San Francisco Estuary Institute

The San Francisco Bay Mercury News

An electronic newsletter of mercury research in the Bay Area

RMP

The *San Francisco Bay Mercury* News, an electronic newsletter issued bi-annually, is a compilation of mercury research activities currently underway in the Bay Area. The newsletter is distributed by the San Francisco Estuary Institute as part of the Regional Monitoring Program.

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Vol 3, No 1 *Winter 2006*

Introduction

Welcome to the third issue of the San Francisco Bay Mercury News! The purpose of this electronic newsletter is to foster communication and collaboration among researchers, regulators, and stakeholders by providing summaries of current mercury research activities in the Bay area. Researchers have provided summary paragraphs regarding the purpose of their research, updates to on-going projects and recently accomplished milestones. Contact information follows each project summary. If you missed the first two issues of the newsletter, you can download them from the SFEI web site at:

http://www.sfei.org/rmp/mercury_newsletter/HgNews_home.html

SFEI welcomes contributions to the newsletter and is actively seeking new contributors for our next issue that will be distributed in October 2006. If you have a summary for the newsletter or questions or comments, please e-mail or call Meg Sedlak at SFEI (meg@sfei.org or tel. (510) 746-7345). Also if you did not receive this newsletter from SFEI directly and you would like to subscribe to this newsletter, please visit the SFEI website to register for the San Francisco Bay Mercury News. Similarly, if you received this newsletter erroneously, you may unsubscribe by going to our web site.

In This Issue…

Upcoming Conferences/Meetings

1. Third Annual SF Bay Mercury Coordination Meeting, Wednesday, February 22nd, 2006 at the SF Bay Regional Water Quality Control Board building, 1515 Clay Street, Oakland (Rooms 2, 3 & 4) – Sign Up Now!

The third annual San Francisco Bay Mercury Research Coordination Meeting is rapidly approaching. The meeting will be held this year on February 22nd, 2006 at the SF Bay Regional Water Quality Control Board building, 1515 Clay St, Oakland, California. The meeting will consist of short presentations by a variety of researchers and regulators from 10 am until approximately 4 pm (lunch will be provided). The draft agenda will be sent out shortly and is posted on the SFEI web site. If you would like to present at this event, please send Meg Sedlak an e-mail at meg@sfei.org. If you would like to register for this event, please register on-line at:

http://www.sfei.org/rmp/mercurymeeting/

Please RSVP by February 15th, 2006.

2. The Eighth International Conference on Mercury as a Global Pollutant, August 6- 11th, Madison Wisconsin

The 8th International Conference on Mercury as a Global Pollutant will be convened in Madison, Wisconsin (USA).

The conference organizing committee has set three principal goals for the conference:

1. To enhance the synthesis of information presented at the conference through an integration of focused plenary sessions, poster sessions, conferee discussions, and synthesis papers;
2. To focus and enhance the integration of science and policy concerning environmental mercury pollution; and
3. To increase participation by under-represented groups, including graduate students, beginning professionals, and representatives of developing nations.

This five-day conference will include a mixture of focused plenary sessions, special sessions, and contributed poster sessions. For more information on this conference, see www.mercury2006.org.

On-going Projects

1. Stanford University Study on the Transformations of Mercury, Iron, and Sulfur During the Reductive Dissolution of Iron-oxyhydroxide by Sulfide

Methylmercury can accumulate in fish to concentrations unhealthy for humans and piscivorous birds. Most sources of mercury (Hg) emit inorganic species to the environment. Therefore, ecological harm occurs when inorganic Hg is converted to methylmercury. Sulfate- and iron-reducing bacteria methylate mercury. Processes promoting the potential bioavailability of inorganic mercury under conditions in which these bacteria live are poorly understood. Researchers at Stanford University showed that sulfide initially decreases the concentration of dissolved and adsorbed mercury in the presence of iron-oxyhydroxide, forming HgS. However, sulfide-promoted dissolution of iron-oxyhydroxide eventually dissolves HgS via formation of ferrous iron-bearing species [Fe(II)]. Our results demonstrate that HgS is much less recalcitrant in the presence of Fe(II) compared to sulfide. The formation of HgS in mercury-contaminated riparian, wetland, or estuarine sediments may not effectively limit bioavailability under conditions that promote the activity of iron-reducing bacteria. Our results emphasize the importance of considering iron in addition to sulfur speciation to effectively predict whether processes promoting Hg bioavailability are likely to dominate. Sulfur and iron speciation are useful geochemical indicators of ecological risk posed by Hg.

