Mercury Cycling in Blacklock Wetland: A Study of a Restored Tidal Marsh

<u>Wesley Heim</u>, Moss Landing Marine Laboratories, wheim@mlml.calstate.edu
Mark Stephenson, California Department of Fish and Game, mstephenson@mlml.calstate.edu
Adam Newman, Moss Landing Marine Laboratories, adam.newman@spyglassbio.com
Stuart Siegel, Wetlands and Water Resources, stuart@swampthing.org
Dan Gillenwater, Wetlands and Water Resources, dan@swampthing.org
Kenneth Coale, Moss Landing Marine Laboratories, coale@mlml.calstate.edu

Historically Suisun Bay Marsh included ~68,000 acres of tidal wetlands. From mid-1800's to early 1900's over 90% of the wetlands were reclaimed for agriculture. Currently, planning efforts to restore 65,000 acres of Delta and Suisun tidal habitat are in final stages of development. The 70 -acre Blacklock tidal marsh restoration site, located in northeast Suisun Marsh, was restored by DWR in 2006 after having been used for livestock grazing and duck hunting activities since 1946. This study is the first effort at estimating the impact on mercury cycling of converting a managed wetland with limited water exchange to tidal marsh with daily tidal inundations. The goals of this study were to estimate changes in total mercury and methyl mercury concentrations in fish, sediment and water within the restoration site before and after restoration. Field sampling took place January, 2005 to September, 2009. Results of two-sample t-test indicate aqueous methylmercury concentrations post breach ($t_{(2), 8} = 6.19$; p < 0.05) were significantly lower than pre-breach concentrations. Lower methylmercury sediment concentrations and less variability between sample locations within the restoration site were observed at Blacklock during the final two years of the study relative to the first year. Inland Silverside mercury concentrations decreased significantly post breach. Greater connectivity of tidal wetlands with surrounding open water areas resulted in decreased methylmercury concentrations in water, sediment, and fish. Two possible explanations may account for these results. First, wetland biogeochemistry in a daily inundated tidal regime does not support mercury methylation at levels observed for the site when it had seasonal wetland inundation regimes. Second, mercury-laden substrate has been buried with new sedimentation, thereby isolating the available mercury from methylation. It is hoped that the scientific knowledge gained as a result of this restoration about mercury cycling will aid future restoration efforts in the Bay-Delta.

Keywords: Mercury cycling; Wetlands; Mercury; Methylmercury

The Song Sparrow as a Biosentinel for Methylmercury in Riparian Food Webs of the San Francisco Bay Area

April Robinson, San Francisco Estuary Institute, april@sfei.org
Letitia Grenier, San Francisco Estuary Institute, letitia@sfei.org
Marcus Klatt, San Francisco Estuary Institute, marcusk@sfei.org
Shira Bezalel, San Francisco Estuary Institute, shira@sfei.org
Meredith Williams, San Francisco Estuary Institute, meredith@sfei.org
Josh Collins, San Francisco Estuary Institute, josh@sfei.org

Recent studies in the Bay Area and elsewhere have documented unexpectedly high concentrations of methylmercury in terrestrial invertebrate-eaters, such as songbirds, indicating that risk from harmful methylmercury exposure can occur in these food webs. Such discoveries, and the knowledge that mercury is already a problem in local watersheds, prompted interest in developing a biosentinel for methylmercury in stream riparian food webs of the Bay Area. The Song Sparrow (Melospizamelodia) was determined to be the best riparian biosentinel candidate on the basis of its natural history, sampling feasibility, and sensitivity to mercury. The ability of Song Sparrows to reflect a wide a range of mercury concentration in their blood, and to therefore distinguish methylmercury risk between conditions, was assessed by sampling individuals from riparian sites across the Bay Area. Sampling sites were chosen according to a conceptual model that identified total mercury in sediment and net methylation environment as the primary drivers for determining methylmercury exposure in riparian wildlife. Sampling sites were classified according to conceptual model categories (High or Low in Total Mercury, and High or Low in Net Methylation Environment) on the basis of reported sediment mercury values from other projects and landscape level indicators of total mercury or methylation environment. The presence of Song Sparrows at all sampling sites, and their ability to distinguish mercury exposure risk between sites, confirms their appropriateness as a biosentinel species. Differences in mercury between conceptual model categories, despite the rough measures used to classify sites, supports the idea that net methylation environment and total mercury are critical factors in determining methylmercury exposure in riparian food webs. Mercury concentrations at the site with the highest risk were associated with a decline in reproductive success in songbirds of greater than 25%, underscoring the need to understand and monitor methylmercury exposure in these systems.

Keywords: Methylmercury, Song Sparrow, Riparian, Biosentinel

Mercury in Motion: Wetland Restoration in South San Francisco Bay and the Legacy of Historic Mercury Contamination

Mark Marvin-DiPasquale, U.S. Geological Survey, mmarvin@usgs.gov

With a 50-year time horizon for its completion, the ongoing 6,500 hectare wetland restoration project in South San Francisco Bay represents one of the largest wetland restoration efforts in the world. Apart from its large scale, one of the biggest challenges faced by project managers is legacy mercury (Hg) buried in primary slough channels and former salt ponds within the restoration area. The source of this Hg is primarily drainage from the former New Almaden mining district, the largest cinnabar (HgS) mine in North America, which produced over 37 tons of Hg from the dawn of the gold rush until 1976. The current restoration project is tasked with the conversion of former salt production ponds ringing South San Francisco Bay, to a mosaic of restored tidal salt marsh and managed ponds for wildlife habitat and flood control. Levee breaches associated with the restoration project are causing vast changes in the hydrology of the restoration area, and these changes are projected to mobilize legacy Hg buried in the sloughs and marshes. Since 2003, USGS scientists have been involved in multiple projects aimed at understanding how much of this Hg has been or will be mobilized as a result of restoration management actions, and to what extent these actions will exacerbate or mitigate Hg bioaccumulation in the local or regional food web. This presentation will highlight a number of these related Hg studies, both past and ongoing, and give a synopsis of 'lessons learned' to date, as well as projection for the future. The insights offered by this body of Hg research has direct implications for wetland restoration efforts that are ongoing and planned in many regions of the San Francisco Bay, its watershed, and globally.

