

Title: Mercury Methylation of Aquatic Plants: Using X-ray Absorption Spectroscopy (XAS) for Speciation

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Due to past mercury mining, in high mercury levels have resulted in the San Francisco Bay Area Delta. Of significant concern is the conversion to methylmercury, which is biomagnified up the food chain. *Eichhornia crassipes* (water hyacinth) is a non-native plant species found in abundance in the San Francisco Delta. The water hyacinth have become a problem by clogging the waterways and wetlands of the San Francisco Bay Delta and San Joaquin river. They are also known to accumulate mercury, especially in their dense and intricate root system. Previous attempts to curb their proliferation have centered on the use of herbicides which has shown to subsequently pose environmental concerns. Current methods include shredding the water hyacinth with specialized boats. The goal of our research is to better understand the ability of water hyacinths to phytoremediate mercury, and to determine the effect of shredding on mercury speciation in the hyacinths.

Plant samples were collected from the Dow Wetlands and grown in 1ppm HgCl₂ under (1) aerobic conditions, (2) anaerobic conditions, and (3) with shredded plant material only. Water hyacinth roots and shoots samples were analyzed for mercury using CVAA. Plants were also analyzed at Stanford Synchrotron Radiation Lab using X-ray absorption spectroscopy (XAS), a method to examine speciation that is element-specific and non-invasive.

As expected the roots had a greater concentration of mercury than the shoots, and shredded hyacinths had a lower mercury uptake than live hyacinths. XAS data on mercury in hyacinths were compared with concurrently collected XAS data on known inorganic and methylmercury forms, to complete the speciation process and determine whether shredding is affecting the degree of mercury methylation. We found that in plants grown live and aerobically, 5% of the mercury was in methylmercury form, with mercury-sulfur ligation to the plant. This percentage increases to 16% in live plants grown anaerobically, and to 22% in shredded anaerobic plants. Our conclusion is that shredding of the hyacinth plants increases mercury methylation, and therefore other methods should be used for hyacinth control. This is strongly relevant to the CALFED goal of minimizing mercury methylation in the Delta.

Cross-seasonal Implications of Hg Bioaccumulation of Mercury by Surf Scoters (*Melanitta perspicillata*) from the San Francisco Bay-Delta

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Abstract

The San Francisco Bay-Delta is one of the most important estuaries for wintering birds on the Pacific coast of North America. Migratory populations far outnumber local breeding species in the estuary; however, little is known about the cross-seasonal reproductive effects of mercury (Hg) accumulated during the winter. Poor body condition in migratory birds may be related to contaminant concentrations, resulting in delayed or depressed breeding, especially in species such as scoters that are long-lived with low annual productivity. To examine Hg effects on reproduction of migratory birds, we followed wintering surf scoters (*Melanitta perspicillata*) to nesting areas in the Northwest Territories (NWT) of Canada. Specifically, our objectives were to determine if Hg: 1) influenced body condition of pre-migratory birds, and 2) was found in eggs of nesting scoters. We collected 159 scoters in the winter of 2004-2005 to measure their body condition and Hg concentrations prior to migration. Preliminary analyses indicated a more than doubling of THg liver concentrations between early (0.4 ppm, wet weight) and late winter (1.1 ppm: $t_{38}=-3.62$, $P=0.01$), with greater site-specific concentrations in the North Bay (0.7 vs. 1.2 ppm: $t_{14}=2.33$, $P=0.01$). Proximate analyses of fat, ash, and protein in these birds were initiated to correlate Hg concentrations with condition effects through multiple regression models. We also captured and radio-marked a sample of nearly 90 scoters during the winter to track them to their boreal forest breeding areas. We successfully located 13 radio-marked and 8 satellite-marked scoters between the Great Slave and Great Bear Lakes in the NWT, and we collected eggs from a nesting female, one of the first nests documented for the species. The albumen and yolk of each egg was frozen separately for MeHg and stable isotope (to determine nutrient origin) analyses. Over the next two years, we will continue our cross-seasonal research to explain how Hg bioaccumulation in the Bay-Delta may be affecting reproduction of scoters breeding in the boreal forest.

Foraging Patterns of American Avocets (*Recurvirostra americana*) in San Francisco Bay

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Abstract

Accumulation of mercury depends, in part, on foraging areas and preferences. We examined variation in American avocet's (*Recurvirostra americana*) foraging patterns and home range sizes throughout the pre-breeding, breeding, and post-breeding seasons to determine dietary exposure. From March through July 2005, we radio-marked 50 avocets in the South San Francisco Bay and monitored 5 individuals from pre-breeding through post-breeding. Our results indicated that American Avocet space use varied with the stage of the breeding cycle. Pre-breeding habitat use was primarily non-tidal salt ponds and some surrounding tidal areas, while avocets used only non-tidal salt ponds for nesting habitat. Pre-breeding home ranges (960 ha) and core use areas (133 ha) were greater than during the incubation stage (151 and 23 ha, respectively). Post-breeding home ranges (5,389 ha) and core use areas (1014 ha) were, in turn, greater than during pre-breeding and incubation stages. Pre-breeding and incubation stage core use areas often overlapped, indicating that avocets were prospecting in potential nesting locations prior to egg-laying. Core use areas during the incubation stage were centered on nest locations. Our results indicate that avocet foraging areas are much larger during the pre-breeding season than during the breeding season when foraging is localized near nesting sites. These results suggest that avocets are likely to be exposed to varying levels of mercury contamination during the egg formation period.