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2. RMP Small Fish Mercury Project

Significant management actions are underway that have the potential to change mercury (Hg) concentrations in fish from the San Francisco Estuary. The Hg TMDL is a major effort to reduce mercury accumulation in Estuary fish, and there is concern that extensive tidal marsh restoration could increase mercury in the food web. Small fish are a useful tool for monitoring inter-annual changes in methylmercury in aquatic ecosystems. They integrate finer-scale spatial and temporal patterns of methylmercury uptake into the food web, while providing more localized data than large fish. From November through December of 2005, SFEI staff sampled small fish (Atherinopsidae and Gobiidae) from two habitat types (benthic and pelagic) at eight locations in the Estuary. Multiple composite samples of five to ten individuals each were collected at each sampling location, weighed, measured, and sent for whole-body analysis of total mercury concentration. When laboratory analyses are complete, these data will provide: 1. estimates of mercury concentrations in prey of piscivorous wildlife; 2. estimates of spatial variation in mercury exposure in San Francisco and San Pablo Bay; and 3. initial data for a long-term biennial monitoring program to evaluate trends in food-web mercury over time, especially with respect to management actions.

Collaborators:
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More information on this study can be found at www.sfei.org, 2006 RMP Program Plan or by contacting Ben Greenfield at Ben@SFEI.org or (510) 746-7385.

3. Results from Interlaboratory Studies for the California Bay-Delta Authority Mercury Studies Quality Assurance Program

One of the primary data quality objectives of the California Bay-Delta Authority (CBDA) Mercury Studies Program is the generation of defensible data that is comparable with other data generated during the project. In order to monitor and support this objective, the CBDA Mercury Studies Quality Assurance Oversight Program has been authorized to conduct a series of intercomparison studies for total mercury and methylmercury in all matrices collected under the broad scope of the program.

The first intercomparison study focused on total mercury in water and methylmercury in sediment. The samples were distributed in June, 2005, with the final report issued in December, 2005. The second intercomparison study focused on the entire spectrum of analyses conducted under the Mercury Studies Program. Samples for total and methylmercury in water, sediment, and tissues were distributed in November, 2005. Results from the participating laboratories were expected in the middle of January, 2006. The third intercomparison study will be conducted in the spring of this year.

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4. Trace Element Concentrations in the Pacific Harbor Seal, *Phoca vitulina richardii*, in Central and Northern California

To determine trace element concentrations in the Pacific harbor seal (*Phoca vitulina richardii*), live (n=186) and dead seals (n=40) were sampled throughout central California from March 2003 to January 2005. Total mercury (THg) concentrations were determined in blood and hair of live harbor seals and hair and liver of dead harbor seals. Concentrations of monomethyl mercury (MeHg), selenium (Se), and lead (Pb) additionally were determined in liver of dead harbor seals. To assess trophic level, carbon and nitrogen stable isotopes were examined in liver. Age class assignments of live harbor seals were based on morphometrics, and ages of dead harbor seals were determined by cementum annuli in teeth. There were significant differences in THg concentrations in blood and hair based on age ($P<0.001$). Adult male harbor seals had greater THg concentrations in their hair than adult female harbor seals ($P<0.003$). THg concentrations in liver increased linearly with age; whereas, MeHg concentrations in liver increased with age exponentially with an asymptote at approximately 1.3 ppm wet weight. MeHg expressed as a percentage of THg (% MeHg) was best described by a decay function ($r^2=0.7961$, $P<0.001$). As harbor seals aged, % MeHg decreased to a minimum and remained constant. Se in the liver also increased with age and was in equilmolar ratios with THg in adults; whereas, molar ratio of Se:THg in pups did deviate from a 1:1 ratio. Significant differences among locations in THg concentrations in blood and hair were not detected. Assessing the possible affect of location of sampling on mercury concentrations, however, is confounded and limited by lack of equal sample sizes for basic age and sex cohorts.

