mV, millivolts

ng, nanogram

ng/g, nanogram per gram

ng/l, nanogram per liter

nm, nanometers

µg, microgram

µm, micrometer

µmol/l, micromoles per liter

wt, weight

>, greater than

>>, much greater than

<, less than

≈, approximately equal to

Chemical Notation

BrCl, bromine monochloride

Cl^-, chloride anion

$CuSO_4$, copper sulfate

H_2SO_4, sulfuric acid

HCl, hydrochloric acid

Hg, mercury

Hg^0, elemental mercury

Hg(II), divalent inorganic mercuric ion

$Hg(II)_R$, inorganic reactive mercury

$HgCl_2$, mercuric chloride

KCl, postassium chloride

KOH, potassium hydroxide

MeHg, methylmercury (monomethylmercury)

Na_2CO_3, disodium carbonate

$NaHCO_3$, sodium bicarbonate

NaOH, sodium hydroxideSO_4^{2-}, sulfate anion

$SnCl_2$, stannous chloride

THg, total mercury

u-MeHg, unfiltered methylmercury

u-THg, unfiltered total mercury

1. Study Background

Mercury (Hg) becomes a problem when the toxic organic form, MeHg, accumulates in food webs to levels that endanger people and wildlife. The Office of Environmental Health Hazard Assessment has issued a Hg advisory for San Francisco Bay that provides guidelines for the safe consumption of Bay fish and shellfish by people (OEHHA 1994). Recent studies of aquatic birds and tidal marsh song sparrows that feed in various San Francisco Bay and wetland habitats (Ackerman et al. 2008a, 2008b, Eagles-Smith et al. 2008, 2009a, Grenier et al., 2007b) provide some of the best evidence to date that wildlife, including both shore birds and tidal marsh plain song sparrows, bioaccumulate Hg from these habitats.

One of the major sources of Hg to South San Francisco Bay has been the New Almaden Mining District in the watershed that drains through Alviso Slough. The New Almaden Mining District was historically the most productive Hg mine in North America, and current runoff into South Bay carries from eight to 116 kg of total mercury (THg) per year (McKee et al. 2006). Not surprisingly, Hg concentrations in sediment and water tend to be greater in South Bay than in other parts of the greater San Francisco Bay (Conaway et al. 2003), and Alviso Slough and the adjacent managed pond system contain more Hg than other areas of South Bay (SFEI 2005), as verified in the first phase of the current study (Marvin-DiPasquale and Cox 2007).

In Phase I of the current study (previously published), it was estimated that there is approximately 1650 ± 310 kg of THg within the upper 2.0 meters of sediment in Alviso Slough and its fringing marshes, between the slough mouth and the proposed construction site of an armored tidal control structure that would reintroduce tidal flow to Pond A8 (Marvin-DiPasquale and Cox 2007). It was further determined that erosion of Alviso Slough, due to increased tidal flows caused by the construction of this control structure, could mobilize 66–125 kg of THg, 54–102 g of inorganic 'reactive' mercury ($Hg(II)_R$), and 76–142 g of MeHg, depending on the size of the structure notch (e.g. 20 or 40 feet). Tidal marshes and other kinds of wetlands have been identified as important areas of MeHg production (Krabbenhoft et al. 1999, Waldron et al. 2000, Marvin-DiPasquale et al. 2003). Therefore, the South Bay Salt Pond Restoration Project (SBSPRP) has been concerned that its draft plans to convert former salt ponds along Alviso Slough into tidal marsh, by reintroducing tidal flow, might increase MeHg production and concentrations in South Bay.

However, the production of MeHg depends on many environmental factors in addition to the amount of THg. High concentrations of THg in Alviso Slough and its associated managed ponds do not necessarily mean that converting the ponds to tidal marsh will increase the risk of a Hg problem. Concentrations of THg are poorly correlated to concentrations of MeHg in sediment or in water across the Bay as a whole (Heim et al. 2007). Data on THg and MeHg concentrations exist for a variety of locations in South Bay (Thomas et al. 2002, Conaway et al. 2003, Topping et al. 2004, Beutel and AbuSaba 2004, SFEI 2005), but little is known about the regional and habitat-specific processes governing the transport and transformations of different Hg species, including Hg(II)-methylation, $Hg(II)_R$ concentrations, and MeHg uptake into food webs. Threshold concentrations of MeHg toxicity are not well known for most wildlife species, and habitat designs or management practices that might minimize MeHg production or bioaccumulation are largely untested.

This study was developed in the context of the complex environmental chemistry of Hg and concerns about health risks to wildlife and humans that could be increased by tidal marsh restoration in South Bay.

2. Study Purpose

The primary purpose of this study was to assess the relative difference in the risk of exacerbating the existing Hg problem, by either continuing to manage Pond A8 as it has been managed or by converting it to tidal marsh. The study was guided by a decision framework (Fig. 2.1) indicating specific needs for data to inform the management choices. One assumption of the study design, which is key to understanding the decision framework, is that the fringing marshes and their tidal channels along Alviso Slough adjacent to Pond A8 were assumed to represent the endpoint of tidal marsh restoration for Pond A8. The study addressed the following questions.

A. *How should the Hg problem be assessed for Pond A8, Alviso Slough, and the greater SBSPRP?* This question was addressed early in the Project while determining the study design and during the pilot study in 2006. The answer to this question is discussed in the 2006 progress report (Grenier et al., 2007a) and in the Study Design section below.

B. *Would erosion of Alviso Slough related to the construction of the Pond A8 armored tidal control structure increase the Hg problem?* This question was addressed in the first phase of this study. The answer is briefly summarized in this report and is discussed in detail in an earlier report (Marvin-DiPasquale and Cox 2007).

C. *Does the risk of a Hg problem differ between characteristic types of habitat for Pond A8 and Alviso Slough?* The answer to this question involves knowing how the conversion of one habitat to another might affect Hg concentrations for the greater tidal marsh and pond ecosystems. It is therefore a prerequisite for answering the next question below. It also can inform habitat designs for tidal marshes and ponds.

D. *Would conversion of Pond A8 to tidal marsh unacceptably worsen the Hg problem in South Bay?* Answering this question is the primary purpose of this study (see decision framework, Fig. 2.1). The answer is discussed at length in this report.

All the results from all three years of the study are discussed in this report, which addresses the most recent results (2008 field collections) in detail and summarizes earlier results that have either already been published (Marvin-DiPasquale and Cox 2007) or have been treated in detail in previous progress reports (Grenier et al. 2007a, 2007b). To adequately address some questions, earlier data have been re-analyzed or pooled with more recent data for new analyses. The results of any such re-analyses are discussed in detail in this report.

3. Approach and Study Design

3.1. The Effect of Alviso Slough Erosion on Mercury Bioavailability

This aspect of the study focused on estimating the amount of Hg in the sediment of Alviso Slough that might be exhumed by erosion due to increases in tidal flows if Pond A8 were restored to full or partial tidal action. The SBSPRP provided results of models predicting the depth and width of erosion in the Slough (Philip Williams & Associates et al. 2006). Based on

these models, sediment cores were taken along five cross-sections distributed between the slough mouth and the proposed site of the Pond A8 tidal control structure. At each cross-section, sediment cores were taken to the depth of the predicted erosion near the middle of the Slough (2m) and near the lateral limits of predicted erosion. Each core was subjected to non-destructive gamma density and magnetic susceptibility analysis to ascertain variations in sediment density and magnetic mineral content, respectively. Cores were then split longitudinally, with one half photographed and archived, and the other half sub-sampled and sectioned into 10-30 cm intervals (depending on the gamma density, magnetic susceptibility, and visual profile analysis) and assayed for the following constituents: THg, MeHg, $Hg(II)_R$, pH, oxidation-reduction potential (redox), bulk density, percent dry weight, porosity, organic content (weight loss on ignition at 500 ^oC), and grain size. A laboratory experiment was conducted on the mid-Slough sediment representing the 50-175 cm depth zone below the current sediment-water interface to assess the effects of a major erosion event on $Hg(II)_R$ bioavailability. The laboratory experiment demonstrated how the pool size of $Hg(II)_R$, which is the fraction of inorganic Hg(II) most readily available for Hg(II)-methylation, can be significantly increased (up to 60-fold) when buried anoxic sediment containing largely non-reactive Hg(II) are scoured and mixed with oxygenated overlying water. The complete results from this study have been published **(**Marvin-DiPasquale and Cox 2007).

3.2. Comparing Mercury Bioavailability and Bioaccumulation in Tidal Marsh and Managed Pond Ecosystems

This aspect of the study focused on answering the question: does the risk of a Hg problem differ between characteristic types of habitat for Pond A8 and Alviso Slough? The answer was developed based on quantifying and comparing Hg concentrations in sediment, water, and biosentinel species indicative of particular habitats that represent restoration or management endpoints for the SBSPRP (Table 3.2.1). For this study, biosentinels are defined as species whose tissue concentrations indicate the amount of MeHg accumulation in the food web of a particular habitat over a short time span. Such biosentinels can be used to compare habitats in terms of the amount of MeHg entering their food webs (i.e., Hg bioavailability). The biosentinel data can also serve as a pre-restoration baseline of Hg concentrations for the purpose of assessing the effects of restoration activities on the risk of Hg problems. 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 the construction of the tidal control structure.
- 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 full tidal action, given its landscape position, anticipated salinity regime, and sediment sources.
- All other tidal marshes south of San Mateo Bridge and all other ponds that are part of the SBSPRP were assumed to represent the reference condition for the South Bay tidal marsh ecosystem and pond systems of the SBSPRP, respectively.

A pilot study was conducted in 2006 to verify that the proposed biosentinel species were present in sufficient numbers, broadly distributed across the study area, readily captured, and had sufficient accumulation of MeHg in their tissues to elucidate spatial and temporal patterns of

bioavailability and accumulation (Grenier 2007a). The target sentinel species were present and readily captured in sufficient numbers (and appropriate sizes for fish) to complete the initial sampling regime from Ponds A8, A7, and A5, and the fringing tidal marshes along Alviso Slough and Guadalupe Slough. Initial comparisons were made among these habitats, but sample sizes were small in the pilot study. Capture techniques were effective, and capture methods and gear were refined during the 2006 field season. The analytical lab was able to provide measures of THg for fish and bird tissues and MeHg for fly tissues, despite extremely small sample masses in many cases. Choice of sentinel species was altered slightly from the original proposal, as fish distributions became better understood.

In later years, the sediment, water, and biosentinel monitoring focused on assessing Pond A8 in the context of the Alviso area (2007; Grenier et al. 2007b) and the SBSPRP and South Bay as a whole (2008; Table 3.2.1). The following assessment questions were addressed as described below.

- *Would conversion of Pond A8 to tidal marsh decrease or increase local Hg bioavailability?*

  This question was approached from a variety of perspectives during 2007 (Grenier et al. 2007b).
  - First, the concentrations of THg, MeHg, and $Hg(II)_R$ were determined for the sediment of Pond A8, Alviso Slough, and the adjacent tidal marsh plain. In addition to comparing habitats, these data were used to evaluate the factors that control the transformation of inorganic Hg(II) to organic MeHg.
  - Second, THg, MeHg, and other water-quality parameters were assessed bimonthly between November 2006 and August 2007 for the water-column habitats of Pond A8 and Alviso Slough, and for tidal water draining from the adjacent tidal marsh plain. 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.
  - Third, the different habitats were compared based on their common biosentinels. For example, concentrations of THg in longjaw mudsuckers from the demersal zone of Pond A8 were compared to those in longjaw mudsuckers from the tidal marsh channels in Alviso Slough.

- *Would conversion of Pond A8 to tidal marsh unacceptably worsen the Hg problem in South Bay, and how do the baseline Hg conditions for Alviso Slough and related pond ecosystems compare to reference conditions of comparable systems in South Bay?*

  This question was addressed in 2008 field collections using a probabilistic sampling design to assure objective representation of the tidal marsh and managed pond ecosystems of South Bay. Sample sites were selected using the Generalized Random Tessellation Stratified (GRTS) approach (Stevens and Olsen 2004). 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. In this study, two sample frames were developed, one for managed ponds and one for tidal marsh. Tidal marsh sample frames included all possible sites south of the San

Mateo Bridge with the exception of Mowry Marsh (excluded to avoid disturbing other wildlife). The pond sample frame included all possible sites in the SBSPRP boundaries. .Using GRTS, 20 tidal marsh sites and 20 pond sites were selected from the sample frame for each biosentinel (Table 3.2.1). Sediment was also collected at the Song Sparrow sampling sites.

4. Methods

4.1. Sediment

Field Sample Collection

Surface Sediment Sampling

Sediment sampling was limited to the upper 2 cm of the substrate because a) this is the depth over which there is typically maximum interaction among edaphic and aquatic biochemical processes affecting Hg bioavailability; b) this is often the most active sediment layer with respect to MeHg production and flux to overlying water; and c) this near-surface layer is most responsive to short-term changes in sedimentary processes, including the deposition and decomposition of organic materials. The surface sediment sampling locations are shown in Figs. 4.1.1 and 4.1.2, with coordinates, sampling dates and habitat type detailed in Table 4.1.1. For samples collected between March 2007 and January 2008, from Pond A8, Alviso Slough and the fringing marsh, sediment was sampled using a polycarbonate core ring (2cm x 8cm i.d.), which was pressed into the sediment until the top edge was flush with the sediment/water interface and then gently lifted out with the support of a stiff plastic sheet on the underside. The resulting sediment patty was transferred into an acid-cleaned mason jar. Each jar was filled with 4−6 patties. Sub-samples were taken in the field for Hg speciation (THg, $Hg(II)_R$ and MeHg), pH, oxidation-reduction potential (ORP), grain size, and organic content as percent weight loss on ignition (%LOI), using a 3-cm^3 cut-off syringe. The jar was stored on wet ice until further processing for pore water constituents back at the USGS Menlo Park, CA, laboratory. The 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.

During July and October 2007, the USGS collected additional surface sediment from high, mid-elevation, and low tidal marsh plant communities at two locations along Alviso Slough (Table 4.1.1 and Fig. 4.1.2). These samples were collected as part of a companion study funded by the San Francisco Foundation to investigate how Hg geochemistry and MeHg production rates in plant root zones vary with plant species composition as affected by marsh elevation. A subset of the data from this companion study (undisturbed vegetated sites only) is included in this report to provide an increased number of observations of sediment Hg chemistry in the tidal marsh ecosystem.

During the March-April 2008 sampling conducted throughout South San Francisco Bay, four sediment patties were collected using the polycarbonate core ring (described above) at equal intervals along the perimeter of a circle with a radius of 2 meters at each biosentinel sampling site. The sediment patties for each site were composited into plastic zip-sealable bags, any air pockets were removed, and the samples were frozen on dry ice in the field. In the laboratory, the zip-sealed bags of frozen sediment were first thawed overnight in a refrigerator and then transferred to an anaerobic glove-bag (N_2 flushed) for sub-sampling to assess THg, $Hg(II)_R$,

MeHg, pH, ORP, grain size, and organic content (as %LOI). Sub-samples for Hg species were immediately refrozen until further processing.

Pore Water Sub-sampling

All sub-sampling of surface sediment and pore water was conducted at the USGS laboratory in Menlo Park, CA, under anaerobic conditions within 24 hours of field collection. Sediment was transferred from the mason jars into plastic bags, where it could be more completely homogenized. Plastic centrifuge bottles (250 cm^3) were filled to the shoulder with the homogenized sediment. The bottles were centrifuged for 20 min at 3500 rpm and subsequently returned to the N_2 flushed glove bag, prior to removing the caps for further sample processing. In all cases, samples collected from vegetated Alviso Marsh sites were too dry to yield enough pore water to collect all of the sub-samples required. Therefore, approximately 30 g of sediment plus 30 g anoxic DI-water (previously N_2 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. Pore water supernatant was filtered through 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) into pre-labeled containers prepared for the collection of the various pore water constituents (SO_4^{2-} and Cl^-, sulfide and specific 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 heated to 50 ^oC in an oven overnight. Once cooled, a 5 ml sub-sample was transferred into a pre-combusted glass container. 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 method is based on the tin reduction of Hg(II) to gaseous Hg^0, trapping Hg^0 on gold sand, thermal desorption, and quantification of Hg^0 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 $HgCl_2$ standard. Quality control acceptance criterion for this assay is detailed in the published methods documents (Olund et al. 2004, USEPA 2002).

Reactive Mercury

Sediment "reactive" mercury ($Hg(II)_R$) is methodologically defined as the fraction of THg, which has NOT been chemically altered (e.g. digested, oxidized or chemically preserved apart from freezing), that is readily reduced to elemental Hg^0 by an excess of stannous chloride ($SnCl_2$) over a defined (short) exposure time. This operationally defined parameter was developed as a surrogate measure of the fraction of inorganic Hg(II) that is most likely available to Hg(II)-methylating bacteria responsible for MeHg production (Marvin-DiPasquale et al. 2009). Upon thawing, sub-samples collected and frozen in the field for $Hg(II)_R$ 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 (0.3-0.8 g wet weight) into plastic centrifuge tubes and extracted with a solution of 25% KOH/methanol (25 g of KOH dissolved in 100 ml of methanol), heated to 60 ^oC for 4 hours (Xianchao et al. 2005). Extracted samples were stored frozen (-80 ^oC). Upon thawing and centrifugation, a 0.15 ml aliquot of the extractant 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. MeHg was converted, within the vial, to volatile methyl-ethyl-mercury, which was subsequently analyzed on an automated MeHg analysis system (Brooks Rand Laboratories, Seattle, WA) using cold-vapor atomic fluorescence spectrometry (CVAFS) detection.

Each batch of analytical samples was accompanied with analysis of the following Quality Assurance (QA) samples: a) at least one certified reference material, b) at least one matrix spike sample, c) at least one analytical duplicate, and d) at least 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 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^3 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 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 ± 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^3 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_h values (which is a standard convention that adjusts the value assuming a normal hydrogen reference electrode), using the following conversion:

E_h = ORP (meter value) + ER

ER =(-0.718 x T) + 219.97

Where: ER = 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^3 of wet sediment was removed from the sample vial using a 3.0 cm^3 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^3) 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 dessicator to cool, and then reweighed. The sediment percent dry weight was then calculated as [dry wt]/[wet wt] x 100. Sediment porosity (mL porewater per cm^3 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 was then placed in a combustion oven at 500 °C for four hours. This completely burned off any organic constituents, leaving only mineral material. After cooling and reweighing, the percent weight loss was calculated.

Grain Size

Grain size, measured as the dry weight percentage less than 63 microns (< 63 µm (%); 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 crimp-sealed serum vials and stored frozen until analysis. Both anions 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_2CO_3 and 1.7 mM $NaHCO_3$. 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 3 ml sulfur antioxidant buffer (2 mol/l NaOH, 35 g/l ascorbic acid, 67 g/l EDTA-disodium salt), and transferred to 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.

Specific 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 sediment analytes are noted above in the Laboratory Analysis section. The specific quantified results for each QA metric are given in Table 4.1.2.

Statistical Analysis

All statistical analyses were conducted using commercial software (TIBCO Spotfire S+®, Version 8.1 for Windows). Due to the limited temporal resolution of the sediment sampling at any given site, the statistical treatment of the sediment data was limited to a spatial comparison based upon sampling area. Sediment data were grouped into three main habitats: Pond A8 benthic habitat, Alviso Slough benthic habitat, and the tidal marsh plain. The Pond A8 benthic habitat was further stratified into Pond A8 mudflats, Pond A8 borrow ditches and remnant slough channels. Analysis of variance (ANOVA) was conducted on each sediment parameter, using habitat as the independent categorical variable, to assess if there were any statistical differences among the habitat types. If a significant difference was found at the probability (P) level $P < 0.05$ (for Type II Error), then a pair-wise multiple comparison analysis among paired groupings was conducted using the Tukey critical-point calculation program provided with the software.

4.2. Water

Field Sample Collection

Surface water was collected from Pond A8, Alviso Slough, and tidal marsh channels draining the marsh plain along Alviso Slough (Table 4.2.1, Fig. 4.1.2) during November 2006, and January, March, May, July, and August 2007, except that no samples were collected from tidal marsh channels during March 2007.

In addition to the water samples sent to commercial analytical laboratories, a one liter bottle of overlying water from each site/depth was initially stored in a cooler with ice, delivered to the USGS laboratory in Menlo Park, CA on the day of collection and stored refrigerated until further processing the next day.

Alviso Slough Main Channel

In Alviso Slough, water samples were taken from just below the water surface and from just above the Slough bottom at mid-channel locations during the early part of the ebb phase of an over-bank tide, near the end of a spring tide series. Station ASW1 was adjacent to the freshwater tidal marsh near the proposed Pond A8 tidal control structure location. Station ASW2 was adjacent to brackish tidal marsh between Ponds A7 and A10, approximately 4.4 km downstream of ASW1. Station ASW3 was adjacent to saline tidal marsh, near the slough mouth between Ponds A6 and A10, approximately 2.0 km downstream of ASW2.

Double-bagged, acid-cleaned, glass containers were used for water sample collection and transport. All water sampling was done using the two-person "clean hands, dirty hands" method **(**USEPA 1996). Surface water was collected directly into the sample container by submerging the bottle from the boat with a gloved hand, removing the cap, filling the bottle, and replacing the cap. Bottom water was collected approximately 25 cm above the sediment-water interface using a 2.2-Liter Van Dorn Beta-type (Wildco) sampling device. After retrieval, sample containers were filled directly from the Van Dorn sampler and then double-bagged and stored on ice in a cooler.

Tidal Marsh Channels

Stations ASMW1, ASMW2, and ASMW3 were located in small, intertidal channels (second-order sloughs) at least 10 m into the fringing tidal marsh along Alviso Slough and roughly adjacent to the mid-channel water sampling stations (Fig 4.1.2). A single depth-integrated water sample was taken at each station on the same dates as the main channel samples were taken, with the exception that no marsh channels were sampled during March 2007. Sampling was timed to assure that the samples represented return water draining from the tidal marsh.

Pond A8

Stations A8WF1 and A8WF2 were located along the northwestern and southeastern shorelines, respectively, within the borrow ditch that parallels the perimeter of Pond A8. Water was sampled from the lower portion of the water column at these two locations. Station A8WD1 was located in a historical slough channel in the interior of Pond A8. Two depths were sampled at this station, one just below the water surface and one approximately 25 cm above the sediment-water interface. Pond A8 was fully flooded (standing water atop the mudflats) from January through March 2007. Evaporative loss led to exposed mudflats during the May thru August 2007 sampling period. All Pond A8 samples were collected within two days of the sampling dates for Alviso Slough and its fringing tidal marsh.

Surface Water Field Measurements

Measurements of pH, temperature, specific conductivity, dissolved oxygen, and turbidity were recorded at each sampling depth using a Horiba U-10 Water Quality Checker (Horiba Instruments Inc., Irvine, CA). The instrument was inserted directly into the water at the appropriate depth, when possible. Otherwise, samples were collected into a triple-rinsed collection beaker into which the instrument was inserted.

Surface Water Laboratory Analyses

Unfiltered Total Mercury

Acid-cleaned borosilicate glass containers (500 ml) with BrCl preservative or unpreserved sets of four 40-ml glass vials provided by the analytical laboratory were used for the collection of unfiltered total mercury (u-THg) water samples. Analyses were conducted by TestAmerica (San Francisco, CA) (November 2006 Pond A8 samples only; January 2007, all sites; March 2007, all sites; May 2007, all sites), its subsidiary (Severn Trent Laboratories, Tacoma, WA) (July 2007, all sites; August 2007, all sites) or Brooks Rand Laboratories (Seattle, WA) (November 2006, Alviso slough and marsh samples). All three labs used EPA Method 1631 (USEPA 2002), with a Reporting Limit of 0.50 nanograms per liter (ng/l). Standard QA for all labs included method blanks, analytical duplicates and matrix spikes, with each analytical batch. While most QA criterion were met, matrix spike analyses did not meet QA criterion for analytical batches that included most of the slough and marsh samples collected during January 2007, all of the pond samples and some of the slough samples collected during March 2007, and all of the slough and marsh samples collected during July 2007. Nevertheless, these data were accepted because a) the other QA criteria were met, b) the results were similar to those from other analytical batches associated with this study where the matrix spike recovery criteria was met, and c) the results were similar to previously values measured surface water u-THg values in Alviso Slough (Conaway et al. 2003) and Pond A8 (Miles and Ricca, in press) from previous studies.

Unfiltered Methylmercury

Acid-cleaned polycarbonate containers (250 ml) with HCl or H_2SO_4 preservative provided by the laboratory were used for the collection, preservation and storage of unfiltered methylmercury (u-MeHg) water samples. Samples were analyzed by Brooks Rand Laboratories (Seattle, WA) using EPA Method 1630 **(**USEPA 2001**)**, with a Reporting Limit of 0.05 nanograms per liter (ng/l). QA consisted of at least one certified reference materials (CRM) sample, two matrix spikes, three continuing calibration verification samples and four method blanks, with each analytical batch. All analyses met QA criteria.

Total Suspended Solids

Both USGS (Menlo Park, CA) and SCVWD (contracted to TestAmerica) analyzed water samples for total suspended solids (TSS). SCVWD analyzed unfiltered samples for TSS according to EPA Method 160.3 (USEPA 1979), with a Reporting Limit of 10 mg/l. 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 criteria for acceptable data was a RPD < 20%. When this criteria was not met the samples associated with those batches were flagged, and while still reported, these data should be used with some caution.

TSS analyzed by the USGS were collected on pre-weighed combusted 0.7 µm glass-fiber filters used during the DOC filtration (see below), with the exact volume of water filtered recorded. The filters were then placed into plastic petri dishes and were dried in a dessicator for 30+ days before a final dry weight was recorded. Lab duplicates were run on 58% of all samples, and the average RPD (± standard error) was 12 (± 2)%**.**

Dissolved Organic Carbon & Specific UV Absorbance

Overlying water DOC and $SUVA_{254}$ 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/$SUVA_{254}$ 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 100 ml of sample prior to final collection. The filtrate was sub-sampled into acid-cleaned pre-combusted glass containers. The sub-samples received a final concentration of 0.1% HCl as a preservative, and to drive off dissolved inorganic carbon. Samples were 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). Sample optical absorbance at the 254 nm wavelength (UVA_{254}) was measured using a Shimadzu Model UV-1601 spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD). Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$, in units of L mg^{-1} m^{-1}) was calculated by normalizing the UVA_{254} measurement to the respective DOC concentration. Higher $SUVA_{254}$ values indicate a higher proportion of aromatic carbon per unit mass of DOC (Chin et al. 1994, Weishaar et al. 2003). Quality assurance measures included calibration standards, laboratory reagent blank, and filter blanks, as detailed in the above EPA method.

Sulfate and Chloride

Overlying water SO_4^{2-} and Cl^- concentrations were measured by the USGS (Menlo Park, CA) 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.

4.3. Biosentinels

Field Sample Collection

Demersal and Water-column Fish

Fish were collected from mid July through the end of August, 2008, in the managed ponds of the SBSPRP and from tidal marshes south of San Mateo Bridge (Table 4.3.1). In ponds, fish were much more abundant in borrow ditches and historical channels than in the shallower areas (47% vs. 7% capture success rate). Furthermore, some ponds lacked fish. Therefore, sampling for fish biosentinels focused on locations within borrow ditches and historical channels that were close to the randomly selected sample locations. Sampling alternated between tidal marsh sites and pond sites and across different parts of South Bay to prevent temporal variability from confounding spatial patterns.

Demersal longjaw mudsuckers (*Gillichthys mirabilis*) were targeted, because they are resident in marshes and reflect local Hg conditions in the marsh channels more closely than transient marsh fish. By-catch included some transient water-column fish, particularly threespine stickleback (*Gasterosteus aculeatus*). Fish were collected using minnow traps baited with cat food and set for 15 – 27 hours in marsh channels and for 17 – 70 hours in ponds. Trapped fish could not access the bait, which was in metal cans with small slits to allow the scent of food to enter the water.

After collection, fish were stored in the field in Ziploc® freezer bags on ice. Fish samples were double-bagged in Ziploc® freezer bags at SFEI and stored at −4 °C until shipment to the analytical laboratory. Before shipment to the analytical laboratory, fish were weighed, measured for total length, and rinsed with de-ionized water. Water-column fish (threespine stickleback) were composited by species and site. Demersal fish (longjaw mudsuckers) were analyzed as individuals. The relationship between fish length and THg concentration was controlled by restricting the fish sample to individuals within a small size range for each species. Fish less than 75% of the length of the largest fish were excluded from composite samples whenever possible (88% of composites met this criterion).

Brine Flies

Brine flies were collected during less than three weeks in June 2008 (Table 4.3.1). Brine flies live and feed at the margin of salty, wetted areas, so field personnel sampled the edge of wet managed ponds near the randomly selected sampling locations. In some cases this meant sampling at the edge of the drying main water body, and in some cases this meant sampling at the edge of a borrow ditch or historical marsh channel. During the 2007 field efforts, flies were observed moving as far as 75m between habitat patches within ponds. In 2008, flies were collected from shorelines < 75m in length, all within the same habitat type, and not separated by a levee or other physical barrier. In the marsh, flies were collected from the panne (naturally occurring salty pond within a tidal marsh) nearest to the GRTS sampling points. At sampling points where birds were captured, flies were collected in the panne nearest to the bird capture location in order to collocate biosentinel samples as much as possible. Flies from pannes within 10 meters of one another were composited.

To capture flies in areas of high population density, sweep nets were used just above the water or sediment surface. In areas of moderate fly density with sufficiently deep water, sweep nets were lowered into the water and raised after a fly landed on the water surface above the sunken net. In areas of low fly density, pan traps were set for 1–4 hours. Pan traps were aluminum pans filled with distilled water plus a minute amount of liquid soap to break the surface tension. Flies captured in pan traps were rinsed with distilled water immediately after collection to remove any soap residue.

Flies were placed in Ziploc freezer bags containing Kimwipes to absorb external moisture and kept on ice in the field until they could be transferred to a freezer (-4 ºC) at SFEI. Before being sent to the analytical lab, flies were rinsed in de-ionized water and sorted to genus under a dissecting scope. Taxonomic identification of *Ephydra* (brine flies) was based on a reference collection identified by Dr. David Herbst at the Sierra Nevada Aquatic Research Laboratory.

Resident Marsh Birds

Song Sparrow and non-target birds were captured by mist net in tidal marsh **(**Table 4.3.1). Birds were sampled in April and May 2008, during the breeding season, when these species were territorial and sex and age could be identified more easily. 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. Birds were weighed, measured, sexed, and aged when 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. Feathers were stored at ambient temperature in paper envelopes, while blood samples were kept on ice in the field and transferred to a freezer (-4 °C) at SFEI to await shipment to the analytical lab. Birds were marked with USFWS metal bands and unique color band combinations (Song Sparrows only) for field identification. All birds were released following sample collection.

Laboratory Analysis

Vertebrate samples were analyzed as THg, because the vast majority (> 90%) of THg in the vertebrate tissues analyzed (whole-body small fish and bird blood) is MeHg. Thus, whether analyzed as THg (vertebrates) or MeHg (flies), the Hg species being measured in the food web was principally MeHg. All biosentinel 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 THg and MeHg. Avian blood and whole-body flies and fish were shipped to the analytical lab on dry ice.

Vertebrate Sample Analysis for Total Mercury

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.