Foraging Areas of Forster's terns (*Sterna forsteri*) at Three Breeding Colonies in San Francisco Bay

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Abstract

We examined Forster's tern (*Sterna forsteri*) foraging patterns and home range sizes at three nesting colonies in the San Francisco Bay to determine dietary exposure and potential sites of mercury accumulation. In 2005, we captured and radio-marked 31 pre-breeding Forster's terns at three colonies and tracked them daily by truck or aircraft throughout the breeding season. We examined space use by each tern colony and estimated home-range and core area sizes. Home-range size of foraging terns averaged $5,843 \pm 1,016$ ha with a core-area size of 864 ± 206 ha. Although there was some overlap in areas used by each of the three tern colonies, foraging areas differed among colonies. Additionally, each colony's core use area encompassed artificial salt evaporation ponds, indicating the importance of salt pond habitat for tern foraging and contaminant exposure. Our results indicate that terns range widely from colonies, forage in distinct areas based on colony location, and primarily use salt pond habitats. These results suggest that terns can be exposed to distant sources of mercury contamination, exposure depends on colony location, and terns mainly forage in salt evaporation ponds where mercury levels can be high.

Mercury Influence on Growth Rates of Forster's Tern (*Sterna forsteri*) Chicks in San Francisco Bay

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Abstract

We examined mercury (Hg) concentrations and growth rates of Forster's tern (*Sterna forsteri*) chicks from four nesting colonies in the San Francisco Bay as part of a CalFed-supported study to examine Hg risks to avian reproduction. Using mark-recapture methods, we captured, banded, weighed, and measured 680 Forster's tern chicks and recaptured 610 marked chicks. We captured all chicks within each breeding colony by hand every other week at A1 and A8 (South Bay) and weekly at A16 (South Bay) and Pond 2 (North Bay). For each chick, we estimated age using a multiple regression developed from a subset of our data that included chicks with known hatching dates. We then calculated mass, wing, culmen, and tarsus growth rates. For Hg analysis, we collected down feathers from the rump when chicks were first captured (to represent Hg levels in the egg) and collected pin or fully grown feathers from the breast of recaptured chicks (to represent Hg accumulated after hatching). We also collected a subset of these chicks just before they fledged at 24.2 ± 4.2 days old. We immediately processed chicks and analyzed Hg levels in blood, feathers, muscle, liver, kidney, and brain. Here, we present only Hg data from muscle as the other Hg analyses are in progress. We found significant differences in chick muscle Hg levels among tern colonies, but no overall difference in growth rates among colonies. However, at the individual level, wing, but not mass or culmen, growth rates of chicks declined with increasing concentrations of muscle Hg. These results underscore the importance of examining effects of Hg at the individual level. In the future, we will use our mark-recapture dataset to relate individual growth rates to Hg concentrations in feathers. This larger dataset will help elucidate the relationship between tern chick growth and Hg levels, and ultimately the ecotoxicological risk of Hg to avian reproduction.

Determining How Avian Embryos Differ In Their Sensitivity To Methylmercury

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Abstract

More field research is needed to study differences in embryo sensitivity under realistic natural conditions, although these studies are complicated by the presence of other environmental stressors. Laboratory breeding studies can control for other stressors, but the great cost and time required to conduct captive breeding studies with wild birds is going to severely limit the number of these studies undertaken. Most of what is known from the lab about toxic levels of methylmercury in bird eggs came from game farm species such as mallards (*Anas platyrhynchos*), ring-necked pheasants (*Phasianus colchicus*), and chickens (*Gallus gallus*). How the sensitivity of the embryos of the game farm species compares to the sensitivities of the embryos of wild birds is unknown. Using mercury injections into the eggs of wild bird eggs complements data from field and controlled feeding studies. In the future, combinations of field, controlled laboratory feeding, and hybrid field-lab studies (such as egg injection studies) will be required to gain a good idea of how the embryos of various birds respond to methylmercury exposure.

Egg Injections as a Hybrid Field-Lab Technique for Assessing the Embryotoxicity of Methylmercury to Different Birds

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Abstract

Part of the challenge in CALFED mercury research is to use controlled laboratory studies to determine how sensitive aquatic birds, particularly fish-eating species, are to methylmercury. Embryos are the most sensitive life stage in birds, so controlled breeding studies would seem to be the most logical approach. Unfortunately, because of the difficulty in raising aquatic birds in captivity to conduct reproductive studies, no controlled laboratory studies have been done to examine the effects of mercury on the reproductive success of fish-eating or other wild aquatic birds. To fill this gap in our knowledge, we developed a hybrid field-lab approach in which wild bird eggs are collected from the field and injected back in the lab with various doses of methylmercury. This approach bypasses the problems of breeding adults in captivity, while allowing control over the dosing of eggs. Our protocol involves injecting various doses of methylmercury dissolved in corn oil into the air cell of the egg. We discovered that the embryos of different species of birds differ in their sensitivity to methylmercury with some species being more sensitive than the mallards that have to date been used as a default species for wild birds.