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5. Mercury Speciation in Tidal Waters, Suspended Solids and Sediments from the San Francisco Bay (Project Led by University of Notre Dame)

This project is funded by the U. S. Army Corps of Engineers (USACE) San Francisco District and the U. S. Army Research Office (Jeffrey Talley, PI; Xiangru Zhang, Co-PI). Initially, a sodium tetraethyl borate derivatization/solid phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS) method was adopted for the analysis of methylmercury and mercuric ion. Some parameters were optimized including SPME fiber coating, extraction time, sample heating temperature, salt effects, GC injection and separation program, MS ionization mode, scan mode, emission energy, etc. Under the optimized conditions, the minimal reporting levels (MRLs) of methylmercury and mercuric ion in water samples were approximately 10 ng/L as Hg. Then, a purge and trap (PT) unit was used instead of the SPME unit. The PT unit was optimized by changing autosampler transfer line, trap coating, purge flowrate, purge time, dry-purge time, trap desorption temperature, trap desorption time, transfer line temperature, and moisture control system temperature. Under the optimized conditions of the PT-GC-MS system, the MRLs of methylmercury and mercuric ion were approximately 2 ng/L as Hg in reagent water with a purge volume of 20 mL, 0.5 ng/L as Hg for purging a 200-mL water sample, and 0.2 ng/L as Hg for purging a 500-mL sample, respectively. Also, the PT–GC–MS generally resulted in lower relative standard deviations than the SPME–GC–MS. By using the PT–GC–MS system, some sediment samples from the San Francisco Bay were readily analyzed with a distillation pretreatment. Such a low minimum reporting level of the PT–GC–MS system, however, still could not meet the needs for the analysis of seawater samples due to the extremely low concentrations of methylmercury and the high concentrations of chloride ions, which adversely affect the derivatization of methylmercury. We developed a solid phase extraction (SPE) protocol with the adsorbent activated coconut charcoal. Some critical factors that affect the recovery of the SPE protocol were identified. With the SPE preconcentration, we were able to determine sub-ppt levels of methylmercury in some water samples from the San Francisco Bay. The possible artifact formation of methylmercury during analysis was corrected.

Presentations/publications:

(1) Zhang, X.; Talley, J. W.; Davis, W. E.; Conn, D. B.; George, J. E.; Li, Y. Comparison of solid phase microextraction and purge trap gas chromatography mass spectrometry for the determination of methylmercury. In Division of Environmental Chemistry Preprints of Extended Abstracts; 231st American Chemical Society National Meeting: Atlanta, GA, 2006; Vol. 46(1).
(2) Zhang, X.; Talley, J. W. Determination of sub-ppt level methylmercury in seawater samples. In Division of Environmental Chemistry Preprints of Extended Abstracts; 231st American Chemical Society National Meeting: Atlanta, GA, 2006; Vol. 46(1).

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

Due to past mercury mining, 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 $HgCl_2$ 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.

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7. New Almaden Quicksilver continues to flow: WY 2003, 2004, and 2005 and beyond

SFEI has been sampling floods on Guadalupe River since November 2002 at the USGS gauge at Hwy 101 using funding from the RMP, CEP, USACE, SCVWD, and SCVURPPP. Water samples have been

analyzed for HgT (n=115), HgD, MeHgT, and MeHgD (n=43) and sediment samples have been analyzed for HgT (n=8) on 8 grain size classes from <0.0625mm to >3.8mm. HgT ranged between DL and 18,673 ng/L. In WY 2005 HgD concentrations on average accounted for 3% of HgT. MeHgT concentrations varied from 0.06 - 1.89 ng/L and exhibited a FWMC of 0.49 ng/L. HgT concentrations in the bed load sediments ranged between 0.03 and 1.8 mg/kg (median of eight samples) and increased with decreasing grainsize. Water-column HgT load varied between years in relation to climatic forcing: WY 2003 (116 ± 36 kg), WY 2004 (15 ± 4.5 kg), and WY 2005 (8 ± 2.5 kg). MeHgT load was 0.04 kg (0.5% of the HgT load) in WY 2005 and HgT transported along the bed (bedload mercury) accounted for an additional 0.08 kg (1%). Our data support a hypotheses that methylmercury is sourced from in-channel production during low flow periods and that the majority of total mercury transported in the system is derived from out of channel sources in the historic New Almaden Mining District when rainfall intensity exceeds 30 mm in a 6-hour period. The development of a calibrated hydrological model would improve data interpretation and would help to prioritize implementation actions aimed at reducing particulate mercury concentrations and mercury loads. Presently, year 4 sampling is 2/3 complete and there is support for continuation during a 5^{th} year in WY 2007.