Whole-body fish and avian blood samples were analyzed for THg by combustion / trapping / cold-vapor atomic absorption using EPA Method 7473 (USEPA 1998). Samples were weighed to the nearest 0.1 mg in tared, combusted nickel boats. The boats were then loaded into the autosampler carousel of a Milestone DMA 80 Hg analyzer and sequentially introduced into the instrument's combustion chamber. Samples were heated in a tube furnace at 850°C under a stream of oxygen, and combustion products were passed through a catalyst and then through a gold-coated sand column where Hg atoms were trapped. Following thermal desorption, the oxygen gas stream carried Hg vapor through two atomic absorption cells that quantified Hg over the range 0.001-0.700 µg. Instrument calibration utilized certified reference materials as standards; calibration was monitored after every 10 samples and at the end of the analysis by analyzing a check standard and a blank. Laboratory quality control samples included a method blank, certified reference material, a duplicate sample, and a spiked sample with each batch of 20 or fewer samples.

Invertebrate Sample Analysis for Methylmercury

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 $CuSO_4$ and KBr into a mixture of methylene chloride and

hexane. Solvent was evaporated, and the extracted MeHg was converted to 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 20 field samples. For lab replicates, the relative percent difference (RPD) was calculated between the parent sample and lab duplicate. The benchmark for acceptable data is a RPD < 25%. All duplicate results were 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%. All CRMs were 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. A few blank values were greater than the MDL of the blank, but none of the field samples were less than three times the blank result. Therefore, all data were deemed usable.

Statistical Analysis

Based on the GRTS approach, cumulative distribution functions (CDFs) were developed to show the Hg condition in marshes and managed ponds across the South Bay for each sentinel species. Area-weighted CDFs were calculated using version 2.6.2 of the psurvey.analysis statistical library, using the R system (Stevens and Olsen 2004).

For these analyses, the Alviso Ponds are defined as those to be involved in the Pond A8 restoration, i.e., Ponds A8, A7, and A5. Alviso Slough is defined as from the Gold Street Bridge to where the slough empties into South Bay/Coyote Creek.

Demersal and Water-column Fish

Fish data analyses were conducted using wet-weight concentrations of THg. To obtain a consistent dataset for analysis of each species, the following approach was taken: first, the average THg concentration for all samples from the same trap was calculated; second, the average THg concentration from all traps in the same tidal marsh or pond site was calculated. This approach prevented any one area of the pond (trap site) from being overly weighted, while

providing a single THg concentration for each species from each GRTS site sampled. This dataset was used in the statistical analysis of 2008 data described below.

Data from sampling in 2007 were generally not pooled with data from 2008 field collections to avoid increasing error from inter-annual, seasonal, and geographic differences. The only instance where fish data from 2007 were included in the 2008 data analysis was the plots at pond sites for both mudsucker and stickleback. This approach was used so that the full distribution of pond data could be visualized at once, as Ponds A8, A7 and A5 were heavily sampled in 2007 and the reference sites across South Bay were sampled in 2008. Therefore, it should be acknowledged that some of the variability in these CDFs may be due to temporal variation. The 2008 fish data were also explored for patterns in THg related to date of sample collection. There was no relationship between THg and date of sampling, based on visual examination of scatter plots of mudsucker and stickleback data.

To examine the length:Hg relationship in biosentinel fish, mudsucker and stickleback samples with wider ranges in length were collected in two habitats in 2007: ponds (A5, A7, A8) and Alviso Marsh and Slough (Grenier et al. 2007b). For each species, one of the sites in 2007 showed a significant ($p < 0.05$) effect of length on THg and the other site did not. Data from mudsuckers collected in marshes in 2008 were also examined for the influence of length on THg. Results indicated a significant effect of length on THg concentrations, though the amount of variation explained was low (Table 4.3.2, $r^2 = 0.09$). Sticklebacks were only analyzed as composites in 2008, except for a few individuals caught from ponds. Using the average length from composites in the ambient population of marsh samples indicated a poor correlation to THg (Table 4.3.2, $r^2 = 0.001$). Therefore, for the analyses of fish data from pond and marsh habitats, size limits (75 – 100 mm) were applied to the longjaw mudsucker samples prior to statistical analysis. Due to the limited evidence for a size effect in the 2008 samples of threespine stickleback, no size limits were applied for this species.

Fish data were analyzed by two-sample t-tests in Systat v.11 (Chicago, IL) to compare mean THg concentrations from pond and tidal channel habitats and to compare Alviso Marsh to ambient South Bay marshes. The THg data were log-10 transformed to meet assumptions of parametric analyses. Therefore, results are reported as geometric means +/- 1SD. Due to sample size differences, t-test results were based on the separate variances calculation.

Resident Marsh Birds

Bird data analyses used wet-weight concentrations of THg in whole blood. As with the fish data, the birds collected in 2008 were primarily from different geographic areas than in 2007, and thus were not pooled in statistical analyses. To obtain a consistent dataset for bird data analysis, an approach similar to that for fish was used. First, multiple samples from the same mistnet were averaged, and then all nets from the same marsh site were averaged. This approach prevented any one area of the marsh from being overly weighted, while providing a single THg concentration for each GRTS site sampled. For the two resident marsh species that were collected in sufficient numbers in 2008, Common Yellowthroat and Song Sparrow, two-sample t-tests were used to examine geographic differences in THg concentrations, as well as age and sex differences. Results are reported as arithmetic means ± 1SD. The geographic test compared the Alviso Slough fringing marsh samples to reference marshes. Due to non-normally distributed values in Song Sparrow, the Mann-Whitney non-parametric t-test was used.

Brine Flies

Brine fly data analyses were conducted using dry-weight concentrations of whole-body MeHg. Data from multiple pannes within the same marsh site were averaged prior to analysis. Two-sample t-tests were used to compare the ponds and marshes and to compare marsh samples from the Alviso area to the reference areas. Since the sample size from ponds and pannes were exactly equal, the pooled variance calculation was used for that t-test. The MeHg data were log-10 transformed, to meet assumptions of parametric analyses. Therefore, results are reported as geometric means +/- 1SD. The same approach taken for the CDF analysis of fish in ponds was used for brine flies. Specifically, 2007 and 2008 data were pooled for the pond CDF, but only 2008 data for marshes were used.

Integration among Biosentinel Species and Sediment

Mercury concentrations in different sentinel species from the same marsh sample locations were compared to each other using linear regression analysis in Systat v. 11 (Chicago, IL). This analysis was not repeated for ponds, because fish and flies could not be co-located at sufficient sites. Mercury data were log-transformed to meet assumptions of normally distributed error values. Due to the small sample size in Alviso Slough, results corresponding to this region were excluded from the analyses.

In addition, each biosentinel species sampled in tidal marsh was examined for a relationship to sediment THg and MeHg. This comparison was designed to be made between Song Sparrows and sediment, because both were sampled at the same time and place from 20 sites (Fig. 4.1.1). Longjaw mudsucker (marsh channel) and brine fly (panne) data were also examined by regression analysis for relationships to sediment.

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 biosentinels) were initially submitted as Excel spreadsheets, with the exception of 2008 bird data which were collected and stored in a database through the use of an Access-based form. These data submittals were reviewed for accuracy and completeness by a data manager at SFEI and revised as needed before being imported into the final Project 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 Hg concentrations per species. The map figures were designed using a combination of ESRI ArcInfo 9.3.1 and Google Earth 4.2 software, and are in California Teale Albers NAD 83 and Simple Cylindrical WGS84 projections, respectively.

5. Results

5.1. Sediment and Pore Water

The complete database and summary statistics for all sediment and pore water results is provided as a Microsoft Excel workbook (Appendix A). Sediment data are graphically presented grouped by the five sampling areas on which statistical analysis was based. These groupings are: a) Pond

A8 mudflats [A8-mudflat], b) Pond A8 borrow ditches and remnant slough channels [A8-slough], c) Alviso Slough main slough channel [AS-slough], d) Alviso Slough vegetated marsh plain [AS-marsh] and e) South Bay vegetated Reference marsh plain [Ref-marsh].

Mercury Speciation

Sediment Hg species concentration (dry weight) is presented as box-and-whisker plots (Fig. 5.1.1), which graphically depict the median, the 25-75% inter-quartile range, the maximum and minimum values, and the Tukey pair-wise comparison results for each sampling area. Median values of sediment THg (Fig. 5.1.1a) ranged from 260 ng/g (Ref-marsh) to 711 ng/g (A8-mudflat) among sampling strata. The Tukey pair-wise comparison among habit types indicated that THg concentration in A8-mudflat was significantly higher than in both vegetated marsh groups (AS-marsh and Ref-marsh).

Median values of sediment $Hg(II)_R$ (Fig. 5.1.1b) ranged from approximately 0.25 ng/g in the deep water channels of both AS-slough and A8-slough to 8.10 ng/g in AS-marsh. Both vegetated marsh sampling areas (AS-marsh and Ref-marsh) had $Hg(II)_R$ concentrations that were significantly elevated over all other areas, while AS-marsh had significantly higher concentrations than Ref-marsh. Similar spatial trends were found when $Hg(II)_R$ was expressed as a percentage of THg (Fig. 5.1.1c), with median values of $\%Hg(II)_R$ ranging from 0.05 % in both AS-slough and A8-slough to 2.43% in AS-marsh. The mean (± std. err.) sediment $\%Hg(II)_R$ value for the complete data set (N = 71) was 1.45 ± 0.18%. Thus, concentrations of $Hg(II)_R$ are a very small percentage of THg at all locations, as was seen in the Phase I (Alviso Slough deep core) study (Marvin-DiPasquale and Cox 2007) and in a recent study of diverse freshwater stream bed sediment (Marvin-DiPasquale et al. 2009)

Median sediment MeHg concentrations (Fig. 5.1.1d) ranged from 1.5-1.6 ng/g in AS-marsh and AS-slough to 7.7 ng/g in A8-mudflat. A8-mudflat and A8-slough had a statistically higher MeHg concentration than both vegetated marsh groupings (AS-marsh and Ref-marsh) and AS-slough. Expressed as a percentage of THg, median values of %MeHg (Fig. 5.1.1e), which is often used as a proxy measure for Hg(II)-methylation efficiency (Benoit et al. 2003, Sunderland et al. 2006), ranged from approximately 0.4% in both AS-slough and AS-marsh to 1.3% in A8-mudflat. The Tukey pair-wise comparison among habitat types for %MeHg yielded slightly different results than what was found for MeHg concentration, as %MeHg was significantly higher in A8-mudflat and A8-slough than in AS-slough and AS-marsh, but not significantly different from Ref-marsh.

A modest (yet significant) positive linear relationship existed between sediment THg and MeHg across all sites, ($r^2 = 0.20$; not shown), although when assessed individually, none of the five habitat type groupings exhibited a significant relationship between sediment THg and MeHg (not shown). A log-transformation of both variables resulted in a slightly better linear fit ($r^2 = 0.24$; Fig. 5.1.2a) across all sites. Plotted as individual habitat types (Fig. 5.1.2b) only the A8-slough grouping exhibited a statistically significant linear relationship ($r^2 = 0.46$) between the log-transformed THg and MeHg sediment data.

There was no significant relationship between THg and $Hg(II)_R$ concentrations, across all sites (Fig. 5.1.3a). However, there was a clear trend in that marsh sites (Alviso Marsh and Ref marshes) had comparatively low THg and a wide range of $Hg(II)_R$ concentrations, while Pond

A8 and Alviso Slough sites exhibited the converse, a wide range of THg values and comparatively low $Hg(II)_R$ concentrations. When assessed by sampling area, a weak positive regression was found for the AS-marsh grouping only (Fig. 5.1.3b).

The relationship between $Hg(II)_R$ concentration and MeHg concentration across all sites was best described with log-transformed data and a 2nd order polynomial fit ($r^2 = 0.28$) (Fig. 5.1.4a), where MeHg concentrations increased with $Hg(II)_R$ for Alviso Slough and Pond A8 sites, and decreased with increasing $Hg(II)_R$ concentration for Alviso Marsh and Reference marsh sites. When log-transformed MeHg and $Hg(II)_R$ concentration data was assessed by sampling area, significant linear regressions were found for Ref-marsh (negative slope) and A8-slough (positive slope) only (Fig. 5.1.4b).

Additional Sediment Characterization

Median values for sediment oxidation-reduction (redox) potentials ranged from strongly reducing in the deep channels of Pond A8 (-135 mv for A8-slough) to strongly oxidized (> +300 mv) in the vegetated marshes (AS-marsh and Ref-marsh) (Fig. 5.1.5a). Sediment pH did not show particularly strong differences among the sampling areas, with median values ranging from 6.4 pH units for the Ref-marsh sites to 7.4 pH units in AS-slough (Fig. 5.1.5b). Sediment organic content (expressed as %LOI) had median values ranging from 6.0% (AS-slough) to > 15.0% in Pond A8 (A8-slough and A8-mudflat) and across South Bay reference marshes (Ref-marsh) (Fig. 5.1.5c). Sediment grain size (expressed as % < 63 µm) had median values ranging from 62-64% for the two Pond-A8 habitats to 84-91% for the two vegetated marsh categories (AS-marsh and Ref-marsh), indicating generally finer grained sediment in the emergent wetland sites (Fig. 5.1.5d).

Not surprisingly, the hypersaline Pond A8 environment had significantly elevated pore water conductivity (Fig. 5.1.6a), chloride (Fig. 5.1.6b), and sulfate (Fig. 5.1.6c), compared to both the AS-slough and AS-marsh settings. Pore water sulfide (Fig. 5.1.6d) ranged over three orders of magnitude among sampling areas, with the highest values associated with A8-slough (median = 281 µmol/l; maximum = 2190 µmol/l), while all other habits were significantly lower (median values: 0.4 to 1.1 µmol/l; maximum values: 0.9 to 3.7 µmol/l). Pore water sulfide was not assayed in AS-marsh samples during July 2007, because the redox measurement exceeded +100 mV (very oxic), indicating that no sulfide was present. No pore water constituents were sampled in the Ref-marsh category (April-May 2008 sampling).

5.2. Surface Water

Mercury Speciation

The surface water samples collected bimonthly between November 2006 and August 2007, from Pond A8, Alviso Slough and Alviso Marsh, lend themselves to a detailed temporal analysis of Hg speciation a) among these three general habitat types, b) with water column depth, and c) along the salinity gradient of Alviso Slough. The complete database and summary statistics for all surface water parameters is provided as a Microsoft Excel workbook (Appendix B).

Surface water u-THg concentrations (Fig. 5.2.1) were generally highest in Pond A8 compared to Alviso Marsh and Alviso Slough, with means (± std. err.) for each sampling area of 60 ± 10 ng/l, 21 ± 4 ng/l, and 23 ± 3 ng/l, respectively (all sampling dates, locations and depths included). One

Pond A8 sampling site in particular (borrow ditch A8WF1) exhibited a dramatic increase in u-THg concentration over the sampling period (Fig. 5.2.1a), whereas none of the other sampling locations showed such a distinct temporal pattern in any of the three sampling areas. From January through August 2007, there was also a pronounced effect of sampling depth within Alviso Slough, with the near-bottom sites having higher u-THg concentrations than the near-surface sites (Fig. 5.2.1c). The water quality objective for u-THg in both fresh and saline water, as set out in the *San Francisco San Francisco Bay Basin (Region 2) Water Quality Control Plan* is 0.025 µg/l (25ng/L) (SFRWQCB 2007). Samples collected from Pond A8 frequently exceeded this objective, particularly as the summer season progressed, while samples from the Alviso Marsh occasionally exceeded the objective, and bottom water samples from Alviso Slough exceeded it consistently between May and August 2007.

Surface water u-MeHg concentrations (Fig. 5.2.2) were also significantly higher in Pond A8 compared to Alviso mash and Alviso Slough, with means (± std. err.) for each sampling area of 2.88 ± 0.44 ng/l, 0.52 ± 0.24 ng/l, and 0.38 ± 0.11 ng/l, respectively (all sampling dates, locations and depth included). Again, Pond A8 sampling site A8WF1 stood out as having the highest overall u-MeHg concentrations and peaking in late May (Fig. 5.2.2a). The seasonal trend in u-MeHg concentration was also more pronounced in Alviso Marsh (Fig. 5.2.2b) and Alviso Slough (Fig. 5.2.2c) than was the case for u-THg, with a modest increase between March and August at most sites, and a dramatic increase for the most freshwater site in Alviso Slough. There was no consistent trend with sampling depth within Alviso Slough, as was noted above for u-THg concentrations.

The percentage of u-THg that was u-MeHg (i.e. % u-MeHg) was also generally higher in Pond A8 (median = 5.2%), compared to Alviso Marsh (median = 1.5%) and Alviso slough (median = 1.1 %) (Fig. 5.2.3). While seasonal trends varied among the individual sites, there was a pronounced spike in % u-MeHg associated with the historic slough channel in Pond A8 (site A8WD1) during late March, with near-surface and near-bottom water samples exhibiting values of 53% and 45%, respectively (Fig. 5.2.3a). There was a similar late-March spike in the freshwater region of Alviso Slough (site ASW1), with near-surface and near-bottom water samples exhibiting values of 19% and 55%, respectively (Fig. 5.2.3c).

Non-Mercury Parameters

Non-mercury surface water parameters provide some evidence as to what may control the observed spatial and temporal trends in surface water and sediment Hg speciation. A number of the key non-Hg parameters monitored for this study are more fully described below and graphically illustrated, while specific numeric information regarding all can be found in Appendix B.

Surface water TSS tended to increase throughout the November 2006 – August 2007 sampling period in all three sampling areas, although this trend was most pronounced in Pond A8 (Fig. 5.2.4). Pond A8 also had significantly higher TSS concentrations than the two other sampling areas, as illustrated by the median and mean (± std. err.) values for the three sampling areas, which were as follows (in mg/l): Pond A8, 215, 303 ± 44; Alviso Marsh, 68, 53 ± 8; Alviso Slough, 65, 75 ± 10. TSS also tended to be higher in near-bottom samples, compared to near-surface samples, from the two most saline sites along Alviso Slough (ASW2 and ASW3) (Fig. 5.2.4c).

It is noteworthy that the TSS data described above and depicted in Fig. 5.2.4 represents that generated by the SCVWD laboratory. The USGS group also ran samples for TSS on sample splits, but generally calculated much higher values than those obtained by the SCVWD lab (> 20X in some cases), particularly for Pond A8 samples, which consisted largely of phytoplankton (see Discussion section). There was much closer agreement between the two laboratories for samples collected from Alviso Slough and marsh, and the spatial and temporal trends for all sites were generally similar. As detailed in the Methods section, the two labs used two different approaches for TSS, with the SCVWD using a heated evaporation technique (no filtration of the water sample), and the USGS group using a filtration technique combined with desiccation. It is not clear why such large differences in results were observed for the two approaches, but for simplicity only the SCVWD data are presented here. However, TSS results from both laboratories can be found in Appendix B.

Dissolved oxygen (D.O.) concentrations in Pond A8 decreased dramatically at all sites during the sampling period, from highs of approximately 6-10 mg/l in near-surface (remnant slough channel) and mid-depth (borrow ditch) waters during November 2006 and January 2007, to sub-oxic levels (≈ 3 mg/l) by March, to anoxic (< 1 mg/l) or near anoxic levels during May thru August 2007 at most sites (Figs. 5.2.5a). In contrast, D.O. concentration declined more modestly across all Alviso Marsh and Slough sampling locations, from highs of approximately 6-12 mg/L in November 2007 to lows of approximately 4-6 mg/l in August 2007(Figs. 5.2.5b and 5.2.5c). A clear trend with depth was evident in Alviso Slough between May and August 2007, where near-bottom waters were consistently lower in D.O. than near-surface waters.

Surface water pH was basic (pH > 7.0) and varied by just under 1.5 pH units (7.4 to 8.8) across all sites and sampling times throughout the study. The seasonal patterns were largely consistent both within and among sampling areas. For Pond A8, after an initial drop in pH between November 2006 and January 2007 in near-surface (remnant slough channel) and mid-depth (borrow ditch) waters, values peaked again during March and May, then fell again to seasonal lows during July and August 2007 (Figs. 5.2.6a). Alviso Marsh and slough seasonal trends in pH were very similar to each other, with the peak (ca. 8.2 to 8.6 pH units) occurring during May 2007 (Figs. 5.2.6b and 5.2.6c).

Surface water specific conductivity (S.C.) exhibited very strong spatial and temporal trends (Fig. 5.2.7), with Pond A8 having much higher values overall (median = 160 mS/cm; mean (± std. err.) = 189 ± 25 mS/cm) than both Alviso Marsh (median = 29 mS/cm; mean = 23 ± 3 mS/cm) and Alviso Slough (median = 33 mS/cm; mean = 26 ± 2 mS/cm). As would be expected, there was a very clear increase in S.C. going from the freshwater sites to the more saline sites for both Alviso Marsh and Slough, and higher S.C. values in near-bottom water samples from Alviso Slough, compared to near-surface waters from the same site. Seasonally, S.C. increased dramatically between March and August 2007 in Pond A8, while only minor increases in S.C. were observed over the sampling period in Alviso Marsh and Slough. Very similar spatial and temporal patterns were observed for both dissolved sulfate (Fig. 5.2.8) and chloride (not shown), as those described above for S.C.

Surface water DOC similarly exhibited strong spatial and temporal trends (Fig. 5.2.9), with Pond A8 having much higher values overall (in mg/L, median = 73.2; mean (± std. err.) = 72.3 ± 6.2)

than both Alviso Marsh (median = 5.7; mean = 5.4 ± 0.4) and Alviso Slough (median = 4.3; mean = 4.6 ± 0.2). Pond A8 also exhibited a clear consistent rise in DOC concentrations between November 2006 and July 2007 in near-surface (remnant slough channel) and mid-depth (borrow ditch) waters (Fig. 5.2.9a). The seasonal trend in the Alviso Marsh and Slough sites was less pronounced and consistent. However, from May thru August 2007, within both Alviso Marsh and Slough, there was a distinct spatial trend in which the most freshwater sites (ASW1 and ASMW1) had the lowest DOC concentrations and the mid-salinity sites (ASW2 and ASMW2) had the highest DOC concentrations (Figs. 5.2.9b and 5.2.9c).

Associated with surface water DOC is $SUVA_{254}$, which provides some measure of dissolved organic quality and source among the various habitats. Across the three habitat types, $SUVA_{254}$ values were significantly lower in Pond A8 (in L/mg-m, median = 1.3; mean (± std. err.) = 1.4 ± 0.1) than in either Alviso Marsh (median = 2.5; mean = 2.8 ± 0.3) or Alviso Slough (median =2.4; mean = 2.4 ± 0.1) (Fig. 5.2.10). These summary statistics confirm that the DOC from Pond A8 has less aromatic character and is indicative of a phytoplankton source, while DOC from the two Alviso habitats is more aromatic and indicative of terrestrial sources (lignin rich vascular plants). Along the Alviso salinity gradient, the most freshwater slough and marsh sites (ASW1 and ASMW1) tended to have higher $SUVA_{254}$ values than the mid and high salinity locations down-stream (Figs. 5.2.10b and 5.2.10c). This likely reflects changes in vascular plant community composition along the salinity gradient, with tule dominating the freshwater end and *Spartina* dominating the more saline end of the slough-marsh complex. In contrast to these distinct spatial trends, there was only minor seasonal variation in $SUVA_{254}$ values within each given habitat type.

5.3. Biosentinels

In 2008, 20 marsh sites were sampled for birds, 51 marsh and pond sites were sampled for fish, and 46 marsh and pond sites for flies (Fig. 4.1.1).

Demersal and Water-column Fish

Longjaw mudsucker (demersal) and threespine stickleback (water-column) were the two most frequently sampled fish. No clear spatial pattern of THg concentration was evident across mudsuckers from South Bay (Fig. 5.3.1). No significant difference was found in mean THg concentrations between tidal marsh channels and pond habitats for either longjaw mudsucker or threespine stickleback (Fig. 5.3.2). Mean THg concentrations in mudsucker from marsh channels measured 0.08 +/- 0.14 µg/g compared to 0.08 +/- 0.32 µg/g in ponds ($t = 0.28$, $df = 23$, $p = 0.78$). Similarly, stickleback exhibited no significant difference ($t = 0.33$, $df = 13$, $p = 0.75$) in mean THg concentrations between the marsh channels (mean = 0.12 +/- 0.37 µg/g) and ponds (mean = 0.11 +/- 0.24 µg/g).

In addition to marsh-pond comparisons, the fish biosentinels also were used to compare the Alviso restoration area (in and around Pond A8) to the South Bay ambient population of marshes and ponds. Mercury did not differ between the Alviso Slough fringing marsh and the reference population of South Bay marshes for either species (mudsucker: $t = 1.52$, $df = 1$, $p = 0.32$; stickleback: $t = 0.18$, $df = 8$, $p = 0.38$; Fig. 5.3.3). One reason for this result is that there were more samples from the reference marshes than from Alviso Slough marsh. Mudsuckers were only collected from two Alviso sites and sticklebacks from three sites, compared to 18 sites and

7 sites in the reference marshes, respectively. This unbalanced sample design was because the sampling design was primarily oriented toward placing the Alviso samples in the context of South Bay ambient using GRTS-based CDFs (see below). Mean THg concentrations in mudsuckers from Alviso Slough marsh measured 0.11 +/- 0.11 µg/g compared to 0.08 +/- 0.14 µg/g in reference marshes. Similarly, stickleback exhibited THg concentrations in Alviso Slough that were slightly higher (0.16 +/- 0.20 µg/g) than in the reference population of marshes (0.11 +/- 0.42 µg/g), but that were not significantly different.

The CDF plot for marsh fish indicates that, relative to ambient condition across South Bay, the tidal marsh channels in the area to be restored (Alviso Slough) do not have particularly high Hg in the food web (Fig. 5.3.4). Approximately 20% of the tidal marsh area sampled in the South Bay has mudsucker THg concentrations that are higher than in Alviso Slough. The CDF plots for pond fish show an opposite result, in that Pond A8 has the highest mudsucker and stickleback THg concentrations of all the SBSPRP ponds (Figs. 5.3.5 and 5.3.6).

Mercury concentrations in small fish from the South Bay managed ponds and tidal marshes are above levels for concern in the Bay. The CDFs indicate that 100% of the South Bay tidal marsh area is currently above the San Francisco Bay Hg TMDL threshold of 0.03 µg/g in small fish (protective of piscivorous wildlife) based on longjaw mudsucker data (Fig. 5.3.7); approximately 90% of the SBSPRP pond area is currently above the 0.03 µg/g TMDL threshold based on longjaw mudsucker data (Fig. 5.3.8); and 100% of the pond area is above the TMDL based on threespine stickleback data (Fig. 5.3.9).

Resident Marsh Birds

The primary bird biosentinels sampled in 2008 were Song Sparrows and Common Yellowthroat. No difference was found in mean THg concentration by sex or age in either species. Mean THg concentrations in male (n = 61, mean = 0.40 µg/g) and female (n = 36, mean = 0.42 µg/g) sparrows were similar (t = 0.66, df = 79, p = 0.51). Song Sparrows of unknown sex were excluded from this comparison (n = 12). Similarly, evaluation of difference in THg by age in sparrows indicated no significant difference (t = 0.16, df = 8, p = 0.88) between after-hatch-year (n = 100, mean = 0.40 µg/g) and hatch-year (n = 8, mean = 0.42 µg/g) birds. Song sparrows aged as second-year after hatching were excluded from this comparison (n = 1). All data for Common Yellowthroat were aged as being after-hatch-year (n = 27, mean = 0.43 µg/g). As with Song Sparrows, males (n = 18, mean = 0.47 µg/g) and females (n = 9, mean = 0.34 µg/g) did not differ in their blood THg concentration (t = 1.65, df = 19, p = 0.12). Based on these analyses, bird data was pooled across sexes and ages within each species for all other analyses.

Mean THg concentrations in Song Sparrow blood varied spatially across marshes in South Bay (Fig. 5.3.10). Both sparrows and yellowthroat from Alviso Slough fringing marsh had THg concentrations similar to those of birds of the same species from reference marshes across South Bay (Fig. 5.3.11). Mean THg concentrations in Song Sparrow were not significantly different (Mann-Whitney U = 827.0, p = 0.06) in Alviso Slough marsh (n = 13, mean = 0.41 µg/g) and reference marshes (n = 96, mean = 0.33 µg/g). Similarly, yellowthroat THg concentrations did not differ (t = 0.24, df = 7, p = 0.82) between Alviso Slough (n = 20, mean = 0.45 µg/g) and reference marsh (n = 7, mean = 0.42 µg/g).

The CDF plot of the sparrow data shows that 80% of the South Bay tidal marsh area had a worse THg condition in the marsh plain food web (as indicated by Song Sparrows) than did the fringing marsh in Alviso Slough (Fig. 5.3.12). Thus, the marshes along Alviso Slough are not remarkable in their Hg condition, relative to South Bay ambient condition. Average sparrow blood THg values from each sampling station were below a suggested toxicity risk threshold of 1.18 µg/g (D. Evers pers. comm.), although some individuals did exceed this value in 2007 and 2008.

Brine Flies

Ephydra was the most frequently captured brine fly genus in 2008. Average brine fly MeHg concentrations throughout the South Bay did not suggest a strong spatial gradient (Fig. 5.3.13). Brine fly MeHg concentrations ranged from 0.0–0.3 µg/g dw at the vast majority of sites. Brine flies also exhibited similar MeHg concentrations in both the managed pond margins and the marsh pannes (Fig. 5.3.14). A two-sample t-test indicated that mean MeHg concentrations were not significantly different ($t = 0.57$, $df = 44$, $p = 0.58$) between pannes and ponds. The overall mean concentration in the ponds was 0.13 +/- 0.24 µg/g compared to 0.12 +/- 0.24 µg/g in the marsh pannes.

The CDF of marshes sampled in 2008 indicates that most of the marsh area in South Bay has brine fly MeHg concentrations in a narrow range from 0.1--0.2 µg/g ww (Fig. 5.3.15). Similar to the result for fish, Pond A8 had the worst MeHg condition for the pond margin habitat (as evidenced by brine fly MeHg) of any of the South Bay ponds sampled. All MeHg concentrations in the brine fly CDF above 0.35 µg/g corresponded to Pond A8 (Fig. 5.3.16). However, the managed pond area in South Bay above this level was small (< 3%).

5.4 Integration across Biosentinel Species and Sediment

Biosentinel species sampled from the same locations did not show the same spatial patterns across South Bay marshes (Fig. 5.3.17). Linear regression indicated weak relationships in Hg concentrations among marsh birds, fish, and flies from the same sites. The relationship between Hg in brine flies and mudsucker from marsh habitats had the highest correlation among the species compared but was not significant ($n = 16$, $r^2 = 0.19$, $p = 0.09$). Similarly, sparrow Hg concentrations were not significantly related to those of either mudsucker ($n = 15$, $r^2 = 0.05$, p-value = 0.43) or brine flies ($n = 13$, $r^2 < 0.001$, p-value = 0.96).

Mercury in Song Sparrows was strongly related to % MeHg in sediment ($n = 19$, $r^2 = 0.50$, p-value = 0.0007; Fig. 5.3.18). One outlier point corresponding to a marsh site near Foster City was removed from the regression ($n = 20$, $r^2 = 0.24$, $p = 0.030$). Similar analyses were performed for mudsuckers and brine flies in relation to sediment MeHg, but no significant relationship ($p > 0.05$) was found. This was expected since neither fish nor brine flies were sampled from the same marsh habitat at the same time as sediment, while sparrows and sediment were both sampled from marsh plain at the same time.

6. Discussion

This study addresses a series of questions to inform decisions by the Project Management Team (PMT) of the SBSPRP about Pond A8 restoration design and management (Fig. 2.1). The

ultimate question is whether or not conversion of Pond A8 to tidal marsh would increase the risk of Hg bioaccumulation in Pond A8, Alviso Slough, or South Bay overall (Grenier et al. 2007b).