Mercury Concentrations Vary Among Waterbird Foraging Guilds And Locations In San Francisco Bay

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Abstract

Legacy mercury (Hg) contamination of the San Francisco Bay (Estuary) and Sacramento-San Joaquin River Delta has resulted in elevated Hg concentrations in some species of invertebrates, fish, and waterbirds. Currently, there is concern that the on-going restoration of the Estuary and associated conversion of salt evaporation ponds to tidal marsh may alter Hg dynamics in the Estuary and adversely affect wildlife. In waterbirds, Hg bioaccumulation results from dietary exposure and is dependent upon several factors including space use, foraging habitat, and diet. We examined liver total mercury (THg) concentrations in four species of birds that occupy three distinct foraging guilds: diving benthivores (surf scoters, *Melanitta perspicillata*), littoral foragers (American avocets, *Recurvirostra americana*), and obligate piscivores (Forster's terns, *Sterna forsteri* and Caspian terns, *Sterna caspia*). We also assessed whether THg concentrations differed among sites for each species (North Bay, Central Bay, South Bay, and Suisun Bay). Between 3 March and 22 April 2004-2005, we collected livers from 32 surf scoters, 44 American avocets, 10 Caspian Terns, and 20 Forster's terns. Across all locations, THg concentrations were highest in Forster's terns, followed by Caspian terns, surf scoters, and American avocets. Both Caspian terns and Forster's terns had liver THg concentrations that were nearly three times those of American avocets and surf scoters. Conversely, THg concentrations did not differ significantly between Caspian terns and Forster's terns or between surf scoters and American avocets. THg concentrations in surf scoters differed between sites with Suisun Bay birds having liver burdens nearly twice those of Central Bay birds. THg concentrations in Forster's terns and American avocets did not differ among sites; however, mean Forster's tern values in the South Bay were nearly twice those from the Central Bay. Our results highlight the importance of foraging strategy and location in assessing the risk of Hg to avifauna and suggest that restoration goals should include an understanding of potential Hg accumulation and effects on reproduction based on foraging guilds.

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Mercury Dynamics in Forster's Terns (*Sterna forsteri*): Influence of Reproductive Status and Sex

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Abstract

The San Francisco Estuary has a legacy of mercury (Hg) contamination resulting from historic mining operations in the Coastal and Sierra mountain ranges. Current and proposed restoration activities in the Estuary have the potential to exacerbate management issues related to Hg. The goal of our CALFED funded project is to quantify the trophic transfer and pharmacodynamics of Hg in waterbirds dependent upon the estuary, and assess the ecotoxicological risk to avian reproduction. We collected adult Forster's terns (*Sterna forsteri*) within three major regions of the San Francisco Bay (North Bay, Central Bay, and South Bay) during both the pre-breeding (23 March – 20 April) and breeding (26 April – 28 June) time periods. We analyzed THg in muscle and liver in 20 pre-breeding (5 South Bay, 5 Baumberg, and 10 North Bay), and 28 breeding (16 South Bay and 12 North Bay) terns. THg concentrations in liver and muscle were highly correlated, with liver concentrations nearly three times that of muscle. We found no regional differences in liver or muscle THg concentrations; however, THg concentrations in both tissues differed among sexes and breeding status. Liver and muscle THg concentrations increased temporally from the pre-breeding to breeding seasons by approximately 50 percent. Although there were no differences in THg levels between sexes during the pre-breeding time period, breeding males had concentrations nearly double those of breeding females. Our results suggest that for piscivorous birds bioaccumulation occurs rapidly in the Estuary and that Hg deposition into eggs likely serves as an important mechanism for reducing overall body burdens in females during the breeding season.

Methyl Mercury Production in Two Freshwater Ponds in the California Delta

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Wetlands are important and vanishing habitats for birds, mammals, reptiles, the recruitment of juvenile fish and act to attenuate hydrological flow through the Bay-Delta complex. The loss and restoration of this habitat is a matter of concern for managers and regulators. Yet these habitats are also important chemical reactors, moderating the flow of carbon and nutrients. In the Delta, they are also sites of methyl mercury production, thus the restoration of wetland habitats must be informed from an understanding of chemical cycling in these systems. In 1997, two 2.7-hectare marshes were restored on Twitchell Island in the northwestern part of the Sacramento-San Joaquin Delta. The marshes, East Pond and West Pond, are rectangular-shaped, wetlands with different water depths, vegetation covers, and water flow patterns. The West Pond and East Pond have been maintained at constant water levels of approximately 25 cm and 50 cm, respectively. We monitored methyl mercury concentrations from the summer of 2003 until the summer of 2005 by periodically sampling import and export water and measuring the rates at which water flooded into and drained from East Pond and West Pond. The West Pond seasonally produced approximately ten times more methyl mercury in its export water than East Pond. There was also a seasonal pattern of methyl mercury production in both ponds that was most apparent in West Pond. Hypotheses to explain these differences include differential photoreduction of methyl mercury, varying rates of production within sediments and matted vegetation and hydraulic residence times. These processes are now being investigated. It is clear from this study that subtle changes in wetland restoration measures may dramatically affect methyl mercury production and could dramatically affect mercury concentrations in food webs from these systems.

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Spatial Relationships of Mercury exposure in California Black Rails along the Petaluma River, California.

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Poster Presentation

California Black Rails (*Laterallus jamaicensis coturniculus*) were captured at three independent sites along the Petaluma River, CA, in spring and summer 2005. Captured birds were radio-marked in the spring, and blood and feather samples collected for mercury analyses in both seasons. Home ranges differed among sites, and males (0.29 ha) had larger home ranges than females (0.18 ha). In spring, Black Rails preferred wet areas dominated by tall *Salicornia virginica* (25.8 - 35.0 cm mean hgt.) situated near upland habitat or other taller vegetation at all sites, where nests would be less likely to be flooded during high tide events. In summer, Black Rails were often found in areas of lower vegetation structure than in spring. Mercury concentrations in tissues differed significantly among sites. Females had lower (not significantly) mercury concentrations than males, possibly due to depuration of mercury into eggs. Understanding the spatial relationships of habitat use and mercury concentrations of threatened species such as the California Black Rail will aid in the design and management of tidal marsh restoration, a major concern in the San Francisco Bay area.

