South Baylands Mercury Project

2006 Year-End Progress Report

Letitia Grenier, Josh Collins, Jennifer Hunt,
Dayna Yocum, Shira Bezalel, and April Robinson
San Francisco Estuary Institute, Oakland, CA

Mark Marvin-DiPasquale
U.S. Geological Survey, Menlo Park, CA

David Drury
Santa Clara Valley Water District, Santa Clara, CA

Elizabeth Watson
University of California, Berkeley, CA

Executive Summary

The South Baylands Mercury Project was launched in 2006. This project is a collaborative effort between San Francisco Estuary Institute, United States Geological Survey-Menlo Park, and the Santa Clara Valley Water District to characterize mercury (Hg) in the sediment, water, and biota of the Alviso Pond and Slough Complex. The results from this study are designed to facilitate decision-making regarding management and restoration options for Pond A8. The Project will also provide baseline data prior to returning the Pond to tidal action and will increase the knowledge base for other South Bay Salt Pond Restoration Project restoration decisions.

Field sampling commenced in the latter half of 2006. Fifteen 2-meter-long sediment cores were taken from Alviso Slough (5 cross-slough transects with 3 sites each, along a 3.5 km stretch, from midway up the Slough to near the town of Alviso). Extensive analysis of their physical and chemical composition is currently underway. Some of the preliminary results are available in this report. These data will characterize total mercury (Hg_T) for the full two-meter depth at all 15 sites, as well as reactive mercury ($Hg(II)_R$) and MeHg (MeHg) at 9 sites (three of the five transects). Ancillary sediment characterization includes: bulk density, organic content, magnetic susceptibility, % dry weight, pH, oxidation-reduction potential, photography, X-ray analysis and detailed lithographic descriptions of each core.

The first water sampling event occurred in November, and these sites will be revisited for seasonal sampling 5 times in 2007. Some of the November water data are currently available and are presented here. Water measurements include total Hg, methylmercury, pH, temperature, specific conductivity, dissolved oxygen, salinity, total suspended solids, dissolved organic carbon, specific UV absorption, sulfide, chloride, and turbidity.

Songbirds, fish, and brine flies were sampled from July through September to characterize Hg bioaccumulation in the food web and to compare Hg concentrations in biota between the managed ponds and the Alviso Slough marsh. Samples from hundreds of individual biota were collected, target sentinel species were present and readily caught in sufficient numbers, and capture techniques were refined during the initial field work of 2006. Data from marsh plain birds have been received from the lab and are presented here. These 2006 data will be used to shape the 2007 sampling plan, which will include sampling biota farther up-estuary toward the proposed Pond A8 notch, a larger sample of brackish-marsh birds, and broader representation of South Bay reference marsh samples.

All results to date are preliminary and are subject to change pending peer review and project completion. They are presented below as a demonstration of the project's progress, and should not be circulated without the express consent of the scientific institutions controlling that data. Results are presented with little or no interpretation, as many samples remain to be analyzed, some samples have not yet been collected, and not enough time has passed to allow the research group to thoroughly synthesize the data in hand. The 2007 sampling plan is currently being developed. Remaining 2006 data that are still pending from the analytical labs will be reported and interpreted at a later date.

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I. Background

This report describes the South Baylands Mercury Project progress during 2006. This project is designed to provide information about Hg bioaccumulation and other Hg processes to facilitate decision-making for the South Bay Salt Pond Restoration Project (SBSPRP). The study area and 2006 sampling locations are in the Alviso Pond and Slough Complex (Figure 1). Project activities in 2006 were funded by the Santa Clara Valley Water District, the California Coastal Conservancy, the San Francisco Foundation Bay Fund, and the Regional Monitoring Program for Water Quality.

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

The South Baylands Mercury Project is a collaborative effort between the San Francisco Estuary Institute (SFEI), United States Geological Survey (USGS) of Menlo Park, and the Santa Clara Valley Water District (SCVWD). The complexity of the Hg problem in wetlands requires a multi-disciplinary approach. Through this combined effort, we will characterize Hg in sediments likely to be scoured during wetland restoration, quantify differences in Hg concentrations between habitats and their sentinel species, develop a baseline of Hg concentrations, and evaluate potential risks of wetland restoration for Hg bioaccumulation.

- The USGS component studies Hg cycling in sediment to quantify reactive Hg available for methylation, the factors that control transformation from inorganic Hg to organic MeHg, the amount of MeHg produced in existing marshes, and the correlation between Hg in sediment and biota. In addition, sediment cores were taken along Alviso Slough, both from the main slough channel and the fringing marsh, to study Hg deposited in previous decades. Deeper sediments may have higher concentrations of Hg from historical mining in the Guadalupe River watershed. These deeper sediments could be remobilized during restoration into the biologically active sediment layer and the food web.

- The SCVWD component measures Hg and other water quality parameters in the water of the slough, adjacent marsh, and salt ponds. Water data will be analyzed for chemical indicators that correlate with Hg concentrations and bioaccumulation in the food web. Tidal water draining from secondary sloughs is sampled to determine if the marsh plain is a source of MeHg to Alviso Slough and the Bay.

- The SFEI component samples sentinel species specific to certain habitats that can be compared between managed ponds and marshes (Table 1). These biota indicate habitat-specific Hg conditions before and after wetland restoration. In 2006, four pairs of habitats were compared between the managed ponds and adjacent marshes. SFEI is also the coordinating agency for the Project.

II. Problem Statement

Mercury is a legacy contaminant, mined historically from the California Coast Ranges and transported to the Sierra Nevada for use in gold extraction during the 19th century Gold Rush. Mercury historically entered and continues to enter the Bay and Baylands from the Sacramento/San Joaquin Rivers and from run-off from mines located around the local Bay watershed. One of the most prolific mercury-producing mining areas was the New Almaden Mining District located in the hills above San Jose in the watershed that presently drains through Alviso Slough.

Mercury is a significant contaminant in the waters and sediment of the Bay as well as in the wildlife that reside here. There is evidence that the transformation from inorganic mercury (Hg(II): not significantly biologically available) to organic methylmercury (MeHg: the form that is most toxic to biota and most readily enters food webs) can occur at high rates in wetlands. Therefore, the potential exists to inadvertently increase the risk of Hg methylation and accumulation in South Bay fish and wildlife through hydrological modification of salt ponds as part of the SBSPRP. Concentrations of Hg in sediment and water tend to be greater in South Bay than other parts of the Estuary; the Alviso Pond and Slough Complex are especially worrisome, because they contain more Hg than other areas of South Bay (SFEI 2005) and are slated for early restoration to tidal action.

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

Although Hg and MeHg concentration data have been previously collected at various locations within the South Bay (David et al. 2002, Thomas et al. 2002, Conaway et al. 2003, Topping et al. 2004, Beutel et al. 2004, SFEI 2005), little is known about the regional and habitat-specific processes governing mercury-species transport and transformations, Hg(II)-methylation, $Hg(II)_R$ concentrations, and MeHg uptake into food webs. Key questions include the following:

- How much legacy Hg is contained in sediments of different depths or in different areas?
- How readily available is this legacy Hg for conversion to toxic MeHg?
- How effectively and by what specific pathways is MeHg incorporated into local food webs?
- How might restoration of managed ponds to tidal wetlands impact the availability of legacy Hg for methylation and uptake into the food web?

The South Baylands Mercury Project is a collaborative and integrative approach to address these questions.

III. Field Sampling Methods

Surface Sediment/Sediment Coring

Surface sediment sampling did not occur in 2006. Surface sediment will be sampled in conjunction with biota in 2007.

Sediment cores were collected in fall 2006 from 15 stations along Alviso Slough in South San Francisco Bay (Figure 1). Samples were collected along a salinity gradient from the more saline part of the slough (nearest the slough mouth) to upstream locations near the town of Alviso. Sediment cores were collected from five transects running perpendicular to the slough. Three sites were sampled along each transect, which included the vegetated marsh plain that fringes either side of the slough (A and C series), as well as the thalweg of the main slough channel (B series). The piston corer used for sediment collection is a hand-operated 2" diameter Livingston coring device with locking piston. Each operation of the device recovers up to 100 cm of sediment; the starting depth of each sample is controlled by locking or unlocking the piston. Cores were collected up to a depth of 255 cm and were collected in sections ranging from 24 cm to 98 cm in total length. Three to four sections were collected at each site in order to reach the selected maximum depth of 255 cm. Due to compaction of sediments during coring, the maximum depth reached was 233 cm.

Water

Water samples for measurement of mercury species and ancillary parameters were collected from Pond A8, the Alviso Slough main channel, and secondary channels in Alviso Slough fringing marsh (Figure 1). Water samples were collected in mid November at the middle of a spring tide (2.9 meter tide). Samples were taken inside Pond A8 in a historical channel (surface and deep sample), at the pond side of the weir (surface sample), and at the A7 inlet gate (surface sample). Water samples were also collected from the fringing marsh along Alviso Slough (surface sample from secondary sloughs) and Alviso Slough main channel (surface and depth sample). Marsh and slough samples were collected at the bay-ward end of the slough, near the dredge lock area, and downstream of the Gold Street Bridge. Sampling occurred close to a slack/ebb tide in order to measure methylmercury export from the marsh. Both total and methylmercury, as well as ancillary parameters, were analyzed for each sample taken.

Alviso Slough Water Station Descriptions

- Station ASW1: mid-channel adjacent to freshwater tidal marsh near the proposed breach at the south end of Pond A8.
- Station ASW2: mid-channel adjacent to brackish tidal marsh upstream of ASW3.
- Station ASW3: mid-channel adjacent to saline tidal marsh and near the existing intake at Pond A7.
- Number of grabs: two per station; one at the water surface and one at one- quarter meter off the bottom.

- Timing: during the early part of ebb tide, after an over-bank tide, near the end of a spring tide series.

Tidal Marsh Water Station Descriptions

- Station ASMW1: secondary channel draining freshwater marshland at least 10 m upstream from the Alviso Slough main channel bank.

- Station ASMW2: secondary channel draining brackish marshland at least 10 m upstream from the Alviso Slough main channel bank.

- Station ASMW3: secondary channel draining saline marshland at least 10 m upstream from the Alviso Slough main channel bank.

- Number of grabs: one at each station that integrated over depth in the channel.

- Timing: during the early part of ebb tide, after an over-bank tide, near the end of a spring tide series. Ideally, the water sampled was in the process of being drained from the marsh interior.

Pond A8N Water Station Descriptions

- Station A8WF1: shallow water along the northwest pond shoreline.

- Station A8WF2: shallow water along the southeast pond shoreline.

- Station A8WD1: deep water of the interior pond.

- Number of grabs: One per station at A8WF1 and A8WF2 just off the bottom; two at Station A8WD1, one at the water surface and one at one-quarter meter off the bottom.

- Timing: Within two days of the Alviso Slough and marsh water sampling event.

Water surface samples were collected directly into the sample container by submerging the bottle, removing the cap, filling, and replacing the cap. Sample containers were double-bagged and handled using the two-person “clean hands dirty hands” method.

Water depth samples were collected 0.25 m off the bottom using a 2.2-Liter Van Dorn Beta-type (Wildco) sampling device. After retrieval, sample containers were filled directly from the device. Sample containers were double-bagged and handled using the two-person “clean hands dirty hands” method.

Marsh water samples were collected into an acid-cleaned glass container by submerging the container into a flowing stream. Each station deployed a dedicated glass container to be used only at that station to avoid cross-contamination. After retrieval, sample containers were filled directly from the glass container. Sample containers were double-bagged and handled using the two-person “clean hands dirty hands” method.

Measurements of pH (Units), Temperature (°C), Specific Conductivity (ms/cm), Dissolved Oxygen (mg/l), Salinity (%) and Turbidity (NTU) are recorded at each sampling depth using a Horiba U-10 Water Quality Checker (Horiba). The Horiba is inserted directly into the water at depth. For some sites, samples are collected into a triple-rinsed collection beaker into which the Horiba will be inserted.

Biota

Marsh Plain Birds

Alameda song sparrows, common yellowthroats, marsh wrens, and other species were collected in September by mist net from the marsh along Alviso Slough and Guadalupe Slough (Reference Marsh). All birds collected were post molt, so their feather Hg values (data not yet available) reflect the post-breeding feather growth in late summer of 2006. Nets were set up in the early morning in areas where birds were active and foraging. Often, nets were set perpendicular to small sloughs in areas of dense *Grindelia* or adjacent to *Scirpus* patches. After being extracted from the nets, birds were weighed and measured, and their sex and age were determined whenever possible. Blood samples of 10-100 µl were collected by brachial veinipuncture. A small needle was inserted to perforate the brachial vein at the angle of the wing, and then blood was collected in a microcapillary tube. Capillary tubes were capped with flexible plastic plugs to prevent moisture loss and then placed in larger tubes for transport and storage. Feather samples were also taken, consisting of several body feathers and the distal half of the first primary flight feather (snipped at the coverts) from the right wing. For each bird, body and flight feathers were stored in separate envelopes at ambient temperature, and blood samples were kept on ice in the field until they could be transferred to a freezer (-4º C) awaiting shipment to the lab. Birds were marked with USFWS metal bands and color bands for field identification, and then they were released following sample collection.

Fish

Fish were no longer present in Pond A8 at the time of sampling, so fish were collected from Ponds A5 and A7 instead. These ponds house the source population of fish that enter Pond A8 when water is transferred during pond management events. Minnow traps and pillow traps were baited to capture demersal longjaw mudsuckers and yellowfin gobies in the marsh channels along Alviso Slough and from Ponds A5 and A7. Traps were baited with mackerel or cat food and set out for a period of 4 – 24 hrs. Trapped fish could not access the bait, which was contained in metal cans with only very small slits that allowed the scent of food to enter the water. Mississippi silversides, three-spined stickleback, and rainwater killifish were collected by beach seine in the pelagic area of tidal channels and managed ponds. At marsh sites, the beach seine was walked out into the channel with a person at either end, then extended to the full length of the net and hauled back to shore. In deeper water, the net was set out from a small boat with one person on the other end of the net in the water. Fish were stored in Zip-Lock© freezer bags on ice in the field.

Fish samples were weighed and measured for total length in the lab after field collection and before shipment to the analytical lab. The fish length:mercury relationship was controlled by sampling fish within a small size range for each species. Mississippi

silversides, three-spined stickleback, and rainwater killifish were grouped into composites by species. Yellowfin gobies and longjaw mudsuckers were analyzed as individuals. Whenever possible, the smallest fish was no smaller than 0.75 of the length of the largest fish, either within a composite for the pelagic fish or within a species for the gobies. Each composite or individual was put in a separate Zip-Lock© freezer bag and stored in a freezer (-4º C) until shipment to the analytical lab. Groups of fish samples were stored in a second bag to prevent moisture loss.

Brine Flies

Brine flies were captured from salt ponds using sweep nets and aspirators. Brine flies were absent from the marsh at the time of sampling, because it was very late in the year. Flies were observed earlier in the year in the areas of interest, so we expect to capture them readily in 2007. Samples were collected from pond edges in areas sheltered from the wind and from stagnant pools where the flies tended to congregate. Most flies were found in small isolated pockets (<1 m^2) with many meters between pockets. Brine fly samples were standardized by collecting adults from different habitats during the same time period. We collected an average of 100-200 flies per composite (range 10-350). Voucher specimens were sent to Dr. David Herbst at the Sierra Nevada Aquatic Research Laboratory, who confirmed that the species we collected were *Ephydra cinerea* and *E. millbrae*.

IV. Sample Analysis Protocols

Sediment

Initial Post-Collection Deep Core Processing

Within 3 – 7 days of field collection, the Alviso deep cores were taken through an extensive and detailed process of characterization and sub-sampling. Each core length (50 in all) went through this five-step process which included a) initial non-destructive imaging of whole core sediment density and magnetic susceptibility, b) core splitting, c) physically describing the 'working' half split-core lithography and entering that information into a database, d) sub-sampling for parameters of interest, and e) photographing the 'archive' half split-core.

Multi-Sensor Core Logger

Sediment wet bulk density (via the gamma-ray method) and magnetic susceptibility (a measure of magnetic mineral content) were first made using the Multi-Sensor Core Logger (MSCL) (Model MSCL-75; Geotek Ltd™; United Kingdom), which is owned and operated by the Coastal Marine Geology unit of the USGS (Menlo Park, CA). By measuring and studying the variation of these two state properties, we were able to get a 'look' inside of each core prior to actually splitting the core tubes. Since down-core variation in these parameters is often not readily apparent to the naked eye even once the cores are split and inspected, this MSCL data was critical in helping us decide exactly how to space the specific sediment intervals to be sub-sampled.