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8. Mercury-Methylation Dynamics in Sediments From Freshwater, Delta, and Salt-Marsh Regions of the San Francisco Bay Watershed

The bacterially mediated conversion of inorganic divalent mercury (Hg(II)) to highly toxic methylmercury (MeHg), and the factors that control it, are active areas 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 change 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-habits, a suite of measurements 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 $^{203}Hg(II)$ incubations to assess the activity of bacteria capable of methylating $Hg(II)_R$; 3) potential rates of benthic MeHg production calculated 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) the observed spatial variation was largely due to 10X to 1000X higher rates of microbial sulfate reduction (and Hg(II)-methylating bacteria activity) in the Petaluma sites, 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 became more oxic (less reducing), iv) the observed trend in $Hg(II)_R$ largely drove the regional trend between the freshwater tributary and the central Delta where the latter was more reducing and had a lower pool size of $Hg(II)_R$ compared with the former; and v) sites dominated by submerged aquatic vegetation had higher rates of MeHg production than open-water and/or emergent salt-marsh sites.

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9. Evaluation Framework for Identifying Mercury Control Options in Tidal Wetlands and Associated Habitats of the San Francisco Estuary

The San Francisco Bay Regional Water Quality Control Board has adopted a Total Maximum Daily Load (TMDL) for mercury in the Bay and has designated this TMDL as one of the highest water-quality priorities for the region. Methyl mercury, the form that is most toxic and most readily available for uptake by organisms, is the primary form of mercury in fish. Therefore, efforts to reduce production of methyl mercury are important components of the Board's mercury control strategy.

The conceptual framework is the central organizing element in the project titled "Wetland Design and Management Options for Control of Mercury in San Francisco Bay" which was initiated in late 2005 and funded by a grant from the Coastal Nonpoint Source (Northern) bond funds established under California's Proposition 13 (Costa-Machado Water Act of 2000). The project is in the early stages of development.

The framework will incorporate ecosystem management, risk reduction, and contaminant remediation perspectives. Four key environmental evaluations will address habitat methylation, habitat spatial extent, environmental parameters, and temporal aspects of the estuarine system. "Habitats" will include landforms as well as dominant plant associations. The process used to identify and evaluate methylmercury reduction strategies will incorporate these evaluations together with information on biogeochemistry of mercury and methylmercury from other sources as well as from data collected as part of the project.

Initial identification of potential control options has been completed and includes approximately thirty-eight options, most of which previously have been implemented in the estuary for purposes other than mercury control. In addition to incorporating the results of the evaluations described above, the control option evaluation will include a net environmental benefit analysis. The process will result in identification of candidate control measures which will be incorporated ultimately into a Wetland Implementation Plan to be submitted to the Board.

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10. Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems- CALFED ERP02D-P62 Annual Project Report 2005

This study focuses on two habitat elements of the tidal marsh physiographic template: moderate sized sloughs (2nd-3rd order channels) and adjoining high marsh plains in wetlands along the main stem of the Petaluma River. We sampled these elements in the habitat of the California Black Rail, a species of special concern targeted as a potential indicator of Hg problems in tidal marshes. Results from our work in 2005 will be discussed.

Total Hg is elevated above natural background but fairly evenly distributed among wetlands, so there does not appear to be any elevated Hg source within the main reach of the Petaluma. Therefore Hg_T from atmospheric deposition, watershed urban and non-urban runoff, and sediments from the Bay are sufficiently uniform or well-mixed within the Petaluma system that no gradient is seen in wetlands along this river.

Wetland slough channel sediments (particularly at the GM site, the lowest salinity site) show higher MeHg concentrations than typically seen in Bay sediments, but slough channel waters show similar concentrations to those already measured in San Pablo Bay. Although much more spatially and temporally intensive sampling would be required to resolve the direction and magnitude of MeHg

transport between the wetlands and Bay, the similarity in concentrations does not suggest large export flux in water or sediments from these wetlands.

Concentrations of MeHg in high marsh sediments are greater than those typically found in Bay habitats. High marsh plain MeHg concentrations at the mid-Petaluma wetland were greater than those in high marsh sites upstream and downstream. Within each of these marshes, high marsh sediments consistently had higher MeHg than slough channel sediments. Sediment MeHg concentrations were moderately correlated to sediment organic content, but did not correlate at all to total Hg. We will continue to examine the data more closely to identify possible causes for these differences.

The higher MeHg in high marsh plains than slough channels and differences among wetlands reflects geomorphological differences affecting wetland hydrology and multiple biogeochemical factors, which mediate relative MeHg production and degradation rates.