Trophic enrichment of Methylmercury in food webs of the Cosumnes River and Frank's Tract: Role of food web structure, habitat utilization and species-specific accumulation

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Biomagnification of Methylmercury in food webs can lead to excessive concentrations of mercury in sport fish that put wildlife and humans at risk. Trophic enrichment of mercury in nature remains poorly understood, although a number of processes have been identified as having an influence on mercury accumulation in ecosystems. These processes include: 1) attributes of the organisms themselves such as their size and age-specific growth rates, 2) food web dynamics (food chain length, community structure), and 3) life history characteristics (herbivory versus carnivory, habitat utilization). Although it is recognized that these processes modify mercury accumulation in food webs what is not often clear is their importance relative to other biogeochemical processes (loading, methylation – microbial processes) in understanding mercury accumulation overall. Here we show how mercury enrichment in food webs from two regions of the California Bay Delta ecosystem, Cosumnes River and Frank's Tract, is relatively insensitive to subtle differences in food web structure and species-specific attributes. The relationship between methylmercury concentration and trophic position in submerged aquatic vegetation (SAV) food webs were virtually identical for the two regions. Yet, the overall concentration in the Cosumnes River SAV food web was approximately twice that of the Frank's Tract food web. These results suggest that the amount of methylmercury entering the base of the Cosumnes River SAV food web was higher than that entering the Frank's Tract food web. It is unclear at this time if the higher concentrations at the base of the Cosumnes SAV food web are simply due to higher aqueous methylmercury concentrations or some other biological process enhancing methylmercury uptake into algae.

Sedimentary Mercury-Methylation Dynamics In Freshwater, Delta and Saltmarsh Regions of the San Francisco Bay Watershed

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The bacteria mediated conversion of inorganic divalent mercury (Hg(II)) to highly toxic methylmercury (MeHg), and the factors that control it, is an active area of ecosystem research. The specific controls on MeHg production in sediments are many, but can largely be grouped into those that either control the activity of the Hg(II)-methylating bacteria or control the availability of Hg(II) to those bacteria. Understanding the relative balance of these two types of controls, and how they changes over various spatial and temporal scales, is a critical step toward developing informed management decisions with a goal of minimizing MeHg production. CBDA sponsored research focused on benthic MeHg production is currently being conducted in multiple regions within the San Francisco Bay watershed. The data presented here compares results of such investigations, in three regions: a) a freshwater tributary (Cosumnes River), b) the fresh to brackish central Delta region (Frank's Tract), and c) a suite of high salinity salt marshes associated with the Petaluma River. In each region, and associated sub-habit, a suite of measures are used to assess controls in MeHg formation, including 1) reactive inorganic mercury (Hg(II)_R), a surrogate measure of the Hg(II) geochemically available to methylating bacteria; 2) radiotracer ²⁰³Hg(II) incubations to assess the activity of bacteria capable of methylating Hg(II)_R; 3) potential rates of benthic MeHg production calculate from (1) and (2); and 4) sediment in situ MeHg concentrations. These data indicate that i) MeHg concentrations and rates of production were highest in salt marsh sediments (i.e. Petaluma River high marsh and sloughs) and lowest in the central Delta; ii) this was largely due to 10X to 1000X higher rates of microbial sulfate reduction (and Hg(II)-methylating bacteria activity) in the Petaluma sites, which was ultimately driven by the significantly higher levels of sulfate in the high saline end of the system; iii) the percentage of Hg(II)_R increased as sediments become more oxic (less reducing), iv) this trend in Hg(II)_R largely drove the regional trend between the freshwater tributary and the central Delta where the later was more reducing and had a lower pool size of Hg(II)_R compared with the former; v) sites dominated by submerged aquatic vegetation had higher rates of MeHg production than open water and/or emergent marsh sites.

Minimizing Mercury Release and Methylation in River Restoration Projects in Watersheds Impacted by Historic Placer Gold Dredge and Hydraulic Mining

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River restoration projects underway in watersheds impacted by historic mining of gold placers and subsequent gravel mining include: (1) the removal of riparian berms; (2) channel and flood plain modification; (3) sediment augmentation; and (4) formation of wetlands. These projects involve redistribution of mercury (Hg)-bearing placer tailings, which can result in mobilization of Hg. Less-toxic species of Hg can be converted to highly toxic and readily bioaccumulated methylmercury (MeHg), if Hg-bearing materials or Hg derived from them enter environments favorable for Hg methylation. MeHg is produced by sulfate-reducing bacteria (SRB) that live in low-oxygen environments such as the uppermost few centimeters of sediments in wetlands and other aquatic environments. Many other types of microorganisms destroy MeHg by de-methylating it. The rates of microbially-controlled Hg methylation and demethylation vary in time and space, and control MeHg accumulation in sediments, waters, and the food web. In order to minimize the mobilization and methylation of Hg in restoration projects, placer mining methods and types of tailings present should be identified; concentration, distribution, and speciation of Hg in tailings should be determined; environments with active SRBs should be identified and methylation and demethylation rates measured; and subsequently this information should be incorporated in the planning, permitting, and implementation phases.