The MSCL-system is described in detail elsewhere (Gardner et al. 1995, Kayen et al. 1999). The MSCL consists of a 4-m-long tracking system that holds three sequential measurement devices: 1) a gamma ray wet bulk density sensor, 2) a primary

compression-wave (P-wave) velocity and core-diameter sensor, and 3) a magnetic susceptibility sensor. A Macintosh computer driven by data acquisition software controls the system. Whole core sections up to 1.5 m in length can be logged. Core movement along the tracking system is run by a computer-controlled stepper motor that advances the core section at 1-cm intervals during logging. Each core section was run consecutively through the sensors, starting with the top of the section and progressing through to the bottom of the core. Core caps at each end (approximately 3 cm at the top and bottom of each core section) generate spurious data, which were subsequently excluded in the sediment profiles depicted in this report (Figs. 2 and 3).

The sediment density sensor functions by sending a beam of gamma radiation (emitted from a ^{137}CsCl solid source) through the diameter (width) of the whole core. A scintillation detector coupled to a photomultiplier measures the attenuated radiation that passes through the core diameter. This attenuated gamma radiation signal is converted to sediment density (g/cm^3) by applying a two-point calibration curve based on the attenuated gamma radiation signal produced by a similar core tube filled with either pure water or a solid cylinder of aluminum (both of accurately known densities: 1.0 g/cm^3 and 2.7 g/cm^3, respectively). Calibration cores containing water and aluminum were run daily to verify the accuracy and consistency of the instrument.

The magnetic susceptibility sensor is set electronically by the manufacturer, based on a single standard of stable iron oxide. Thus, this sensor is calibrated absolutely and requires no additional calibration during daily operation.

The quality of the P-Wave velocity data was inconsistent due to a combination of factors including: the lack of water-saturated sediment in some core sections, incomplete coupling of the sediment with the interior core liner wall in some core sections, and the comparatively high degree of flexibility of the thin-walled core liner that was used for sediment collection. Thus, P-wave velocity data generated by the MSCL were not used in our determination of sediment intervals to sub-sample, and are not presented in this report.

Deep Core Splitting

After the data from the MSCL are obtained and assessed, each core section is split into two equal halves, representing the ‘working’ and ‘archive’ split core halves. The core end-caps are first removed. The whole core section is then placed into an aluminum core cradle with an inner diameter that exactly matches the outer diameter of the core tube, and which includes a top and bottom half, and thus totally encases the core liner. The core cradle also has two slits running along the length of each half, which act as a straight-line guide for the cutting tool. A utility knife blade is inserted at one end of the guide-slit, cutting into the core liner. The blade is run along the guide-slit until the core liner is cut from the top to the bottom ends on one side. The whole cradle is rotated 180^o, and the core liner is again cut along a line that is parallel and exactly opposite (180^o) the first. The core is then removed from the cradle and a very thin stainless steel wire is run longitudinally through the center of the core, along its full length. The two halves are then carefully pried apart and laid open-faced on the work bench. A film of plastic-wrap is gently placed over the exposed sediment of the ‘archive’ split core to minimize drying

and chemical oxidation. This core is then stored in a walk-in cooler at 3 ^{o}C until photographing can be later conducted (see below).

Deep Core Descriptions & Database

The 'working' half split-core is moved to the work table outfitted with bright 'full spectrum' lights. The surface of the sediment is gently smoothed (horizontally) with an acid-clean stainless steel spatula, removing the surface 1-2 mm of material to expose fresh sediment. Always measuring from the top of the core down, the following lithological parameters are noted for the complete core section: sediment color (hue/chroma) using the standard Munsell® soil color chart (Greta Macbeth LLC, New Windsor, NY), grain-size via texture to touch (e.g. sand, silt, clay), the position and nature of stratigraphic contacts, and sedimentary structures (e.g. plant roots, shell fragments, etc.). All of this information is input into a sediment profile description database created in FileMaker Pro 6.0 (FileMaker, Inc. Santa Clara, CA) by the Coastal Marine Geology group at USGS (Menlo Park, CA). Ultimately, this database information will be used to create graphical descriptive representations of each core, which will appear along side the photograph of the archive half split-core, the x-ray image and the MSCL data.

Deep Core Sub-Sampling

After fully describing the core section and assessing the MSCL density and magnetic susceptibility data, a decision is made as to the specific intervals to be sampled. Depth intervals typically ranged 10 – 30 cm in length. Priority of interval placement is given to obvious peaks in density and/or magnetic susceptibility, and to visible changes in sediment color and/or texture. Such discrete features were bracketed and typically sampled in one interval. When no such obvious features were noted, specific intervals were typically set to 20 or 30 cm, depending on the total number of intervals already identified for that whole 2 meter core profile. When core sections from the same site overlapped (which was typically the case), sub-sampling in the next lower core section would begin at the sediment depth associated with the bottom of the last interval from the core section just above it. This allowed for collection of sub-samples representing the complete 2 meter length of the core site, without overlapping data. The only exception to this was profile T5A, which was the first one sampled, and where there was some depth overlap during the sub-sampling between core sections D1, D2 and D3.

Once all depth intervals had been determined for the whole core section, tape was placed on a ruler that ran along side the core to mark-off each interval. Beginning with the top interval, an acid cleaned 1x1x1 cm plastic U-shaped sampling channel is placed 'open-face down along the length of the desired interval (just left of center) and then pushed evenly into the sediment until the top edge is flush with the sediment surface. A thin acid-cleaned stainless steel wire is then run along the bottom edge of the sampling channel to make a clean cut between the sediment inside and outside of the sampling channel, which is then gently extracted from the core section. This approach ensured that no sediment that had been in contact with the interior surface of the core liner was sub-sampled. The sediment filling the channel is immediately scraped from the interior into a 4 ounce (114 cm^3) plastic Whirl-Pak™ bag (Nasco, Inc., Fort Atkinson, WI). A second channel is similarly sub-sampled (just right of center), and the extracted sediment is added to the

same plastic bag. This results in 20 cm^3 (for a 10 cm interval) to 60 cm^3 (for a 30 cm interval) of sediment for each sub-sample. All sediment is squeezed to the bottom of the bag and all air is squeezed out of the bag, which is then sealed at the top. The sediment in the bag is then well homogenized by hand manipulation of the bag for approximately 1 minute.

The bag is reopened and sub-samples are taken with an acid-cleaned 3 cm^3 plastic syringe (with the needle-end cut off) for the following parameters: a) total mercury (Hg_T) [3-6 cm^3, frozen immediately on dry ice, all intervals], b) reactive mercury ($Hg(II)_R$) [3-6 cm^3, frozen immediately on dry ice, all intervals from transects 1, 3 and 5 only], c) MeHg (MeHg) [3-6 cm^3, frozen immediately on dry ice, all intervals from transects 1, 3 and 5 only], d) organic content / % dry weight [6 cm^3, refrigerated, all intervals], and e) grain size [6 cm^3, refrigerated, all intervals]. Collection vials for all HgT, organic content and grain size were 20 ml screw top PET bottles (acid-cleaned). Collection vials for Hg(II)R and MeHg were acid cleaned pre-combusted 20 ml screw-top glass vials. Sub-sample duplicates were taken for all of the above constituents at a frequency of approximately 10% of all samples collected.

After sub-sampling for the above parameters, the sediment remaining in the Whirl-Pak™ bag was again squeezed back to the bottom, and sediment pH and oxidation-reduction potential measurements are immediately taken on this material (see below for procedure). The excess sediment that remained in the core liner was used to fill a new Whirl-Pak™ bag that is saved as an archive sample for that particular core section / depth interval. Sediment was squeezed to the bottom of the bag, and air was squeezed out, prior to sealing (as above). These archived sub-samples are stored refrigerated. The above sub-sampling procedure was repeated for all core sections and depth intervals.

Deep Core Photographing and Archiving

The ‘archive’ half split-core sediment surface is gently smoothed (horizontally) with an acid-clean stainless steel spatula, removing the surface 1-2 mm of material to expose fresh sediment. The core is returned to the MSCL-system (described above) which is equipped with an overhead mounted Geoscan-colorline scan digital camera (using 3x1024 pixel charge-couple device arrays, Pentex™ k mounting lens; Geotek Ltd™; United Kingdom). The system takes a digital photograph of the whole core in one shot, while the core is mechanically moved down the MSCL track by the computer-controlled stepper motor. The image processing software (Geoscan™ Digital Imaging, version 5.2) creates a high resolution (approximately 25 Mb) JPG file. These images will ultimately be included as part of the final report that will be constructed with the FileMaker Pro™ database (as described above).

After photographing, the exposed sediment surface of the archive half split-core is again covered with plastic wrap, and the core is placed into a D-tube for long-term storage in the USGS (Menlo Park) core refrigerator (at 3 ^oC). A piece of wet sponge is added to the D-tube to maintain a high moisture atmosphere, and the end of the D-tube is sealed with duct-tape and appropriately labeled. These archive core metadata will be entered into the National Geophysical Data Center – Marine Geology and Geophysics (NGDC-MGG) database (http://www.ngdc.noaa.gov/mgg/curator/curator.html).

Mercury Speciation Analyses

Three specific Hg parameters (Hg_T, $Hg(II)_R$ and MeHg) have been (or will be) measured on the Alviso deep core sub-samples. This will allow us to calculate an inventory of these Hg species in the top 2 meters of sediment along the stretch of Alviso Slough that was sampled, and which has been estimated by Philip Williams & Associates (Ltd.) modeling efforts (Don Danmeier, personal communication) to be the section of the slough most likely to scour once the hydrodynamics of the system are changed due to opening up of the salt pond to tidal action.

Total Mercury Analysis

Sub-samples for total mercury (HgT) were taken at every depth interval for all sites, and were frozen at the time of sampling and maintained frozen until analysis. The procedure used for HgT analysis generally follows that of an approved USGS method (Olund et al. 2004), with modifications as to the approach for sample digestion. Once thawed, sediment samples (approximately 0.1 – 0.4 g wet weight) are initially digested in 10 ml concentrated nitric acid (or a mix of concentrated nitric and hydrochloric acids) in a Microwave Accelerated Reaction System (MARS-X™) (CEM Corp., Matthews, NC) according to EPA Method 3051a (USEPA 1998), designed for the microwave assisted digestion of sediments and soils. After samples are cooled, a 2 – 3 ml sub-sample is transferred into a pre-combusted glass container and held until further analysis. The digestate is then analyzed on an Automated Mercury Analyzer (Tekran Model 2600, Tekran, Inc., Canada), according to EPA Method 1631, Revision E (USEPA 2002). This standard method is based on the tin reduction of Hg(II) to gaseous Hg^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 is accompanied with analysis of the following Quality Assurance (QA) samples: a) 1 certified reference material, b) 1 matrix spike sample, c) 1 analytical duplicate, and d) 1 method blank. Calibration standards are prepared from a NIST-certified commercially obtained $HgCl_2$ standard. Quality control acceptance criteria for this assay is detailed in the published methods documents (Olund et al. 2004, USEPA 2002). In addition, the USGS Mercury laboratory in Menlo Park has been taking part in the QA/QC program overseen by Van Buuren Consulting LLC, for the CALFED/CBDA Ecosystem Restoration Program funded Hg studies throughout the San Francisco Bay region. Participation in this program includes: a) standard operating procedure documentation review, b) conducting a mean detection limit prove-out exercise, and c) inter-laboratory comparison analysis of HgT in sediment and water matrices (VBC, 2005; VBC and CDFG, 2005).

Reactive Mercury Analysis

Sediment "reactive" mercury ($Hg(II)_R$) is methodologically defined as the fraction of HgT in a sediment sample that has not been chemically altered (e.g. digested, oxidized or chemically preserved) and that is readily reduced to elemental Hg^0 by an excess of tin 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. While there is no standard method for this parameter, the procedure described below is modified from that described elsewhere (Kieu 2004), and has been used extensively in a number of research studies led by USGS researchers (Marvin-DiPasquale et al. 2006).

Recent experimental evidence suggests that the $Hg(II)_R$ assay effectively measures the fraction of Hg(II) that is associated with simple anions (e.g. $HgSO_4$, $HgCl_2$) in sediment pore water and/or Hg(II) that is weakly adsorbed to particle surfaces (Marvin-DiPasquale et al. 2006). Both of these fractions are indeed likely available to sediment microbes for Hg(II)-methylation. In a related set of experiments, the concentration of $Hg(II)_R$ measured in a suite of freeze-dried and homogenized environmental samples ranging over four-orders of magnitude in HgT (1-24,000 ppm), was strongly correlated ($r^2 = 0.97$) with the amount of MeHg produced when these freeze-dried samples were mixed (at a constant HgT amendment level) with fresh sediment containing active populations of Hg(II)-methylating bacteria (Bloom et al. 2006). These results suggest that the $Hg(II)_R$ fraction, as measured below, does provide a reasonable surrogate measure of the fraction of HgT that is potentially available for Hg(II)-methylation.

Sub-samples for inorganic reactive mercury ($Hg(II)_R$) were taken at every depth interval for the following Alviso Slough (AS) sites [T1A, T1B, T1C, T3A, T3B, T3C, T5A, T5B and T5C], and were frozen at the time of sampling and maintained thus until analysis. Upon thawing, sediment is initially processed in an anaerobic chamber. Sediment is first homogenized in the original collection vial, using an acid cleaned stainless steel spatula. Subsamples (0.1-1.0 g) are then accurately weighed in 15 ml plastic centrifuge tubes, to which 10 ml of anoxic 0.5% HCl solution is added. The tubes are capped and the resulting sediment slurry is homogenized on a vortex shaker. Samples are then removed from the anaerobic chamber and immediately refrozen on dry ice to minimize any oxidation reactions prior to transfer into the reaction bubblers. The reaction bubbler rig, the dual gold trap analytical set-up, and the CVAFS detection system employed for the remainder of the assay is exactly that which is described in EPA Method 1631 (USEPA, 2002) for the analysis of HgT in an aqueous samples.

A set of four environmental samples are allowed to thaw only 15 minutes prior to the actual analysis. The 200 ml glass gas-flushing bottles (bubbler flasks) are filled with 40 ml of anoxic 0.5% HCl. The sample slurry is briefly remixed and the whole contents of a single centrifuge tube is quickly and completely transferred to a single bubbler. A 0.5 ml aliquot of 20% (w/v) $SnCl_2$ is added to each and the system is sealed and purged with nitrogen gas for exactly 15 minutes while gently shaking. The evolved gaseous Hg^0 is subsequently trapped on a gold-sand trap. A soda-lime trap is located between the bubbler and the gold trap to protect the latter from acid fumes, as detailed in EPA Method 1631. The Hg^0 is then thermally desorbed from the gold trap to the analytical system and detected using CVAFS detector (Brooks Rand Model III Mercury Analyzer; Brooks Rand Inc., Seattle WA). Peak integration software (Peak Simple) is used to convert the analog signal output from the CVAFS to an integrated peak area value. Standard curves generated from aqueous $HgCl_2$ calibration standards, assayed as above, were used to calculate $Hg(II)_R$ concentrations.

Daily analytical batches consisted of a set of 4 (minimum) calibration standards, 8-16 $Hg(II)_R$ samples, 1-2 additional replicates of a single randomly picked $Hg(II)_R$ sample, and 4 bubbler blanks. Bubbler blanks consisted of 50 ml of 0.5% HCl and the $SnCl_2$ amendment only (no sediment). Calibration standards are prepared by dilution of a NIST-certified commercially obtained $HgCl_2$ standard. In addition, a precisely calculated

amount of gaseous elemental Hg^0 is injected into the analytical rig to verify the results (peak area vs. total Hg added) of the aqueous standards.

Methylmercury Analysis

Sub-samples for MeHg (MeHg) were taken at every depth interval for the following sites [T1A, T1B, T1C, T3A, T3B, T3C, T5A, T5B and T5C], and were frozen at the time of sampling and maintained thus until analysis. A standard USGS approved method is used for the sediment MeHg extraction and quantification (DeWild et al. 2004). In summary, MeHg is first extracted from sediment (0.5 to 1.0 g) with a mixture of potassium bromide, copper sulfate, and methylene chloride. A sub-sample of the organic phase (methylene chloride) is added to a container of water, which is then slowly heated. This results in the evaporation of the organic phase and the back-extraction of the MeHg into the aqueous phase. The pH is adjusted to 4.9 using acetate buffer. The extractant is then ethylated using sodium tetraethyl borate. The ethylated Hg species are purged from solution with N_2 gas, collected on a carbon-trap, thermally desorbed, separated using a gas chromatographic (GC) column, reduced using a pyrolytic column, and detected using CVAFS.

Additional Sediment Characterization

Sediment pH

Sub-samples for sediment pH were taken at every depth interval for all sites, and were measured immediately after sub-sampling (as described above). 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 then fully inserted into the homogenized sediment, which was squeezed into a ball around the probe tip (to exclude any air bubbles) in the bottom of the plastic Whirl-Pak™ bag.