These MeHg production and degradation rates vary seasonally, with higher net production in summer. The seasonal differences in measured ambient concentrations mirror patterns in net rates derived from laboratory incubations, further evidence of the role of bacterial activity in the methylation of mercury under suboxic conditions.

Despite high spatial and temporal variability in sediment MeHg measurements within wetlands, mercury in Black Rail feathers mirrors differences in high marsh MeHg among wetlands. Published effects levels for Hg in Black Rails are lacking, but at two of three sites feather Hg concentrations are at the low end of the published effects range (or the high end of the background range) for other bird species. Maximum concentrations found thus far exceed this threshhold by a factor of two, but the severity of specific effects on Black Rails at these levels is currently unknown. Although the linkage between MeHg concentrations in wetland habitat elements and their resident biota is not yet complete, these data support the expectation that the resident biota would integrate and reflect moderate to long-term contaminant concentrations in these environments. It therefore appears likely that management actions that reduce MeHg in sediments could reduce the Hg risk to high marsh biota.

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11. Guadalupe River Watershed Mercury TMDL

In Guadalupe and Almaden reservoirs, the increase in the concentration of methylmercury in the hypolimnion is pronounced, increasing from concentrations of less than 1 ng/L to greater than 10 ng/L. Fish mercury concentrations are also elevated, particularly in Guadalupe Creek and Reservoir where they are as high as 0.83 mg/kg average total mercury, wet weight in age-1 largemouth bass (90 mm), and 6.1 mg/kg in adult (420 mm). In contrast, in Lexington Reservoir located outside of the mining district, the concentration of methylmercury in the hypolimnion increases from 0.2 to 3.0 ng/L over the course of the dry season. Mercury concentrations in largemouth bass in Lexington Reservoir were 0.09 mg/kg in age-1 (89 mm) and 0.6 mg/kg in adult (410 mm).

The proposed TMDL numeric targets are fish tissue methylmercury concentrations protective of human health and wildlife:

Fish Targets (ppm methylmercury, wet weight)		
Protection of Wildlife	Protection of Wildlife	Protection of Human Health
TL3 Fish 50 – 150 mm	TL3 Fish 150 – 350 mm	Typical Size and Species of Fish Consumed
0.05 ppm	0.10 ppm	0.3 ppm

Achieving the load allocations will be part of a two-phase TMDL implementation process in which the loads will decline as source control measures are implemented and as more data on the efficacy of methylation control methods becomes available. In general, the goals for the first phase of implementation are to a) implement effective source control measures for mining waste in the New Almaden Mining District, b) complete studies to reduce discharge of mining waste accumulated in downstream beds, banks, and floodplains, and c) attain the urban runoff interim loading milestone of 11 kilograms per year. The goal for the second 10-year phase of implementation is to achieve the watershed fish tissue targets and the total mercury load allocation assigned by the San Francisco Bay Mercury TMDL. Throughout both phases, the mercury load, concentrations, and bioaccumulation will be monitored to ensure that total and methylmercury levels have adequately declined. Monitoring may be undertaken in a coordinated effort by many entities. Guiding both phases, and remaining central to the implementation process, will be specific allocation amounts for each source. (Specific allocation categories and amounts can be obtained from Carrie Austin at the San Francisco Regional Water Quality Control Board).

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12. Monitoring and assessment of mercury bioaccumulation and environmental mercury in the South Bay Salt Pond Restoration Project

The South Bay Salt Pond Restoration Project (SBSPRP) encompasses 15,100 acres of commercial salt ponds that nearly surround the extreme southern sub-embayment of San Francisco Bay, California, USA. A historic mercury (Hg) mine in the watershed has left a legacy of mercury in the South Bay, adjacent wetlands and salt ponds (the baylands), and in the uplands and streams of the watershed. The potential exists to inadvertently increase the risk of mercury accumulating in South Bay fish and other wildlife through hydrological modification of salt ponds as part of the SBSPRP. The concern is that some management actions will favor conversion of Hg into toxic methylmercury (MeHg) and its uptake into local food webs. Bayland managers need to know how their actions may affect the risk of mercury toxicity in wildlife.