Knowledge of various methods of gold placer mining employed in a watershed is important to understanding and predicting the distribution of Hg and its potential for methylation, because Hg is associated with silt- and clay-size particles in tailings and sediments. In hydraulic mining, all but the coarsest material was washed through Hg-charged sluices, resulting in poorly-sorted tailings enriched in Hg. In contrast, dredges size-sorted material prior to gold recovery: pebbles and cobbles were discharged using a conveyor-belt stacker and only the finer material was exposed to Hg in sluices or on separating tables. The result is that piles of coarse poorly-sorted stacker tailings generally have low Hg concentrations, whereas the fine-grained, relatively well-sorted sluice tailings are enriched in mercury. Where floating dredges were used, sluice tailings were commonly discharged near the dredge and settled to the bottom of the dredge pond, then were covered by meters to tens of meters of stacker tailings as the dredge moved forward. Consequently sluice sands are rarely exposed at the surface, but they may be exposed during flood-plain restoration. These fine grained, well bedded deposits are easily distinguished from the coarse non-bedded stacker tailings. The basal part of the overlying stacker tailings may be enriched in mercury because of mixing with the sluice sands.

Much of the Hg^0 introduced into placer tailings has been transformed to other Hg species; now Hg^0 comprises less than half the total Hg present. However, Hg^0 may remain dominant at locations where large amounts of Hg were lost or spilled, such as drainage ditches and tunnels that were lined with sluices, and sites where dredges sank. Hg speciation studies by sequential chemical extraction indicate that organic-bound Hg, Hg sulfide, and Hg adsorbed on iron and aluminum oxyhydroxides comprise most of the

Hg present in dredge sluice tailings and in sediments contaminated with such tailings. Water-soluble Hg species are relatively minor (less than 5 percent). Column leaching studies and studies of Hg transport in lower Clear Creek indicate that soluble Hg and colloidal HgS can be removed from tailings during wetting and drying cycles such as those that accompany flood plain inundation, whereas other forms of Hg, especially Hg adsorbed on iron oxyhydroxides, are only removed and transported when tailings are eroded and physically entrained in stream waters.

Hg methylation has been examined in many environments in the lower Clear Creek restoration area, including dry tailings, stream waters and sediments, placer mine drainage sluiceways, ponds in tailings, flood-plain ponds and backwater areas, and constructed wetlands ponds. Measurement of MeHg concentrations has shown that some methylation occurs in all quiet-water environments, and some ponds, especially in tailings, support high methylation rates. These ponds have elevated levels of sulfate derived from various local sources, and their bottom sediments provide conditions ideal for the growth of SRBs. Determination of methylation-demethylation rates has shown that Hg-bearing muds in all pond environments generally have significant Hg methylation potential. The aquatic habitat supports a highly varied community of microorganisms; resulting Hg bioaccumulation and biomagnification in the vicinity of lower Clear Creek ponds has been verified by studies of Hg in biota at various trophic levels.

Based on speciation and column leach studies, tailings removed to lower the floodplain at Hocker Flat, in the Trinity River Restoration Program (TRRP), were disposed of on top of existing piles of stacker tailings located above the 100 year flood level. Recognition of sluice tailings in an area planned for wetland conversion in the TRRP resulted in redesign and relocation of the wetland. The Clear Creek and TRRP examples demonstrate that the management of unwanted Hg release during river restoration projects must address Hg sources and mobility, and also juxtaposition of Hg-bearing materials with environments that may enhance Hg methylation and bioaccumulation.

The Delta Watershed Fish Project: Reducing Exposure to Mercury in Fish through Outreach and Education

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1. Problem

Elevated levels of mercury in fish are present throughout the Sacramento-San Joaquin Delta watershed due to historic mercury and gold mining activities. The watershed is also an area with abundant fishing and a diverse multilingual population, who may be exposed to harmful levels of mercury by consuming contaminated catch. Remediation efforts are not likely to reduce mercury levels in fish for many years. The California Department of Health Services (DHS) coordinates the Delta Watershed Fish Project, an inter-organizational effort to increase public awareness about fish contamination problems and reduce human exposure to mercury in fish through a variety of research, outreach, education, and training activities.

Recent research activities include a survey of low-income women at a Women, Infants, and Children clinic to learn about fish consumption practices and advisory awareness in an ethnically diverse population. DHS convenes a stakeholder advisory group, comprised of community group, environmental organizations, and local agencies, to guide the project's outreach and education activities. The advisory group helps DHS to develop, translate, test, and distribute written educational materials (cards, brochures, posters, and warning signs) in multiple languages. DHS also awards mini-grants to local groups to support community-based outreach and education projects, provides training about fish contamination issues, and is convening a public forum on fish contamination issues in December 2005. DHS' outreach and education activities will continue through 2007 as part of the Fish Mercury Project, a three-year effort to monitor mercury levels in fish.

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CALFED Ecosystem Restoration Program
A Pilot Program for Monitoring, Stakeholder Involvement, and Risk Communication
Relating to Mercury in Fish in the Bay/Delta Watershed