Oxidation-Reduction Potential (ORP)

Sub-samples for sediment ORP were taken at every depth interval for all sites, and were measured immediately after sub-sampling (as described above). Measurements of sediment ORP 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 electrodes accuracy was tested daily with freshly made buffer solutions (pH = 7 and pH = 4) saturated with quinhydrone, as per the manufacturer's instructions (Cole-Parmer document #P1937). The ORP potential for each solution is measured and the difference between them calculated. If this value falls 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 the homogenized sediment, which was squeezed into a ball around the probe tip (to exclude any air bubbles) in the bottom of the plastic Whirl-Pak™ bag. The ORP meter was allowed to equilibrate for a minimum of 10 minutes, until a stable reading is achieved, prior to recording the milli-volt (mV) value. All measurements were taken while sediment was at room temperature (19-22 ^oC). The ORP meter values were converted to Eh values (which is a standard convention that adjusts the value assuming a normal hydrogen reference electrode), using the following conversion:

$Eh = ORP\ (meter\ value) + E_R$

$E_R = (-0.718 \times T) + 219.97$

Where: E_R = is the standard potential for a normal hydrogen reference electrode;
T = temperature (^oC)

Bulk Density, Percent Dry Weight, Porosity and Organic Content

Sub-samples for sediment bulk density, dry weight, porosity and organic content were taken at every depth interval for all sites. All of these parameters are assayed in order from a single sediment sample. An exact 3.0 cm^3 of wet sediment is removed from the sample vial using a 3.0 cm^3 plastic syringe that has the needle end cut off of the syringe barrel. This sub-sample is transferred into a small crucible and weighed. Sediment bulk density (g/cm^3) is then calculated as the weight:volume ratio.

Sediment dry weight and porosity are measured using standard drying techniques (APHA, 1981a).The crucible is then placed in an oven over-night at 105 ^oC. The next day, the sample is placed in a dedicator to cool, and is then reweighed. The sediment percent dry weight is then calculated as [dry sed wt./wet sed wt. x 100]. Sediment porosity (ml porewater per cm^3 of wet sediment) is calculated as the volume of water lost upon drying divided by the original sediment wet volume.

Organic content is calculated via the Loss on Ignition (LOI) standard assay (APHA, 1981b).The crucible is then placed in a combustion over at 500 ^oC for four hours. This completely burns off any organic constituents, leaving only mineral material. After recooling and reweighing, the weight loss is calculated, which is a measure of total organic content.

Grain Size

Sub-samples for sediment grain-size were taken at every depth interval for all sites. Grain size, greater or less than 62 microns (the sand/silt split), was assayed using a standard wet sieve method (Matthes et al. 1992).

Water

Total Mercury (low level)

500-ml acid-cleaned borosilicate glass containers with BrCl preservative provided by the laboratory are used for sample collection. Unfiltered samples are analyzed for Hg using EPA Method 1631, with a Reporting Limit of 0.50 nanograms per liter (ng/l). Total Hg was analyzed by TestAmerica (Morgan Hill, CA).

Methylmercury

250-ml acid-cleaned polycarbonate containers with HCl preservative provided by the laboratory were used for sample collection. Unfiltered samples were analyzed for Hg using EPA Method 1630 (modified), with a Reporting Limit of 0.050 nanograms per liter (ng/l). Methylmercury was analyzed by Brooks Rand Laboratory (Seattle, WA).

Total Suspended Solids

1-Liter polycarbonate containers provided by the laboratory are used for sample collection. Unfiltered samples are analyzed for total suspended solids using EPA Method

160.3, with a Reporting Limit of 1 milligram per liter (mg/l). TestAmerica analyzed TSS.

Dissolved Organic Carbon & Specific UV Absorption

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

Sulfate and Chloride

Overlying water sulfate and chloride are measured using ion chromatography according to EPA Method 9056A (USEPA, 2000), using a Dionex Ion Chromatograph (Model DX-300, Sunnyvale, CA). Samples are processed along with those for DOC (as above), but are not preserved with 0.1% HCl. Quality assurance measures include calibration standards, laboratory reagent blank, filter blanks, field blanks, laboratory fortified matrix sample, field duplicate samples, and continuing calibration check standards, as detailed in the above EPA method.

QA Procedures for Water

All field samples will be stored in wet ice-filled chests and delivered to the laboratory within 24 hours of collection.

Approximately 10% of the total number of water samples are field duplicates. TestAmerica is conducting analyses for unfiltered Hg and total suspended solids. TestAmerica will run the following QA samples per batch: one method blank, one matrix spike, one matrix spike duplicate, one laboratory control sample. The reporting limit for unfiltered Hg is 0.50 ng/l; the reporting limit for TSS is 1mg/l.

Brooks Rand is conducting analyses for unfiltered MeHg. Brooks Rand runs the following per batch: one laboratory fortified blank, several (> 5) continuous calibration verifications using an aliquot of the CRM DORM-2, one matrix spike, one matrix spike duplication, one method blank, two independent calibration verifications, and individual sample specific detection limits. The method used for MeHg is EPA Draft Method 1630 (Mod), as detailed in BRL SOP BR-0011. The MDL=0.020 ng/l and the PQL=0.050 ng/l.

Biota

Bird Blood and Feathers

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

Only avian blood data have been received back from the lab to date. Therefore, we report only the relevant analytical methods here. The remaining data and methods will be reported in future documents.

Blood samples were extracted from capillary tubes and diluted with 2.0 ml of double deionized water. Blood was then homogenized and prepared for total Hg analysis according to TERL SOP-ST16, reducing volumes of reagents to account for small sample volume. Prior to analysis, blood samples were digested using nitric acid, sulfuric acid, potassium permanganate, and potassium persulfate. Digest solutions were then reduced with hydroxylamine hydrochloride to eliminate excess MnO_2. Feather total Hg analysis utilized the same digestion process as blood. Blood and feathers were analyzed for total Hg using a Milestone DMA 80. Samples were placed in a nickel boat, combusted in an oxygen rich atmosphere, passed through a heated catalyst to complete oxidation, and then passed through a gold column which traps Hg. Post combustion, the gold column was heated and trapped Hg was released to quantify by atomic absorption.

For the blood samples, a laboratory blank, sample duplicate, matrix spike and duplicate, and two Certified Reference Materials (NRC-DORM-2 and NRC-DOLT-3) were run with each batch. A batch represents 20 samples. There was no Hg contamination in the lab blanks. Relative percent differences (RPD) for duplicates of blood analysis ranged from 7-24%, recoveries on the spike and spike duplicates ranged from 103-108%, CRM recoveries ranged from 98-103%. All QA were within acceptable guidelines for the project. For the 2006 lab analyses we used the CalFed QAPP for QA guidelines (Puckett and Van Buuren, 2000). Method blank concentrations for total Hg need to be below 0.002 ug/g, recoveries between 75-125%, and RPDs less than 25%.

V. Results and Discussion

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

Sediment

Multi-Sensor Core Logger Data

Sediment magnetic susceptibility and sediment density (via the gamma radiation method) results from the MSCL are provided in Figs. 2 and 3 respectively. These data were one of the screening methods used to determine specifically which depth intervals would be sub-sampled. Peaks in magnetic susceptibility indicate a higher concentration of magnetic minerals (e.g. Fe_3O_4) in that particular stratum. All analyses are complete and presented for these two parameters. The depth interval specific sediment bulk density, measured on sub-samples, is also shown in Fig. 3, demonstrating a good match between the two methods, particularly when the variation in sediment density was high for a given profile (e.g. T3-B and T4-B).

Mercury Speciation

Six (of nine total) profiles for Hg(II)R are complete and shown in Fig. 4. One notable feature is that the concentration of Hg(II)R tends to be higher at the sediment surface, particularly in vegetated marsh plain sites (i.e., A and C series). This parallels our findings in other San Francisco Bay studies and other ecosystems, which suggest that the proportion of HgT that exists as Hg(II)R is dependent on sediment redox conditions (Kieu 2004, Marvin-DiPasquale et al. 2006, Marvin-DiPasquale et al. 2005, Yee et al. 2005). Depth-integrated concentrations of Hg(II)R for the 0-200 cm profiles analyzed to date range from 376-1590 µg/m2.

Due to technical problems that we experienced throughout December 2006 with our automated total mercury analyzer, we have no HgT data to show at this time. However, the problems with the system have since been resolved and the HgT analysis is scheduled to commence in January 2007. Further, no sediment MeHg samples have yet been analyzed. The analysis of these samples is scheduled to take place in February 2007.

Additional Sediment Characterization Analyses

Oxidation-Reduction Potential and pH

Sediment ORP (converted to E_h) and pH measurements that were taken immediately after sub-sampling each depth interval are depicted in Figs. 5 and 6, respectively. All measurements for both parameters are complete. Sediment E_h values were generally highest at the sediment surface and decreased with sediment depth. This trend was most notable in the vegetated marsh sites (series A and C). Conversely, sediment pH was typically lowest (most acidic) at the sediment surface and increased with depth, and again this trend was most pronounced in the vegetated marsh sites.

Organic Content

All profiles for sediment organic content (as %LOI) are complete and shown in Fig. 7. Not surprisingly, organic content tends to be highest at the sediment surface and decreases with depth, particularly in the marsh profiles. Specific discrete zones of low organic content can be seen in a number of cases (e.g. 100-140 cm in profile T4-B), which correspond to zones of high sediment density (Fig. 3).

Percent Dry Weight

All profiles for sediment % dry weight measurements are complete and shown in Fig. 8. Many of the down core variations in this parameter correspond to down core variations in many of the above parameters. Sites T3-B and T4-B are among the best examples of these multi-parameter correlations. Sediment porosity measurements are also fully complete, but are not graphically represented in the current progress report.

Water

Sampling was conducted on November 14 and 16, 2006. On November 14, samples were collected from three locations in Pond A8. On November 16, samples were collected from three locations in the slough and from three locations in marsh adjacent to the slough sampling locations.

As of this writing, laboratory results for only a portion of samples have been received. The objective of this sampling effort is to establish a baseline of environmental Hg and ancillary water quality measurements for comparing conditions before and after any operational changes in Pond A8. There are no historical or other data collected from Pond A8 for comparison to these data. Overlying water DOC and SUVA are described below. Field measurements and the available laboratory results are presented in Table 2 and Table 3. The results received to date meet quality assurance/quality control criteria.

The applicable water quality criterion for total mercury in water is found in the California Toxics Rule (CTR). For the Lower South Bay, the CTR criterion of 0.051 ug/l (51 ng/l) applies for both fresh and saline waters. One sample collected from Pond A8 exceeded the criterion (A8WF1: 54 ng/l).

The Regional Monitoring Program for Water Quality (RMP) collects water samples from several locations in the Lower South Bay. Although not directly comparable to Pond 8A, in 2004-2005 the RMP samples contained less than 0.010 ug/l (10 ng/l) of total mercury (SFEI 2006).

The data indicate that water in the pond is significantly more saline than water in the slough. Salinity values [4.00 percent (%) or 40.0 parts per thousand (ppt)] were identical at all pond sample locations and were twice as high as the values of 2.22% (22.2 ppt) and 2.39% (23.9 ppt) measured in the bay end of the slough (ASW3). At the fresh water end of the slough (ASW1) the measured salinity of 0.12% (1.20 ppt) was about forty times lower than the pond salinity. In the middle of the slough (ASW2) salinity at the surface (1.19% or 11.9 ppt) was about half the salinity measured at depth (2.09% or 20.9 ppt). Salinity values measured at the marsh sample locations were similar to the values measured at corresponding slough locations. Specific conductivity measurements varied with salinity.

The pH measurements were similar at all locations in the slough and marsh, ranging from 7.74 to 7.97. In the pond, pH was measured to be more alkaline in the surface samples (8.68 to 8.78) than in the marsh or slough; pH in the deep sample from the pond (A8WD1Deep) was measured at 7.43, which was slightly more acidic than the marsh and slough samples.

Dissolved oxygen concentrations were similar at all locations (ranging from 5.70 to 7.10 milligrams per liter [mg/l]) except for the deep pond sample (A8WD1 Deep, 1.73 mg/l) and one of the marsh samples (ASMW1, 12.3 mg/l). The low value in the pond may be the result of higher oxygen demand in the bottom sediments. The high value in the marsh was probably a sampling error.

Turbidity (ranging from 145 to 999 NTU) was higher in the pond than in the slough or marsh. In the middle (ASW2) and bay end (ASW3) of the slough, turbidity in samples at the surface (48 and 40 NTU, respectively) was about half that measured at depth (73 and 72 NTU). At the fresh water end of the slough (ASW1), turbidity was slightly higher than the other slough samples, and was about the same at the surface and at depth (89 and 90 NTU). Turbidity in the marsh samples ranged from 56 to 77 NTU, which were slightly lower than the slough samples.

In the pond, Total Suspended Solids (TSS) values reported by the laboratory ranged from 27 to 120 mg/l, with the lowest and highest values from the historic channel sampling location (A8WD1). TSS values reported for the borrow ditch samples (A8WF1 and A8WF2) were 52 and 34 mg/l, respectively.

THg values reported by the laboratory ranged from 28 to 54 ng/l, with the lowest value from the deep water sample (A8WD1 Deep). MeHg values reported by the laboratory ranged from 0.532 to 3.480 ng/l, also with the lowest value from the deep water sample (A8WD1 Deep).

Overlying Water DOC and SUVA

Concentrations of DOC (and associated SUVA values) for water samples collected during November 2006 from Alviso Slough, adjacent marsh sloughs draining back into Alviso Slough (during ebb tide) and Pond A8, are given in Table 3. Notable observations include: a) similar DOC concentrations between Alviso Slough and draining adjacent marsh sites, b) 6-10X higher DOC concentrations in surface waters of Pond A8, compared to Alviso Slough and marsh sites, c) extremely high DOC levels (> 100 ppm) in deeper bottom waters of Pond A8, d) similar SUVA values for Alviso Slough and draining marsh sites, and e) significantly lower SUVA values associated with pond A8. Since the SUVA measurement is a surrogate for the relative amount of optically active aromatic organic compounds (e.g. terrestrially derived lignins), the differences between SUVA values inside and outside of Pond A8 seem to be indicative of the fact that the DOC in the pond is derived largely from autochthonous sources (i.e. phytoplankton), while the DOC in Alviso Slough and the marsh sites is derived from a higher percentage of allochthonous material (i.e. terrestrial plants). All DOC/SUVA measurements are completed for the samples collected to date.

Overlying sulfate and chloride samples are awaiting analysis, scheduled for January.

Biota

Biota collections were successful in that sentinel species were present and readily captured in sufficient numbers (and appropriate sizes for fish) to complete the initial sampling regime (Table 4). Capture techniques were effective, and capture methods and gear were refined during the 2006 field season. The analytical lab was able to provide

total Hg measurements for all blood samples taken, despite the sample volume being extremely small (< 10 µL) in some cases. The conditions in the sloughs and ponds were challenging, given the unconsolidated sediment and varied terrain and rubble in the ponds. Choice of species was altered slightly from the original proposal to those in Table 1, as fish distributions became better understood. Extra samples of fish outside the target size ranges were given to USFWS for analysis of total Hg and stable isotopes of carbon and nitrogen. These data will be shared between the Project and the CalFed Bird Mercury Project.

We collected blood and feathers from Alameda song sparrows (n = 15), common yellowthroats (n = 4), marsh wrens (n = 1), and barn swallows (n = 1) from the marsh along Alviso Slough and the reference marsh along Guadalupe River. Longjaw mudsuckers and yellowfin gobies were collected from Alviso Slough Marsh, Pond A5, Pond A8SW, and Pond A7. Composites of Mississippi silversides (6 – 27 fish/composite) and three-spined stickleback (4 – 15 fish/composite) were collected from Alviso Slough Marsh, Pond A5, Pond A8SW, and Pond A7. Composites (6 – 22 fish/composite) of rainwater killifish were collected only from the ponds; killifish do not occur in the tidal marsh. Brine fly composites (10 – 350 flies/composite) were collected from ponds A5, A7, A8N, A8SE, and A8SW; flies were not present in the marsh so late in the year.

To date, we have received only the bird blood Hg results from the analytical lab. We are anticipating fly MeHg results later in January, and fish and bird feather total Hg results following receipt of the fly data.

Blood Hg levels in song sparrows ranged from 0.01 – 0.34 µg/g (Figures 9 and 10). Common yellowthroat Hg concentrations ranged from 0.22 – 0.58 µg/g ww. The barn swallow concentration was 0.1 µg/g ww, and the marsh wren had the highest value at 0.82 µg/g ww. Common yellowthroats had higher blood Hg concentrations than song sparrows (Wilcoxon $z = 2.75$, $p = 0.006$; Figure 11). Song Sparrows provided the largest sample size and are used for the statistical comparisons to follow. Sparrow blood Hg concentrations did not differ between Alviso Slough Marsh and Guadalupe River Marsh (Wilcoxon $z = 0.00$, $p = 1.0$; Figure 12). None of the South Bay bird blood samples were above the lowest observed adverse effects level (LOAEL) of 0.96 ug/g ww (Table 5; Evers et al. 2005).