In a collaborative three-year project (2006-2008), we will directly assess that risk by monitoring Hg in 'biosentinel' wildlife species that represent bayland conditions. This bio-monitoring effort is coupled with studies of MeHg production in sediment and concentrations in water and is stratified across habitats to understand how the risk of Hg bioaccumulation can be reduced in light of the various management options under consideration. Each of the sentinel species has been chosen to reflect food-web contamination in a specific major habitat type in the baylands. The habitat types are distinguished by differences in attributes that may affect Hg cycling, such as frequency of tidal inundation and density of vegetation. Thus, our sampling design will provide habitat-specific data on MeHg production and food-web contamination, geographically broad mapping of the mercury problem to place the risk of restoring specific marshes in the context of the larger project, and comparative data for risk assessment in the short-term as well as a baseline for tracking the effects of management actions on the Hg problem into the future.

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13. Methyl Mercury Sources and Sinks in the Tidal Wetlands of Suisun Marsh, California

Suisun Marsh, located 56 km northeast of San Francisco, California is a key part of the San Francisco Bay estuary ecosystem providing 47,000 hectares of managed wetlands, upland grasses, tidal wetlands, and bays and sloughs. Recent studies have shown there is a significant mercury problem in the watershed with many species of fish having mercury concentrations exceeding the threshold for human health concern. Marshes are generally accepted as locations favorable for methyl mercury production. The objective of this study was to determine the net import/export of methyl mercury from two tidal marshes over a complete tidal exchange. Automated samplers were used to collect aqueous samples at preprogrammed intervals over a complete tide cycle. Samples were analyzed for methyl mercury and total suspended solids. Acoustic Doppler instrumentation was used to measure water mass transport. The natural marsh site (First Mallard Branch), in the upper marsh, was a source of methyl mercury, while the site near the mouth of Suisun Marsh (SS1) was a sink. A strong correlation between methyl mercury and total suspended solids was observed at SS1. We hypothesize that the methyl mercury imported to the system is bound to particles resuspended from the adjacent, shallow, Grizzly Bay. Results from this study were used to construct a simple box model of methyl mercury cycling in Suisun Marsh. This study illustrates the complexity of determining whether wetlands import or export methyl mercury.

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14. The CBDA Fish Mercury Project (a.k.a. A Pilot Program for Monitoring, Stakeholder Involvement, and Risk Communication Relating to Mercury in Fish in the Bay-Delta Watershed)

In November 2004, SFEI and several partners began a $4.5 million project to monitor mercury in fish in the Bay-Delta watershed, establish an organizational structure to allow stakeholder input on the monitoring, and conduct risk assessment and risk communication activities to raise public awareness about fish contamination issues with the goal of reducing human exposure to methylmercury in the watershed. SFEI's partners in this project include UC Davis, Moss Landing Marine Lab, the California Department of Health Services, and the California Office of Environmental Health Hazard Assessment. This project includes monitoring of 1) sport fish to characterize human exposure and spatial patterns and 2) small fish as an indicator of temporal and spatial patterns and exposure of piscivorous wildlife. The sampling will include trend monitoring sites, sampling to support advisory development, and monitoring of restoration projects. A Steering Committee has been formed to guide the design of the monitoring program. A Peer Review Panel provides technical oversight of the Project. Sampling began in summer of 2005. The Project will continue through 2007.

Contact Information:

Stakeholders interested in participating in this study should contact Jennifer Hunt at the San Francisco Estuary Institute, jhunt@sfei.org.

Other contacts:
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Small fish sampling: Darell Slotton, UC Davis, dgslotton@ucdavis.edu.

Stakeholder involvement and risk communication: Alyce Ujihara, DHS, aujihara@dhs.ca.gov.

Advisory development: Bob Brodberg, OEHHA, rbrodber@oehha.ca.gov.

15. Update on the San Jose/Santa Clara Water Pollution Control Plant Mercury Fate and Transport Study

Sampling began in October 2004 and continues currently. Phase I sampling, which included weekly sampling of 8 process locations, was concluded in August 2005. Phase I data are currently undergoing thorough evaluation while baseline Phase II sampling continues weekly. Results show a highly efficient removal rate for total mercury (over 98%) correlated with the removal of solids. Methylmercury and filtered (dissolved) mercury are also efficiently removed (97% and 50%, respectively). Flows and concentrations of mercury in digested sludge appear sufficient to account for the mercury removal. There is no evidence of mercury methylation in the Plant. Twenty-four hour sampling efforts have shown a consistent increase in influent total mercury later in the day into early evening. Sampling was predominantly carried out during morning hours, suggesting that even this high removal rate may be an underestimation. Dissolved mercury fluctuates similarly, but influent methylmercury concentration does not change throughout the day. After the evaluation and discussion with Water Board staff, modifications for the remainder of the study duration may be made to the Phase II sampling and analysis plan. The 2005 progress report for the project will be available by the end of February at http://www.sanjoseca.gov/esd/pub_res.htm.