Multiple lines of evidence were developed to answer this question. Mercury concentrations in sediment, water, and food webs from characteristic habitats of South Bay tidal marsh and managed pond ecosystems were compared over three years of field and laboratory research. Most lines of evidence indicate that conversion of Pond A8 to tidal marsh is likely to reduce the local risk of Hg bioaccumulation, and that this risk reduction will be most pronounced within the current Pond A8 footprint.

6.1 Mercury Bioavailability and Bioaccumulation in Pond A8 and Adjacent Tidal Habitats

There is abundant evidence that the bioavailability and bioaccumulation of Hg is greater in Pond A8 than in either Alviso Slough or its fringing tidal marsh.

- MeHg concentrations in sediment were greater in Pond A8 than in Alviso Slough or its fringing tidal marsh (Section 5.1 and Fig. 5.1.1d).

- MeHg concentrations in water were greater in Pond A8 than in Alviso Slough or in fringing tidal marsh channels (Section 5.2 and Fig. 5.2.2).

- Biosentinels representing benthic and shoreline habitats indicated more Hg bioaccumulation in Pond A8 than in the tidal marshes along Alviso Slough (Grenier et al. 2007b):

    - Benthic fish (longjaw mudsucker) had accumulated more THg from Pond A8 than from tidal marsh channels (Fig 5.3.5 in Grenier et al. 2007b);

    - Brine flies had accumulated twice the MeHg from the margins of Pond A8 than from tidal marsh pannes (Fig 5.3.7 in Grenier et al. 2007b).

It is important to note that this study has not assessed possible changes in MeHg that might occur within Pond A8 as it evolves into a tidal marsh. After construction and implementation of the tidal control structure, Pond A8 will become a sediment sink. As new sediment is added to the pond bottom, it will rise in elevation as a tidal mud flat. Marsh vegetation will colonize the ecotone between the tidal flat and the surrounding levee. The flat will eventually attain heights suitable for plant colonization. These elevations are likely to first occur in areas inboard of the tidal control structure, where sediment tends to accumulate. There may be a protracted period during which the pond, now open to tidal flow, is a mixture of mud flat and marsh. The duration of evolution from mud flat to fully vegetated tidal marsh will depend on many factors, including the initial elevation of the pond bottom, the amount of available sediment and its fertility, the temporal and spatial patterns of tidal flooding and drainage, the salinity regimes, the rates and patterns of sediment deposition, the species of plants that colonize the mud flats, and the health and vigor of the plant colonies. All of these factors can affect the bioavailability of Hg.

Controls on Mercury Speciation and Methylmercury Production among Habitats

The weak relationships between THg and MeHg, and between THg and $Hg(II)_R$ (Figs. 5.1.2a and 5.1.2b, respectively), indicate that factors other than the concentration of THg play a

significant role in mediating both the pool size of $Hg(II)_R$ 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 ($Hg(II)_R$ is the surrogate measure of this pool) and the activity of those bacteria in a given setting. Bacterial activity is in turn a function of suitable organic matter and the availability of suitable electron acceptors (i.e., sulfate for sulfate reducing bacteria, iron(III) for iron reducing bacteria, etc.).

Thus, the two key questions 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 $Hg(II)_R$ that is available to those Hg(II)-methylating microbes? This project did not employ isotope tracer experiments typically used to directly measure MeHg production rates associated with the Hg(II)-methylating community activity, so the answer to the first question is still somewhat unresolved. However, the negative sediment redox conditions (< 0 mV; Fig. 5.1.5a), the high sediment organic content (Fig. 5.1.5c), and the high concentrations of pore water sulfate (Fig. 5.1.6c) and sulfide (Fig. 5.1.6d) observed in Pond A8 all suggest that microbial sulfate reduction is generally higher in this pond, as compared with either the Alviso Slough or marsh habitats. This result is relevant in that sulfate-reducing bacteria are the primary drivers of MeHg production in saline aquatic systems (Compeau and Bartha 1985).

The $Hg(II)_R$ pool and how it varied among the habitats as a function of sediment redox conditions was assessed, and thus the second question posed above can begin to be examined. The strong exponential increase in sediment $\%Hg(II)_R$ as a function of redox (Fig. 6.1.1a) sorts out along habitat type, with Pond A8 exhibiting both reducing conditions and low $\%Hg(II)_R$ values, and the vegetated marsh sites exhibiting comparatively oxidizing sediment conditions and much higher $\%Hg(II)_R$ values. This trend is presumably reflective of the fact that high sulfate, chemically reducing sediments (such as those in Pond A8) typically have high concentrations of solid-phase reduced sulfur containing minerals (such as FeS and FeS_2; Marvin-DiPasquale and Capone 1998), and that these minerals can bind strongly to Hg(II), making it less available (i.e., decreasing the $\%Hg(II)_R$; Huerta-Diaz and Morse 1992, Marvin-DiPasquale et al. 2009). A positive linear relationship between sediment redox and log-transformed sediment $Hg(II)_R$ concentration was also observed (Fig. 6.1.1b), and again the data sorted out along similar habitat groupings. These findings are important in that they rule out the possibility that the high MeHg concentrations observed in Pond A8 sediment are due to high concentrations of $Hg(II)_R$, but instead support the idea that enhanced rates of microbial activity associated with Hg(II)-methylation are responsible. Conversely, even though vegetated marsh plains had significantly higher $Hg(II)_R$ concentrations, and $\%Hg(II)_R$ values, compared to Pond A8, they still had much lower MeHg concentrations than Pond A8, again pointing to the critical role of microbial activity in mediating MeHg concentrations among these habitat types. This point is further illustrated in the negative linear relationship observed for log-transformed MeHg concentration as a function of sediment redox (Fig. 6.1.2). While this relationship was weaker than that for $Hg(II)_R$ as a function of sediment redox, it also demonstrates how the data sort out by habitat type, with the more oxidized marsh plain sites having lower MeHg concentrations than the more reducing Pond A8 sites.

Rates of Hg(II)-methylation or microbial sulfate reduction in this study were not directly measured. However, a number of lines of evidence support the conclusion that microbial activity

overall is enhanced in Pond A8, relative to both Alviso Slough and vegetated marsh plain habitats sampled throughout South Bay, and that this enhanced microbial activity is driven by high rates of phytoplankton production in Pond A8. These lines of evidence include the following: a) The comparatively high concentration of overlying water TSS (Fig. 5.2.4) and DOC (Fig. 5.2.9), as well as the low $SUVA_{254}$ values (Fig. 5.2.10) and the green appearance of the water samples from Pond A8, compared to all other habitats, all indicate that Pond A8 is dominated by particulate organic matter in the form of phytoplankton, while Alviso Slough and vegetated marshes are dominated by organic matter that is largely terrestrial in nature; b) The dramatic seasonal drop in surface water D.O. in Pond A8, and the lack of a similarly pronounced drop in D.O. in Alviso Slough and the marsh plains (Fig. 5.2.5), indicates a high rate of aerobic microbial respiration, driven by an ample pool of readily degradable organic matter (i.e. phytoplankton) in Pond A8; and c) the build-up of pore water sulfide concentrations in the deep portions of Pond A8, to levels > 1000X those observed in Alviso Slough or marsh habitats (Fig. 5.1.6d) indicates that microbial sulfate reduction is quite active in Pond A8.

Taken as a whole, the above data suggest that opening up Pond A8 to tidal flushing will likely lead to less phytoplankton production within A8, which will eventually lead to less MeHg production within Pond A8, as a result of reduced loading of easily degradable phytoplankton to the benthos. This conclusion is supported by data recently gathered in a parallel study of Pond A11 (low in phytoplankton production) and Pond A12 (high in phytoplankton production), where particulate and dissolved MeHg concentrations in surface water were higher in A12, as were THg concentrations in waterbird eggs and fish (Marvin-DiPasquale, Ackerman, and Eagles-Smith, unpublished data).

Alviso Slough Sediment Remobilization: Potential Impacts on Methylmercury Production

Immediately after Pond A8 is reconnected to tidal flow through the control structure, Alviso Slough is likely to begin to erode. This will exhume and mobilize buried sediment in the Slough that is laden with legacy Hg from the New Almaden mining district. The exposure of this buried sediment to oxygenated overlying water will likely increase the availability of Hg(II) for methylation (increase the $\%Hg(II)_R$ associated with suspended particles), as experimentally demonstrated during Phase I of this project (Marvin-DiPasquale and Cox 2007). While the ultimate fate of remobilized sediment is uncertain, it is likely that sediment will be largely deposited in three general areas: within Pond A8, on the existing Alviso tidal marsh, and throughout South Bay. The relative proportions in which remobilized sediment will be deposited in these three areas are currently unknown. Ultimately, this spatial distribution will dictate the extent to which $Hg(II)_R$ is actually converted into MeHg, as geochemical and microbial conditions at the sediment surface are primary drivers of MeHg production. Sediment elevated in $Hg(II)_R$ that is deposited within Pond A8 will likely exhibit the highest conversion to MeHg, given its current status as a reducing environment with high levels of readily degradable organic matter. A similar result might be predicted for sediment deposited in the deeper sub-tidal portions of South Bay. In contrast, the comparatively oxidized vegetated tidal marsh plain will likely not produce as much MeHg for an equivalent amount of deposited $Hg(II)_R$-laden sediment. Since the increase in the $Hg(II)_R$ pool size, associated with exposure of reducing sediment to oxygenated overlying water, was rapid (on the order of days) in the laboratory experiments upon which these conclusions are based (Marvin-DiPasquale and Cox 2007), it would be expected that the reverse reaction (a decrease in the $Hg(II)_R$ pool-size) may be similarly rapid in situations

where $Hg(II)_R$-laden sediment is deposited in strongly reducing environments (e.g. borrow ditches, historic slough channels in Pond A8, and deep channels in South Bay).

Thus, to the extent that there is a rise in MeHg production, as a result of remobilized Alviso Slough sediment, the duration of this spike will largely depend upon both the time for the slough scour event to unfold, and on the spatial distribution of this deposited sediment with respect to habitat. Eventually, remobilized Hg-laden sediment will be reburied through normal tidal sedimentary processes. However, close monitoring of both $Hg(II)_R$ and MeHg distributions in water, sediment and biota of Pond A8, Alviso Slough and South Bay, in the period before, during and after the construction of the A8 notch is warranted. In support of this goal, the SBSPRP has recently approved a follow-up study designed to examine mercury dynamics in the water column, sediment and biota in Alviso Slough, Mallard Slough (control slough), Pond A8, Ponds A16 (positive control pond), and Pond A3N (negative control pond) over a two year window (beginning in early 2010) and covering the period during and after the construction of the Pond A8 notch (Eagles-Smith et al. 2009b).

6.2 Mercury Bioavailability and Bioaccumulation in South Bay Managed Pond and Tidal Marsh Ecosystems

Mercury concentrations in sediment and bioaccumulation in sentinel species were surveyed for managed ponds and tidal marshes throughout South Bay during spring and summer 2008. The survey design accounts for the probability of any particular pond or tidal marsh area being included or excluded from the survey sample. The results can therefore be used to estimate the percent of ponds or marshes (by area) that are likely to have any particular value for either Hg bioavailability or bioaccumulation. The results can also be used to compare any particular pond or tidal marsh area to all the others in South Bay. Key findings from the survey are presented below.

- There was no significant difference between the sediment of tidal marsh plains along Alviso Slough and marsh plains elsewhere in South Bay with regard to THg, %Hg(II)R, MeHg, and %MeHg (Fig. 5.1.1). However, the marsh sediments along Alviso Slough had greater concentrations of $Hg(II)_R$ (Fig. 5.1.1b). This trend in $Hg(II)_R$ was modest, and may be partially explained by the fact that compared to the Ref-marsh grouping, Alviso Slough fringing marsh sediment: a) trended towards higher THg concentrations (although not significantly different from Ref-marsh, Fig. 5.1.1a), b) had lower organic content (suggesting a more mineral soil, Fig. 5.1.5c) and c) had a finer grain size (Fig. 5.1.5d).

- Based on THg concentrations in resident marsh fish (longjaw mudsuckers), bioaccumulation of Hg in the food web of tidal marsh channels along Alviso Slough is similar to other South Bay tidal marshes, although somewhat on the higher end (Fig. 5.3.4). About 20% of the tidal marshland of South Bay had greater THg concentrations in longjaw mudsuckers than did the tidal marshes along Alviso Slough.

- Based on THg concentrations in Song Sparrows, bioaccumulation of Hg in the food web of tidal marsh plains along Alviso Slough is similar to other South Bay tidal marshes, although somewhat on the lower end (Fig. 5.3.12). About 80% of the tidal marshland of South Bay had greater THg concentrations in Song Sparrows than marsh along Alviso Slough.

- Based on statistical tests, rather than the CDFs (two bullets points above and Fig. 5.3.4), THg concentrations in biosentinels were either similar for tidal marshes along Alviso Slough relative to elsewhere in South Bay (i.e., marsh fish and marsh birds during 2008; Figs. 5.3.3 and 5.3.11), or were lower for the Alviso Slough marshes (i.e., Song Sparrows in 2007; Grenier et al., 2007b).

- Hg bioaccumulation was greater for Pond A8 than for any other South Bay managed pond in the survey; Pond A8 had the highest Hg concentrations for all pond biosentinels (benthic fish, water-column fish, and brine flies; Figs. 5.3.5, 5.3.6, and 5.3.16).

- Overall across South Bay, there was no difference in Hg bioaccumulation in the biosentinels from tidal marsh habitats compared to managed pond habitats. (Figs. 5.3.2 and 5.3.14).

Apart from the potential risk associated with the remobilization of Hg-laden sediment due to scour from increased tidal prism following the reconnection of ponds to tidal flow through the construction and implementation of armored tidal control structures, these findings suggest that the conversion of former salt ponds to tidal marsh should not be expected to increase Hg bioaccumulation in local food webs. However, there are many factors not addressed in this study that could alter this interpretation. For example, food webs can change in complexity (number of trophic levels), connectivity and the importance of different food-web pathways, species composition and relative abundance, etc. The results of this survey do not replace the usefulness of case-specific studies of the relative risks of managing ponds or converting them to tidal marsh. This survey should help guide more detailed studies designed to help the PMT decide where and when ponds should be converted to tidal marsh to reduce the risks of Hg bioaccumulation for ponds and tidal marsh ecosystems, and South Bay as a whole.

These findings suggest that, despite being directly exposed to sediment and water from the New Almaden Mining District, the tidal marshes along Alviso Slough show no evidence of having greater Hg bioaccumulation than other tidal marshes in South Bay. This is probably due to a variety of factors. From about 1930 to 1969, the tidal marshes and salt ponds along Alviso Slough were subject to severe subsidence due to groundwater extraction in Santa Clara Valley (Poland and Ireland 1988). This subsidence increased the frequency and duration of tidal inundation of the marshes, and thus increased the rate of deposition of sediment, mostly clays and silts, across the marsh plains. As a result, the marsh surface is clayey, has scant organic material, and seldom desiccates. Furthermore, the clays seal the marsh surface, inhibiting exchanges of water between the surface and the underlying plant root zone. These factors in combination likely result in the elevated $Hg(II)_R$ concentrations observed in Alviso Marsh, but not in enhanced MeHg production.

The observed differences in Hg bioavailability and bioaccumulation between Pond A8 and the adjacent tidal marsh along Alviso Slough appear to be unusually large, relative to other ponds and other marshes in South Bay. Pond A8 was created by diking marshland that had been accumulating Hg-laden silts and clays from the New Almaden Mining District. Once diked, the historical marsh sediment was no longer subject to tidal action, so it could not be buried by new sediment carried by the tides. This situation was in contrast to adjacent Alviso Slough and its tidal marsh, where ongoing tidal deposition buried the historic Hg-laden sediment associated

with upstream mining (Marvin-DiPasquale and Cox 2007). The near-surface sediment is where most of the MeHg production occurs, and in Pond A8, this process is enhanced by deposition of phytoplankton and other algae (fuel for Hg(II)-methylating bacteria) and seasonal patterns of wetting and drying (ideal redox conditions for methylation). These factors help explain the relatively large concentrations of THg and MeHg in Pond A8 and its sediment (Fig. 5.1.1), water column (Figs. 5.2.1 and 5.2.2), and biosentinels (Figs. 5.3.5, 5.3.6, and 5.3.16). Other managed ponds have lower concentrations of MeHg in their food webs, when compared to adjacent marshes. For example, in 2007, three of four fish biosentinels had lower THg in Pond A5, which is adjacent to Pond A8, than in the adjacent tidal marsh along Alviso Slough (summary table p. 27, Sec. 5.3 in Grenier et al. 2007b). Thus, in the case of Pond A5, conversion to tidal marsh might cause a local increase in MeHg bioaccumulation through the food webs of these fish.

6.3 Differences in Mercury Bioaccumulation among Tidal Marsh Habitats

Given that tidal marshes are the intended endpoints for much of the SBSPRP, an analysis of relative differences in Hg accumulation among marsh habitats was undertaken to inform restoration design.

There are three basic approaches to compare bioaccumulation across different habitats. The first is to compare Hg concentrations in biosentinels to their Hg toxicity thresholds. However, these thresholds are unknown for most species. Another approach is to compare Hg concentrations for the same biosentinels in all the habitats. This method usually involves biosentinels that move among the habitats, which greatly decreases their value for distinguishing one habitat from another. The third approach, which was used in this study, involves using biosentinels that are habitat-specific in their feeding and have small home ranges or territories within their habitats. The habitats may occur in different ecosystems, but individuals rarely move from one ecosystem to another. For example, longjaw mudsuckers reside in benthic habitats of ponds and tidal marsh channels, but individual mudsuckers are unlikely to move back and forth between marsh channels and ponds.

There was no correlation among Hg concentrations from biosentinels from different tidal marsh habitats within the same marsh (Section 5.4; Fig. 5.3.17). These results indicate that, as expected, the biosentinels are habitat-specific, and that the food webs they represent are relatively distinct and not closely coupled (Grenier 2004). The pannes, channels, and vegetated plains of tidal marshland have their own food webs and the lack of connection between them inhibits the movement of Hg from one habitat to another through food-web pathways.

The close connection between Song Sparrows and the marsh plain habitat was indicated by a strong, positive correlation between the %MeHg in marsh plain sediment and sparrow blood (Fig. 5.3.18). A novel conclusion of this study is that Song Sparrows are especially useful for assessing Hg bioaccumulation in tidal marsh plains (Section 6.4).

These results also may suggest that MeHg is not being transported from one marsh habitat to another by physical processes, such as the movement of water. For example, if the marsh plain were the predominant source of MeHg for the tidal channels within the marsh, then THg concentrations in longjaw mudsuckers from the marsh channels would be positively correlated to

THg concentrations in sparrows from the marsh plains. However, no such correlation was detected.

The upshot of these findings for marsh design and monitoring is that each habitat within a marsh behaves independently of the other habitats with respect to Hg bioaccumulation. Therefore, no one biosentinel will provide information about Hg bioaccumulation in the full tidal marsh ecosystem. Brine flies indicate bioaccumulation in the panne food web, but do not provide information about the marsh channels. Fish provide information about the marsh channels but not the marsh plain. And so forth. Designing marshes with low bioaccumulation potential will mean understanding what creates low bioaccumulation potential for each marsh habitat separately.

6.4 Monitoring Considerations

For this report to inform decisions about alternative restoration designs and management schemes for Pond A8, it must include tentative conclusions with appropriate disclaimers and qualifying statements. Decisions about the future of Pond A8 and other SBSPRP activities must be based on incomplete and sometimes equivocal information. The decisions will therefore always have some risks. One way to manage this uncertainty about Pond A8 is to track the effects of every action and to minimize irreversible actions until the uncertainties about them are acceptable. This approach requires an ongoing gathering of empirical information about field conditions that relate as directly as possible to management concerns and actions. To maintain the flow of needed information, the program of data collection, management, interpretation, and reporting must be affordable. Based on these considerations, this study provides the following ideas about monitoring Hg for the SBSPRP.

- Mercury monitoring should focus on biosentinels. They are the most direct measure of a Hg problem or the potential for a problem to occur. However, biosentinels vary in their usefulness. To be very useful, a biosentinel must have a distribution in time and space that clearly relates to the geographic scope and timing of specific management actions or concerns. For example, the risk of bioaccumulation within habitats, where habitats are defined as physiographically distinct landscape features having their own characteristic food webs (e.g., tidal flats, tidal channels, marsh plains, pond benthos or water-column, pond shorelines, etc.) must involve biosentinels indicative of those food webs. Relative differences among ecosystems, such as managed ponds and tidal marshes, can be assessed by combining analyses of component, habitat-specific biosentinels or by monitoring other biosentinels that feed among all the habitats of an ecosystem but not among the ecosystems.

- Once habitats have been identified and prioritized in terms of concerns about Hg bioaccumulation, then biosentinels for those habitats can be developed. Mercury concentrations in biosentinels should strongly and positively correlate to the bioavailability of Hg in their habitats. This correlation should be quantified using paired measurements of bioaccumulation and bioavailability.

  For example, this study measured a remarkably strong, positive correlation between THg bioaccumulation in tidal marsh Song Sparrows (THg in whole blood) and the %MeHg in surface sediment of tidal marsh plains (Fig. 5.3.18), with half the variance in Song

Sparrow THg concentration being explained by the %MeHg in sediment. This result was not unexpected. Song Sparrows feed on invertebrates on the marsh plain vegetation and the sediment surface (Grenier, 2004). They spend much time feeding directly in the active MeHg production zone (on surface sediment), where bacteria are methylating Hg(II). Given that vegetated marsh plains are the largest habitat component (by area) of the tidal marsh ecosystem that is targeted for restoration by the SBSPRP, and given the clear ecological and statistical relationships between Hg bioavailability on marsh plains and bioaccumulation in Song Sparrows, plus their widespread distribution among tidal marshes but close affinity to marsh plain habitat, Song Sparrows meet the criterion for being useful biosentinels.

- Knowing the toxicity threshold of a biosentinel is not essential for the biosentinel to be useful in a monitoring program. The purpose of the biosentinel is to monitor risk at the habitat scale, not to monitor risk to the biosentinel. Biosentinels are especially useful for tracking changes in ambient condition and for comparing individual sites to baseline data or ambient condition. In the context of monitoring management effects on ecosystem health, having multiple biosentinels clearly representing different habitats and food webs is more important than knowledge of their particular toxicity thresholds. Different biosentinels have different toxicity thresholds, and it is unlikely that resources will be available to determine thresholds for all useful biosentinels. It is more likely that the PMT, with input from scientists responsible for biosentinel data, might decide that an upward trend in bioaccumulation for one or more biosentinels, rather than the exceedance of a finite threshold, warrants a management action. The PMT response to a Hg problem might involve further data collection, a change in habitat management, or a change in ecosystem design.

- Solving a Hg problem will require knowledge about functional relationships between management actions and Hg bioaccumulation. In some cases, especially when the problem is defined by a trend in biosentinel data rather than a finite bioaccumulation threshold, strong correlations between management actions and bioaccumulation may provide the basis for solving the problem by adjusting the actions. Such correlations are unlikely to be known except through experimentation or long-term monitoring of management effects. In other cases, especially when the problem is defined relative to the toxicity threshold for a particular biosentinel, the solution might require understanding the problem's causal processes and mechanisms. In these cases, special studies may be needed to drill down through the physiology and ecology of the biosentinel into the Hg chemistry of the water or sediment of its habitat.

- To assess the risk of Hg bioaccumulation during the evolution of tidal marsh, biosentinels should be monitored during each successive stage. The monitoring might focus on resident fish biosentinels during the evolution of mudflat, and then marsh biosentinels might be added to the monitoring program after the mudflats have been colonized by marsh vegetation.

- A regional perspective is needed to distinguish the local effects of SBSPRP activities on Hg bioaccumulation from regional or larger scale variability and trends. The SBSPRP is likely to move forward with individual, local restoration actions at various places within

the larger geographic scope of the SBSPRP over many decades. In addition to this shift from ponds to marshes, other factors that are likely to affect Hg bioavailability will also change during this timeframe. The continuing rise of sea level will affect salinity and tidal regimes. Changes in rainfall and land use in the watersheds draining to San Francisco Bay will alter sediment supplies. As the distribution and abundance of wildlife species adjust to climate change, the food webs of salt ponds and tidal marsh ecosystems might also change. Being able to distinguish between the effects of the SBSPRP and regional trends is essential to define and detect problems. To provide the regional perspective that is needed, probabilistic surveys using biosentinels, such as the survey conducted for this study, should be repeated often enough to partition the variability in bioaccumulation among restored habitats between regional influences and local SBSPRP actions. Regional surveys should also guide more detailed studies designed to help the PMT decide which ponds should and should not be converted to tidal marsh, and when they should be converted, to reduce Hg bioaccumulation for San Francisco Bay as a whole.

- Effective and affordable monitoring of the effects of the SBSPRP on Hg bioaccumulation will require standard methods of data collection, data analysis, and a common system of data management. All monitoring data need to be safely and routinely archived and readily available for interpretation and reporting. A data management system that integrates Hg data from the SBSPRP with comparable data from other restoration projects and research efforts in the region should be a high priority for the SBSPRP. All data from this study (see Appendices A, B and C) are available in digital format from SFEI.

7. Acknowledgements

The authors thank the many field technicians and volunteers who collected and processed biosentinel samples, especially Katie Harold, Alicia Gilbreath, Dayna Yocum, Tiffany Hernandez, Karen Peluso, Jackson Gentry, Juan Flores, Guy Canha, Rebecca Wolff, Joe Mello, Karla Guevarra, and most of all Celia Norman. Thanks to Dr. Robert Taylor, Deborah Perry, and the other TAMU laboratory staff for finding ways to successfully analyze some difficult biosentinel samples. Sincere thanks are extended to the following USGS employees for their invaluable assistance in sediment field collection, laboratory analysis and data analysis: M.H. Cox, J. Kanerva, S. Quistad, S.Wren, K. Akstin, and C. Coates. Steve Ritchie, Beth Dyer, Clyde Morris, Cheryl Strong, Joy Albertson, and Eric Mruz provided valuable input and kept this project coordinated with other efforts in the region. Input from Don Danmeier has been particularly helpful as well. Thanks to the Don Edwards National Wildlife Refuge, California Department of Fish and Game, Cargill Incorporated, and Palo Alto Baylands for allowing us access to the sampling locations. Thanks to Tony Olsen for providing the GRTS-based sample locations and to Kerry Ritter, Meredith Williams, and John Oram for working on the GRTS design. The authors are also grateful for the identification of brine flies by David Herbst. Finally, the financial support of this project from the following institutions made this work possible and is greatly appreciated: the San Francisco Foundation, the Santa Clara Valley Water District (South San Francisco Bay Shoreline Study), and the California State Coastal Conservancy. This work was conducted with permits from the Patuxent Bird Banding Laboratory, the USFWS, and CA DFG.

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Tables

Table 3.2.1. Sampling design for biosentinels in 2008. Each biosentinel reflects the food web of a particular habitat. Demersal fish and brine flies reflect the food webs of particular habitats in both managed ponds and tidal marshes, so that the two can be directly compared.

Biosentinel	Common and Scientific Names	Habitats	Sites Sampled in Managed Ponds	Sites Sampled in Marshes
Demersal Fish	Longjaw mudsucker (*Gillichthys mirabilis*)	Managed pond benthos and tidal marsh channels	20	20
Brine Flies	Brine fly (*Ephydra*)	Managed pond margins and tidal marsh pannes	20	20
Marsh Birds	Alameda Song Sparrow (*Melospiza melodia pusillula*)	Tidal marsh plain	NA	20

Table 4.1.1. Surface sediment (top 0-2 cm) collection stations and dates.

Station Code	Sampling Dates[1]	Latitude[2]	Longitude[2]	Datum	Location	Feature Type
A8SEBD1	05/08/07, 01/15/08	37 25.373	121 58.802	NAD27	Pond A8	Borrow Ditch
RA8N-200	05/08/07, 01/15/08	37 25.537	121 58.775	NAD27	Pond A8	Borrow Ditch
A8NPH	05/08/07, 01/15/08	37 26.323	121 59.824	NAD27	Pond A8	Borrow Ditch
A8NRS4	05/08/07, 01/15/08	37 25.908	121 59.804	NAD27	Pond A8	Historic Slough Channel
A8NRS5	05/08/07, 01/15/08	37 25.856	121 59.751	NAD27	Pond A8	Historic Slough Channel
A8NMF1	05/08/07, 01/15/08	37 25.460	121 58.814	NAD27	Pond A8	Historic Marsh Plain
A8NMF2	05/08/07, 01/15/08	37 25.860	121 59.765	NAD27	Pond A8	Historic Marsh Plain
A8NMF3	05/08/07, 01/15/08	37 25.968	121 59.820	NAD27	Pond A8	Historic Marsh Plain
A8NMF4	05/08/07, 01/15/08	37 25.987	121 59.818	NAD27	Pond A8	Historic Marsh Plain
A8NMF5	05/08/07, 01/15/08	37 26.016	121 59.804	NAD27	Pond A8	Historic Marsh Plain
ASW3	05/22/07, 01/29/08	37 27.507	122 01.237	WGS84	Alviso Slough	Main Channel
ASW2	05/22/07, 01/29/08	37 26.816	122 00.742	WGS84	Alviso Slough	Main Channel
AST2B	05/22/07, 01/29/08	37 26.316	121 59.588	WGS84	Alviso Slough	Main Channel
AST1B	05/22/07, 01/29/08	37 25.912	121 59.313	WGS84	Alviso Slough	Main Channel
ASW1	05/22/07, 01/29/08	37 25.499	121 58.746	WGS84	Alviso Slough	Main Channel
ASM-WS3	07/05/07, 01/17/08	37 27.496	122 01.310	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASM-501	07/05/07, 01/17/08	37 25.711	121 58.897	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASM-505	07/05/07, 01/17/08	37 25.856	121 58.765	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASM-506	07/05/07, 01/17/08	37 26.359	121 59.516	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASM-504	07/05/07, 01/17/08	37 26.779	122 00.715	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-2LO *	07/05/07, 10/29/07	37 26.803	122 00.732	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-2MID *	07/05/07, 10/29/07	37 26.795	122 00.699	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-2HI *	07/05/07, 10/29/07	37 26.780	122 00.711	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-3LOW *	07/05/07, 10/29/07	37 27.468	122 01.266	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-3MID *	07/05/07, 10/29/07	37 27.462	122 01.285	WGS84	Alviso Marsh	Vegetated Marsh Plain
ASWM-3HI *	07/05/07, 10/29/07	37 27.460	122 01.305	WGS84	Alviso Marsh	Vegetated Marsh Plain
Ref-Y24 (Net4)	04/07/08	37 36.245	122 05.400	NAD83	Old Alameda Cr.	Vegetated Marsh Plain
ASM-01 (Net2)	04/08/08	37 25.433	121 58.658	NAD83	Alviso Marsh	Vegetated Marsh Plain

Station Code	Sampling Dates[1]	Latitude[2]	Longitude[2]	Datum	Location	Feature Type
Ref-O22 (Net4)	04/09/08	37 30.501	122 5.847	NAD83	Audubon Marsh	Vegetated Marsh Plain
Ref-Y26 (Net2)	04/10/08	37 26.61	121 57.733	NAD83	EEC Alviso	Vegetated Marsh Plain
Ref-Y27 (Net1)	04/11/08	37 35.479	122 08.763	NAD83	Whale Tail South	Vegetated Marsh Plain
Ref-O16 (Net3)	04/16/08	37 31.330	122 11.997	NAD83	Greco Island	Vegetated Marsh Plain
Ref-O29 (Net2)	04/17/08	37 31.864	122 13.951	NAD83	Bair Island	Vegetated Marsh Plain
Ref-Y13 (Net2)	04/18/08	37 33.101	122 14.905	NAD83	Foster City	Vegetated Marsh Plain
Ref-Y37 (Net5)	04/24/08	37 30.703	122 10.822	NAD83	Greco Island	Vegetated Marsh Plain
Ref-O50 (Net2)	04/25/08	37 28.272	122 07.552	NAD83	Laumeister Marsh	Vegetated Marsh Plain
ASM-Y2 (Net4)	04/28/08	37 26.893	122 01.102	NAD83	Alviso Marsh	Vegetated Marsh Plain
Ref-O14 (Net1)	05/01/08	37 30.374	122 05.411	NAD83	Dunburton Marsh	Vegetated Marsh Plain
Ref-O42 (Net3)	05/02/08	37 27.703	121 59.329	NAD83	Traingle Marsh	Vegetated Marsh Plain
Ref-O18 (Net2)	05/05/08	37 27.667	122 06.485	NAD83	Palo Alto Baylands	Vegetated Marsh Plain
ASM-04 (Net1)	05/08/08	37 26.375	121 59.497	NAD83	Alviso Marsh	Vegetated Marsh Plain
Ref-Y47 (Net1)	05/12/08	37 26.477	122 02.182	NAD83	Guadalupe Slough	Vegetated Marsh Plain
Ref-O20 (Net3)	05/13/08	37 30.955	122 04.889	NAD83	Dunburton East	Vegetated Marsh Plain
Ref-Y15 (Net2)	05/14/08	37 28.179	122 01.561	NAD83	Calaveras Point	Vegetated Marsh Plain
Ref-O35 (Net1)	05/16/08	37 30.046	122 00.934	NAD83	Upper Mouny Slough	Vegetated Marsh Plain
Ref-O52 (Net1)	05/17/08	37 31.688	122 03.861	NAD83	Newark Slough	Vegetated Marsh Plain

[1]Sampling dates are in given in the [mm/dd/yyy] format

[2]Coordinates for latitude and longitude are given in degrees decimal-minutes [DDD MM.MMM]

* These Alviso vegetated marsh sediment sites were sampled as part of a parallel USGS project (funding awarded to Dr. Lisamarie Windham-Myers by the San Francisco Foundation). The data associated with them are included in the current report to increase the number of Alviso Marsh observations, relative to South San Francisco Bay reference marsh observations.