The lack of difference in sparrow Hg between marshes indicates no extraordinary Hg exposure in the sampled area of Alviso Slough as compared to the reference marsh (Guadalupe Slough). Future sampling to further examine the question of how Hg exposure of tidal marsh birds in Alviso Slough compares to that in ambient marshes throughout the South Bay will occur in 2007. This future comparison will be much broader and more complete, because it will include a more extensive sampling of the South Bay ambient marshes (rather than just Guadalupe Slough) and will continue farther upstream into Alviso Slough, where watershed-specific Hg exposure may be more apparent.

The higher Hg concentrations in yellowthroats and wrens, in comparison to sparrows, suggest that insectivorous birds feeding on the aerial insect/vascular plant food chain may have higher Hg exposure than the more benthic-feeding sparrows. This difference could arise from wrens and yellowthroats feeding at a higher trophic level (e.g., they eat more predatory invertebrates such as spiders), or from the aerial food chain having higher baseline Hg due to a difference in primary producer uptake of Hg. Sampling in 2007 will include yellowthroats and wrens, both because they are more freshwater species that can be sampled farther up-estuary toward the proposed notch site in the Pond A8 levee, and to include in the sampling the species that may be most impacted by Hg.

In a related project, song sparrow blood recently was collected from three marshes along a salinity gradient on the Petaluma River with no known local Hg source upstream (SFEI unpublished data). Song sparrow blood Hg from the North Bay ranged from 0.06 – 1.04 µg/g ww, with an average concentration of 0.43 µg/g ww. North Bay data were more variable than South Bay data, due to differences among North Bay marshes. Despite the variability, North Bay ($n = 22$) sparrow blood Hg (ug/g wet weight) was significantly higher ($t = 5.48$, $p < 0.001$) than in the South Bay ($n = 15$; Figure 13). These results suggest that processes occurring in the North Bay marshes lead to higher bird blood Hg. Based on our general knowledge of these specific sites, marsh ecology, and Hg ecology, we hypothesize that differences in marsh plain elevation (or a correlate such as marsh age or organic matter content) may account for these differences in MeHg in the food web.

Extrapolations from studies of other species are necessary to compare the bird blood Hg we sampled with effects thresholds. Evers et al. (2003) found that common loon egg Hg levels were highly correlated with female blood Hg levels. Correlations can be confounded by intra-clutch (egg-laying order) differences in egg Hg levels, but as a generality we accept the correlation. A predictive effects model was developed based on egg Hg thresholds in songbirds (Evers and Duron 2006); bird blood Hg effects thresholds were predicted from a linear model of the relationship between egg and blood Hg. This model predicts thresholds for songbird reproductive effects (Table 5). It's important to note that these thresholds are not species-specific, but they are the best thresholds available to date.

None of the birds sampled from the South Bay had blood Hg levels above the predicted LOAEL. However, these thresholds were established for tree swallows and common grackles; song sparrows may be more sensitive to Hg effects at lower concentrations. Comparison to effects thresholds is useful in getting a general idea of the potential for effects from Hg exposure, but these results should not be interpreted as a true indication of risk. Species-specific thresholds are needed to fully quantify the risk.

VII. Phase 1 Sampling in 2007

Sediment

There are a number of ongoing analyses regarding the Alviso Slough deep cores that will carry on through March 2007. These include completing all Hg species analyses, taking X-ray images of the archive cores, putting together the FileMaker Pro output files of lithography descriptions, photography and X-ray images.

In addition, early 2007 will find us moving into Phase II of this project, which will include two shallow sediment sampling events focused in Pond A8, Alviso Slough and nearby salt marsh habitats.

Water

To examine seasonality, water will be sampled every other month (6 sampling events), and sediment will be sampled twice (once each during the wet and dry seasons), during Phase 1 in 2007. This temporal sampling is aimed at documenting the changes in Hg speciation that are likely to be associated with the strong seasonal shifts in multiple environmental parameters (drawdown through evapotranspiration, temperatures, DO, salinity and organic matter accumulation) that are typically observed in both pond and marsh environments.

Biota

The results from 2006 available to-date were useful for comparing Hg exposure in marsh plain birds in the bay-ward reaches of Alviso and Guadalupe Sloughs and for recognizing differences in Hg between species. Future sampling will be aimed at capturing more of the variation in tidal marsh songbird Hg by sampling farther upstream, sampling in more marshes, and sampling a variety of species along the salinity gradient (song sparrows, marsh wrens, common yellowthroats). Forthcoming laboratory results will be useful in refining the sampling plan for fish and flies.

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Tables

Table 1. Habitats to be compared between Alviso Slough Marsh, Pond A8, and reference marsh along Guadalupe Slough using the sentinel species listed.

Alviso Slough Marsh Habitat	Pond A8 Habitat	Sentinel Species
Marsh pannes and exposed slough sediment	Margins of managed pond	Brine fly *(Ephydra spp.)*
Benthic/demersal zone of tidal channels	Benthic/demersal zone of managed pond	Longjaw mudsucker *(Gillichthys mirabilis)* Yellowfin goby (*Acanthogobius flavimanus*)
Pelagic zone of tidal channels	Pelagic zone of managed pond	Mississippi silversides (*Menidia audens*) Three-spined stickleback (*Gasterosteus aculeatus*)
Vegetated marsh plain	Vegetated marsh plain (reference marsh Guadalupe Slough)	Alameda song sparrow *(Melospiza melodia)* Marsh wren *(Cistothorus palustris)*

Table 2. Surface Water Field Measurements, Total Mercury, Total Methyl-Mercury, and Total Suspended Solids. NA denotes data still pending, salinity is in percent (multiply by 10 to convert to parts per thousand).

	Total Hg ng/l	Total Methyl Hg ng/l	Total Suspended Solids mg/l	Salinity %	Dissolved Oxygen mg/l	Temperature °C	pH Units	Turbidity NTU	Specific Conductivity mS/cm	Sample Depth
Pond A8N Results	**November 14, 2006**									
A8WF1	54	3.480	52	4.00	6.91	14.6	8.78	173	83.5	Surface
A8WF2	32	2.460	34	4.00	6.51	14.9	8.68	145	77.8	Surface
A8WD1Surface	49	2.770	27	4.00	7.12	15.7	8.68	150	77.2	Surface
A8WD1Deep	28	0.532	120	4.00	1.73	16.2	7.43	999	100.0	1.25 meters
Alviso Slough Results	**November 16, 2006**									
ASW1Surface	NA	NA	NA	0.12	5.90	16.2	7.87	89	2.52	Surface
ASW1Deep	NA	NA	NA	0.12	6.90	16.2	7.91	90	2.49	2.75 meters
ASW2Surface	NA	NA	NA	1.19	5.70	16.0	7.83	48	20.1	Surface
ASW2Deep	NA	NA	NA	2.09	7.00	15.5	7.74	73	33.5	2.5 meters
ASW3Surface	NA	NA	NA	2.22	5.86	14.9	7.87	40	35.2	Surface
ASW3Deep	NA	NA	NA	2.39	6.08	14.9	7.85	72	37.8	1.75 meters
Marsh Results	**November 16, 2006**									
ASMW1	NA	NA	NA	0.16	12.3	15.0	7.97	69	3.19	Surface
ASMW2	NA	NA	NA	1.26	6.83	15.5	7.95	56	21.2	Surface
ASMW3	NA	NA	NA	2.00	6.70	13.5	7.96	77	32.3	Surface

Table 3. Alviso Slough and Pond A8 Water DOC and SUVA.
Concentrations of Dissolved Organic Carbon (DOC) and Specific Ultra-Violate Absorption (SUVA) in overlying water collected on November 14-16, 2006 from a) Alviso Slough, b) from adjacent marsh sites draining into Alviso Slough (during ebb tide), and c) from Pond A8. The deviation (DEV) for a single site is given in ( ), and represents the deviation about the mean from n=2 analytical samples. The DEV for a group of similar sites (e.g. Alviso Slough surface water), is given in bold below that grouping and represents the Standard Deviation of n=3 sites. In both cases, the percent deviation (% DEV) is also given. Quality control results for filter blanks and rinse water is also given.

Sampling Site	DOC AVG. (mg/L)	DEV	% DEV	SUVA @ 254 nm AVG. (L/mg/m)	DEV	% DEV
ASW1 surface SL	6.09			3.00		
ASW2 surface SL	6.24			2.34		
ASW3 surface SL	4.11	(0.02)	0.6	2.18		
Alviso SL Surface	**5.48**	**(1.19)**	**21.7**	**2.51**	**(0.43)**	**17.3**
ASW1 deep SL	5.52			3.21		
ASW2 deep SL	4.07			2.23		
ASW3 deep SL	3.47			2.21		
Alviso SL Deep	**4.35**	**(1.05)**	**24.2**	**2.55**	**(0.57)**	**22.4**
ASMW1 Marsh	5.72			3.25		
ASMW2 Marsh	6.16			2.46		
ASMW3 Marsh	6.87	(0.16)	2.3	2.68		
Adjacent Marsh Water	**6.25**	**(0.58)**	**9.3**	**2.80**	**(0.41)**	**14.6**
A8WF1 pond	41.47			1.32		
A8WF2 pond	36.64			1.39		
A8WD1 surface pond	36.41			1.40		
Pond A8 Surface	**38.17**	**(2.86)**	**7.5**	**1.37**	**(0.04)**	**3.2**
A8WD1 deep pond	101.65	(0.24)	0.2	1.12		
filter blank	0.33					
Rinse Water Avg.(n=3)	0.37	(0.03)				

Table 4. Sample size and size (length) limits for fish by species**.**

Species	Number of Samples from Ponds	Number of Samples from Marsh	Min. Length (mm)	Max. Length (mm)
Longjaw Mudsucker	5	5	82	110
Yellowfin Goby	5	5	90	119
Mississippi Silversides	5	5	39	66
Three-spined Stickleback	5	5	34	52
Rainwater Killifish	5	Not Present	33	56

Table 5. Blood mercury effects thresholds extrapolated from tree swallows and common loons and applied to songbirds (as per Evers et al. 2005).

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

Figure Legends

Fig. 1. Map of Alviso Slough/Marsh, Alviso Ponds, and Guadalupe River Marsh sampling locations for fish, flies, birds, water, and sediment coring in 2006.

Fig. 2. Magnetic susceptibility profiles for Alviso Slough deep sediment cores measured with the non-destructive MSCL prior to core sub-sampling. The various colored traces represent individual cores (D1, D2, D3, etc..) from a given sampling site, which were scanned separately.

Fig. 3. Sediment gamma density profiles for Alviso Slough deep cores measured with the non-destructive MSCL prior to core sub-sampling. The various colored traces represent individual cores (D1, D2, D3, etc..) from a given sampling site, which were scanned separately. The symbols (red circles) and connecting red lines represent the calculated sediment bulk density from the weight/volume measurements made on homogenized discrete depth-interval composites after core processing and sub-sampling. The Y-error bars indicate the width of the composited sediment interval.

Fig. 4. Sediment 'reactive' inorganic mercury ($Hg(II)_R$) profiles for Alviso Slough deep cores, as measured on homogenized discrete depth-interval composites. Symbols (blue diamonds) and Y-error bars as per Fig. 3. When shown, the X-error bars indicate the deviation about the mean of n = 2 samples. Note logarithmic (base10) scale on the X-axis. The 0 – 200 cm depth-integrated average $Hg(II)_R$ concentration is inset (yellow box).

Fig. 5. Sediment oxidation-reduction potential profiles for Alviso Slough deep cores, measured on homogenized discrete depth-interval composites immediately after core splitting and sub-sampling. Symbols and Y-error bars as per Fig. 4.

Fig. 6. Sediment pH profiles for Alviso Slough deep cores, measured on homogenized discrete depth-interval composites immediately after core splitting and sub-sampling. Symbols and Y-error bars as per Fig. 4.

Fig. 7. Sediment organic content profiles for Alviso Slough deep cores, as measured via the percent weight loss on ignition (%LOI) on homogenized discrete depth-interval composites. Symbols and Y-error bars as per Fig. 4. Symbols, Y-error bars and X-error bars as per Fig. 4.

Fig. 8. Sediment percent dry weight profiles for Alviso Slough deep cores, as measured on homogenized discrete depth-interval composites. Symbols, Y-error bars and X-error bars as per Fig. 4.

Fig 9. Blood mercury concentrations (ug/g wet weight) for Alameda song sparrow (*Melospiza melodia pusillula*), barn swallow (*Hirundo rustica*), marsh wren (*Cistothorus palustris*), and common yellowthroat (*Geothlypis trichas*) in South San Francisco Bay, 2006. Lower and upper end of box represents the 25^{th} and 75^{th} percentiles, horizontal line within the box represents the median value for the sample, and the whiskers show the minimum and maximum values of the sample.

Fig 10. Average blood mercury concentrations (ug/g wet weight) for BARS (barn swallows - *Hirundo rustica*), COYE (common yellowthroat – *Geothlypis trichas*), SOSP (Alameda song sparrow - *Melospiza melodia pusillula*), and MAWR (marsh wren - *Cistothorus palustris*) in South San Francisco Bay, 2006. Symbols represent bird species and colors represent mercury concentrations.

Fig 11. Common yellowthroats (n = 4) had higher mercury than song sparrows (n = 15; Wilcoxon z = 2.75, p = 0.006). Bars represent means, dots represent individual sample measurements, and error bars are 95% confidence intervals.

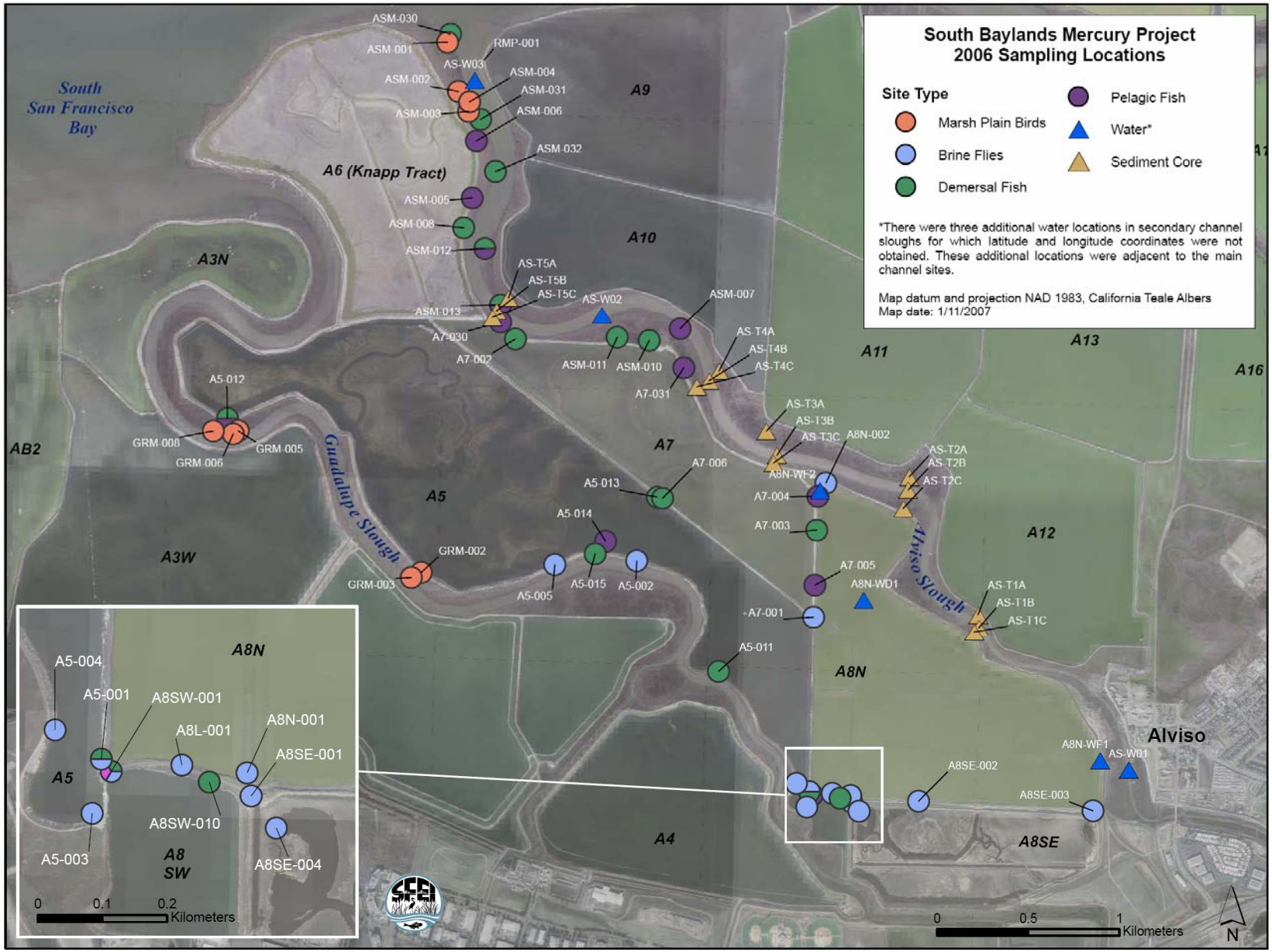
Fig 12. Sparrow blood mercury concentrations (ug/g wet weight) did not differ (Wilcoxon z = 0.000, p = 1.0) between Alviso Slough Marsh (n = 9) and the reference marsh (Guadalupe Slough; n = 6).