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16. Mercury in Birds of the San Francisco Bay-Delta: Trophic Pathways, Bioaccumulation and Ecotoxicological Risk to Avian Reproduction

Reduction and control of legacy Hg within the San Francisco Bay-Delta watershed should be guided by appropriate human and ecotoxicological endpoints as well as an understanding of the factors affecting Hg bioaccumulation. Avian reproduction is a sensitive endpoint used to evaluate methylmercury (MeHg) toxicity in aquatic environments. However, assessing the ecotoxicological risk of Hg is hampered by an inadequate understanding of MeHg exposure among different foraging guilds of birds, and the lack of integration between field and laboratory approaches. The goal of our current work is to combine a field assessment of Hg exposure and effects with a laboratory assessment of avian embryo sensitivity to MeHg to better define the risks of Hg to birds. Our field objectives are to quantify dietary Hg exposure in three different avian foraging guilds, as well as determine Hg effects on adult birds and reproduction. Our complementary laboratory approach is designed to aid in interpretation of our field data, provide vital data on the variation in Hg sensitivity among avian species, and establish and refine MeHg dose-response relationships.

Results from our first year in the field indicated that total mercury (THg) varied significantly among species representing the three foraging guilds, and increased in the following order: American avocet, surf scoter, Forster's tern, and Caspian tern. THg varied spatially and temporally in all the guilds we studied. Forster's tern males accumulated more THg during the breeding period than did females,

implying females deposited Hg into their eggs. Hatching success at nesting colonies we monitored ranged between 81-85% for avocets, 88% for stilts, and 78-83% for Forster's terns. We collected eggs from each species and will examine whether Hg levels in eggs influences hatching success in the wild. These data will also complement lab egg injection studies started at Patuxent Wildlife Research Center during the past year. While the majority of birds in the Bay-Delta are migratory, it is not known if mercury accumulated by wintering birds can have cross-seasonal effects on their reproduction. Thus, we have initiated work to follow Bay-Delta surf scoter to their breeding areas and examine egg contaminant concentrations and sources. We estimated survival to 21 days after hatching for avocet and stilt chicks, and will compare these data to Hg concentrations in downy feathers. Avocet and stilt chicks accumulated THg rapidly in some South Bay sites. We determined growth rates and survival of tern chicks, and found wing growth rates of chicks declined with increasing concentrations of liver THg. Our results thus far highlight the importance of foraging area, diet, and life stage in determining Hg risks to avian species.

Collaborators:
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17. Pre-Construction Biogeochemical Analysis of Mercury in Wetlands Bordering the Hamilton Army Airfield Wetlands Restoration Site

Over 90 percent of the coastal wetlands in San Francisco Bay have been lost since the industrial revolution. The U.S. Army Corps of Engineers (USACE) is working with the California State Coastal Conservancy and the San Francisco Bay Conservation and Development Commission (BCDC) to reconstruct wetlands at HAAF and restore 203 ha of tidal habitat to endangered species such as the clapper rail and the salt marsh harvest mouse. HAAF has subsided below mean sea level and will require 10 million cu yd of fill material to elevate the site to the point where typical marsh vegetation can colonize and the natural sediment trapping, marsh-building physical dynamics can proceed. Wetlands are believed to be sources of methylmercury (MeHg) production and export, and HAAF represents only 203 ha of the additional 23,300 ha of wetlands to be established around the bay by 2055. Means to mitigate MeHg magnification in bay aquatic food webs are needed but currently unknown. This interim report describes site-specific information collected in 2003 on the geochemical/geophysical, microbial, predominant plant- and animal-related interactions that affect stabilization and mobilization of Hg and MeHg in the sediments/soils of the area.