Table 4.1.2. Quality Assurance Metrics for sediment, pore water and surface water analyses conducted by the USGS. The values listed represent the mean (± standard error) in each case. The relative percent deviation (RPD) is given for analytical duplicates. 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, RPD (count)	Certified Reference Material % Recovery (count)	Matrix Spike % Recovery (count)
Sediment Total Mercury	0.013 ± 0.006 µg/g dw (12)	7.7 ± 2.1 (14)	96 ± 3 (13)	98 ± 3 (12)
Sediment Methylmercury	0.10 ± 0.02 ng/g dw (11)	10.5 ± 3.0 (19)	107 ± 2 (23)	95 ± 3 (27)
Sediment Reactive Mercury	0.21 ± 0.06 ng/g dw (10)	6.2 ± 1.7 (11)		
Sediment Dry Weight		1.7 ± 0.2 (71)		
Sediment Bulk Density		2.3 ± 0.3 (71)		
Sediment Loss on Ignition		5.1 ± 0.6 (71)		
Sediment Porosity		2.4 ± 0.3 (71)		
Sediment Grain size (< 63 µm; %)		4.8 ± 0.7 (45)		
Pore Water Sulfate	< 0.6 µmol/L DDL (8)	5.4 ± 1.2 (49)		
Pore Water Chloride	< 1.7 µmol/L DDL (8)	4.5 ± 0.6 (49)		
Pore Water Sulfide	< 0.2 µmol/L DDL (2)	11.8 ± 1.7 (39)		
Pore Water Conductivity		1.6 ± 0.5 (26)		
Overlying Water Dissolved Organic Carbon	< 0.5 mg/L DDL (2)	6.0 ± 2.1 (13)		
Overlying Water Sulfate	< 0.6 µmol/L DDL (8)	1.7 ± 0.5 (5)		
Overlying Water Chloride	< 1.7 µmol/L DDL (8)	0.6 (1)		
Overlying Water Total Suspended Solids		12.1 ± 2.1 (43)		

Table 4.2.1. Surface water collection stations and dates.

Station Code	Sampling Dates[1]	Latitude[2]	Longitude[2]	Datum	Location	Feature Type
A8WD1[Surface and Deep]	01/25/2007, 03/27/2007, 05/17/2007, 07/16/2007, 08/29/2007	37.4331	121.99577	WGS84	Pond A8	historic slough channel
A8WF1	01/25/2007, 03/27/2007, 05/17/2007, 07/16/2007, 08/29/2007	37.4254	121.98087	WGS84	Pond A8	borrow ditch
A8WF2	01/25/2007, 03/27/2007, 05/17/2007, 07/16/2007, 08/29/2007	37.4385	121.99862	WGS84	Pond A8	borrow ditch
ASW1 [Surface and Deep]	11/16/2006, 01/30/2007, 03/29/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.42503	121.97909	WGS84	Alviso Slough	main channel
ASW2 [Surface and Deep]	11/16/2006, 01/30/2007, 03/29/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.44705	122.01232	WGS84	Alviso Slough	main channel
ASW3 [Surface and Deep]	11/16/2006, 01/30/2007, 03/29/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.45827	122.02056	WGS84	Alviso Slough	main channel
ASMW1	11/16/2006, 01/30/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.42477	121.97920	WGS84	Alviso Marsh	2nd–order channel draining the vegetated marsh plain
ASMW2	11/16/2006, 01/30/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.44636	122.01186	WGS84	Alviso Marsh	2nd–order channel draining the vegetated marsh plain
ASMW3	11/16/2006, 01/30/2007, 05/14/2007, 07/12/2007, 08/27/2007	37.45807	122.02126	WGS84	Alviso Marsh	2nd–order channel draining the vegetated marsh plain

[1]Sampling dates are given in the [mm/dd/yyy] format.

[2]All latitude/longitude coordinates are given in decimal degrees (DDD.DDDDD).

Table 4.3.1. Number of samples analyzed for THg (vertebrates) and MeHg (brine flies) from 2008 field collection. Numbers for fish indicate total number of samples (no size limits applied).

Biosentinel	Alviso Ponds	Reference Ponds	Ponds Total	Alviso Marsh	Reference Marsh	Marsh Total
Demersal fish						
Longjaw mudsucker	7	36	43	7	43	50
Water-column fish						
Threespine stickleback	7	14	21	3	7	10
Brine Flies						
Ephydra spp.	3	19	22		33	33
Resident marsh birds						
Song Sparrow				13	96	109
Common Yellowthroat				7	20	27

Table 4.3.2. Length: mercury relationship for longjaw mudsucker and threespine stickleback from reference marshes in 2008.

Species	Sample type	Sample size	R^2	*p*
Longjaw mudsucker	Individuals	43	0.09	0.048
Threespine stickleback	Composites	7	0.001	0.943

Figures

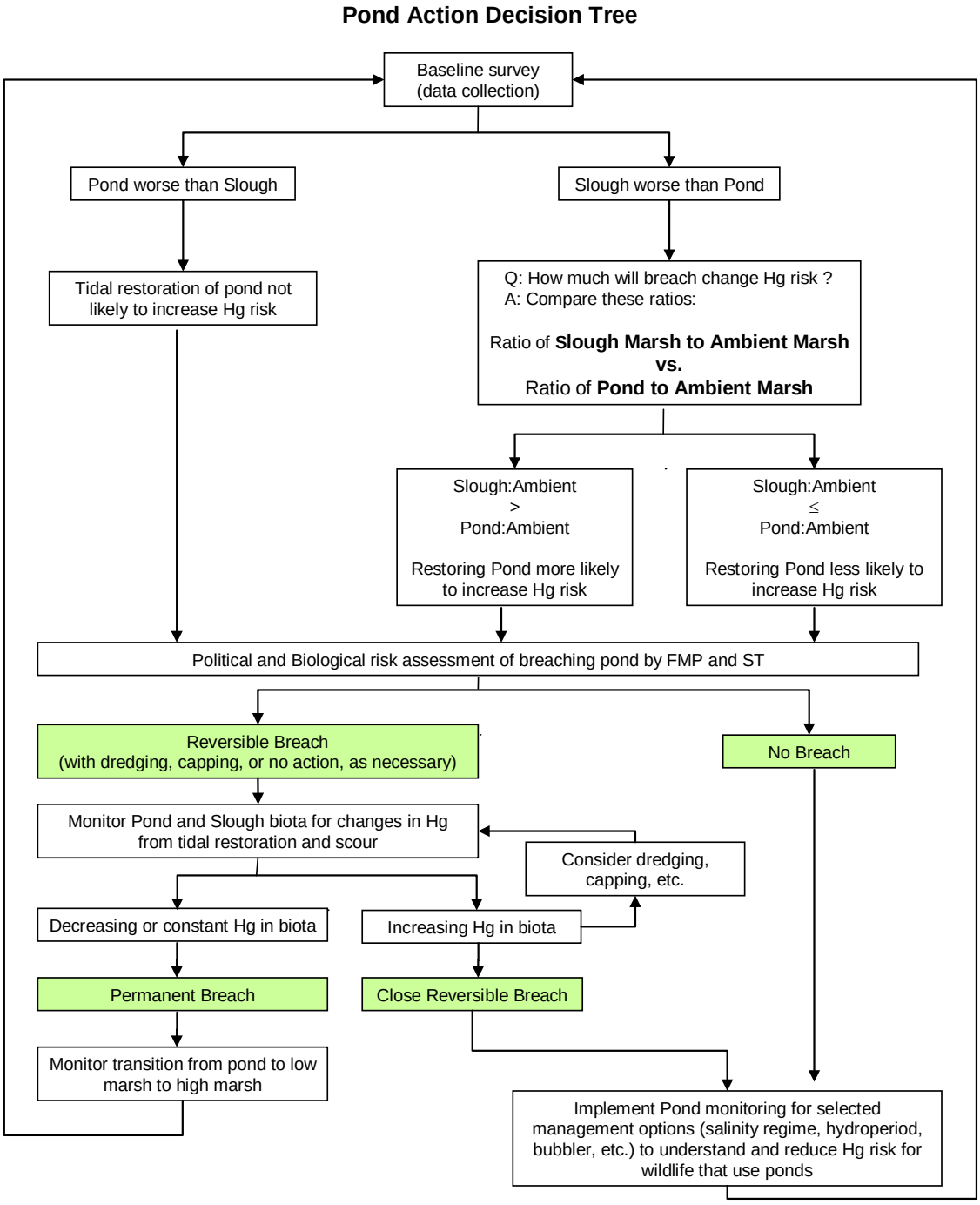

Figure 2.1. Decision framework for how results from this project could be used in management decisions for the SBSPRP. Data from other sources would also be relevant to making the decisions addressed in this framework, such as concentrations of contaminants in sediments likely to be scoured after construction of the Pond A8 tidal control structure..

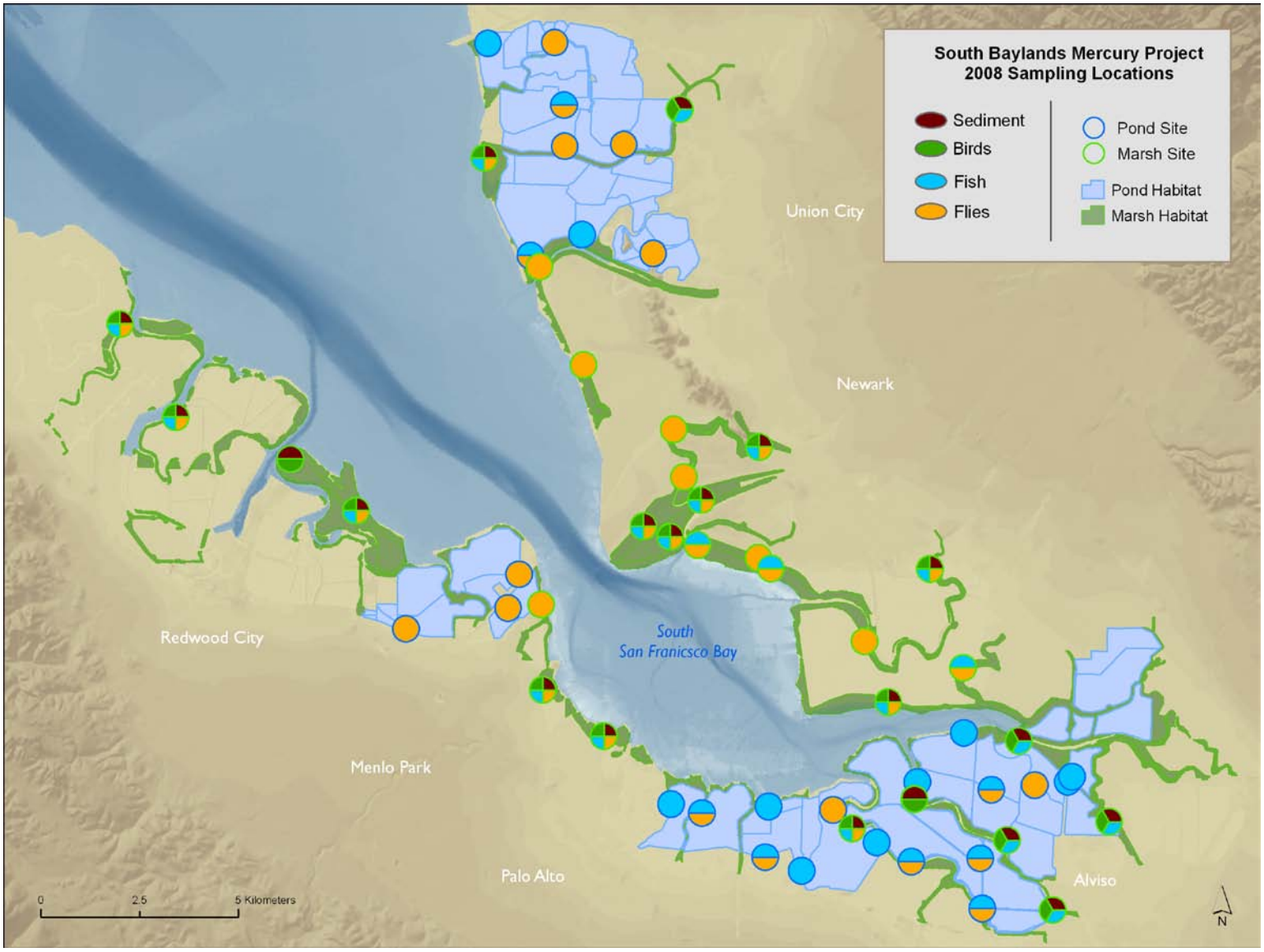

Figure 4.1.1. Sampling locations in 2008 for biosentinels and sediment.

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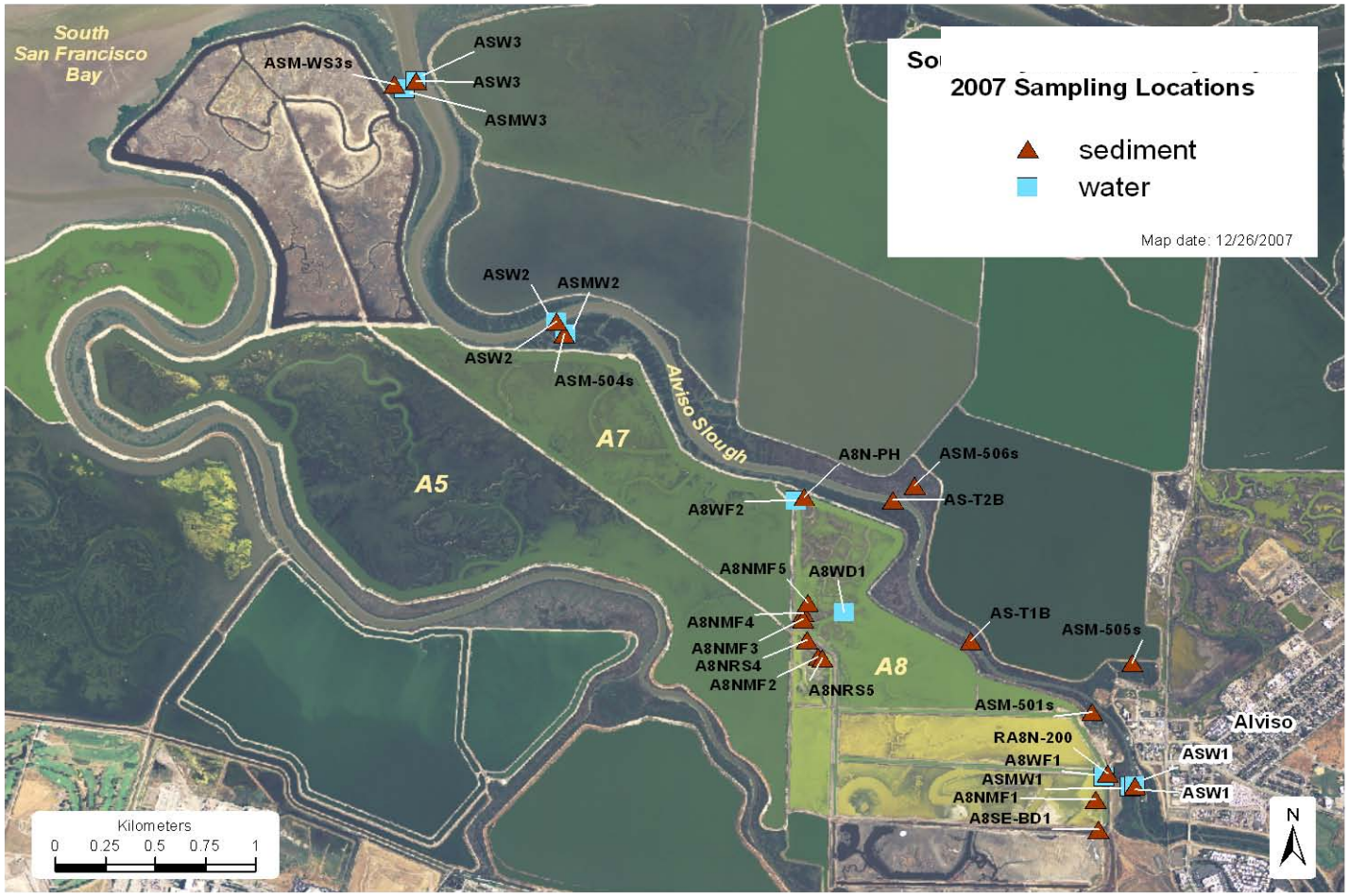

Figure 4.1.2. Sampling locations from May 2007 – January 2008 for sediment and water.

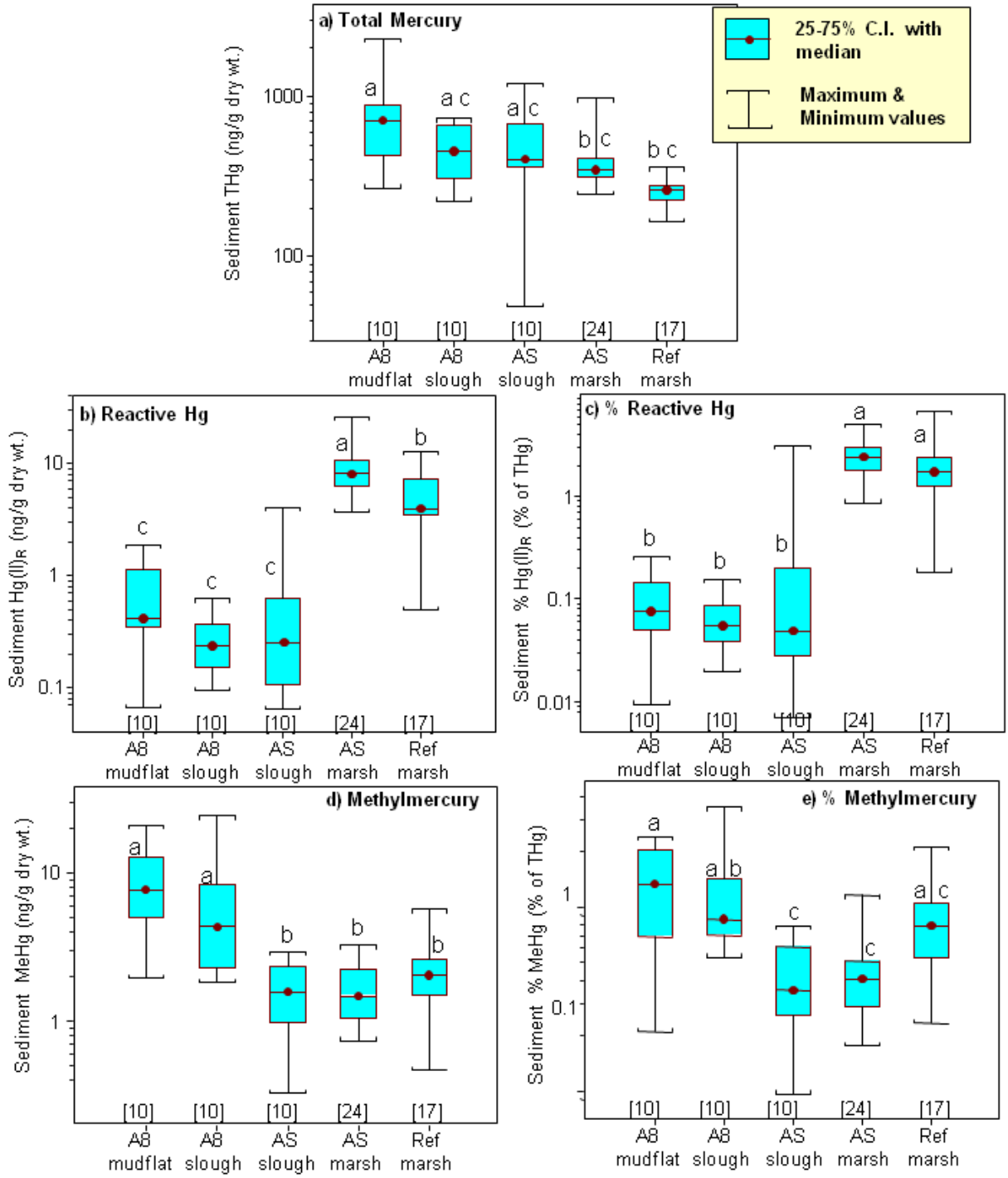

Figure 5.1.1. Box-and-whisker plots of sediment mercury species (total mercury (THg), methylmercury (MeHg) and reactive mercury ($Hg(II)_R$) by habitat type, as sampled between May 2007 and May 2008. The number of observations for each category is given in [#]. Results of Tukey's pair-wise comparison (by habitat type) are indicated by letters (a thru c), where groups sharing any single letter are not significantly different.

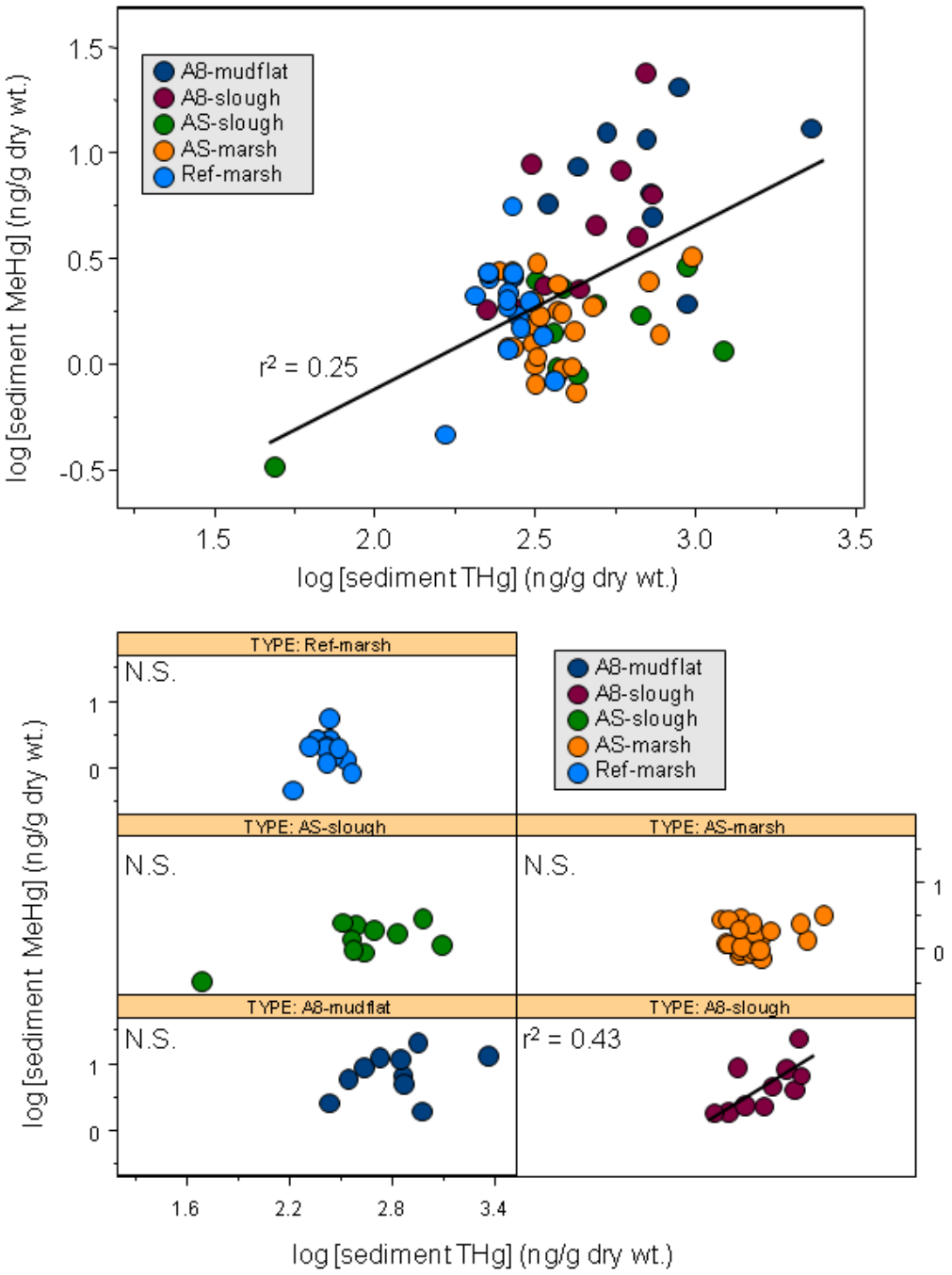

Figure 5.1.2. Linear regression analysis of log-transformed sediment total mercury (THg) versus log-transformed methylmercury (MeHg) plotted with all data (A), and by habitat type (B). The coefficient of determination (r^2) is given for significant regressions only (non-zero slopes at $P < 0.05$). Non-significant regressions are indicated with [N.S.].

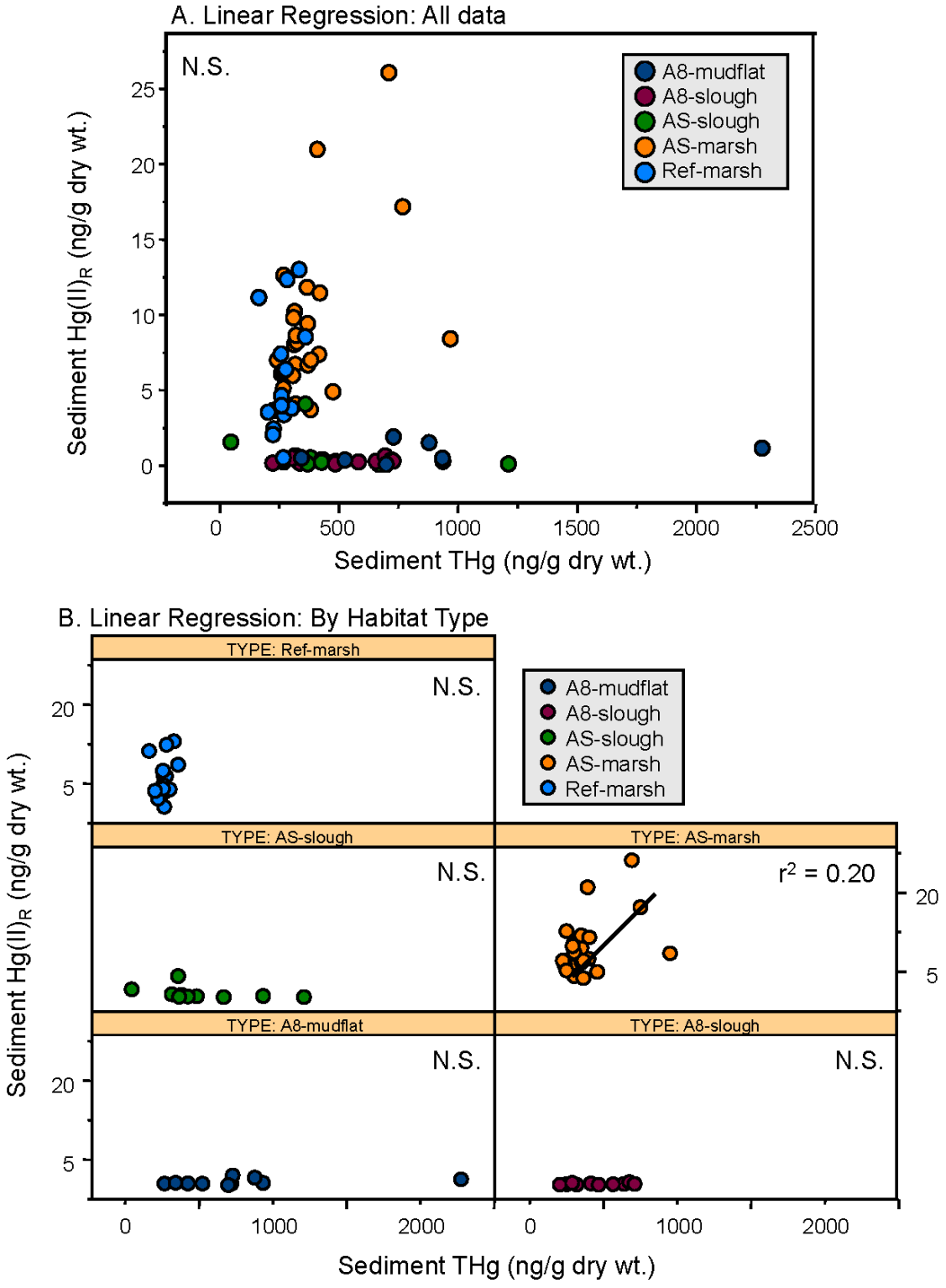

Figure 5.1.3. Linear regression of sediment reactive mercury ($Hg(II)_R$) versus sediment total mercury (THg) concentration, plotted with all data (A), and by habitat type (B). The coefficient of determination (r^2) is given for significant regressions only (non-zero slopes at $P < 0.05$). Non-significant regressions are indicated with [N.S.].