Bars represent means, dots represent individual sample measurements, and error bars are 95% confidence intervals.

Fig 13. North Bay (n = 22) sparrow blood mercury (ug/g wet weight) was significantly higher ($t = 5.48$, $p < 0.001$) than in the South Bay (n = 15). Bars represent means, dots represent individual sample measurements, and error bars are 95% confidence intervals.

Figures

Figure 1.



Alviso Slough Deep Cores (October 2006)

Magnetic Susceptibility

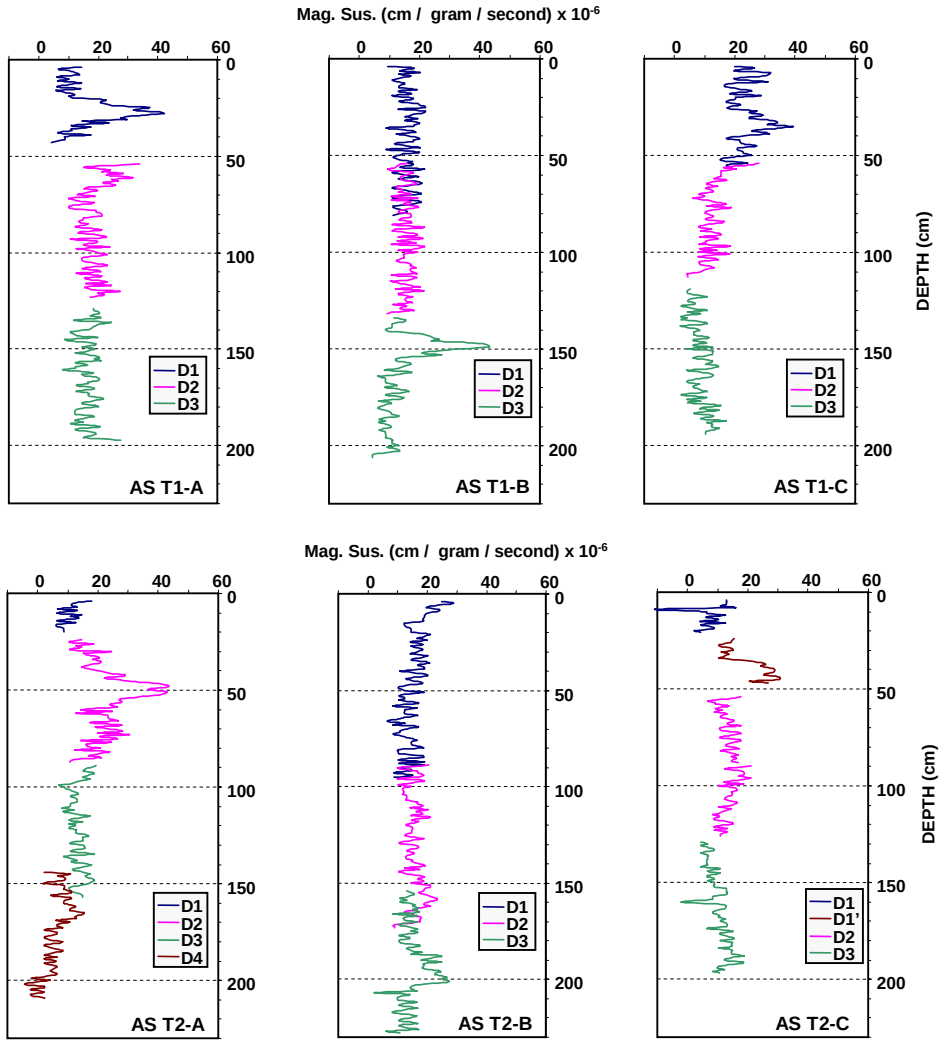
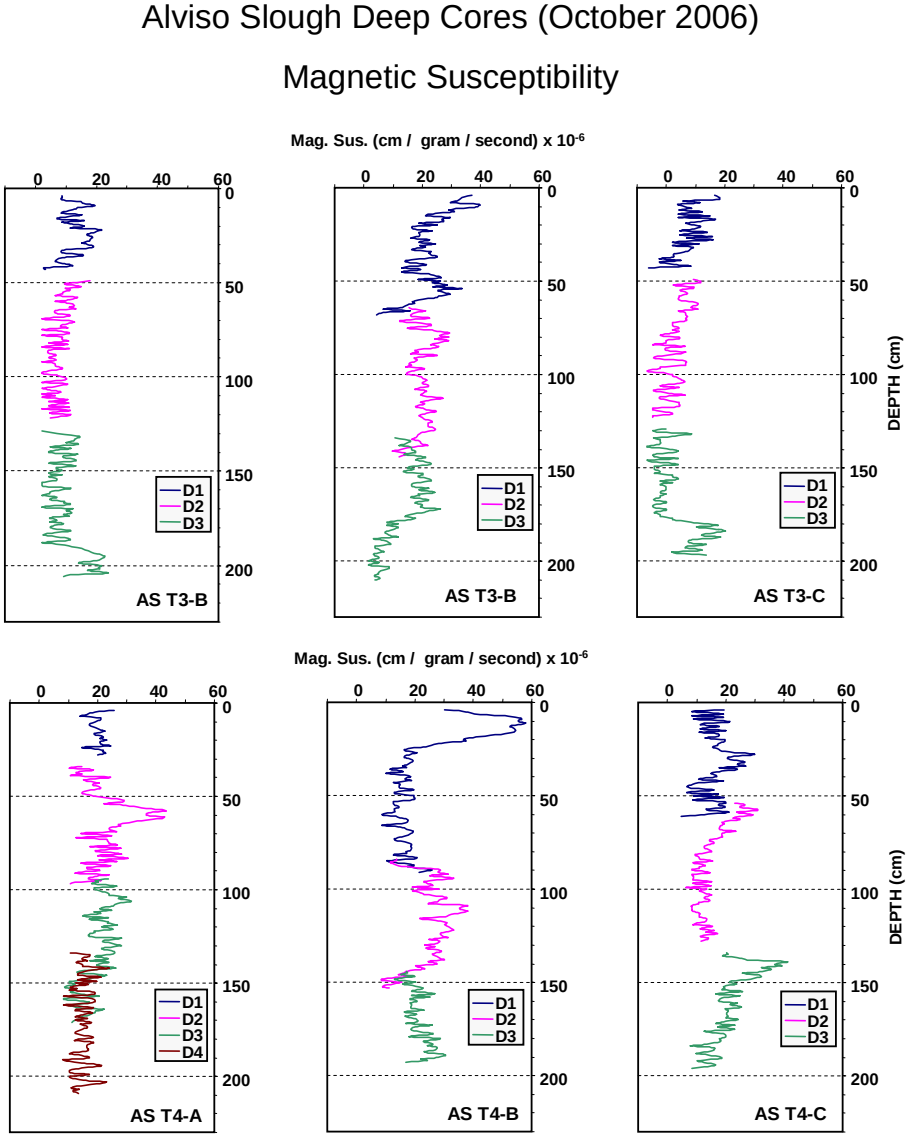


Figure 2.



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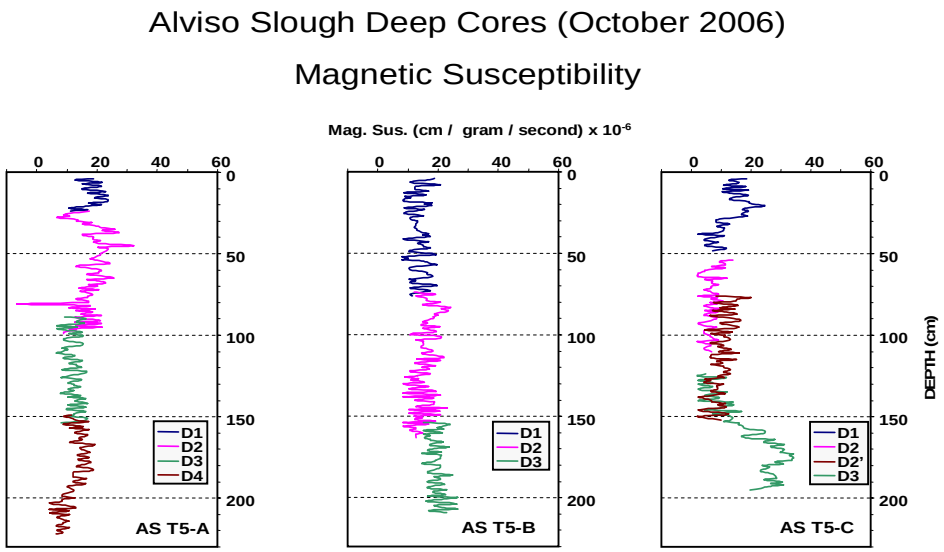


Figure 2. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Bulk Density

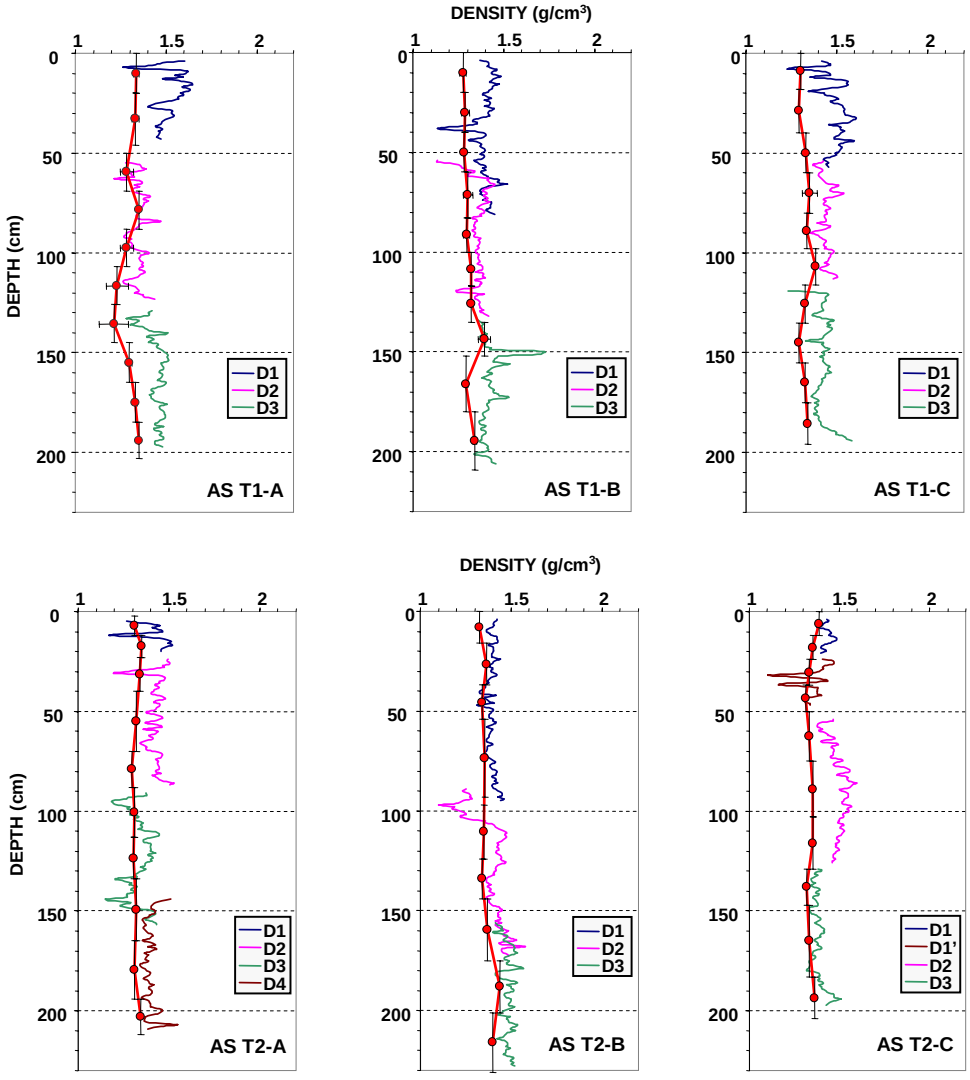


Figure 3.

Alviso Slough Deep Cores (October 2006)

Sediment Bulk Density

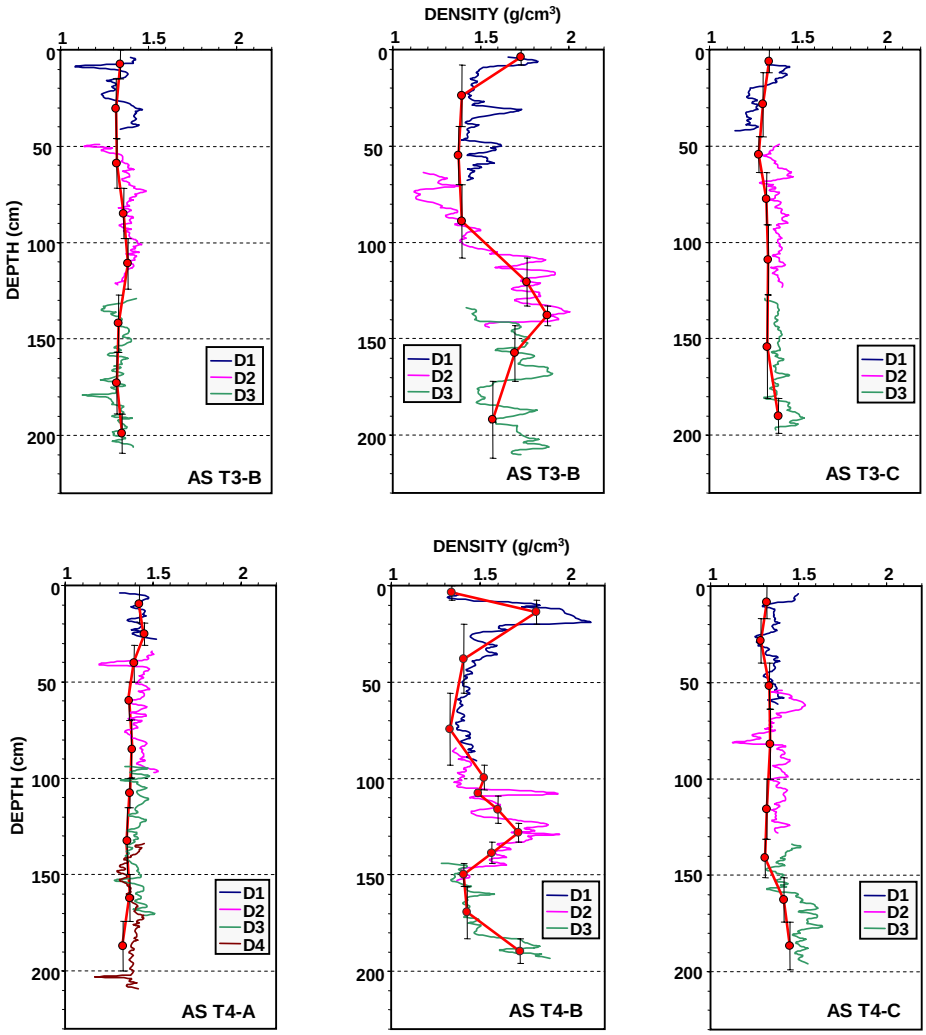


Figure 3. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Bulk Density

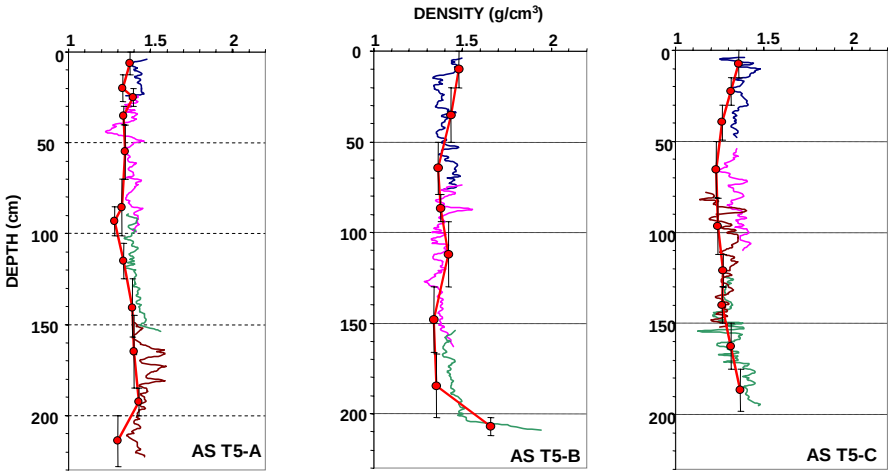


Figure 3. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Reactive Inorganic Mercury