Total mercury (THg) and MeHg levels were measured in June 2003 in the sediment in relation to depth at intertidal sites at HAAF and the China Camp State Park (as a reference), as well as at inland sites at HAAF and Bel Marin Creek. Other parameters important for the cycling of Hg and MeHg in sediments were determined also to establish site-specific relationships between these parameters and THg and MeHg. The highest MeHg concentrations (range 0.8-4.4 mg g^{-1} DW) were found in the upper 2.5 – 5.1 cm of the cores and levels decreased with depth. THg levels (range 160 – 550 ng g^{-1}) increased with depth,

correlating inversely with MeHg. MeHg correlated directly with redox potential (E_h), total organic carbon, and phosphorus. Net MeHg production is the result of methylation and demethylation rates in the sediment. Methylation and demethylation rates were determined by on site incubations of mud- and vegetated-mud-cores with stable Hg isotopes at the HAAF and China Camp sites. Methylation rates were 1.44 ng MeHg g^{-1} per day in non-vegetated sediments of HAAF. Rates were usually lower in vegetated than in non-vegetated sediments. Rates were usually higher in the light than in darkness. Methylation rates varied with location within the bay on bare and epipelon-vegetated sites and were lower at HAAF than at China Camp. Epipelon is the complex of microalgae, bacteria and detritus on the sediment surface. Demethylation rates were 1.281 ng MeHg g^{-1} per day in non-vegetated sediments at HAAF and 0.78 ng MeHg g^{-1} per day at China Camp.

Mean THg concentrations in the macrophytic vegetation, predominated by *Spartina foliosa* and *Salicornia virginica*, ranged from 13 to 158 ng g^{-1} in shoots and from 217 to 297 ng g^{-1} in roots. Mean MeHg concentration ranged from 0.55 to 4.75 ng g^{-1} in shoots and from 2.83 to 5.26 in roots. Plant levels usually exceeded those in the sediments in which they rooted. The THg and MeHg levels in plant detritus were far higher than in live shoots, i.e., by a factor of 5 to 8. Significant levels of THg and MeHg were detected in tissues of macrofauna collected at intertidal sites of HAAF and China Camp. MeHg comprised on average 40 percent of THg (range 20- 70 percent). Biota to sediment accumulation factors (BAFs) for MeHg ranged from about 3 to 50. Snails were the highest Hg bioaccumulators. Because the diet of these animals is composed largely by plant material, it is likely that MeHg in plants represents an important MeHg source for trophic transfer in the marsh. A preliminary annual MeHg mass balance for a 203-ha HAAF system indicated a net MeHg production of 12.8 kg and MeHg export in the order of 0.1 kg with tidal waters to the bay. These values serve as the basis for research hypotheses and future work. Measures to decrease bioavailability were explored as a management tool. The bioavailability characteristics of Hg species in HAAF sediments were evaluated experimentally. The MeHg body burdens of the experimentally 2-56 days exposed *Macoma nasuta* clams were only approximately half of those recorded in clams inhabiting bay edge sediments while elimination was slow, suggesting that exposure periods longer than 56 days are needed for Hg to approach apparent steady state in clam tissues. Bioavailability decreased more by sediment amendment with granular activated carbon (GAC) than with Kraft-lignin.

A screening-level model pertaining to HAAF (QnD HAAF) was created to serve as a tool to incorporate ecosystem characteristics and management measures into a user-friendly framework. This model links the spatial components within GIS files to the prevalent abiotic, climatic, and biotic interactions in the ecosystem. It has a simple design and can be upgraded easily. The current QnD:HAAF version 1.0 integrates the field and laboratory data pertaining to HAAF and other related systems. The model was run to simulate two 14-day scenario's, representing the wet and dry season, respectively. Simulated sediment MeHg concentrations exceeded the measured levels while simulated methylation and demethylation rates were in the same order of magnitude as measured values. Elevation proved to be an important factor influencing net MeHg production. The differences between the simulated and measured THg and MeHg levels in sediment and biota may provide leads to identify areas in which more information is needed. Future research efforts will address processes determining net MeHg production, atmospheric flux of Hg, exchange of Hg and MeHg between sediment and tidal waters, biomagnification of Hg up relevant aquatic food webs, data integration, and management issues.

Collaborators:
Best, E.P.H., Fredrickson, H.L., McFarland, V.A., Hintelmann, H., Jones, R.P., Lutz, C.H., Kiker, G.A., Bednar, A.J., Millward, R.N., Price, R.A., Lotufo, G.R., Ray, G.A., 2005. Pre-construction biogeochemical analysis of mercury in wetlands bordering the Hamilton Army Airfield (HAAF) wetlands restoration site. ERDC/EL-TR-05-15.

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Additional information about this project can be found at:
Our first Progress Report has appeared and can be downloaded from our website, summarizing the work completed in FY2003. Interim Report 2004 for USACE District, San Francisco, September 2005.
http://el.erdc.usace.army.mil/elpubs/pdf/trel05-15.pdf

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