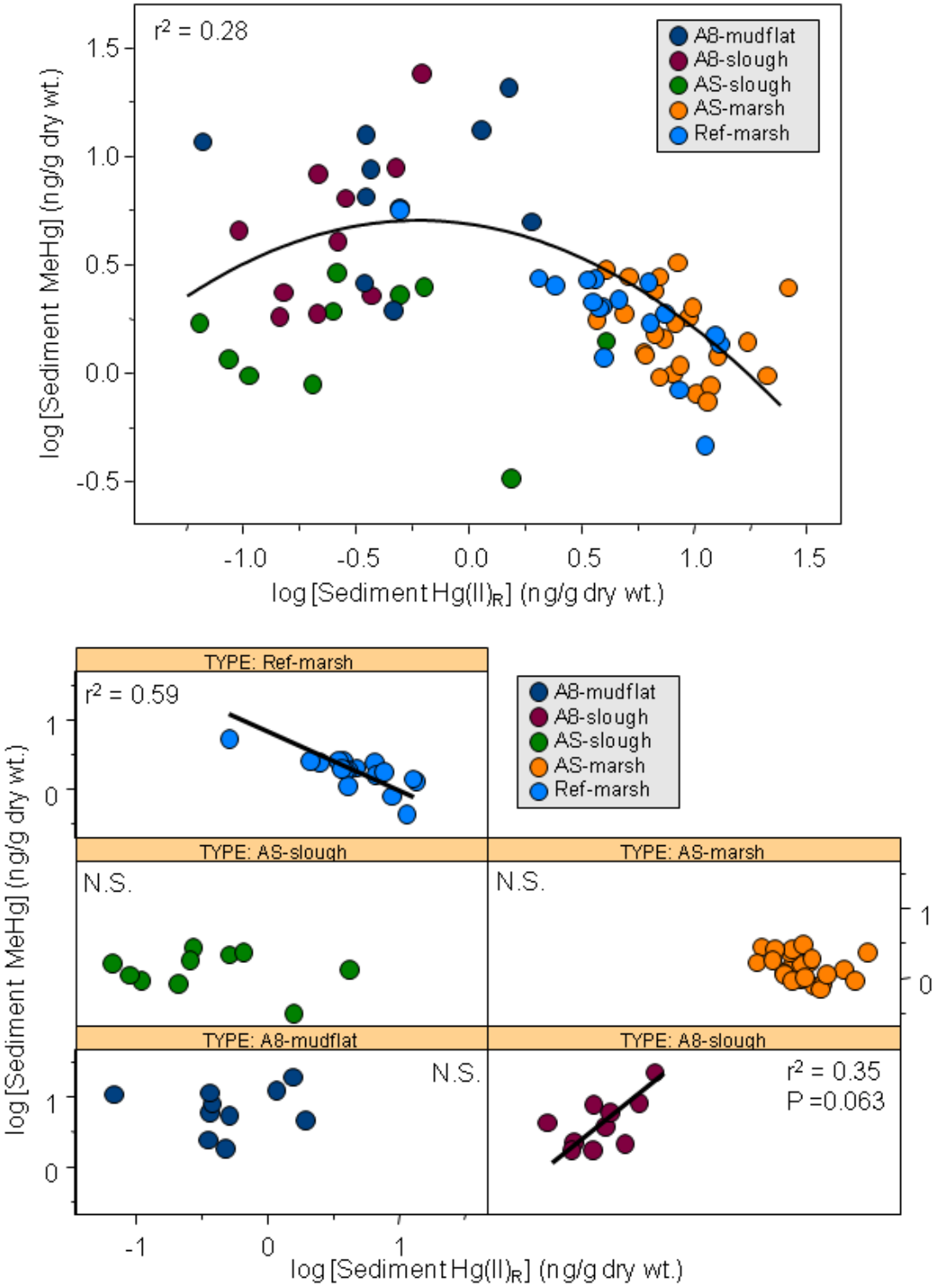

Figure 5.1.4. Second-order polynomial curve fit to log-transformed sediment reactive mercury ($Hg(II)_R$) versus log-transformed methylmercury (MeHg), plotted with all data (A), and linear regression fits to log-transformed data by habitat type (B). The coefficient of determination (r^2) is given for significant regressions only (non-zero slopes at $P < 0.05$, except where indicated). Non-significant regressions are indicated with [N.S.].

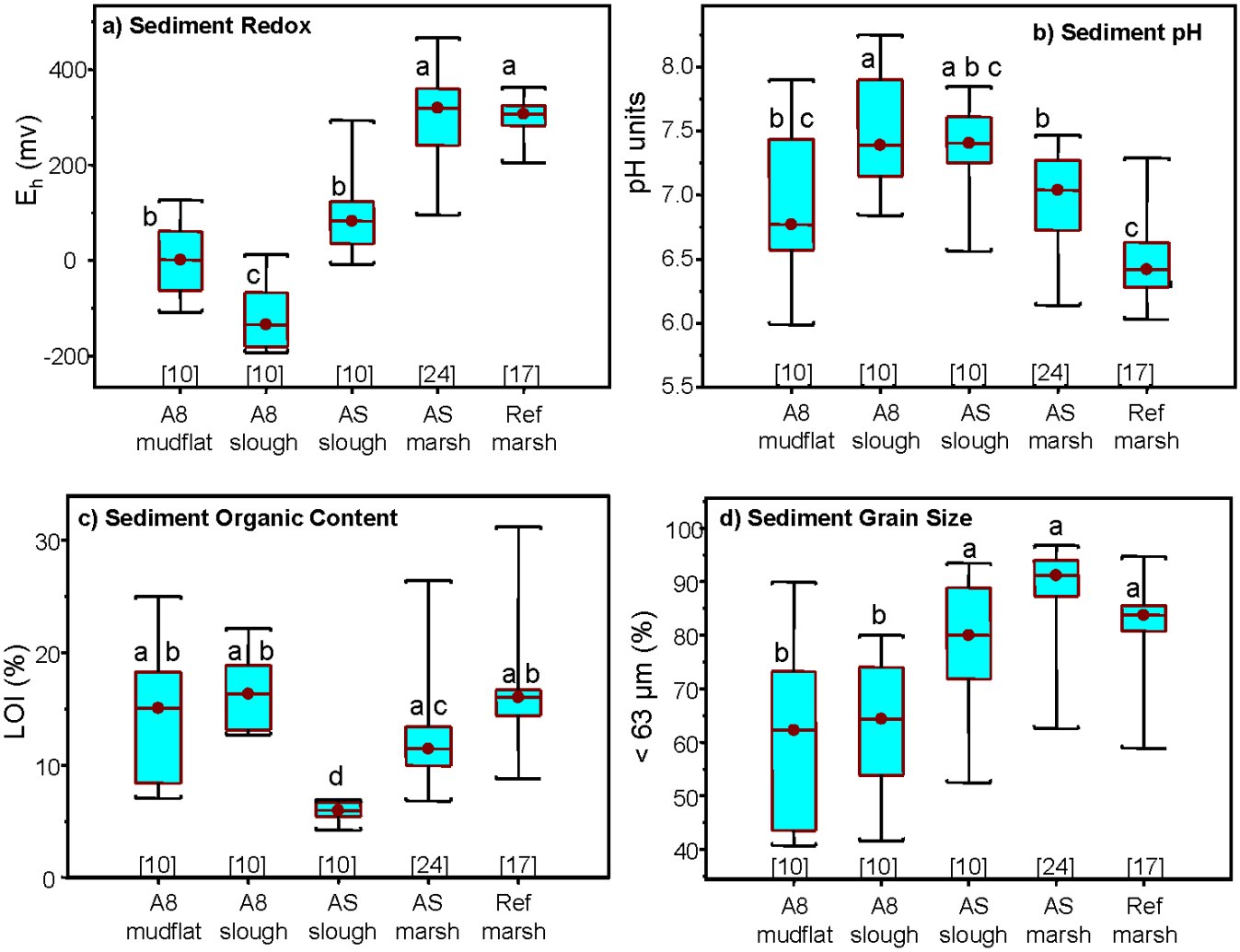

Figure 5.1.5. Box-and-whisker plots of sediment redox (a), pH (b), organic content as percent loss on ignition (LOI) (c) and grain size (as percent less than 63 microns) (d) by habitat type for all data sampled between May 2007 and May 2008. The number of observations for each category is given in [#]. Results of Tukey's pair-wise comparison (by habitat type) are indicated by letters (a thru d), where groups sharing any single letter or letter pair are not significantly different.

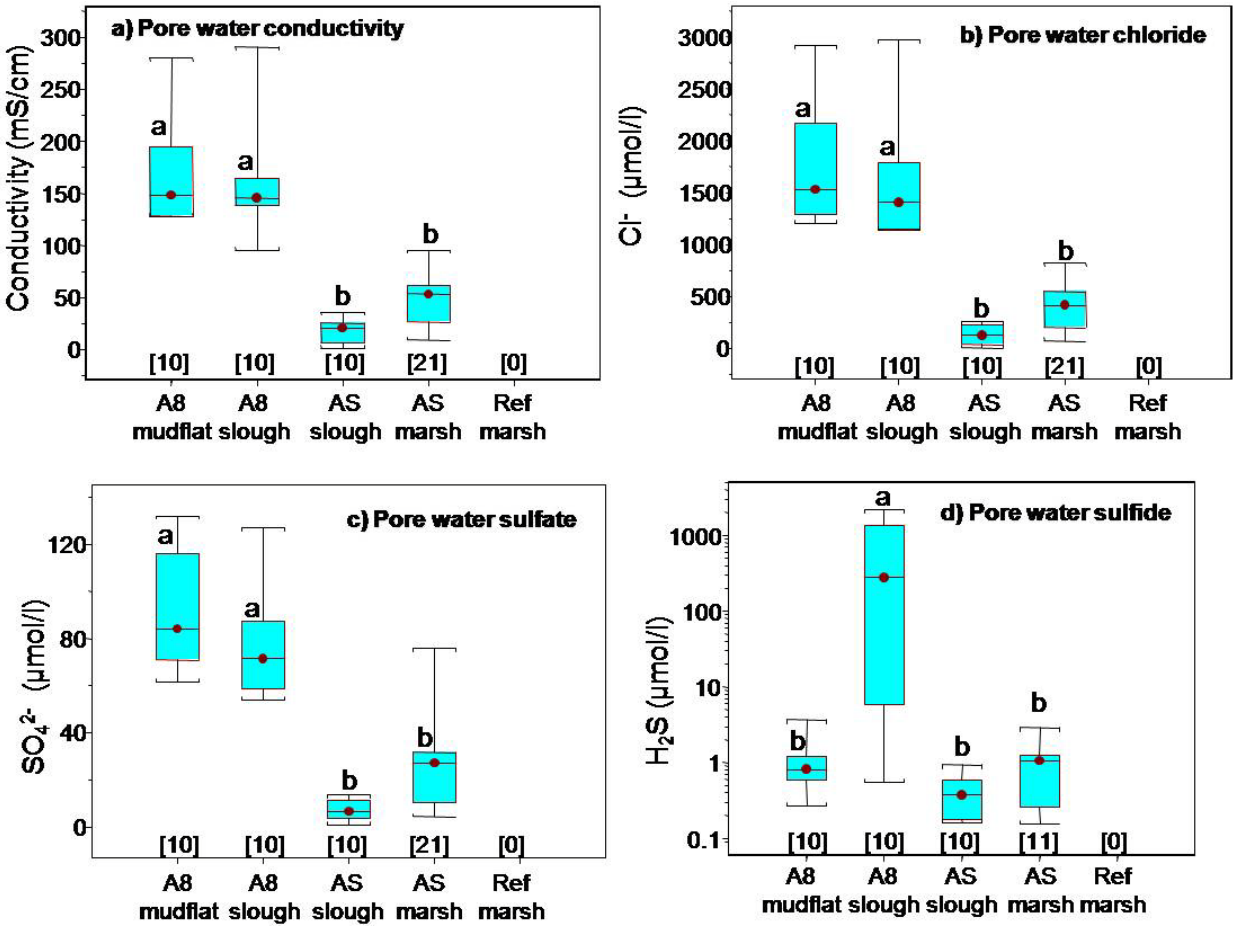

Figure 5.1.6. Box-and-whisker plots of sediment pore water parameters: conductivity (a); chloride (b); sulfate (c); and sulfide (d), by habitat type for all data sampled between May 2007 and January 2008. The number of observations for each category is given in [#]. Results of Tukey's pair-wise comparison (by habitat type) are indicated by letters (a thru b), where groups sharing the same letter are not significantly different. No pore water samples were collected during the April-May sampling of the 20 wetland sites throughout South San Francisco Bay (including any of the 17 Ref-marsh sites).

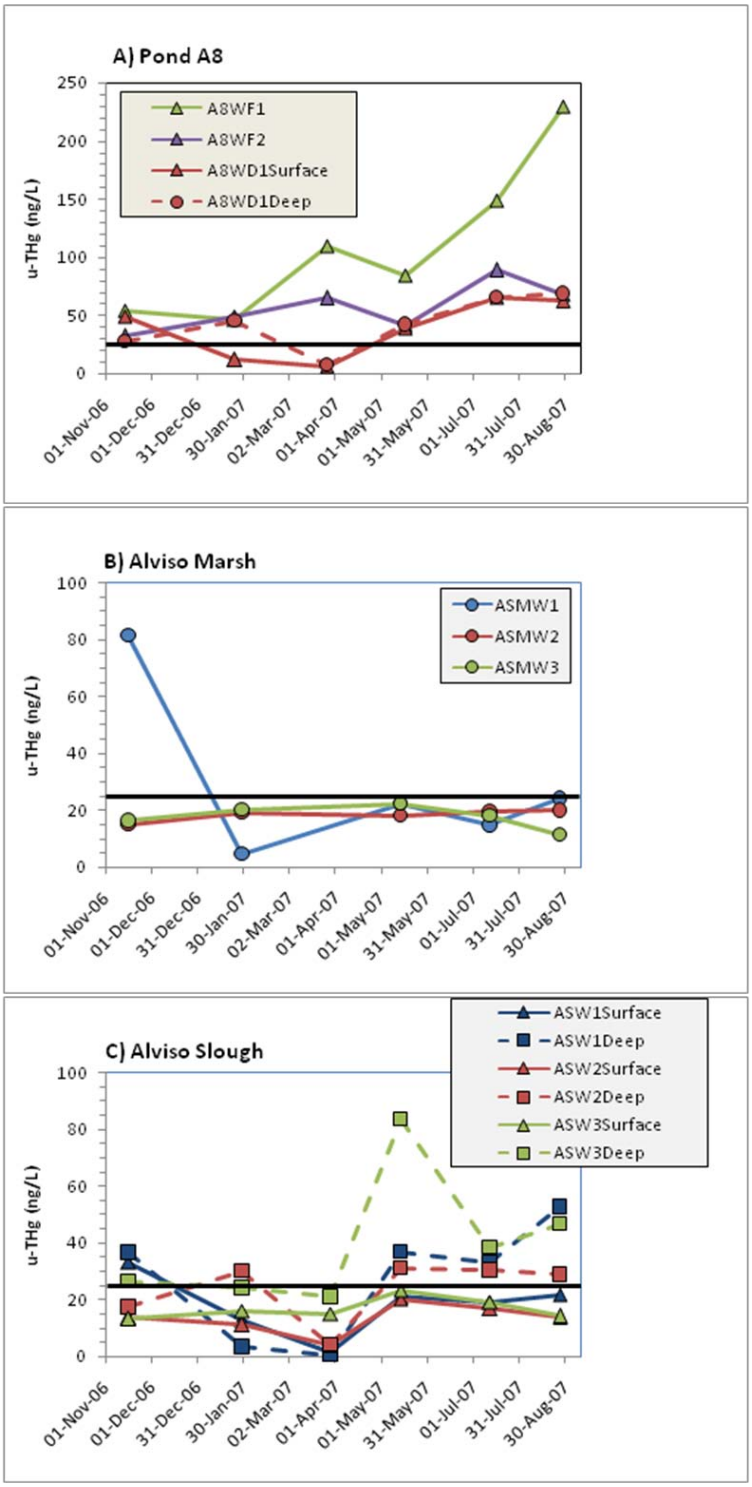

Figure 5.2.1. Time series of water column unfiltered total mercury (u-THg) concentration in Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity. The solid black horizontal line represents the 25 ng/L water quality objective set forth in the *San Francisco Bay Basin (Region 2) Water Quality Control Plan (*SFRWQCB, 2007).

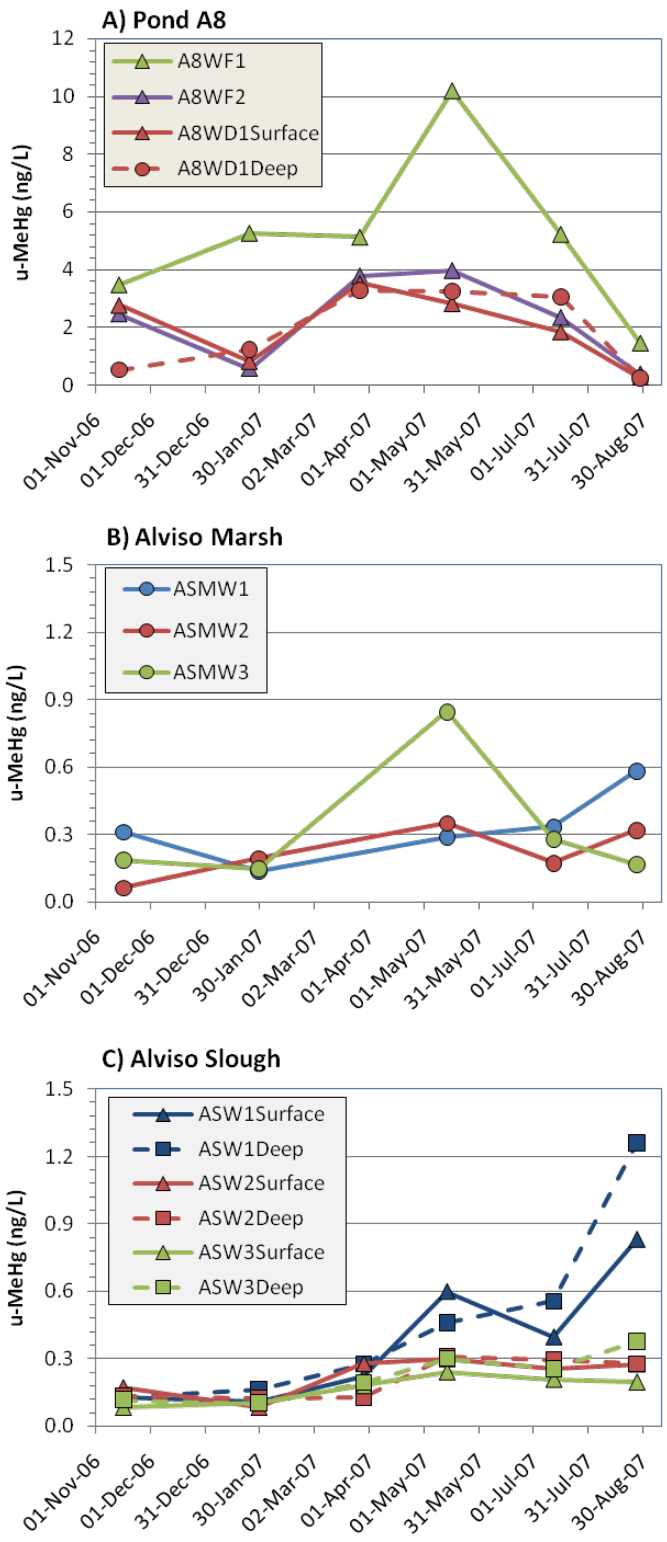

Figure 5.2.2. Time series of water column unfiltered methylmercury (u-MeHg) concentration in sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

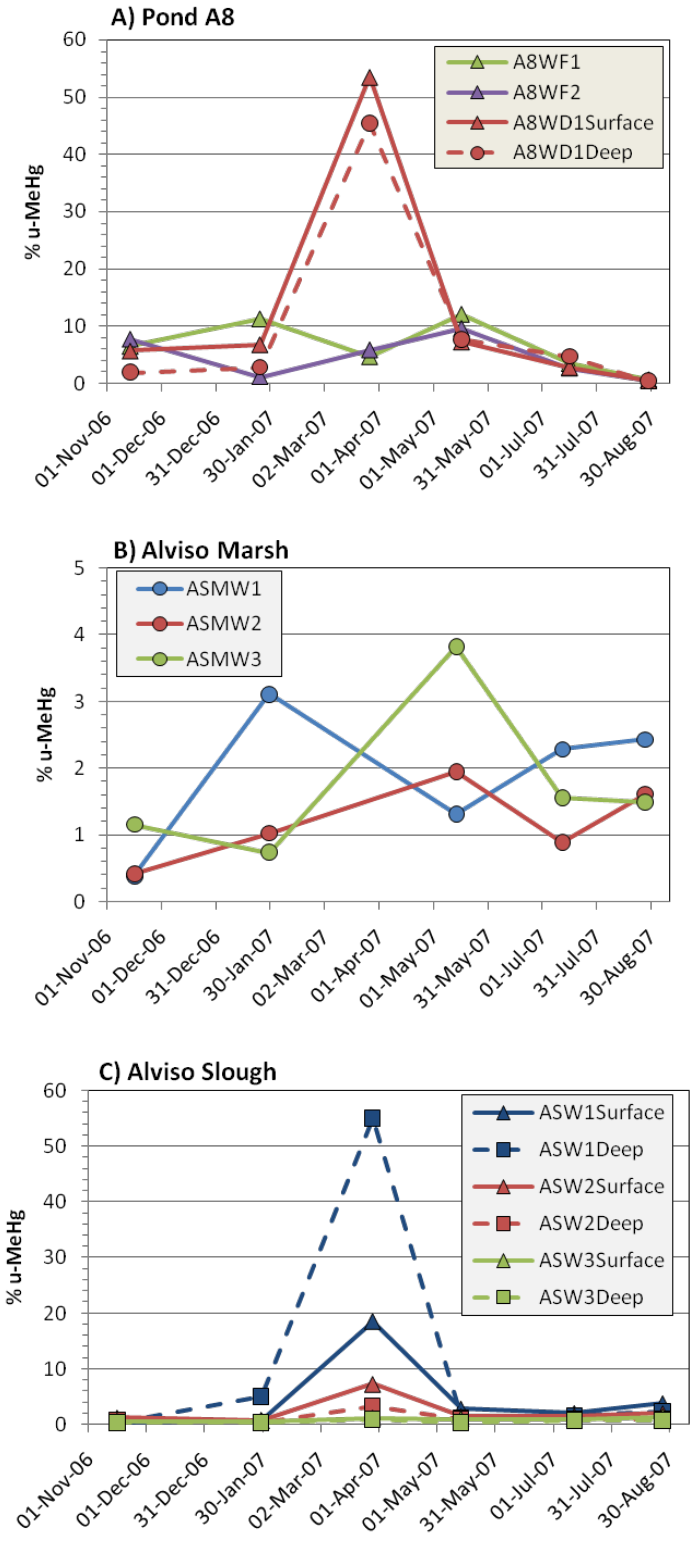

Figure 5.2.3. Time series of water column percent unfiltered methylmercury (% u-MeHg; as a percentage of unfiltered total mercury) at sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

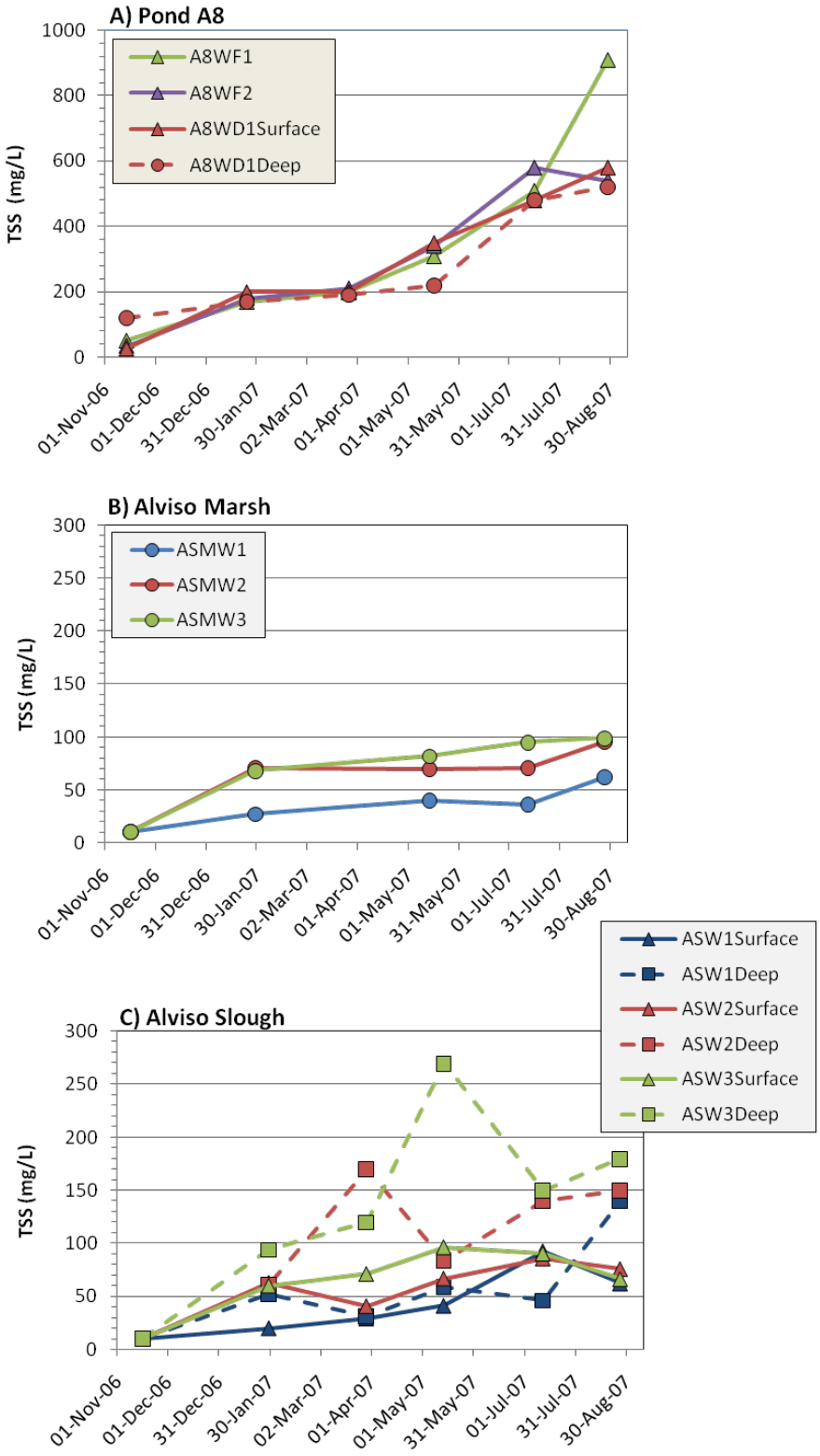

Figure 5.2.4. Time series of water column total suspended solids (TSS) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

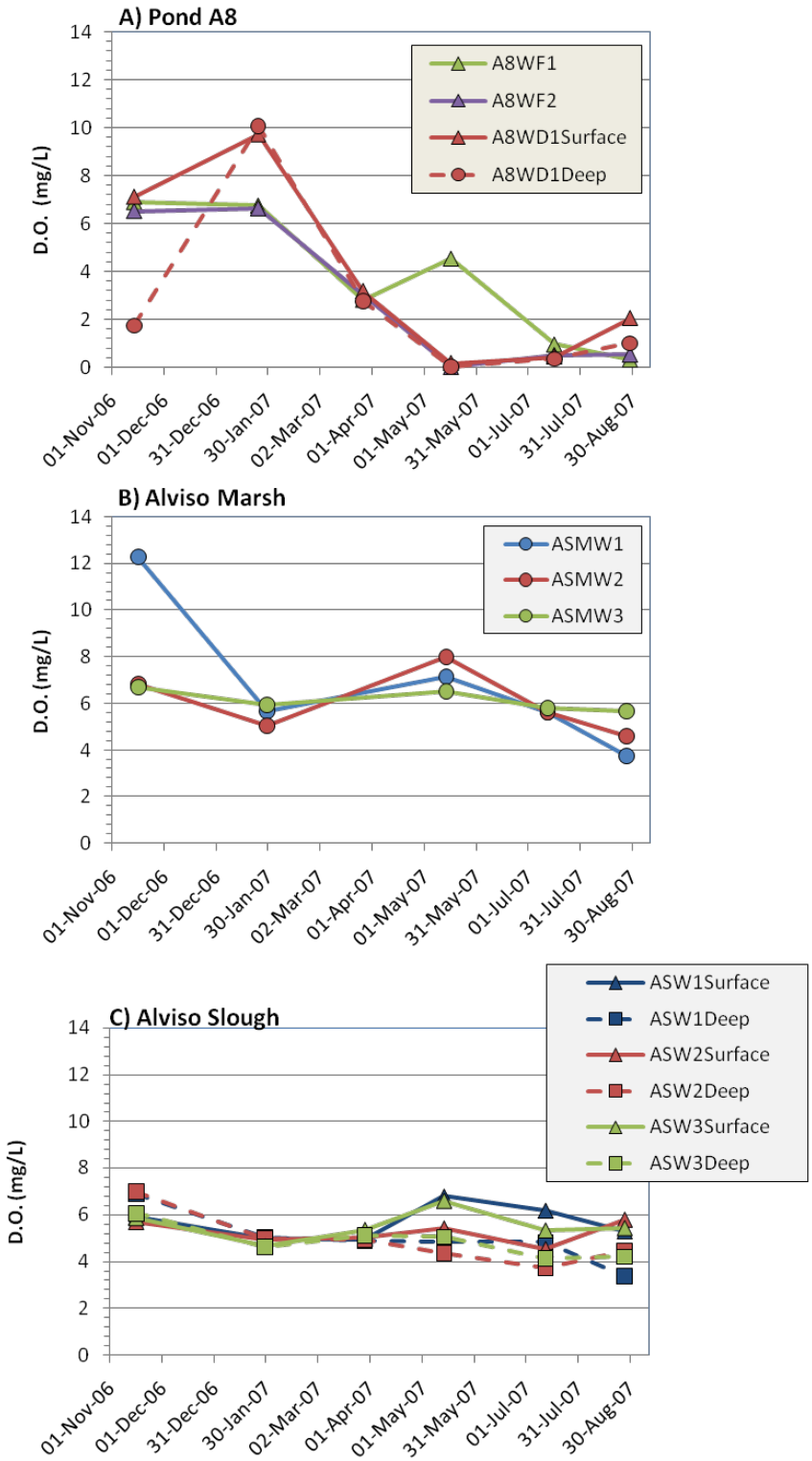

Figure 5.2.5. Time series of water column dissolved oxygen (D.O.) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