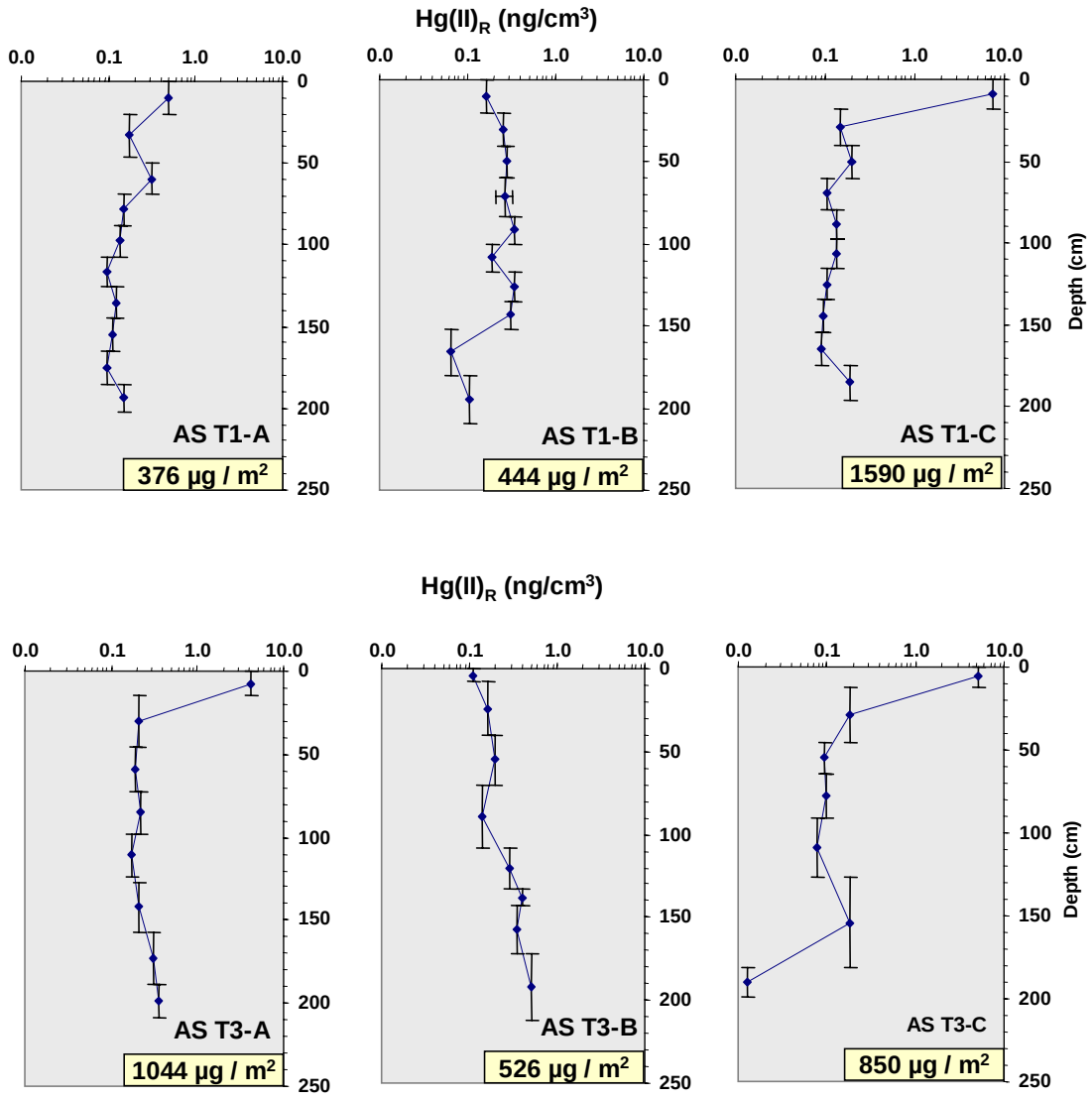


Figure 4.

Alviso Slough Deep Cores (October 2006)

Sediment Oxidation-Reduction Potential

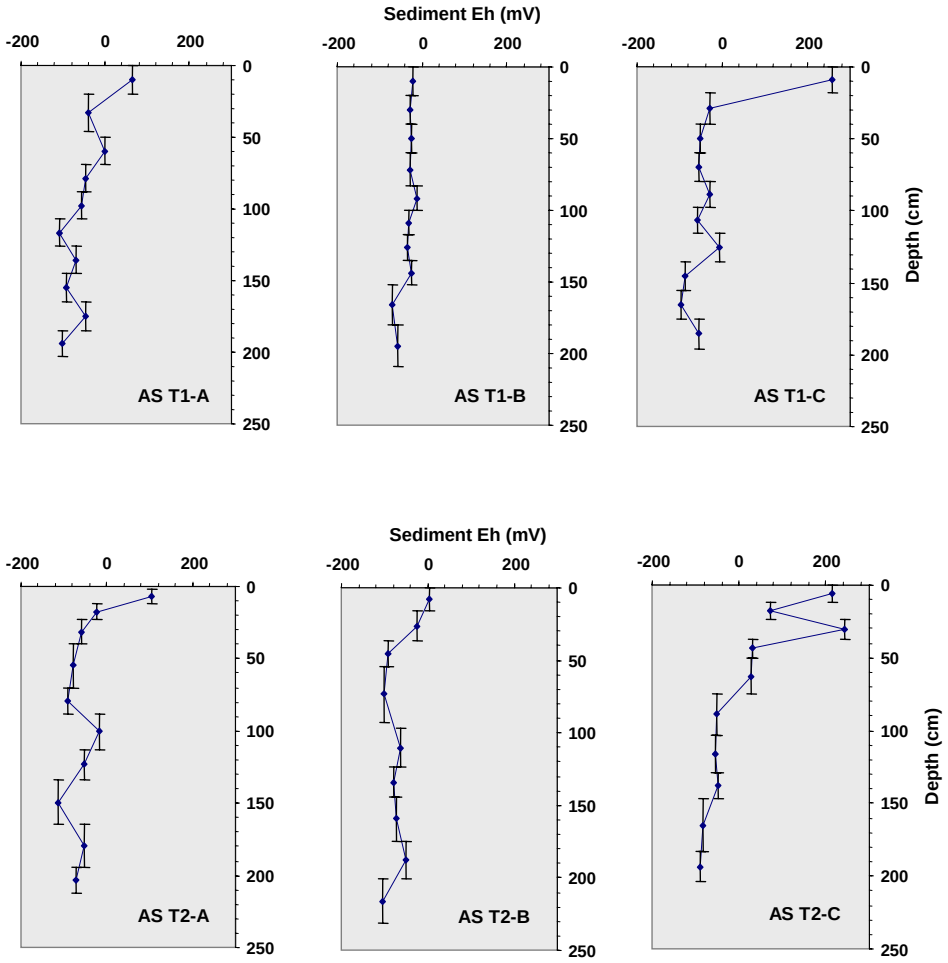
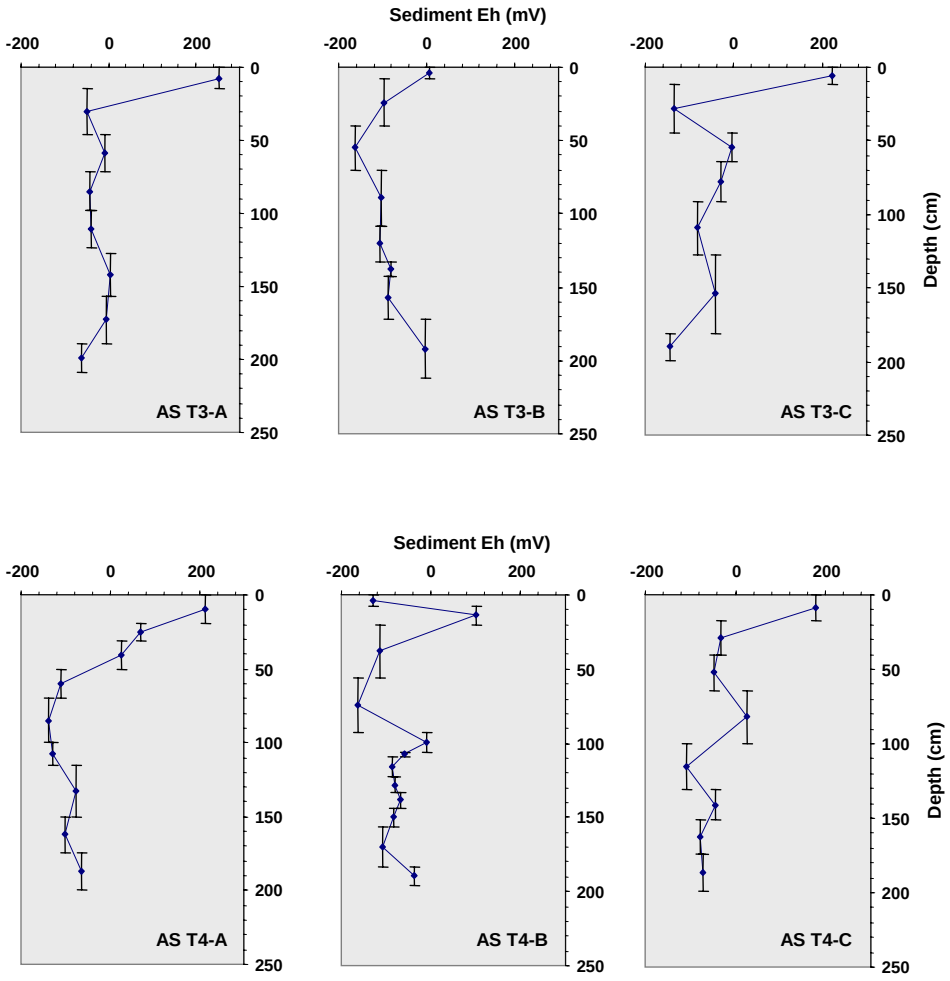


Figure 5.

Alviso Slough Deep Cores (October 2006)

Sediment Oxidation-Reduction Potential



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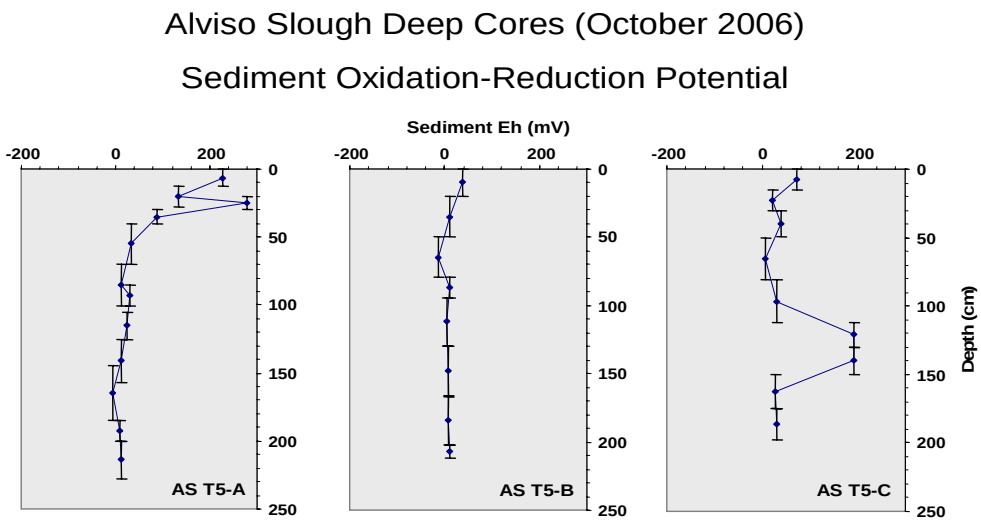


Figure 5. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment pH

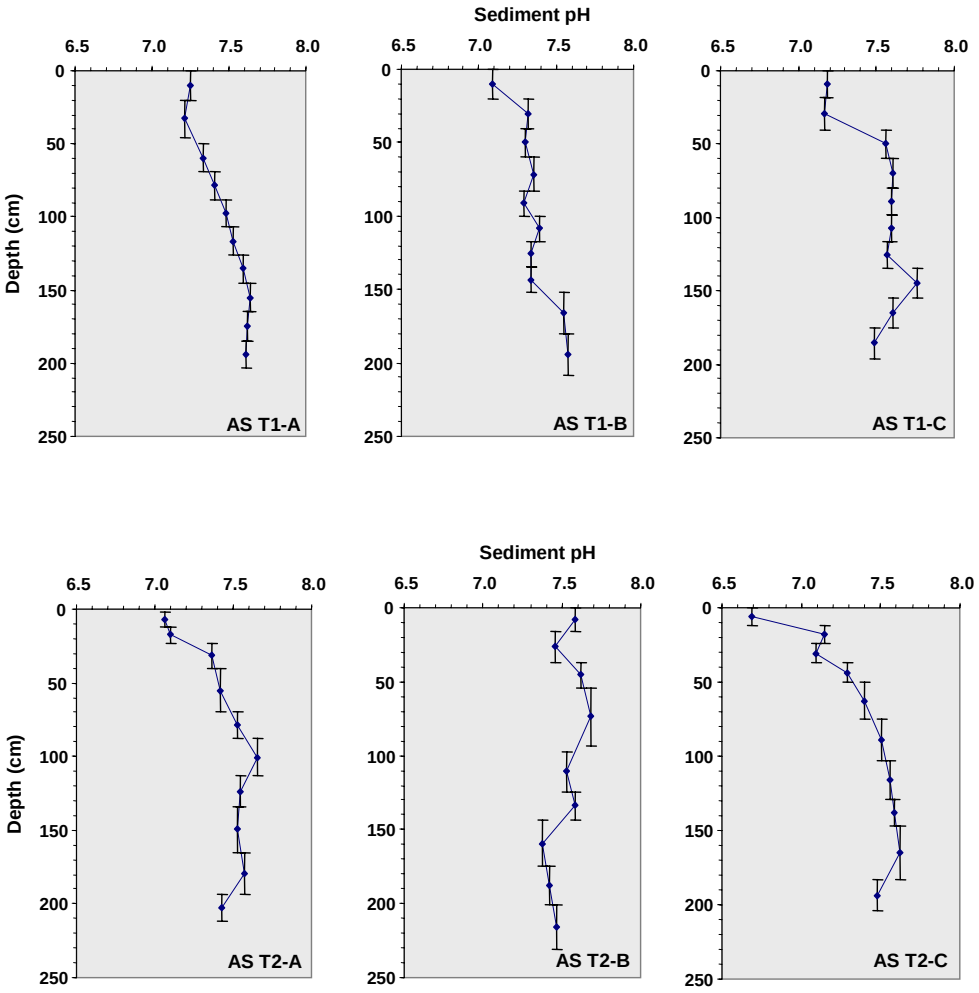


Figure 6.