ERP-02D-P67

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Poster Abstract

Mercury contamination in the Bay-Delta watershed is a legacy from the California Gold Rush of the 1800s. Top aquatic predators, such as seals, humans, and some fish, can accumulate high concentrations of mercury by consuming contaminated fish. Methylmercury is the most harmful form of this element since it can accumulate in biological tissues. Methylmercury formation has been linked to processes that occur in wetlands. Consequently, there is concern that large-scale wetland restoration in the Bay-Delta watershed could increase concentrations of methylmercury in the food web (Davis et al., 2003). Mercury in Bay-Delta fish has been detected at concentrations exceeding human health guidelines (Greenfield et al., 2003; Davis et al., 1999; Davis et al., 1998). The California Bay Delta Authority has developed a Mercury Strategy to provide a scientific framework for identifying sources of mercury, measuring mercury concentrations in fish and wildlife, assessing and communicating associated health risks, and finding ways to reduce sources of mercury and wetland methylation of mercury (Wiener et al., 2003). Following recommendations of the Mercury Strategy, the CBDA-funded Fish Mercury Project is currently monitoring the Delta watershed for mercury in fish in order to 1) assess and communicate human health risk, 2) measure how wetland restoration is affecting methylmercury accumulation in the food web, and 3) establish a scientifically defensible fish mercury monitoring protocol for the Delta watershed. Results of sport fish mercury analysis will aid in the development of fish consumption advisories for affected areas. In addition, small, short-lived fish species (biosentinels) will be used to measure short-term temporal and spatial changes in mercury concentrations due to CBDA wetland restoration projects in the watershed, as well as protocols that can be used to monitor future restoration projects.

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The Role of Submerged and Emergent Macrophytes in the Mercury Cycle of San Francisco Bay Wetlands

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A number of interactions between macrophytes and the mercury (Hg) cycle have been reported in recent years, such as the uptake and/or release of soluble or gaseous Hg species by wetland plants. While these processes may play an important role in the biogeochemical cycling of Hg, few if any plant-Hg process studies have been conducted in the San Francisco Bay (SFB) ecosystem. The current study examines regional differences in macrophyte characteristics and associated plant-Hg speciation concentration and fluxes in two dominant SFB vegetation zones: emergent marsh (dominated by tule, *Scirpus acutus*) and submerged aquatic vegetation (SAV; dominated by invasive *Egeria densa*). This research is one part of a larger multi-investigator study examining the processes underlying the previously reported regional differences in biota-Hg levels, which are generally low in the central Delta and high in the tributaries. Patches of SAV sampled in both regions had greater biomass (both live and dead) and a higher leaf:stem ratio in Frank's Tract (FT; central Delta study area) compared to SAV patches sampled in the Cosumnes River (CR; representative tributary study region). However, total mercury [THg] concentrations were consistently greater in CR SAV, such that areal pools of SAV-THg were not significantly different between the two regions. However, higher rates of SAV productivity, turnover and Hg uptake were evident in FT, when measurements of live and dead SAV biomass were compared for the March and July Sampling dates. A series of short-term (28 day) *E. densa* decomposition experiments demonstrated higher biomass loss rates under oxic conditions and higher THg release rate under mesohaline conditions. In comparison with the pool size of inorganic reactive mercury [Hg(II)_R] in sediments (~2000-6000 ng m⁻²), THg in SAV biomass (~200 ng m⁻²) is small on an areal basis in SAV dominated areas for both regions. However, this rapidly cycling reservoir of SAV-THg may serve as an important labile and readily available pool of Hg(II) to Hg(II)-methylating bacteria at the sediment water interface. Gaseous Hg⁰ flux measurements associated with *S. acutus* stems exhibited a high level of variability, but did show a net release of Hg⁰ from the plant to the atmosphere at both sites. While regional differences were demonstrated for various macrophyte characteristics, as well as for some plant-Hg concentrations and flux rates, the amount of data collected to date is not yet sufficient to readily assess the relative importance of plant-Hg interactions with respect to playing a dominant role in mediating regional differences in biota-Hg levels.

**Methyl mercury concentrations and loads in the Sacramento River Basin
(Task 2, CALFED contract ERP-02-C06-A)**

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The Sacramento River and Sacramento-San Joaquin Bay Delta Estuary are on the State of California 303(d) list because of elevated concentrations of mercury in fish. The Sacramento River is also the single largest source of methyl mercury to the Delta. Methyl mercury is a developmental neurotoxin. The primary route of exposure is from consumption of mercury-contaminated fish. Statistically significant correlations have been observed in the Delta and elsewhere between average annual unfiltered methyl mercury concentrations in water and in fish caught in fall. The relationship suggests that aqueous methyl mercury is an important factor controlling methyl mercury bioaccumulation in the aquatic food chain.

Methyl mercury samples have been collected almost monthly between March 2003 and September 2005 (22 months) at 16 sites with flow gauges in the Sacramento Basin and methyl mercury loads calculated. The study represents the first comprehensive methyl mercury monitoring in the watershed. Important findings are that the three largest reservoirs—Shasta, Oroville, and Folsom—discharged 65% of the water but only 20% of the methyl mercury at Freeport (Delta boundary). Methyl mercury concentrations increased 3-fold in the 150 river miles between Redding and Colusa. The Sacramento River at Colusa (43%), Feather River (24%), Colusa Basin Drain (10%) and American River (8%) watersheds are the main sources of methyl mercury at Freeport. Fifteen percent of the load is unaccounted for. Finally, a positive correlation exists between the sum of the monthly upstream methyl mercury loads from the Sacramento River at Colusa, Feather River, Colusa Basin Drain and American River and the downstream load at Freeport. The correlation is consistent with these being the primary sources of methyl mercury in the Basin and methyl mercury being transported in a conservative fashion down river to Freeport.