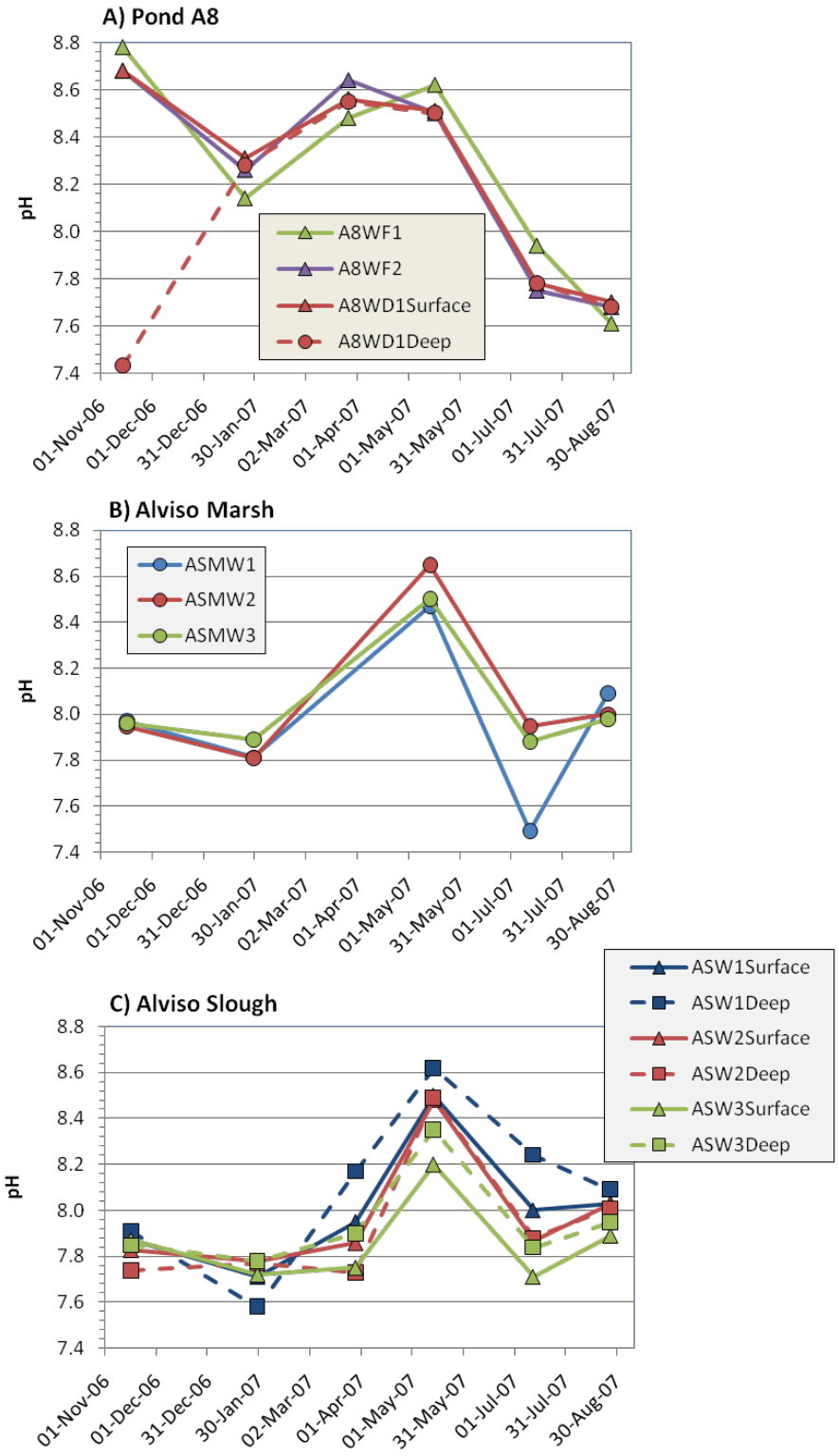

Figure 5.2.6. Time series of water column pH for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

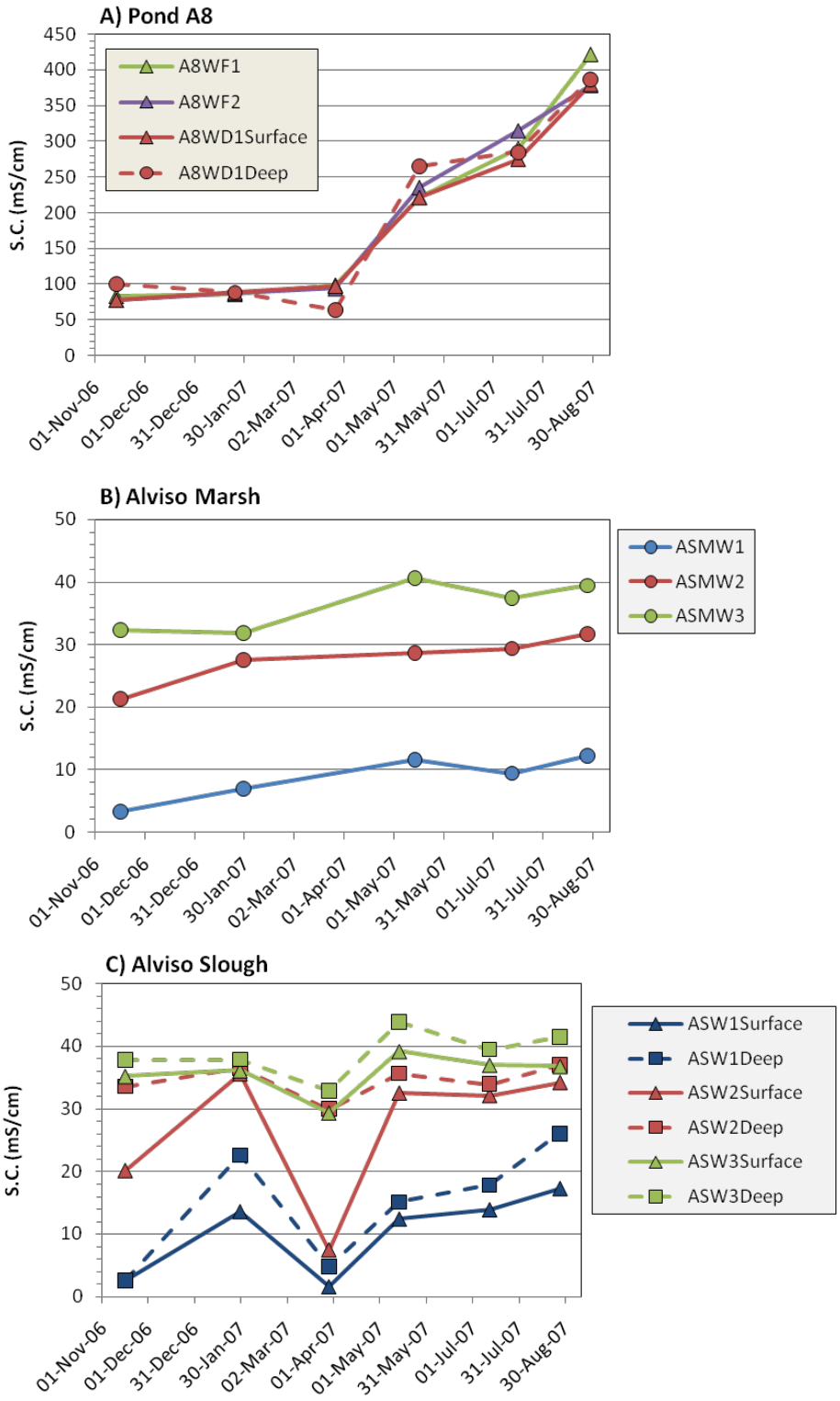

Figure 5.2.7. Time series of water column specific conductivity (S.C.) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

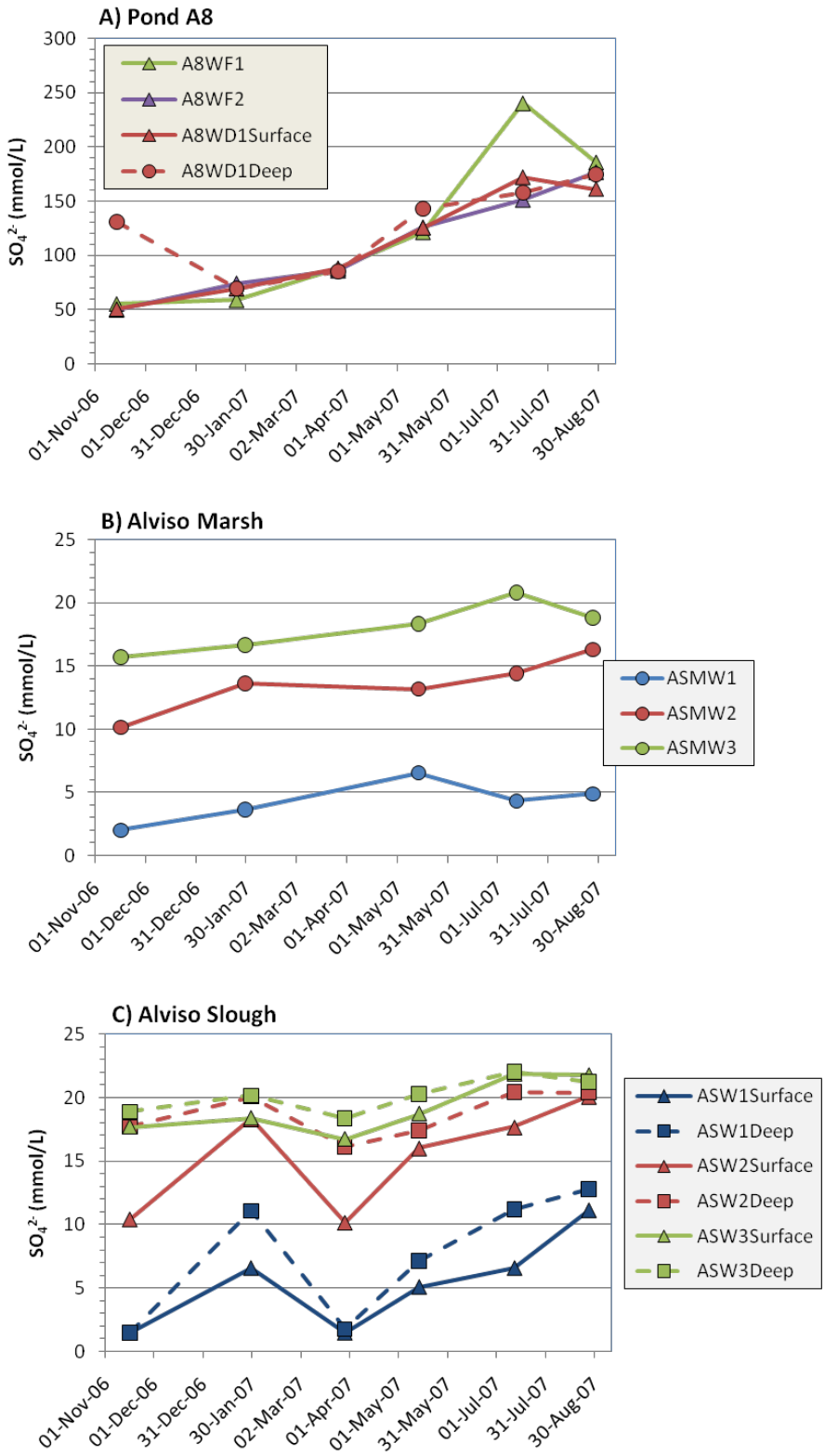

Figure 5.2.8. Time series of water column sulfate (SO_4^{2-}) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

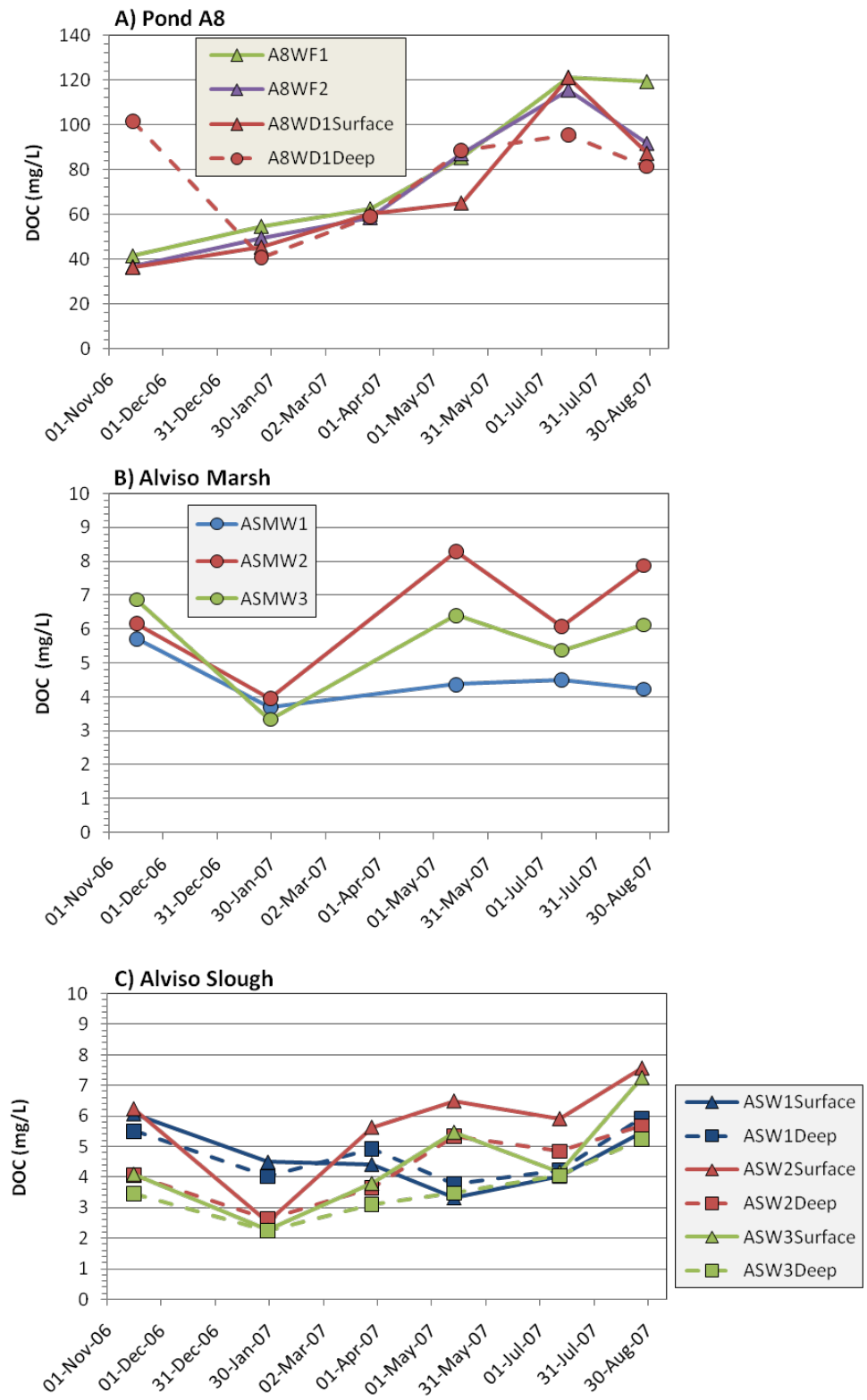

Figure 5.2.9. Time series of water column dissolved organic carbon (DOC) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). Note variable scales for Y-axis. 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

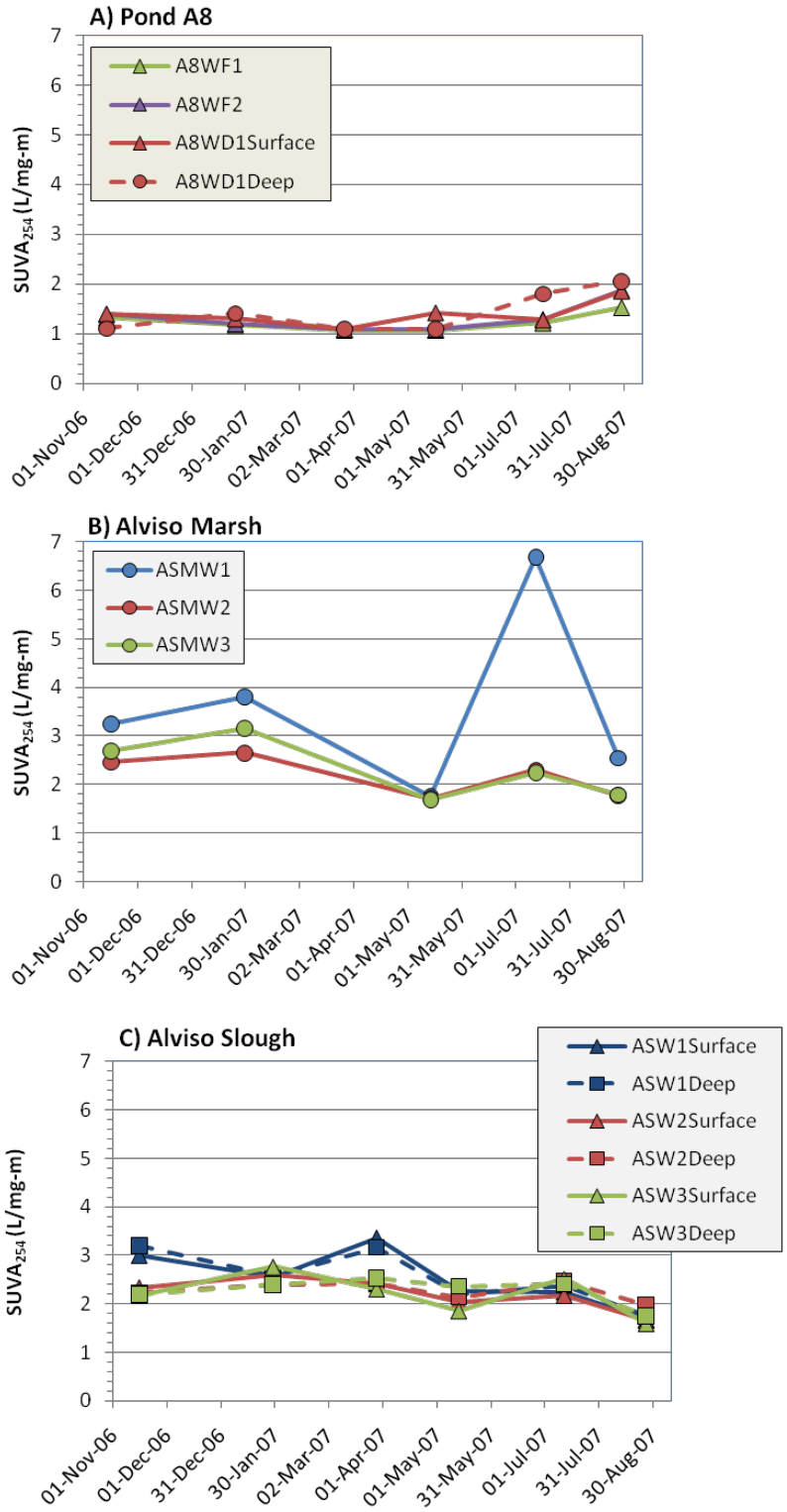

Figure 5.2.10. Time series of water column specific ultraviolet absorption at 254 nanometers (SUVA245) for sampling sites within Pond A8 (A), Alviso Marsh (B), and Alviso Slough (C). 'Near-bottom' water column sites are depicted with a dashed line. Figure legends for Alviso Marsh and Slough list sites from low (ASMW1 and ASW1) to high (ASMW3 and ASW3) salinity.

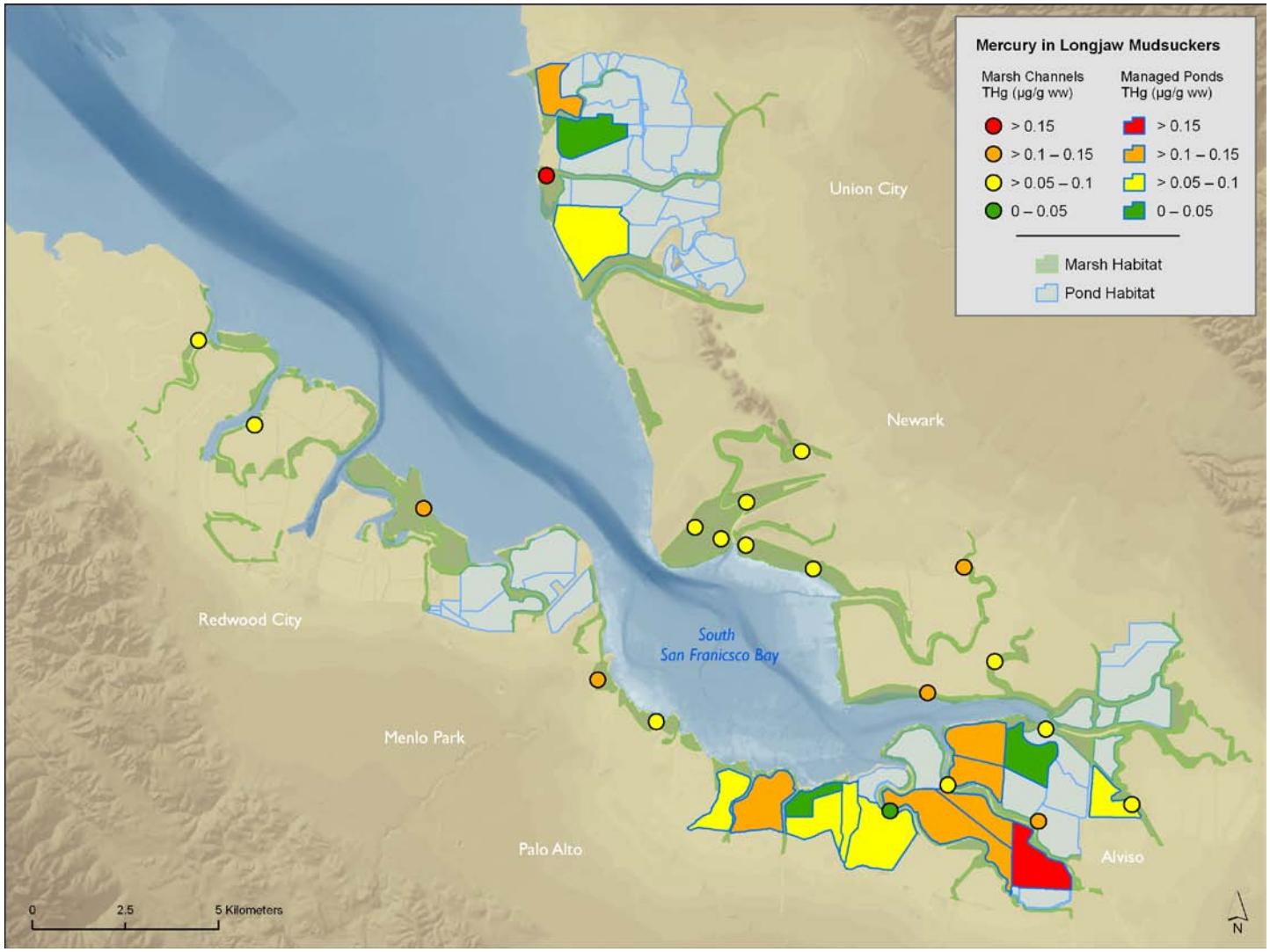

Figure 5.3.1. Map of mean total mercury (THg) concentration (whole body) in longjaw mudsucker for each tidal marsh (n = 20) and pond (n = 16) sampled during 2008. When more than one sampling location was located in the same pond, the average of the locations was used.

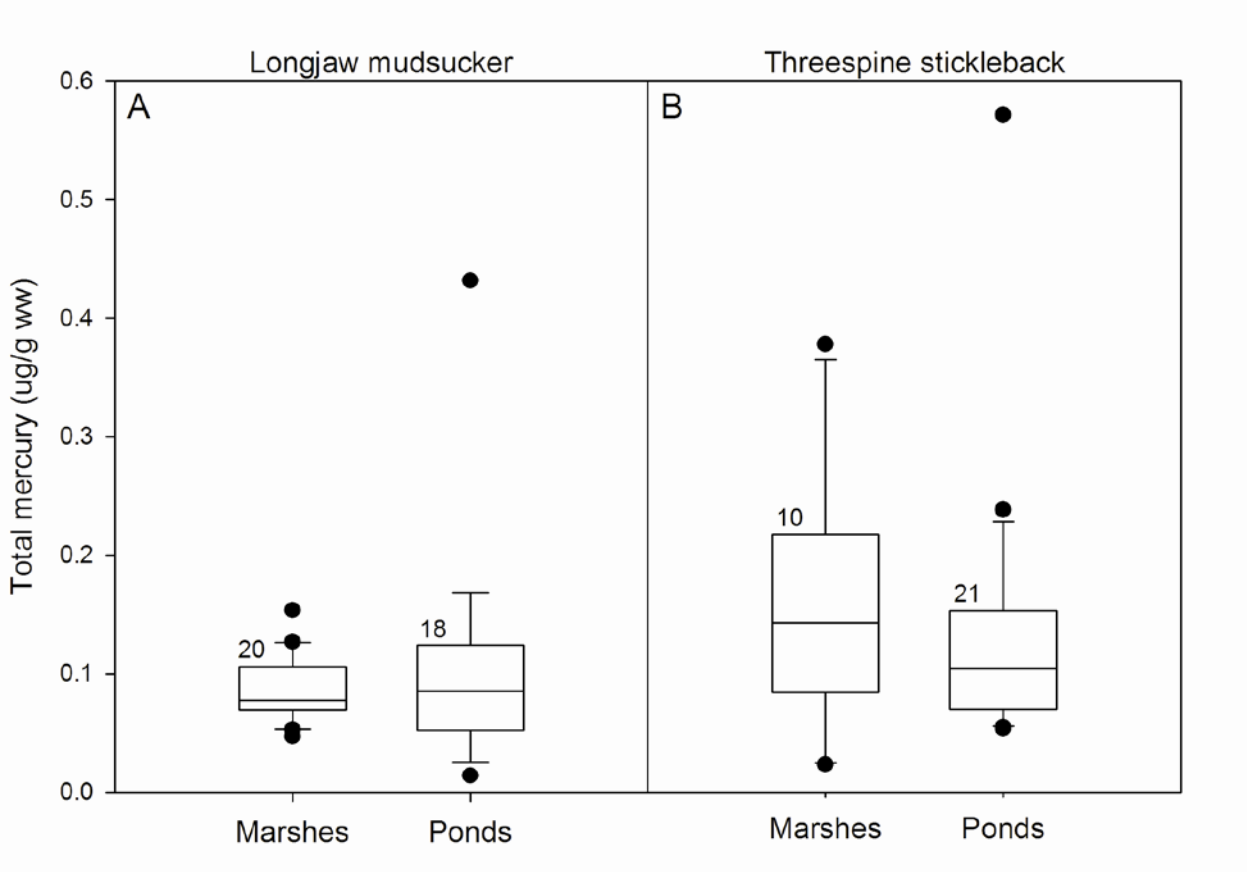

Figure 5.3.2. Box-and-whisker plots of mean total mercury (THg) concentrations (whole body) in longjaw mudsucker (A) and threespine stickleback (B) in tidal marsh channels and managed ponds. Mean THg concentrations in longjaw mudsucker and threespine stickleback were no different in tidal marsh channels and salt ponds sampled in 2008. Stickleback had more variable THg concentrations (and smaller sample sizes) than mudsucker. In each box plot, the lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median, and the lines extending above and below the box represent values that fall within ±1.5 times the inter-quartile range. Outliers beyond the whiskers are represented by black dots. The number above each box represents the sample size (n).

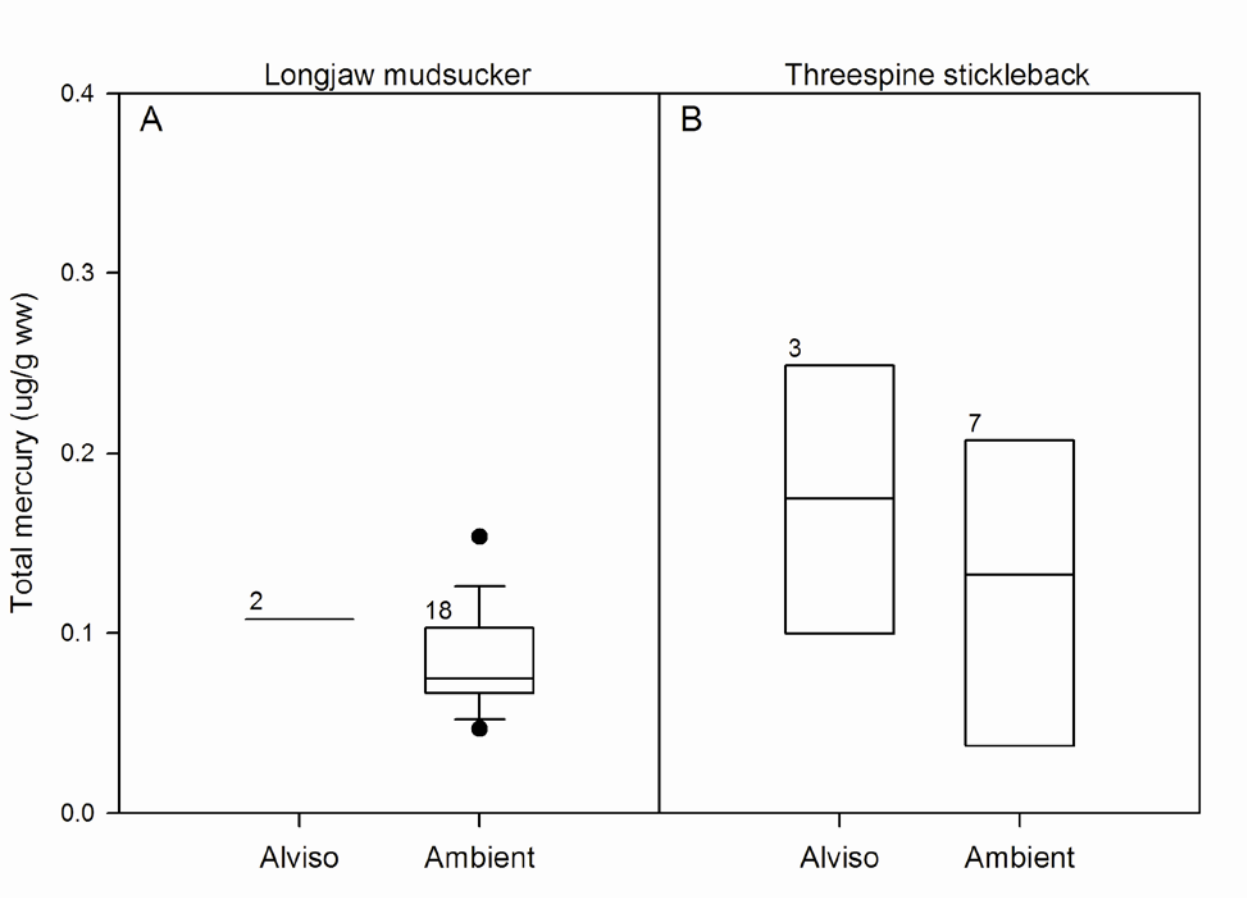

Figure 5.3.3. Box-and-whisker plots of total mercury (THg) concentrations in longjaw mudsucker (A) and threespine stickleback (B) in Alviso marsh and reference (ambient) marshes. Mean THg concentrations in longjaw mudsucker and threespine stickleback did not differ between the Alviso Slough fringing marsh (near Pond A8) and the reference marshes across South Bay. In each box plot, the lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median, and the lines extending above and below the box represent values that fall within ±1.5 times the inter-quartile range. Outliers beyond the whiskers are represented by black dots. Percentiles and inter-quartiles range could not be calculated for all comparisons due to small sample sizes ($n < 9$). The number above each box is the sample size (n).