Alviso Slough Deep Cores (October 2006)

Sediment pH

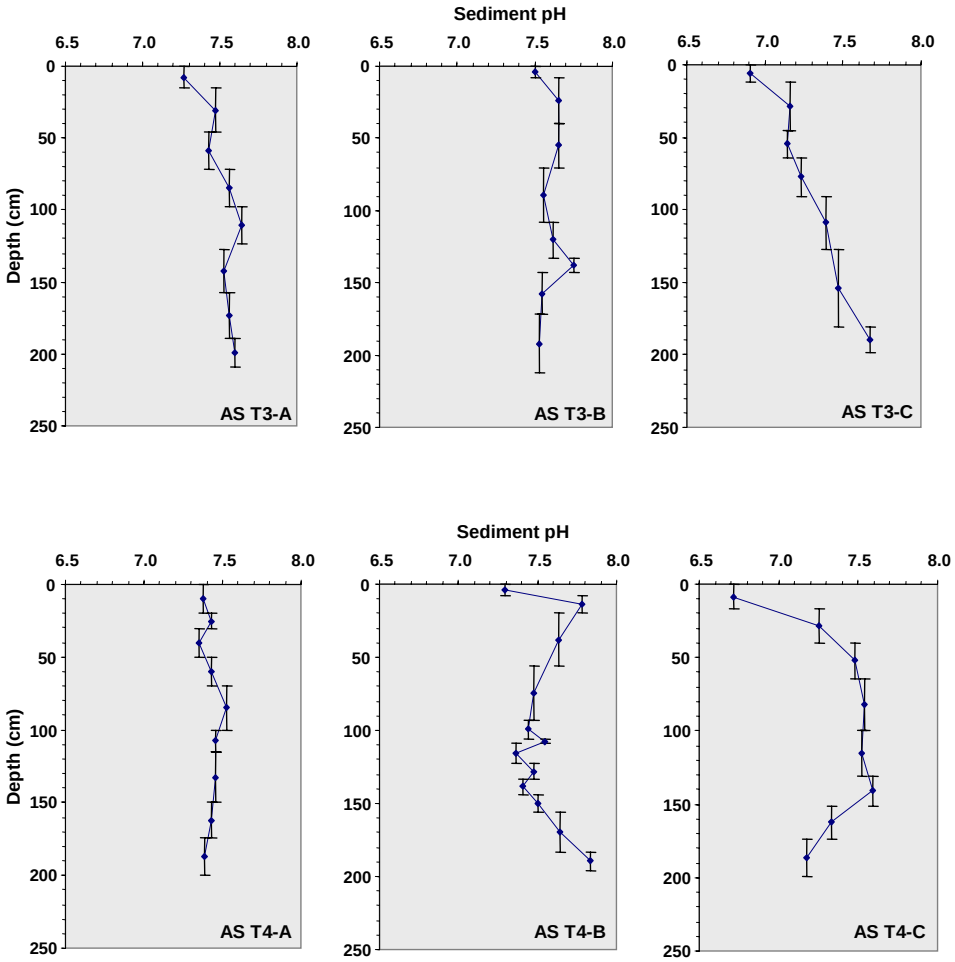


Figure 6. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment pH

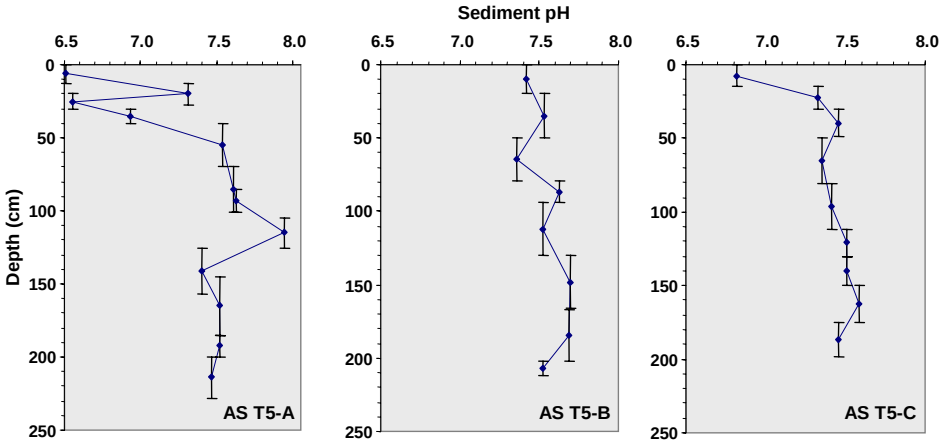


Figure 6. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Organic Content

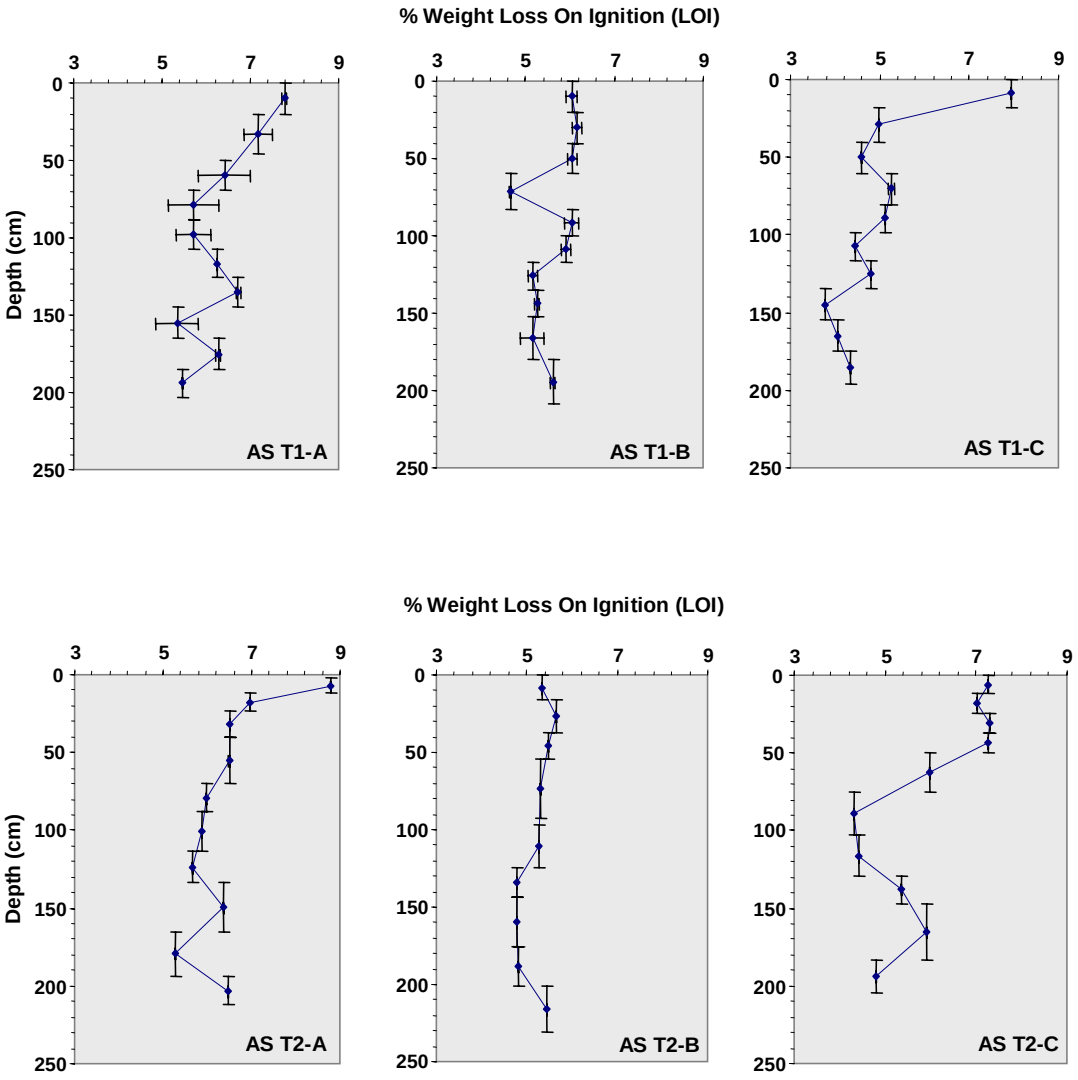
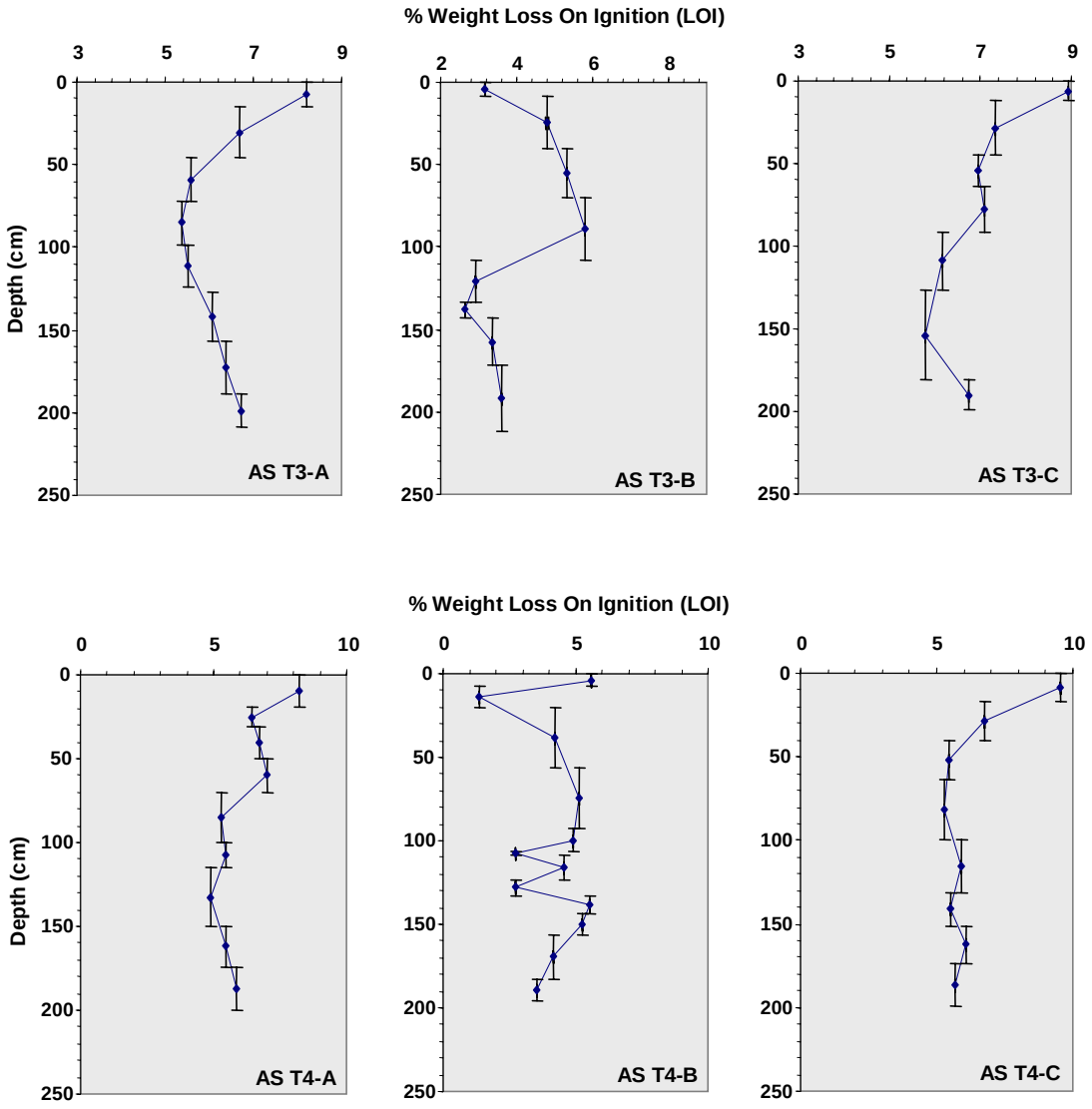


Figure 7.

Alviso Slough Deep Cores (October 2006)

Sediment Organic Content



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Alviso Slough Deep Cores (October 2006)

Sediment Organic Content

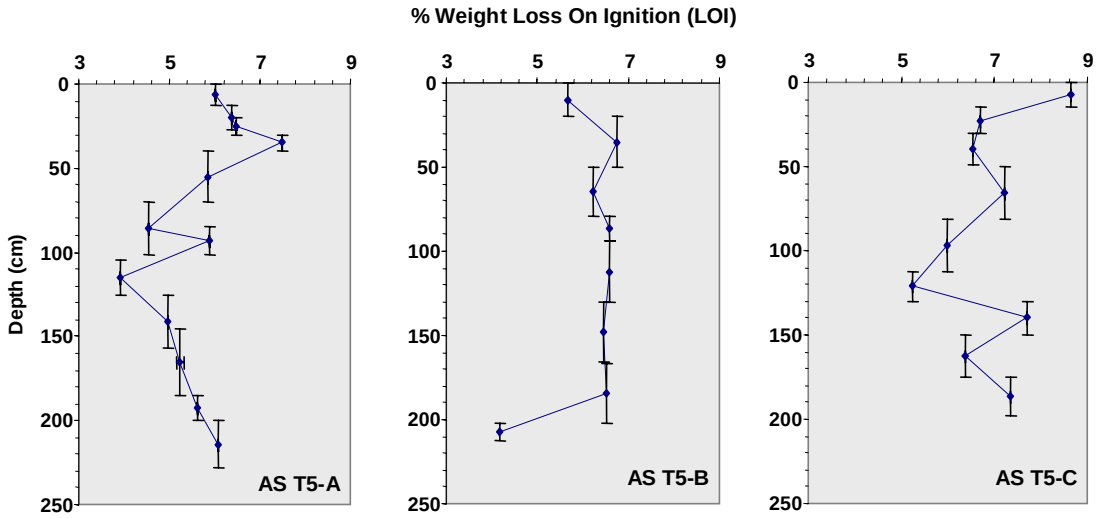

Figure 7. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Percent Dry Weight

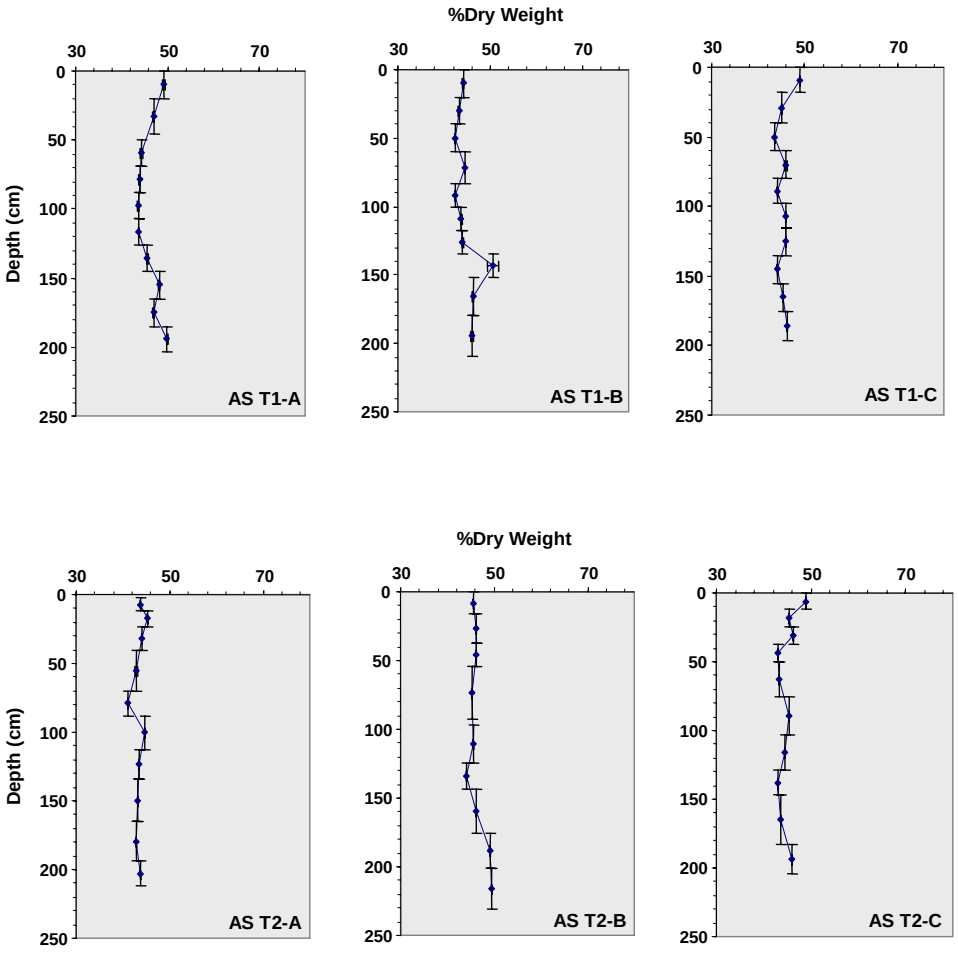

Figure 8.