**Methyl mercury concentrations and loads in the San Joaquin River Basin
(Task 2, CALFED contract ERP-02-C06-A)**

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The San Joaquin River and Sacramento-San Joaquin Bay Delta Estuary are on the State of California 303(d) list because of elevated concentrations of mercury in fish. The San Joaquin River is the major source of methyl mercury to the southern Delta. Methyl mercury is a developmental neurotoxin. The primary route of exposure is from consumption of mercury-contaminated fish. Statistically significant correlations have been observed in the Delta and elsewhere between average annual unfiltered methyl mercury concentrations in water and in fish caught in fall. The relationship suggests that aqueous methyl mercury is an important factor controlling methyl mercury bioaccumulation in the aquatic food chain. Therefore, an understanding of the primary sources and sinks of methyl mercury are essential for understanding the contamination problem and for developing control programs to reduce fish tissue levels.

Methyl mercury samples have been collected almost monthly between April 2003 and September 2005 (25 months) at 11 sites with flow gauges in the San Joaquin Basin and methyl mercury loads estimated. The study represents the first comprehensive methyl mercury monitoring in the watershed. Important findings are that Mud Slough contributed 49% of the methyl mercury at Vernalis (Delta boundary) but only 9% of the flow during the non-irrigation season. In contrast, the three eastside rivers—Merced, Tuolumne, and Stanislaus—discharged 61% of the flow but only 39% of the methyl mercury at Vernalis. A positive relationship exists between methyl mercury loads at Crows Landing and at Vernalis. The result is consistent with the conclusion that most of the methyl mercury is produced in the top of the Basin and is transported in a conservative fashion down River to Vernalis.

Methyl mercury loads in the Yolo Bypass
(Task 2, CALFED contract ERP-02-C06-A)

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The Yolo Bypass is engineered to operate as a flood conveyance system for diverting Sacramento River water around the City of Sacramento during high flow. The Bypass also receives water from the Knights Landing Ridge Cut, Cache and Putah Creeks. Previous monitoring has found that water leaving the Yolo Bypass at Prospect Slough has the highest average annual methyl mercury concentration in the Delta (0.27-ng/l). The Bypass also appears to be the single largest source of methyl mercury to the Delta when discharging Sacramento River floodwater. However, the source and fate of the methyl mercury in the Yolo Bypass is not known. Mass balance calculations demonstrate that 27-66% of the methyl mercury at Prospect Slough in winter and spring is produced in the Bypass. The remainder predominately comes from the Knights Landing Ridge Cut and Cache Creek. No estimate of methyl mercury production is available for the Bypass when operated in winter as a flood conveyance system. However, the highest methyl mercury concentrations ever measured in the Bypass were recorded when flood water exited in June 2005 (1.2 to 1.5-ng/l). Methyl mercury concentrations increase about 20% in the Yolo Bypass Toe drain between Lisbon and ½ Lisbon. The source appears to be water draining from wetlands. Methyl mercury concentrations in drain water ranged between 0.2 and 5.2-ng/l. The flooded Liberty and Little Holland Islands at the base of the Bypass are net methyl mercury sinks. Finally, the Cache Creek Settling Basin is located at the confluence of Cache Creek and the Yolo Bypass. The Settling Basin is a methyl mercury source at Cache Creek flow rates less than 400-cfs. In contrast, a negative relationship exists between flow and production when the Settling Basin is full and discharging over the high flow weir. The compensation point appears to be about 4,000-cfs with production being positive at lower flows and negative at higher ones.

Photo-degradation of Methyl Mercury in the Sacramento-San Joaquin Delta

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Methyl mercury is photo-degraded to less toxic forms of mercury. Photo-degradation is thought to be a removal mechanism for methyl mercury in the surface waters of the Delta as water flows from the Sacramento River to the export pumps. The results of this study indicate that photo-degradation does decrease methyl mercury concentrations in the surface water of Steamboat Slough and the Mokelumne River. Methyl mercury degradation rates (average of 15 to 34% per day – preliminary data) were calculated from bottle incubation experiments that were performed at various times of the year. Degradation rates were also shown to decrease with depth below the river surface. Measurements of dissolved organic carbon, total suspended solids, UV-A and UV-B, and photosynthetically active radiation were also collected. Preliminary findings suggest that photo-degradation is an important removal mechanism for methyl mercury and has important implications for the understanding of mercury cycling in the Sacramento- San Joaquin Delta.

Methyl Mercury Import/Exports in Wetlands in the San Francisco Delta
and Tributaries--A Mass Balance Assessment Approach