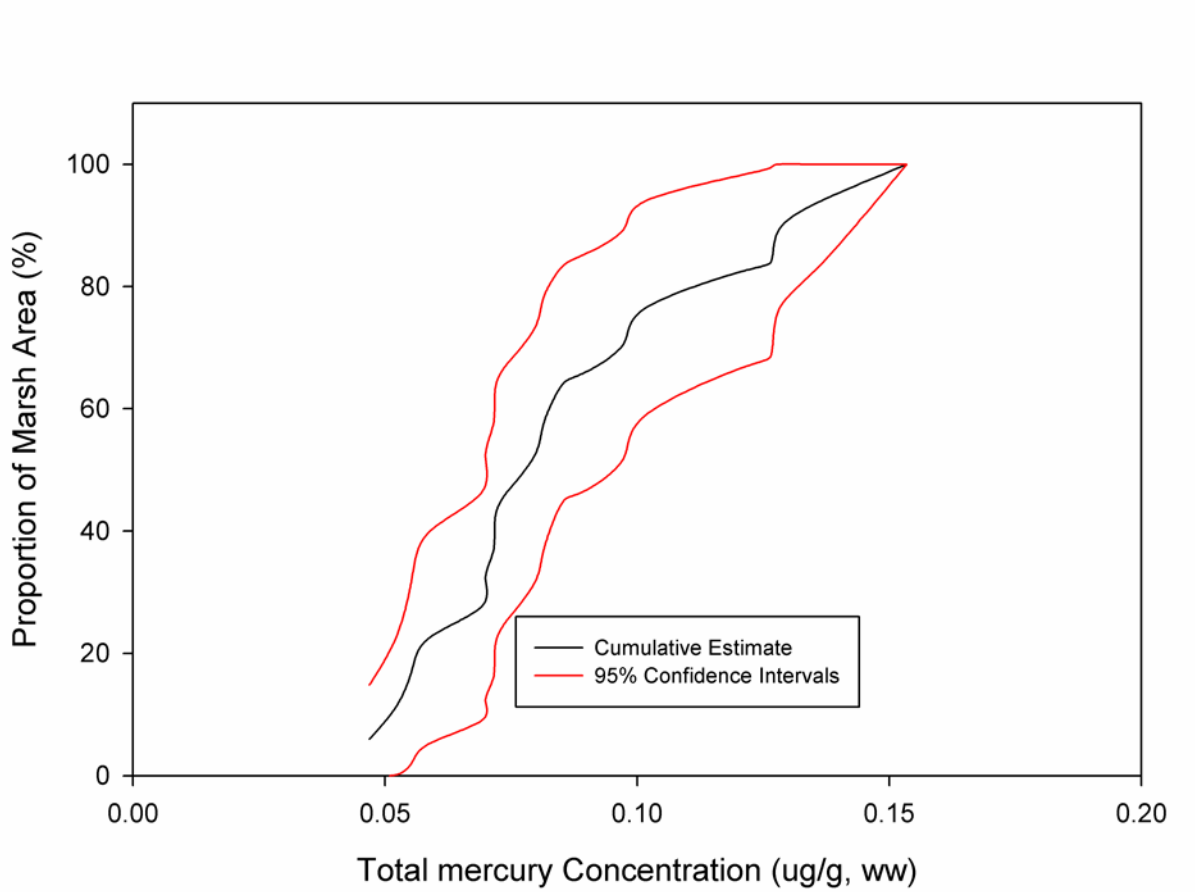

Figure 5.3.4. Cumulative distribution function plot of total mercury (THg) concentrations in longjaw mudsucker from tidal marsh locations sampled during 2008. Twenty percent (20%) of the reference marsh area sampled had higher mercury than Alviso Slough marsh, indicating that Alviso Slough marsh channels are not exceptionally high in food-web mercury.

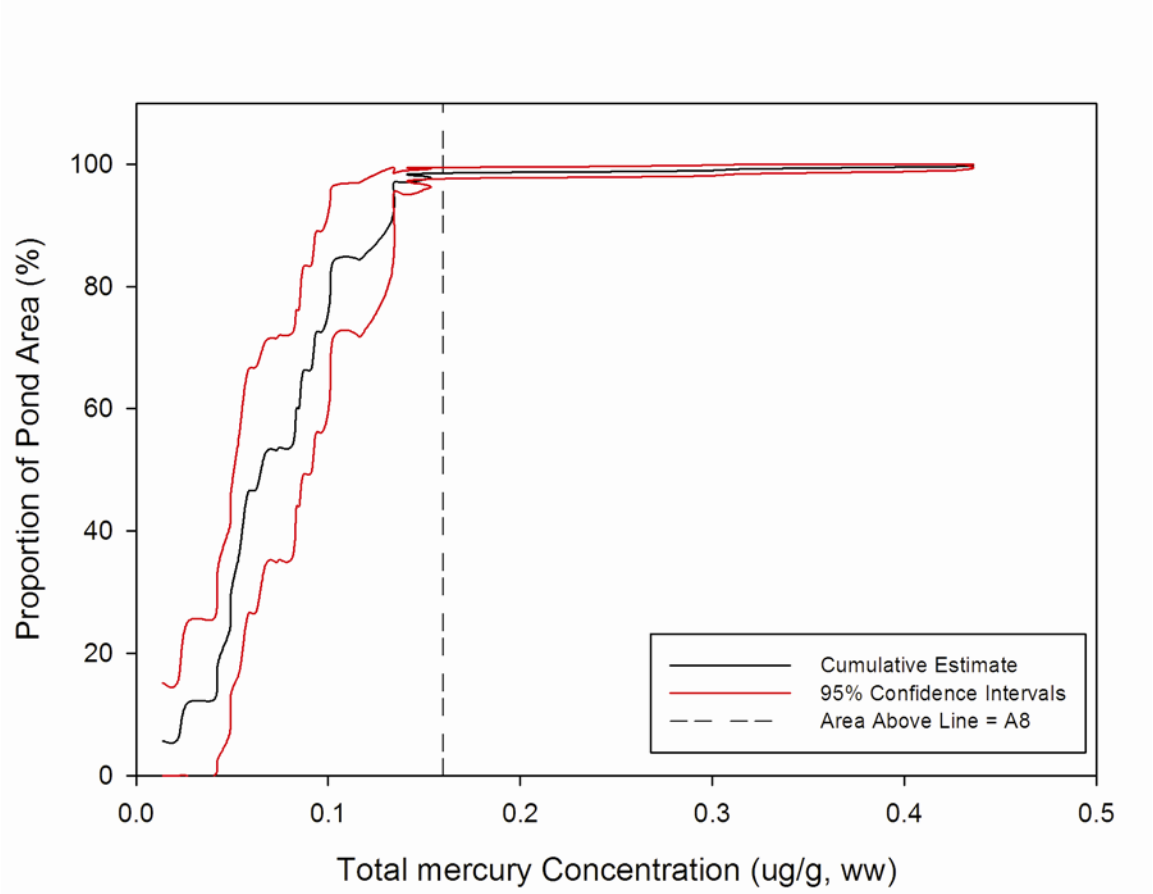

Figure 5.3.5. Cumulative distribution function plot of total mercury (THg) concentrations in longjaw mudsucker from managed ponds sampled during 2007 and 2008. Pond A8 has the highest mercury concentrations in mudsucker (to the right of the dashed line) of any pond in South Bay. Less than 1% of the South Bay pond area sampled corresponded to concentrations in Pond A8 (to the right of the dashed line).

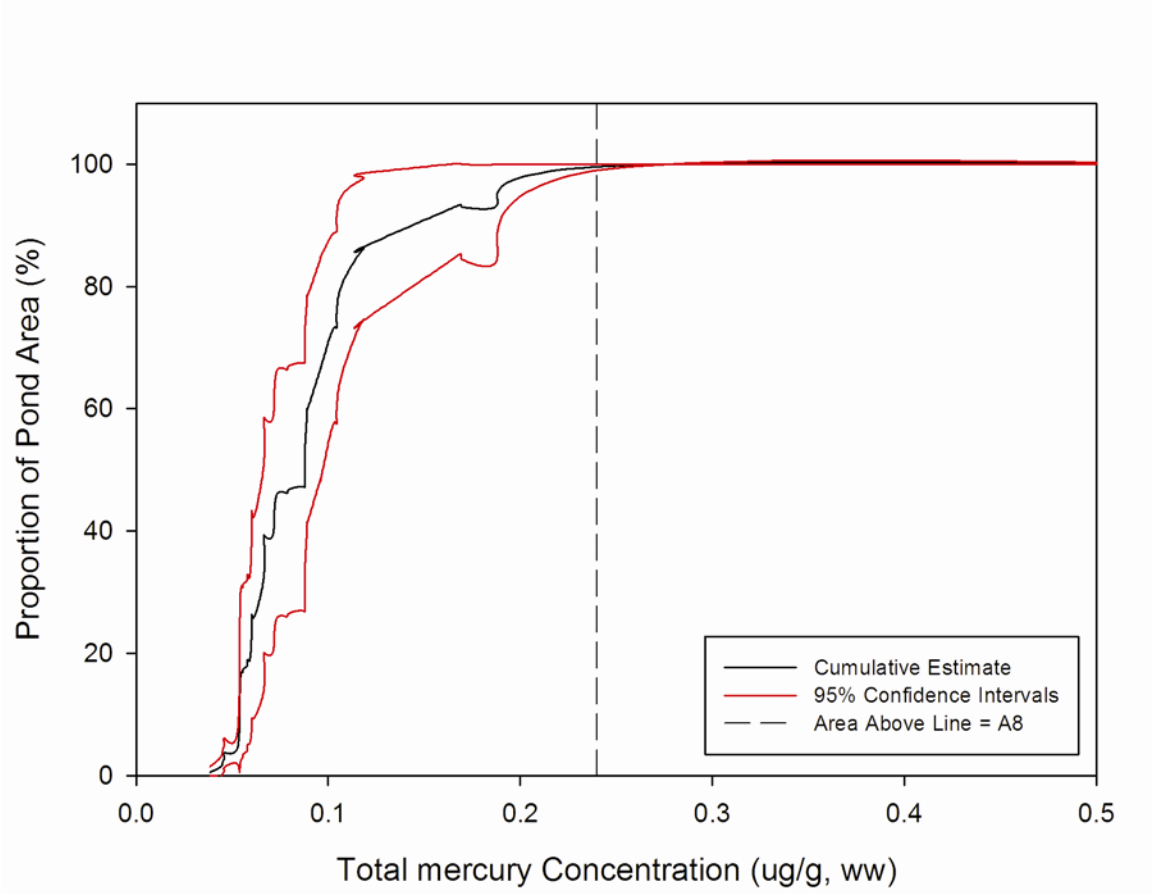

Figure 5.3.6. Cumulative distribution function plot of total mercury (THg) concentrations in threespine stickleback from managed ponds sampled during 2007 and 2008. Pond A8 has the highest mercury concentrations in stickleback (to the right of the dashed line) of any pond sampled in the South Bay. Less than 1% of the South Bay pond area sampled corresponded to concentrations in Pond A8 (to the right of the dashed line).

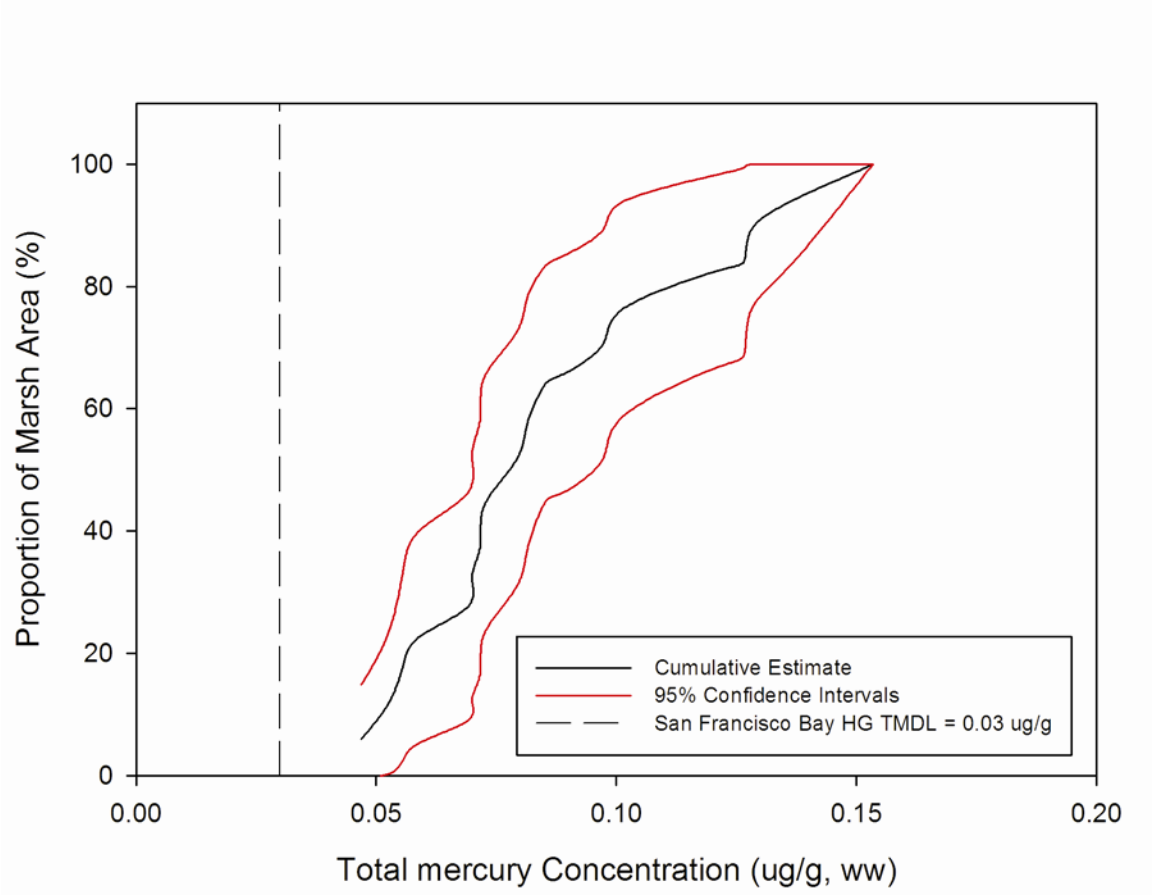

Figure 5.3.7. Cumulative distribution function plot of total mercury (THg) concentrations in longjaw mudsucker from tidal marsh locations sampled during 2008, compared to the San Francisco Bay Hg TMDL target for small fish tissue.. All (100%) of the marsh area sampled was above the San Francisco Bay mercury TMDL threshold (0.03 µg/g ww) for small fish to protect piscivorous wildlife.

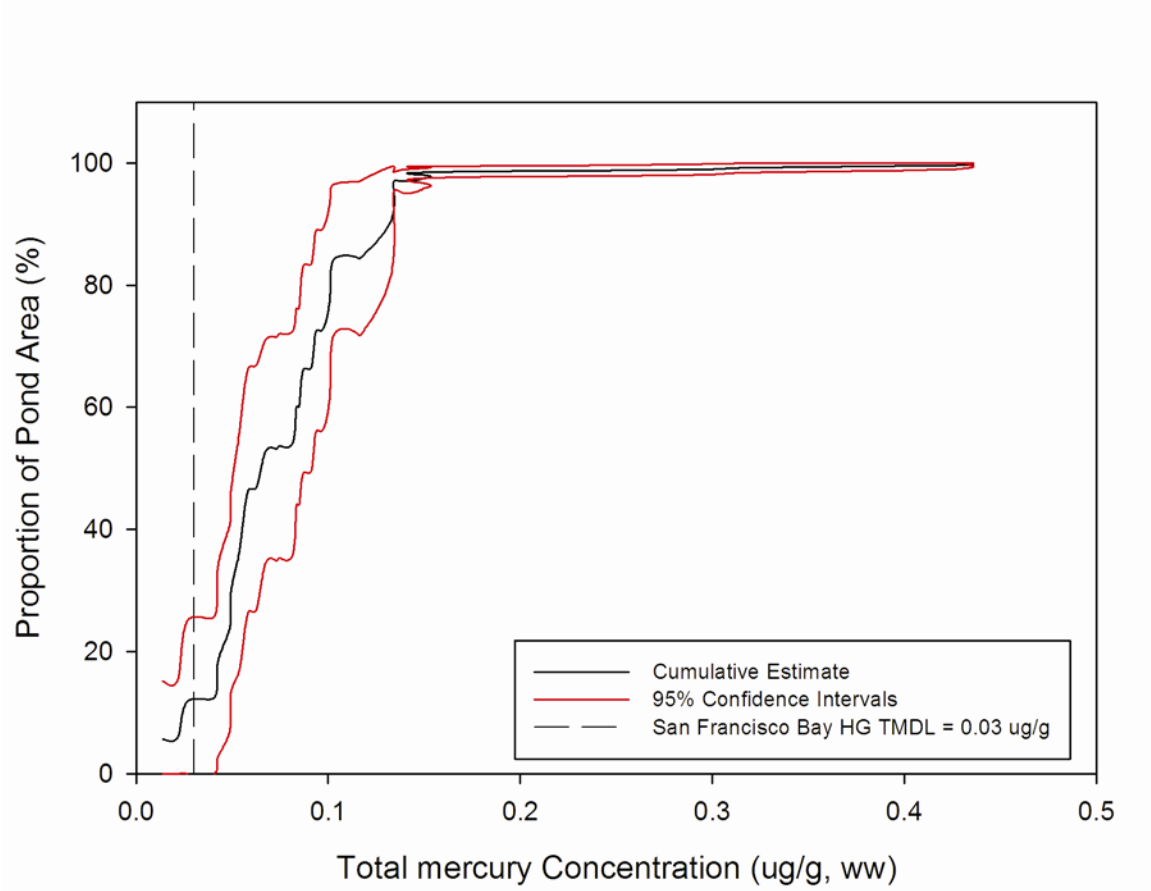

Figure 5.3.8. Cumulative distribution function plot of total mercury (THg) concentrations in longjaw mudsucker from managed ponds sampled during 2007 and 2008, compared to the San Francisco Bay Hg TMDL target for small fish tissue. Nearly all (90%) of the pond area was above the San Francisco Bay mercury TMDL threshold (0.03 µg/g ww) for small fish to protect piscivorous wildlife.

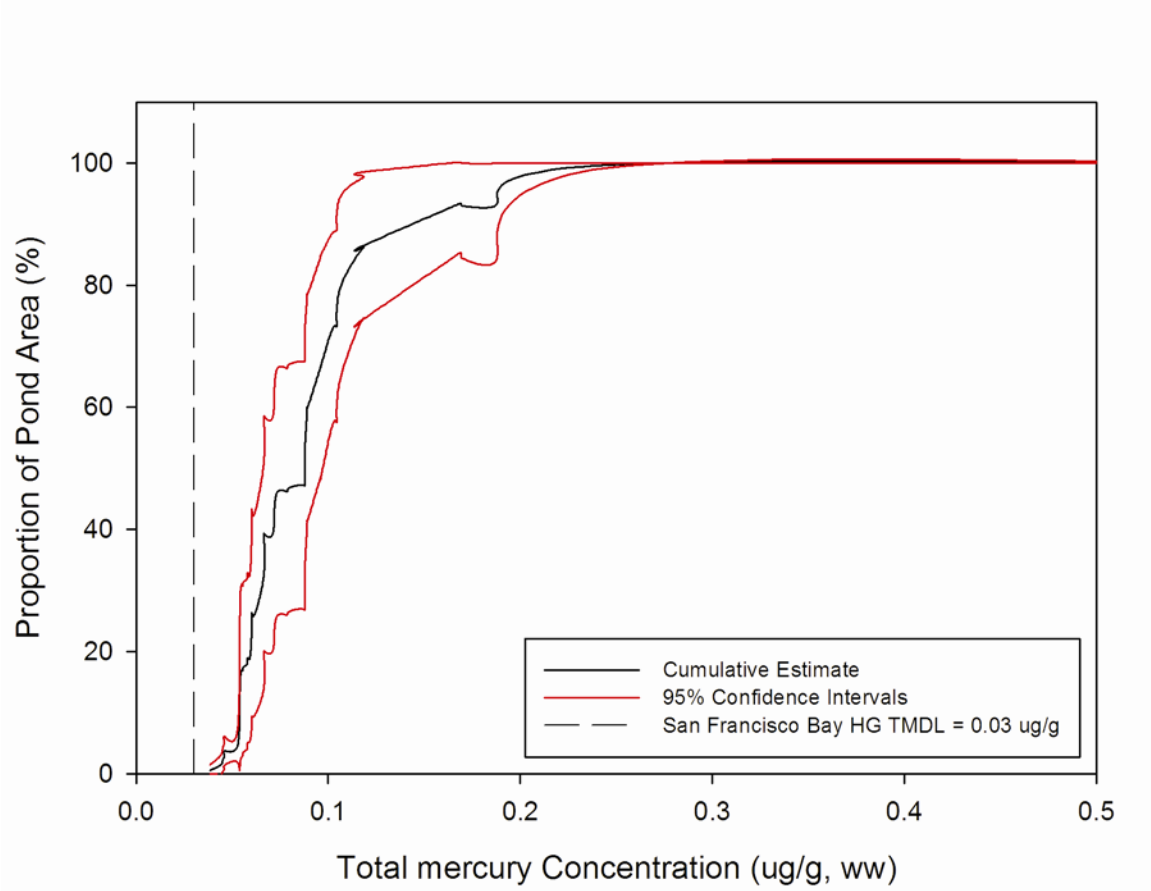

Figure 5.3.9. Cumulative distribution function plot of total mercury (THg) concentrations in threespine stickleback from managed ponds sampled during 2007 and 2008, compared to the San Francisco Bay Hg TMDL target for small fish tissue. All (100%) of the pond area sampled was above the San Francisco Bay mercury TMDL threshold (0.03 µg/g ww) for small fish to protect piscivorous wildlife.

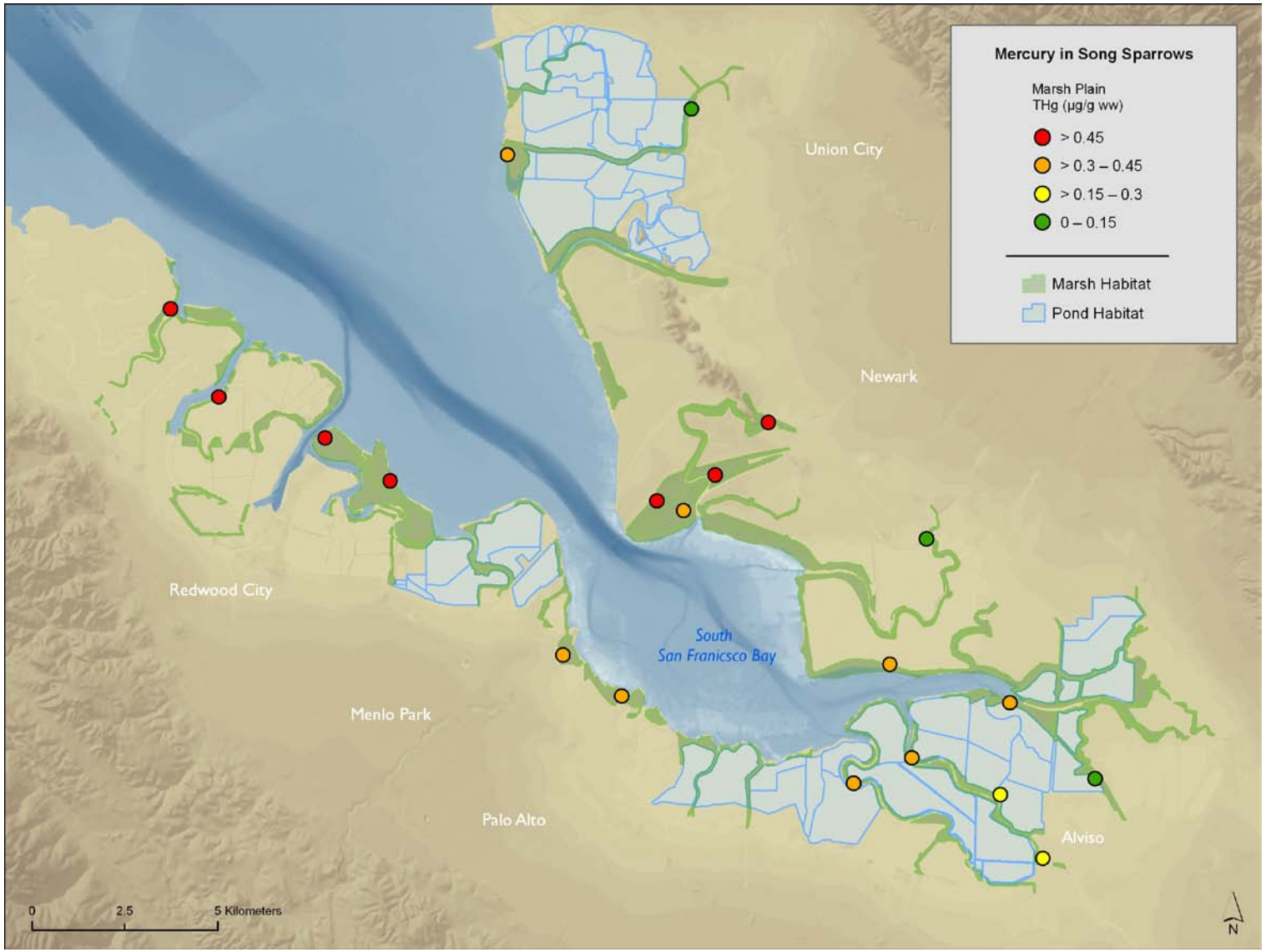

Figure 5.3.10. Map of mean total mercury (THg) concentrations in Song Sparrows (whole blood) from South Bay tidal marshes (n = 20) sampled during 2008.

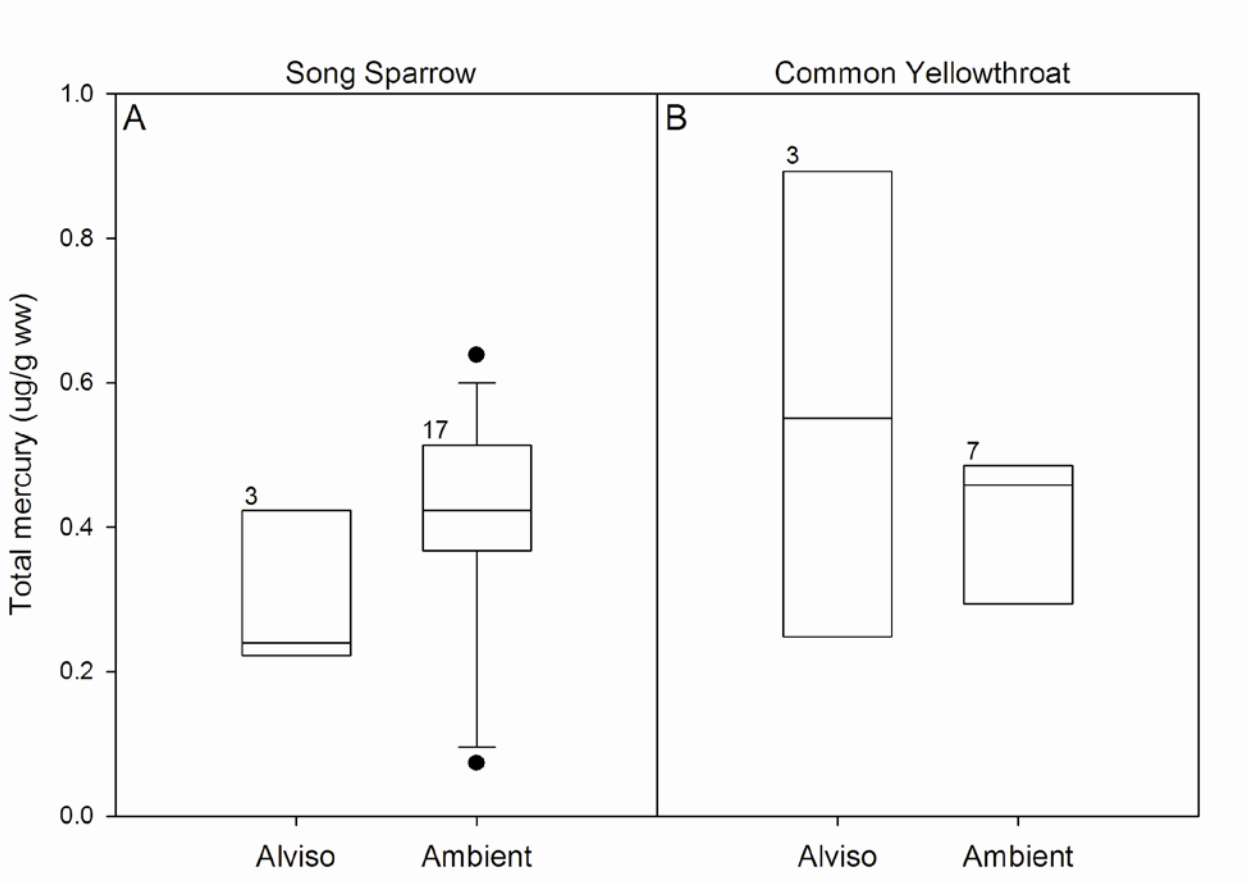

Figure 5.3.11. Box and whisker plots of marsh bird total mercury (THg) concentrations in Song Sparrow (A) and Common Yellowthroat (B) specimens collected from Alviso marsh and South Bay reference (ambient) marshes during 2008. Marsh birds from Alviso Slough fringing marsh (n = 3) had THg concentrations similar to birds of the same species (Song Sparrow, Plot A, and Common Yellowthroat, Plot B) from reference marshes across South Bay (n = 17). In each box plot, the lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median, and the lines extending above and below the box represent values that fall within ±1.5 times the inter-quartile range. Outliers beyond the whiskers are represented by black dots. Percentiles and inter-quartiles range could not be calculated for all comparisons due to small sample sizes (n < 9). The number above each box is the sample size (n).