Alviso Slough Deep Cores (October 2006)

Sediment Percent Dry Weight

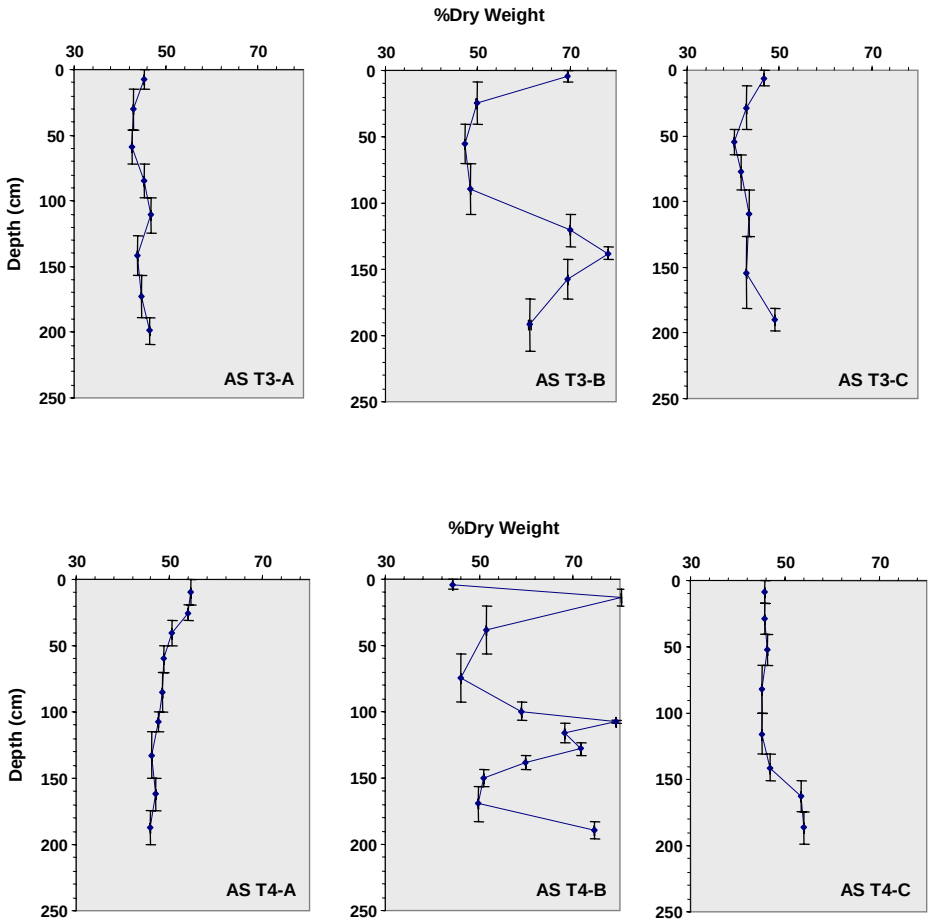

Figure 8. (continued)

Alviso Slough Deep Cores (October 2006)

Sediment Percent Dry Weight

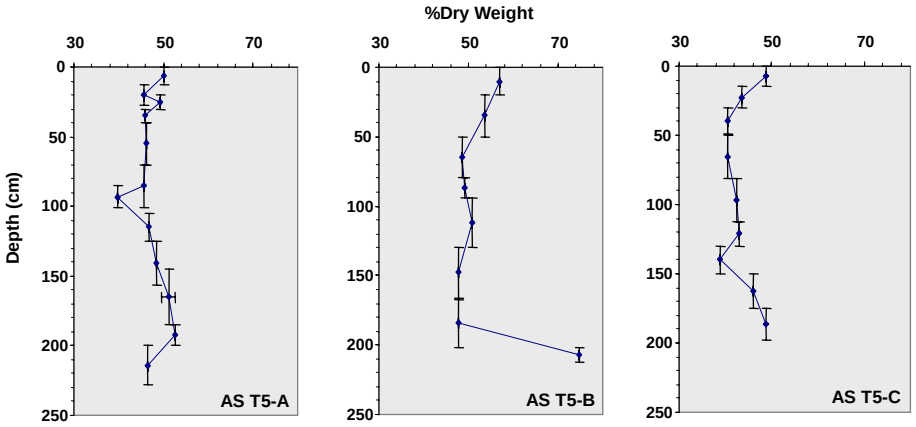

Figure 8. (continued)

Avian Blood Data by Species

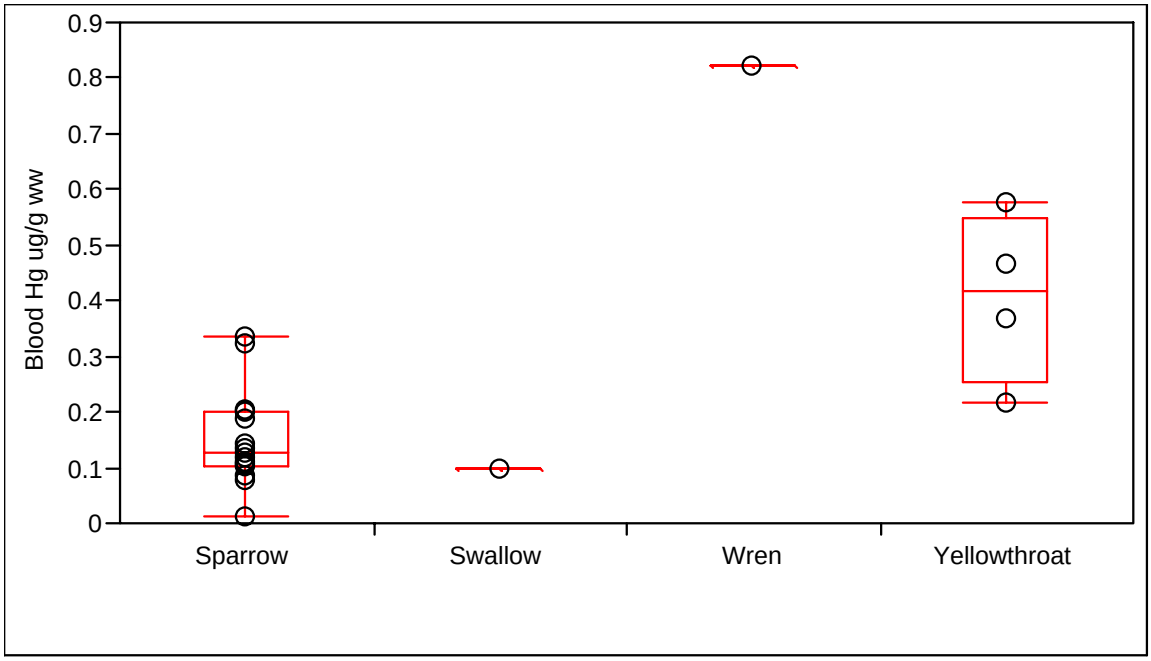

Figure 9

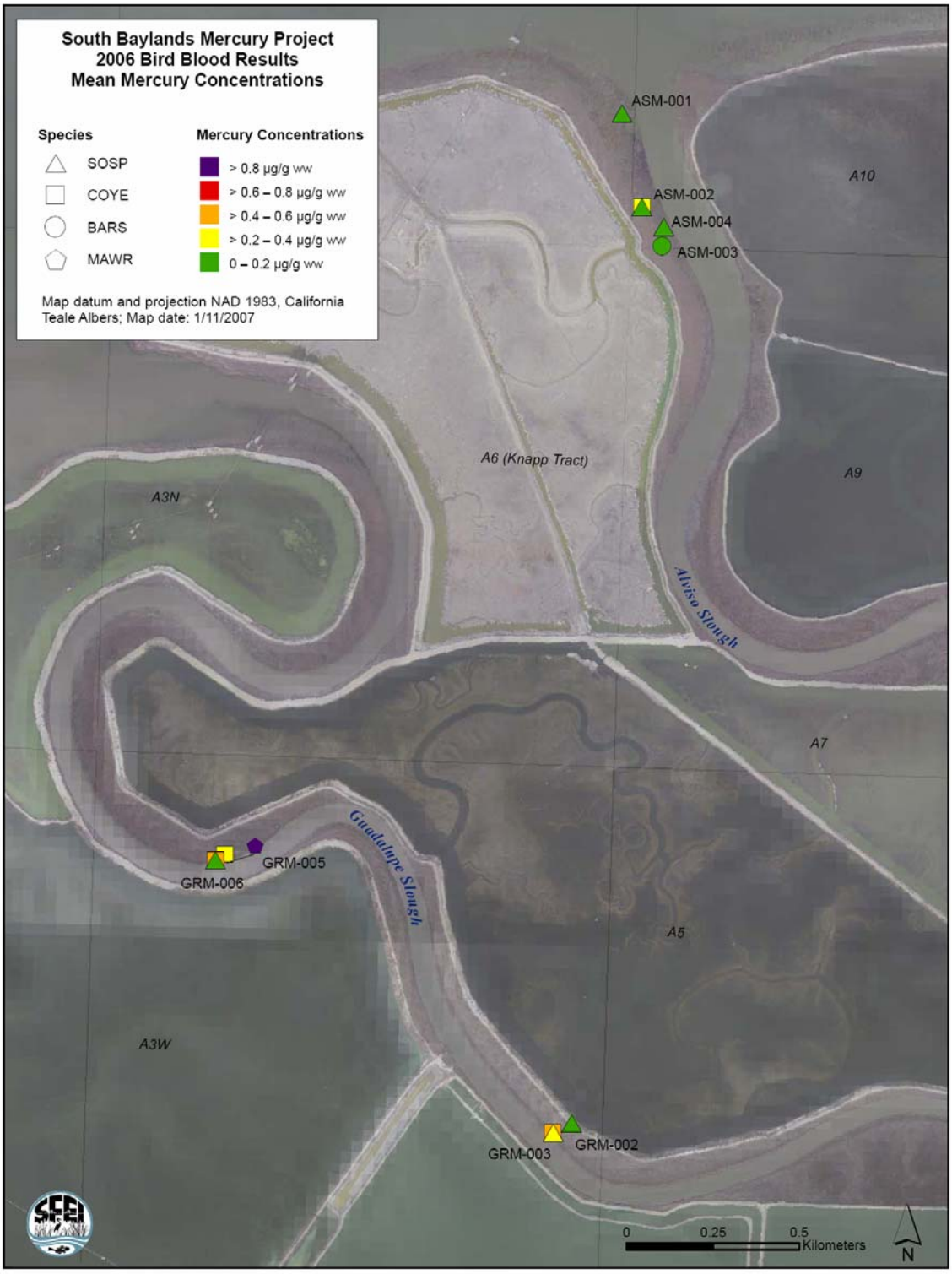
South Baylands Mercury Project
2006 Bird Blood Results
Mean Mercury Concentrations
Species
SOSP
COYE
BARS
MAWR
Mercury Concentrations
> 0.8 µg/g ww
> 0.6 – 0.8 µg/g ww
> 0.4 – 0.6 µg/g ww
> 0.2 – 0.4 µg/g ww
0 – 0.2 µg/g ww
Map datum and projection NAD 1983, California Teale Albers; Map date: 1/11/2007
ASM-001
ASM-002
ASM-004
ASM-003
A10
A9
A6 (Knapp Tract)
A3N
Alviso Slough
A7
GRM-005
GRM-006
Guadalupe Slough
A5
A3W
GRM-003
GRM-002
0
0.25
0.5
Kilometers
N

Figure 10

Yellowthroat and Sparrow Mercury Concentrations

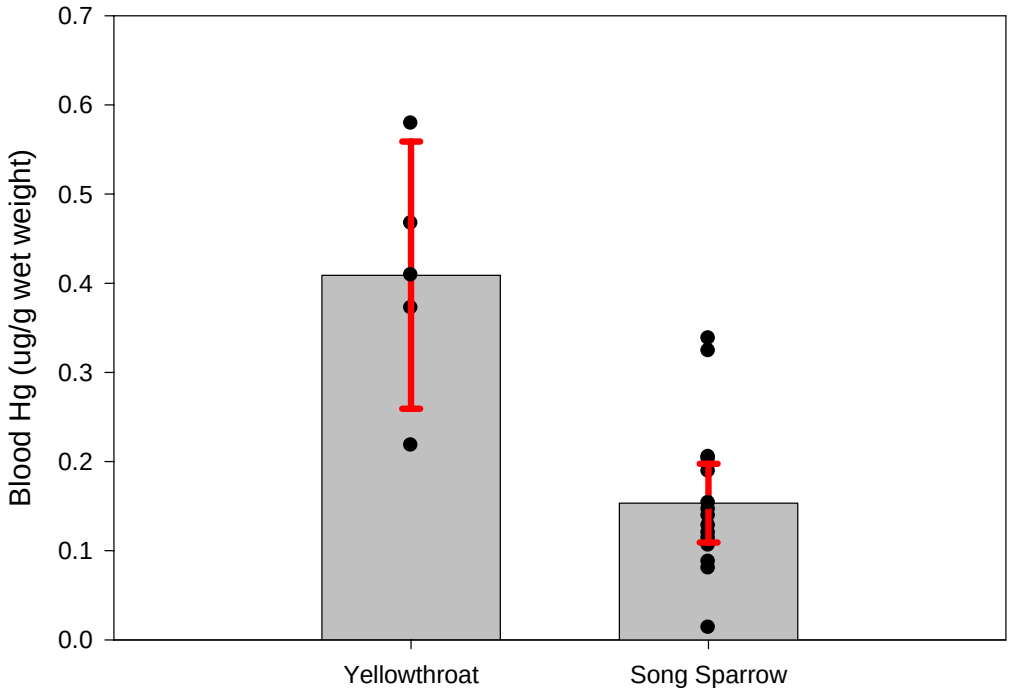

Figure 11

Sparrow Mercury Concentrations from Alviso Slough and the Reference Marsh

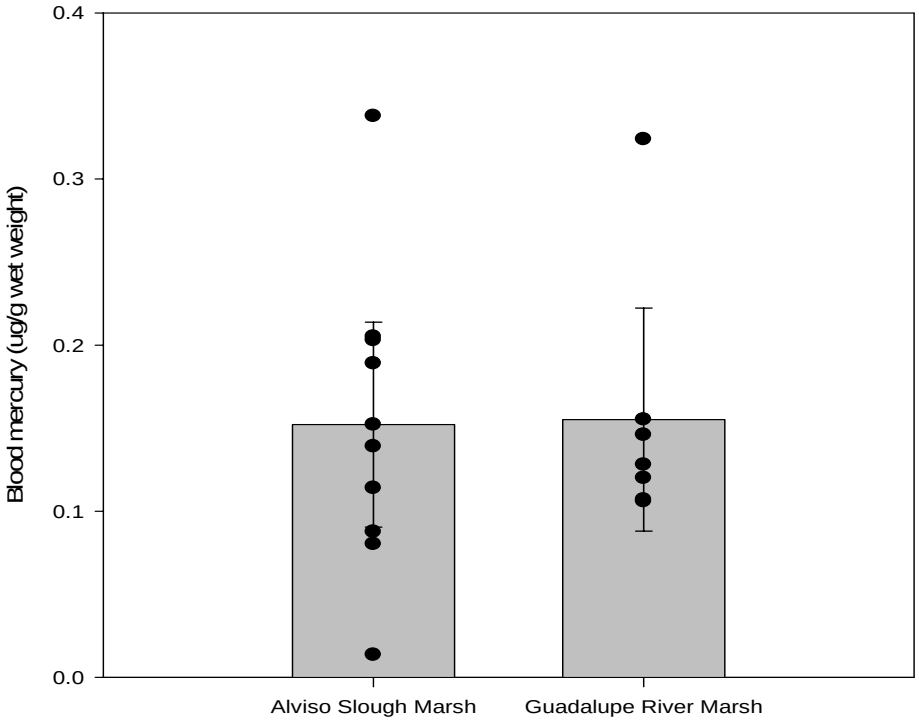

Figure 12

Sparrow Mercury Concentrations from North and South San Francisco Bay

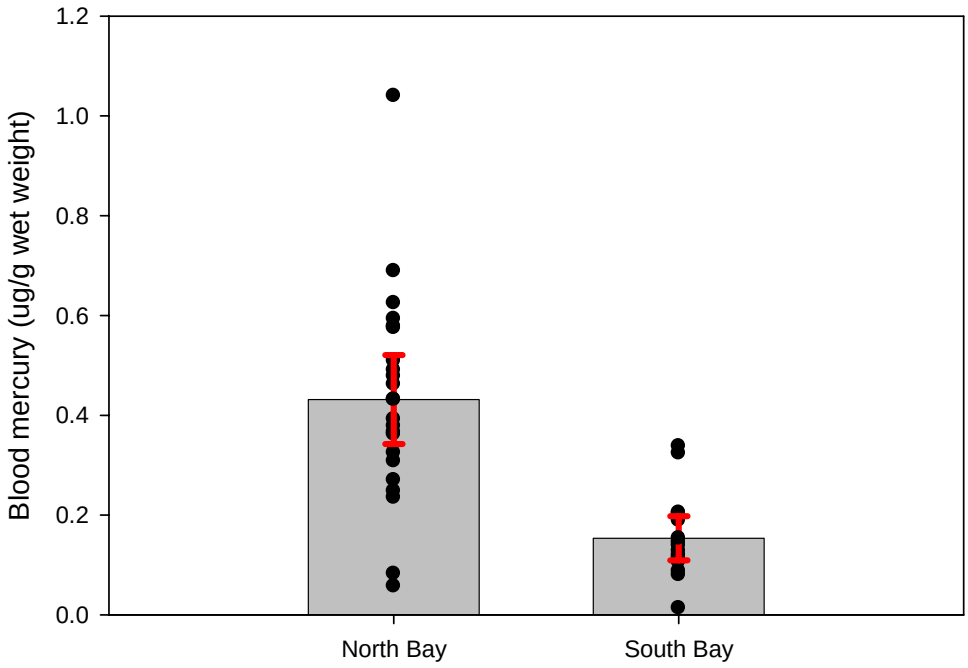

Figure 13