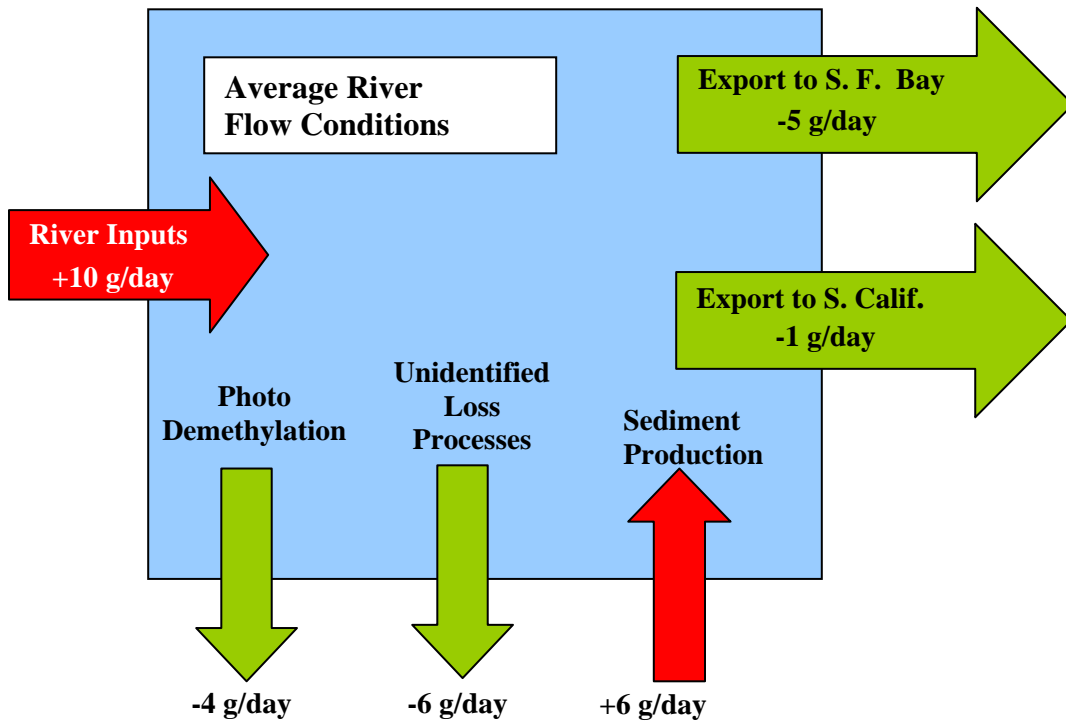
Mark Stephenson, CDFG
Kenneth Coale, MLML
Wesley Heim, MLML
Chris Enright, DWR
Jon Burau, USGS

The objective of this study was to determine whether wetlands import or export methyl mercury during tidal exchanges. We are in the process of conducting studies at Suisun Marsh, Snodgrass Slough, Hog Slough, Sycamore Slough, Brown's Island, and seasonal and permanent wetlands on Grizzly Island. Most of these studies are still in progress. However, we have finished one study at Suisun Marsh during the summer of 2004. This study was conducted with hydrological support from Chris Enright (DWR) and Jon Burau (USGS).

In this study we found that methyl mercury was exported at a natural marsh (First Mallard Branch) and methyl mercury was imported at the mouth of Suisun Slough (See Figure 1). The amount of MMHg imported at the mouth of Suisun Slough is .03 g/day which can account for a small amount of the total loss term of 10g/day in the mass balance box model (Figure 2). We hypothesize the import at the mouth of Suisun Slough was caused by the import of high levels of methyl mercury on suspended sediments from Grizzly Bay during flood tide. Approximately 70-80% of the methyl mercury was on particles at this station. Further evidence is provided by Figures 3 and 4 which show the strong TSS—Methyl Mercury relationship at the mouth of Suisun Slough. We also hypothesize the export at First Mallard branch was caused by the export of high levels of methyl mercury from the small tidal channels in that area. This study illustrates the complexity of determining whether wetlands import or export methyl mercury. We conclude that: 1. Methyl Mercury was imported at the mouth of Suisun Slough—probably associated with particles; 2. Methyl Mercury was exported in the upper marsh at First Mallard Branch; and 3.

these data show methyl mercury can be either imported or exported from wetlands.

Figure 5. Monomethyl mercury fluxes in the Bay-Delta Estuary. The flux associated with the unidentified loss processes was determined by mass balance. Rainfall is estimated to introduce 0.05 g/day MMHg into the Bay Delta (not shown in model).



A Comparison of the Biogeochemical Cycling of Mercury and Methylmercury within Frank's Tract and the Consumes River

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As part of the project '*Evaluation of Mercury Transformations and Trophic Transfer in the San Francisco Bay/Delta*' research program, total Hg (HgT) and methylmercury (MeHg) have been measured in overlying water, sediment and porewater samples collected from Frank's Tract (FT) and the Consumes River (CR).. These studies are aimed at investigating the hypotheses that previously reported differences in MeHg concentration in fish from the central Delta (represented by FT) and inflowing tributaries (represented by CR), are driven by regional differences in both the net MeHg production and food chain biomagnification of MeHg. This poster examines the hypothesis that not only is the CR region a better locale for MeHg formation, but that MeHg is more readily transported from sediments to the water column, where it ultimately enters the food web base. The water column data indicates that dissolved HgT and MeHg are generally similar between the two locations. On average, 5-15% of dissolved HgT was as MeHg. Similarly, the HgT and MeHg in sediments were similar and comparable to those measured throughout the SFB watershed. The relationship between Hg, MeHg and organic matter (OM) shows some interesting differences between the sites, and likely reflects distinct differences in cycling of MeHg within the sediments. There was a regional distinction in the porewater data, in which porewater HgT at the CR was significantly greater than porewater HgT at FT, and the partitioning coefficients (K_d 's) were significantly lower in CR. This suggests that inorganic Hg(II), the bulk of HgT, may be more readily available for methylation in the CR region as a larger proportion exists in the porewater phase, compared with FT. Additional equilibrium speciation modeling of porewater constituents has been done to examine this notion in more detail. There was also a strong regional difference in porewater MeHg concentrations, with CR having generally higher levels. This could be an important factor driving the higher observed MeHg concentrations in the food chain of CR and other local tributaries. Sediment/water Hg flux studies were conducted to examine this notion further. Overall, the various lines of biogeochemical evidence suggest that there is more MeHg in available and cycling fractions in the CR sediments and porewaters, compared with the central delta (FT). These differences are not due to differences in HgT levels and thus, one must conclude that the CR region represents a biogeochemical setting that is more conducive to net Hg(II)-methylation, and as a result, MeHg is accumulated to an overall greater extent into the tributary (CR) food chain than in the central Delta (FT) region.