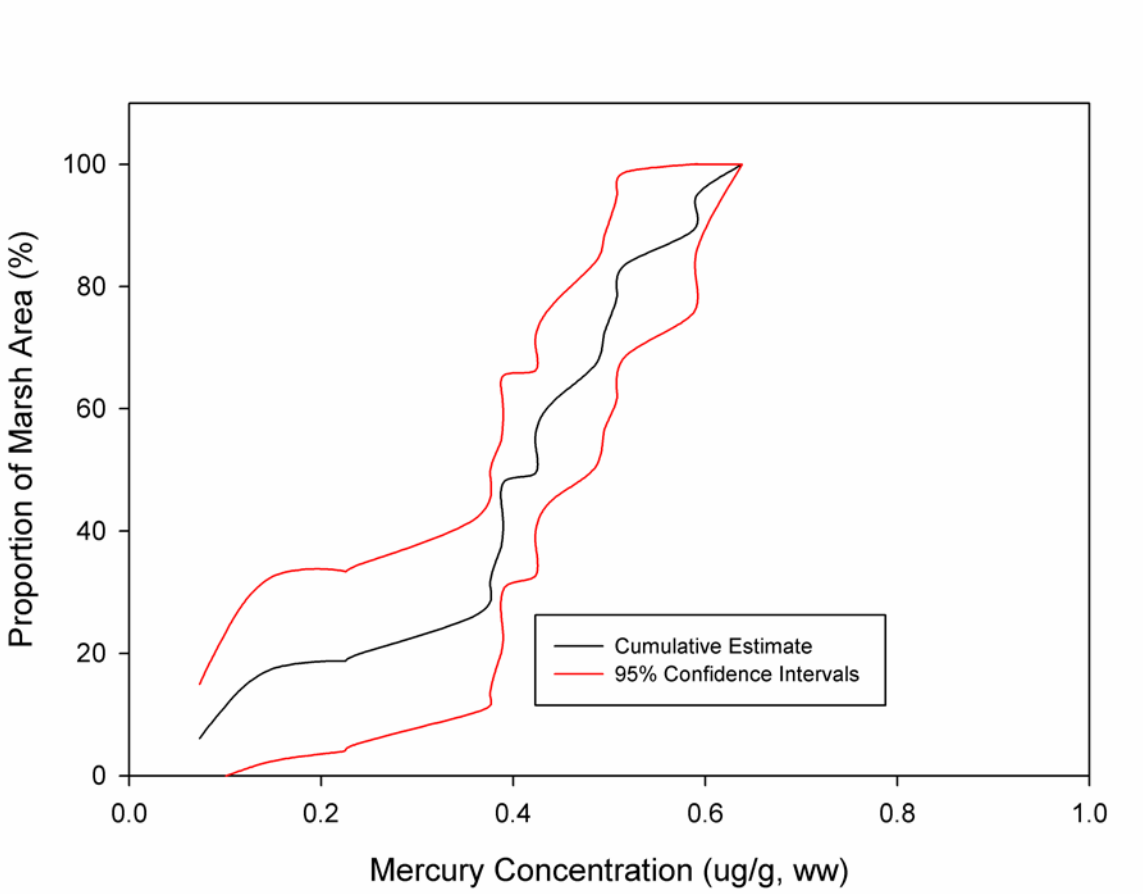

Figure 5.3.12. Cumulative distribution function plot of total mercury (THg) concentrations in Song Sparrow blood from tidal marsh locations sampled during 2008. Eighty-percent (80%) of the marsh area sampled in South Bay had a poorer mercury condition in the marsh plain food web than what was observed in Alviso Slough fringing marsh, based on the sparrow biosentinel data

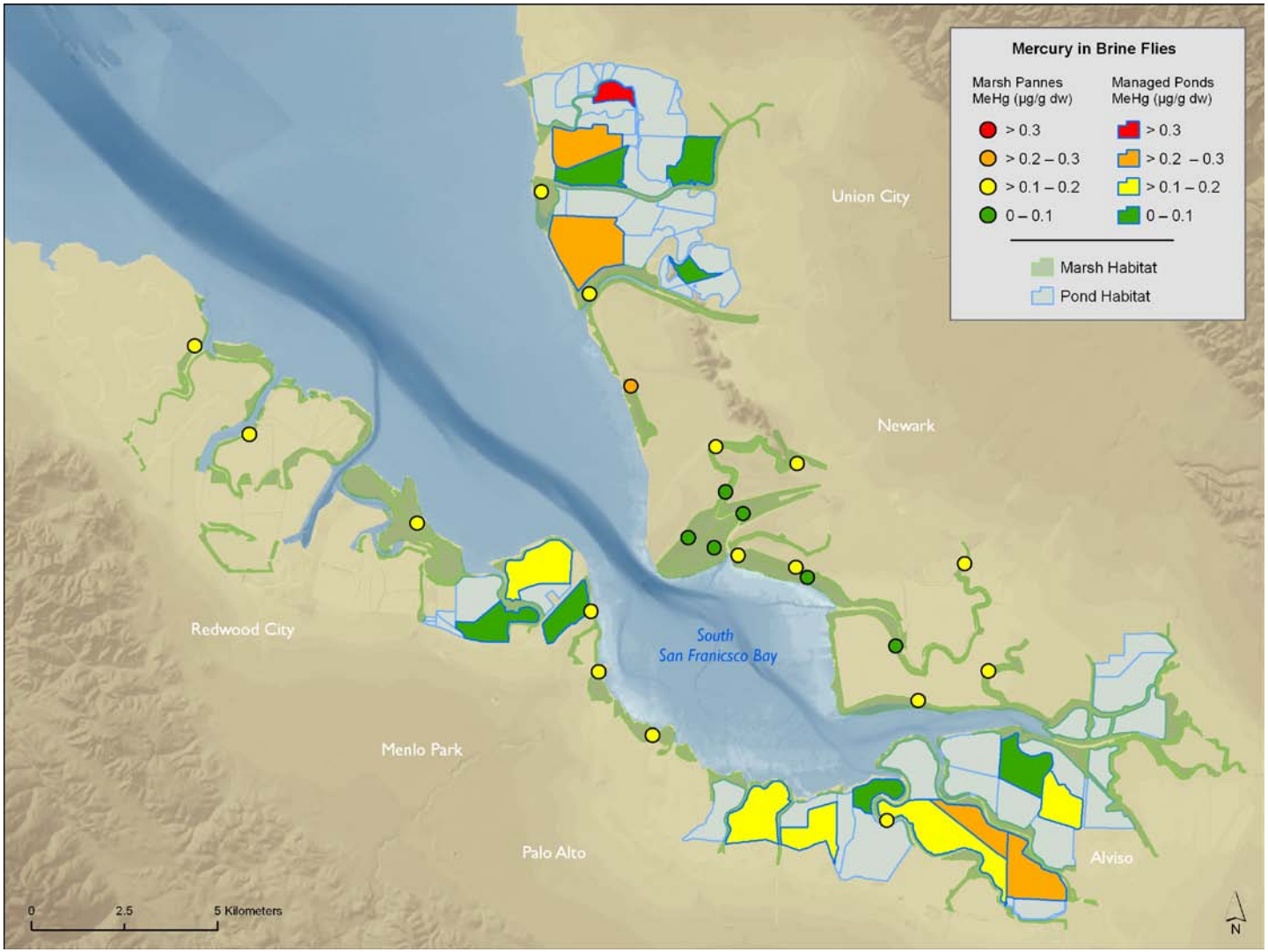

Figure 5.3.13. Map of mean methylmercury (MeHg) concentrations in brine flies sampled from tidal marsh pannes (n = 23) and managed ponds (n = 17) during 2008. When more than one sampling location was located in the same pond, the average of the locations was used.

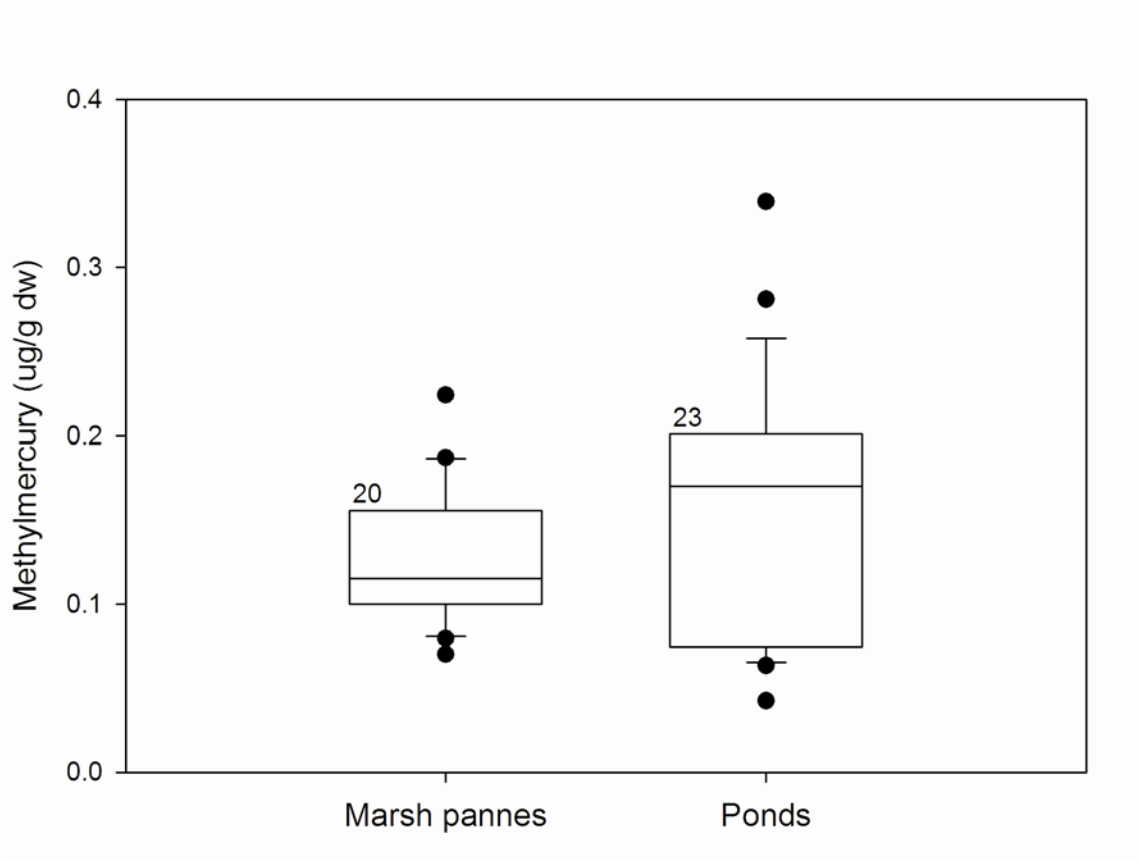

Figure 5.3.14. Box and whisker plot of methylmercury (MeHg) concentrations in brine flies sampled from tidal marsh pannes (n = 23) and managed pond margins (n = 17) during 2008. In each box plot, the lower and upper ends of the box represent the 25th and 75th percentiles, the horizontal line within each box represents the median, and the lines extending above and below the box represent values that fall within ±1.5 times the inter-quartile range. Outliers beyond the whiskers are represented by black dots. The number above each box is the sample size (n).

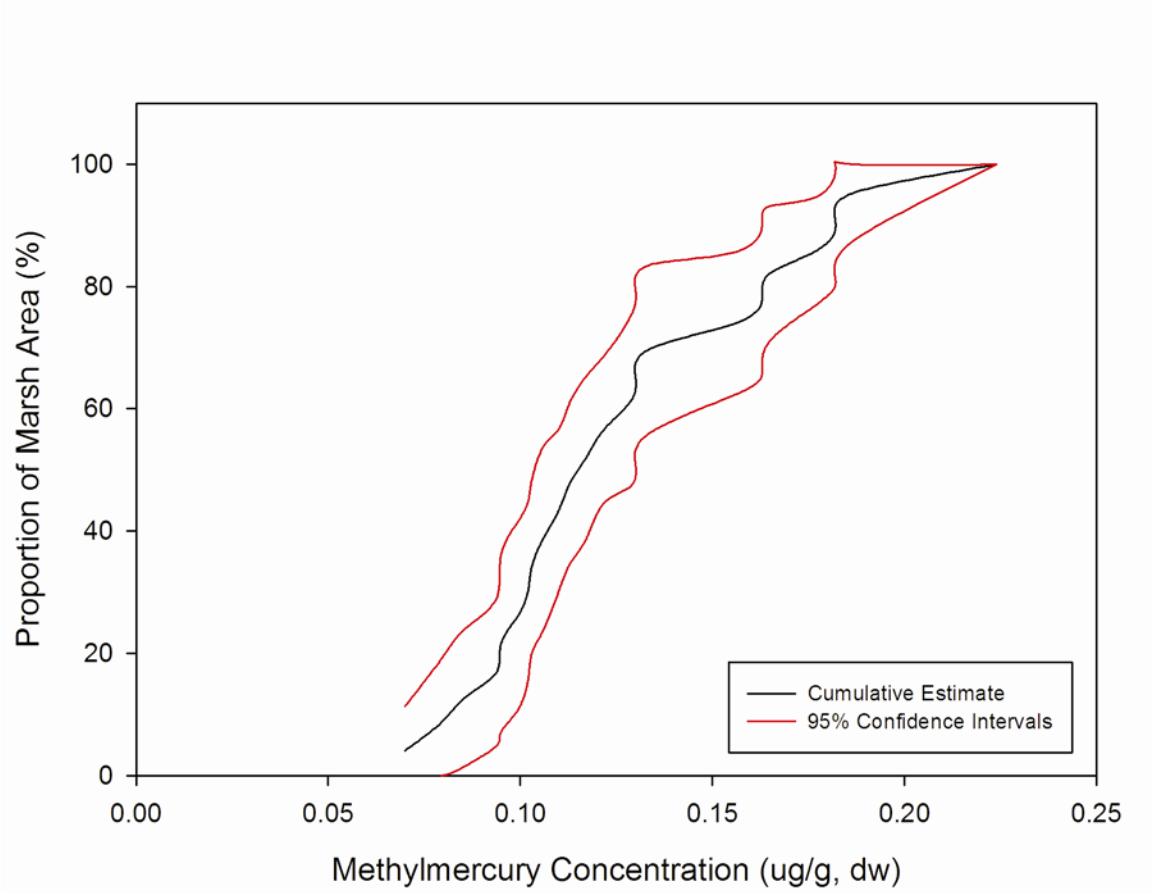

Figure 5.3.15. Cumulative distribution function plot of methylmercury (MeHg) concentrations in brine flies from tidal marsh pannes sampled during 2008.

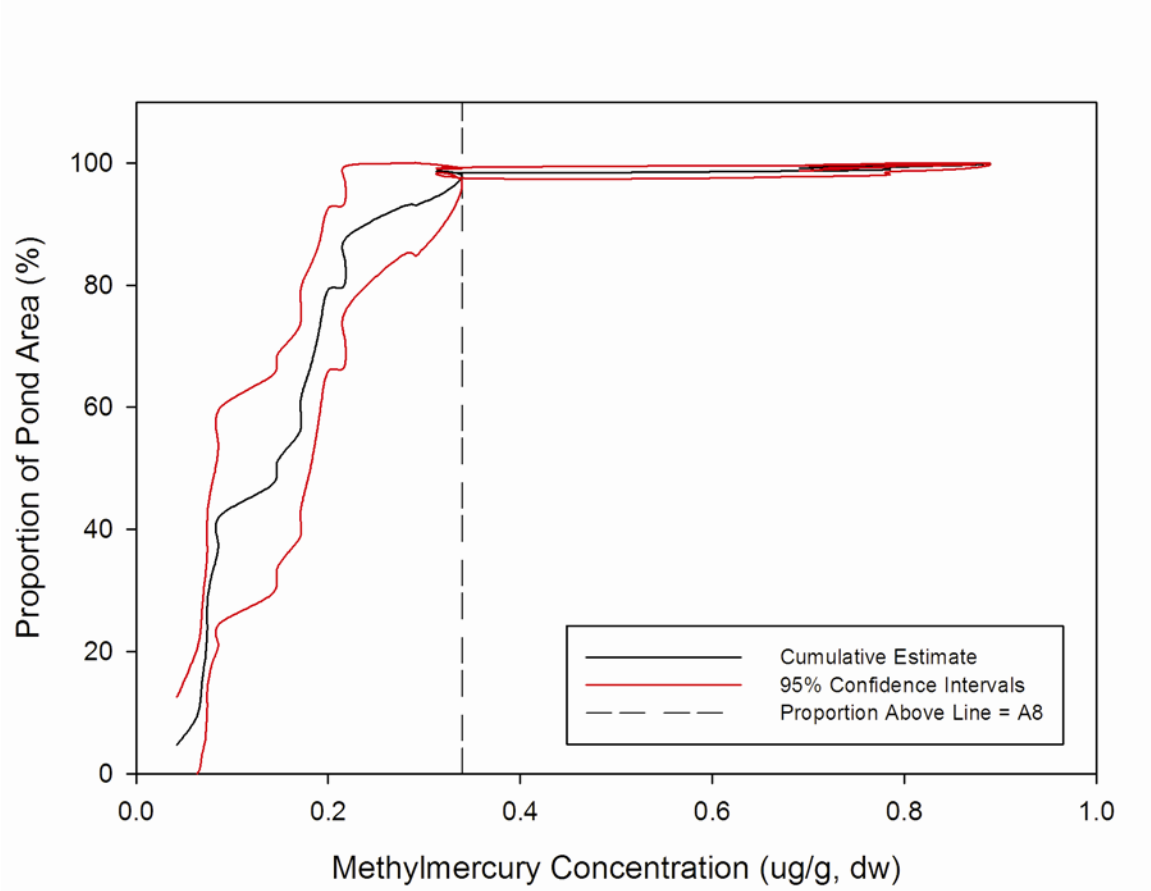

Figure 5.3.16. Cumulative distribution function plot of methylmercury (MeHg) concentrations in brine flies from managed pond margins sampled during 2007 and 2008. Pond A8 exhibited the worst mercury condition for brine flies, but less than 1% of the south bay pond area sampled corresponded to concentrations in Pond A8 (to the right of the dashed line).

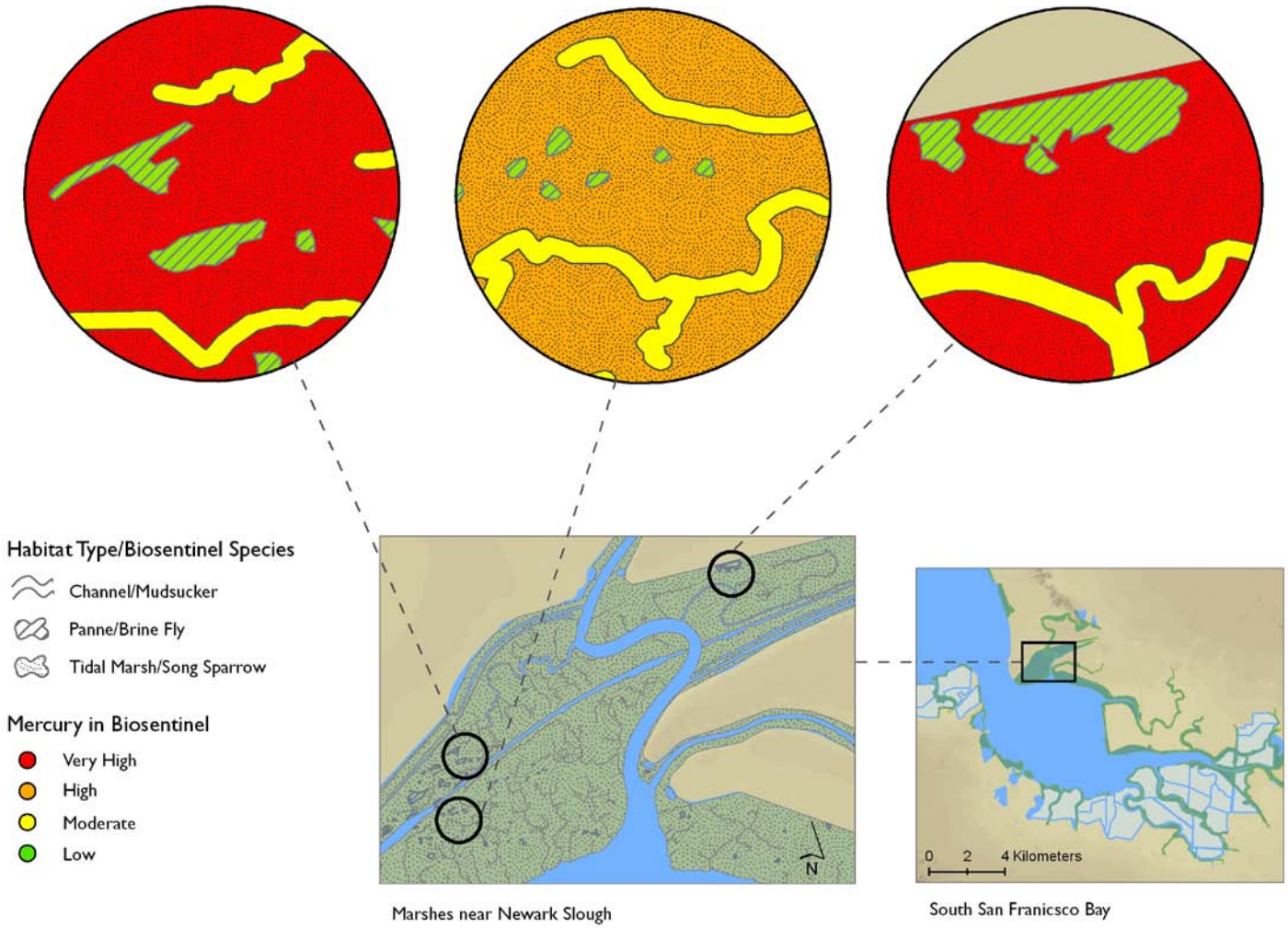

Figure 5.3.17. Conceptual map showing a) how mercury concentrations in biosentinels relate to marsh habitats, and b) the lack of correlation among mercury concentrations in biosentinels from the same marsh site. Sampling areas depicted in detail correspond to sampling stations: left) Ref-022, center) Ref-014, and right) Ref-020. Mercury categories are identical to those in the species-specific concentration maps (Figs. 5.3.1, 5.3.11, and 5.3.14).

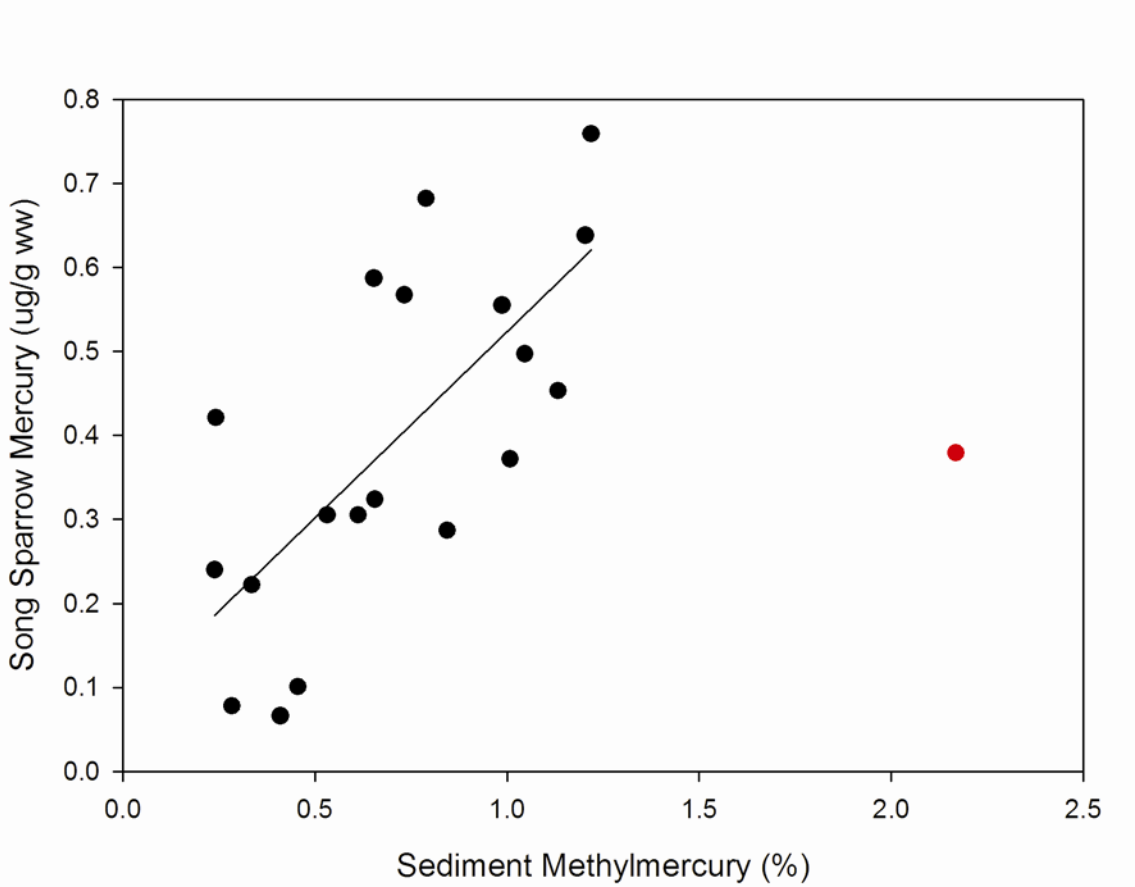

Figure 5.3.18. Linear regression analysis of Song Sparrow blood total mercury (THg) concentrations as a function of tidal marsh sediment percent methylmercury (% MeHg, as a percentage of total mercury). Total Hg in song sparrow blood was strongly related to percent MeHg in sediment sampled at the same time from the same locations ($n = 20$, $r^2 = 0.50$, $p < 0.05$). Red dot indicates an outlier from a marsh near Foster City not included in the regression.

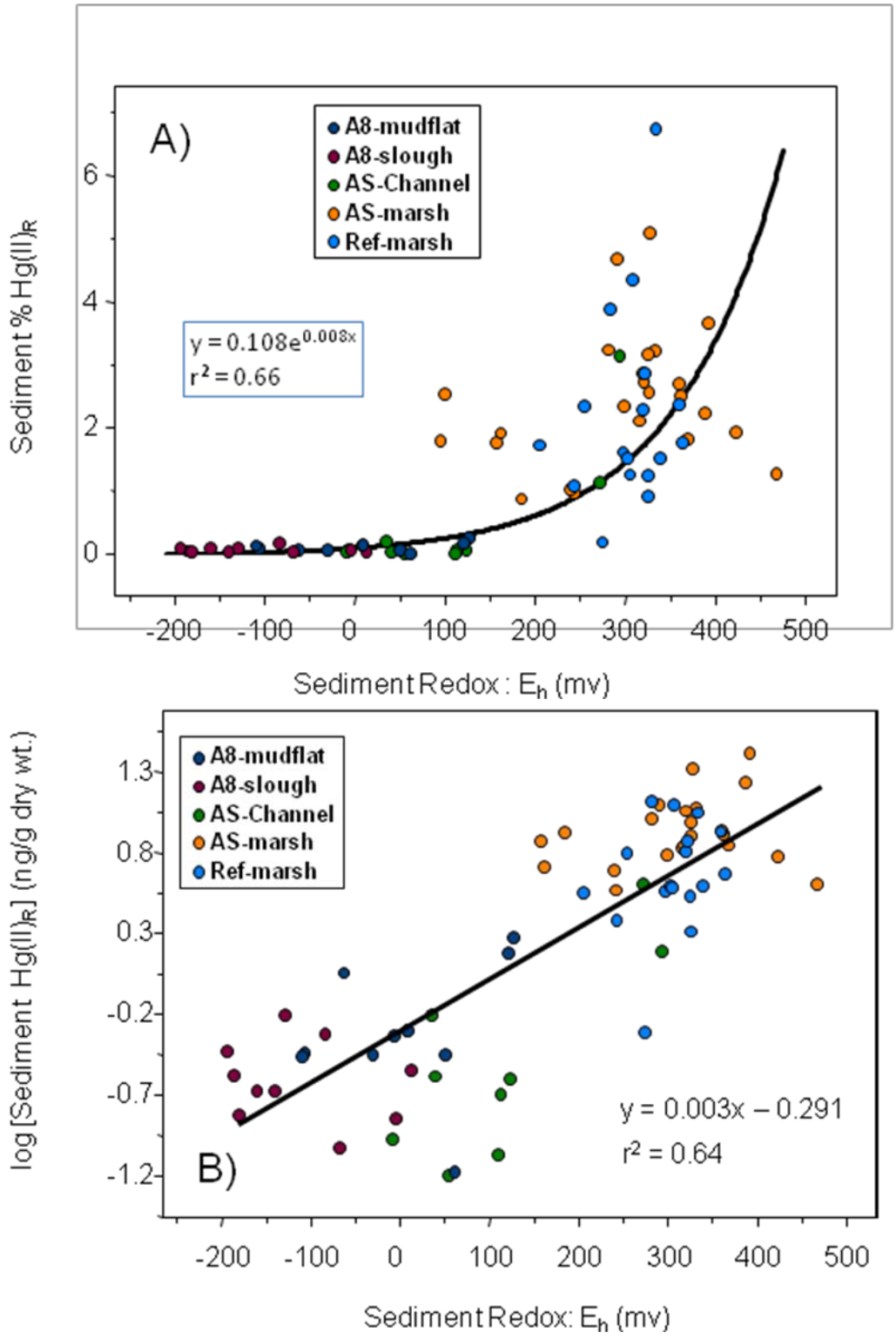

Figure 6.1.1. Non-linear curve-fit of sediment percent reactive mercury (%$Hg(II)_R$) as a function of sediment redox (A) and linear regression analysis of log-transformed sediment reactive mercury ($Hg(II)_R$) concentration as a function of sediment redox (B). The five habitat types are identified in the figure legend inset.

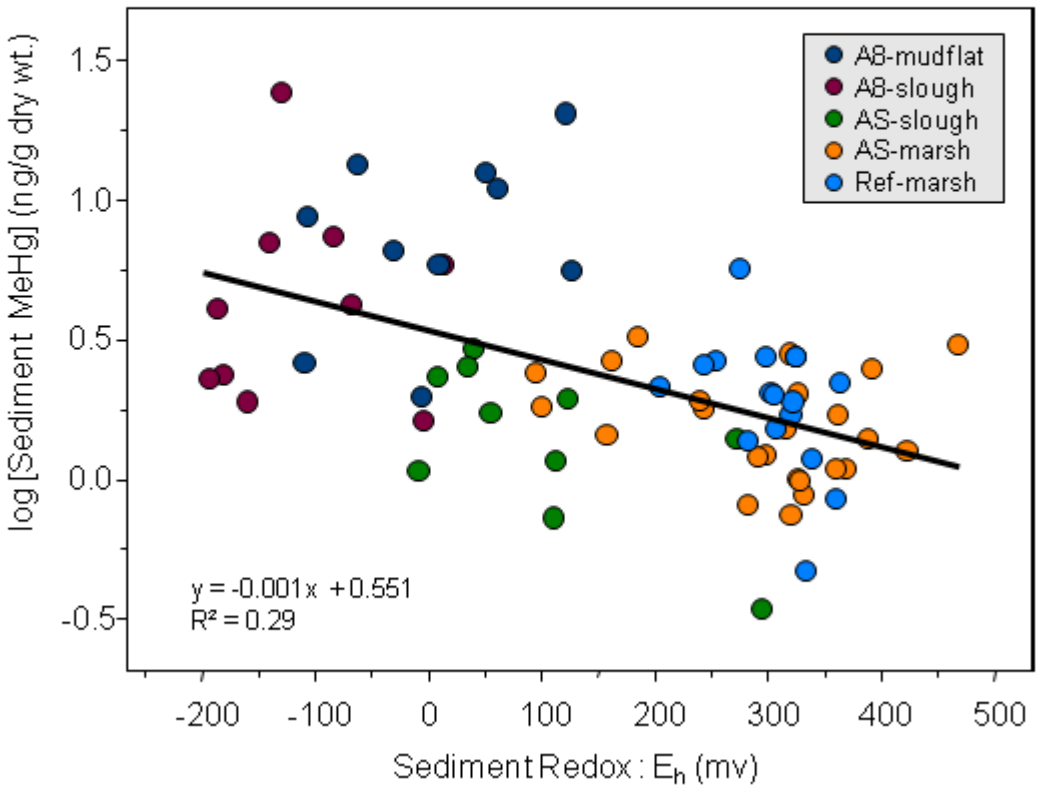

Figure 6.1.2. Linear regression analysis of log-transformed sediment methylmercury (MeHg) concentration as a function of sediment redox. The five habitat types are identified in the inset figure legend.

Appendicies

Appendix A Sediment and pore water data from the South San Francisco Bay Salt Ponds Mercury Study, Alviso, California.

[See Microsoft Excel Workbook: **Appendix A - Sediment SBMP.xls**]

Appendix B Surface water data from the South San Francisco Bay Salt Ponds Mercury Study, Alviso, California.

[See Microsoft Excel Workbook: **Appendix B - Water SBMP.xls**]

Appendix C Biosentinel mercury and methylmercury data for 2006, 2007, and 2008 sampling efforts.

[See Microsoft Excel Workbook: **Appendix C - Biota SBMP.xls**]