Keywords: mercury, wetland restoration, biogeochemistry

Use of Coagulation to Remove Inorganic Mercury and Methylmercury from Solution

Yumiko Henneberry, University of California, Davis, yumberry@ucdavis.edu

<u>Tamara Kraus</u>, US Geological Suvery, California Water Science Center, tkraus@usgs.gov

William Horwath, University of California, Davis, wrhorwath@ucdavis.edu

Phillip Bachand, Bachand and Associates, phil@bachandassociates.com

Jacob Fleck, US Geological Survey, California Water Science Center, jafleck@usgs.gov

David Krabbenhoft, US Geological Survey, Wisconsin District, dpkrabbe@usgs.gov

Peter Nico, Earth Sciences Division, Lawrence Berkeley National Laboratory, psnico@lbl.gov

The approval of the methylmercury (MeHg) TMDL for the Sacramento – San Joaquin Delta (Delta) has highlighted the need to identify best management practices that will reduce the concentration and export of mercury (Hg) from both point and non-point sources. Results from our laboratory studies demonstrate the promise of metal-based coagulants (e.g. iron sulfate, polyaluminum chloride) for removing Hg and MeHg from water. These coagulants are commonly used in the drinking water industry to remove dissolved organic matter (DOM) prior to disinfection to reduce the formation of toxic disinfection by-products. Because both inorganic Hg and MeHg are known to associate closely with DOM, it follows that removal of DOM leads to the concomitant removal of Hg from solution and its incorporation into the organo-metal complex, termed floc, which precipitates out of solution. Previous studies which concluded that coagulation does not effectively remove Hg from solution were conducted using high concentrations of Hg that do not apply to natural waters. Treatment of water collected from Delta subsided island drainage water high in both DOM and Hg demonstrated up to 97% of inorganic Hg and 80% of MeHg can be removed from solution by coagulation. Once formed, the organo-metal floc shows the capacity to adsorb additional Hg. Exposure of the floc to highly reducing conditions in the laboratory indicated that this material may remain stable in a wetland environment, potentially sequestering both carbon and Hg in the sediment over the long-term. Further research is being conducted on Twitchell Island to assess the feasibility of using on-site coagulation to 1) remove constituents of concern including DOM and Hg, and 2) mitigate land-surface subsidence through retention of the floc in constructed wetlands. If proven effective, coagulation may be a feasible technique to reduce Hg and MeHg concentrations and loads in Delta waters.

Keywords: mercury, methylmercury, coagulation, best management practices, Hg, MeHg, TMDL

Strategies for Resolving Low Dissolved Oxygen and Methylmercury Events Originating in Diked Managed Wetlands of Suisun Marsh

Stuart Siegel, Wetlands and Water Resources, stuart@swampthing.org
Phil Bachand, Tetra Tech Research and Development, phil.bachand@gmail.com
Dan Gillenwater, Wetlands and Water Resources, dan@swampthing.org
Stephen Chappell, Suisun Resource Conservation District, schappell@suisunrcd.org
Bruce Wickland, Suisun Resource Conservation District, bwickland@suisunrcd.org
Orlando Rocha, Suisun Resource Conservation District, orocha@suisunrcd.org
Mark Stephenson, Moss Landing Marine Lab, DFG, mstephenson@mlml.calstate.edu
Wes Heim, Moss Landing Marine Laboratory, DFG, wheim@mlml.calstate.edu
Chris Enright, Delta Science Program, cenright@deltacouncil.ca.gov
Peter Moyle, UC Davis, pbmoyle@ucdavis.edu
Bryan Downing, United States Geological Survey, bdowning@usgs.gov
Brian Bergamaschi, United States Geological Survey, bbergama@usgs.gov

Suisun Marsh diked seasonal marshlands management is geared toward wintering waterfowl habitats: mixed open water and emergent vegetation. Management includes summertime drawdown for vegetative growth and wetland maintenance, fall flood up for wintering waterfowl habitat, and late winter/early spring drawdown and flushing for salt leaching. The high organic matter of wetland vegetation plus soil organic carbon in these peat-rich diked wetlands, when flooded in the fall after the summer drawdown, provide ideal conditions for depleting water column dissolved oxygen. Discharging carbon-rich, oxygen-depleted waters into smaller tidal sloughs during fall flood up and, to a lesser extent during winter/spring leaching, can lead to periods of low dissolved oxygen in those sloughs. This hypoxia, and occasionally anoxia, can block access to upstream aquatic habitats and, in the most severe cases, has resulted in fish kills. Wetland soil biogeochemistry also supports methylmercury production via anaerobic microbial activity, resulting in methylmercury loadings to the tidal sloughs. Methylmercury is a potent neurotoxin and export to the tidal sloughs make it bioavailable to fish populations and ultimately poses a human health risk through consumption of mercury contaminated fish. Fishing is commonplace in Suisun Marsh. Our study explored processes affecting production of low DO and methylmercury in Suisun managed wetlands and identified management practices that might reduce or eliminate these problems while supporting productive waterfowl habitats. The study found that human management activities (water, soils, and vegetation management) interact with three key environmental variables (wind, air temperature, and tides). When fall flood up corresponds with windy conditions, cooler air temperatures, and spring tides, modifying managed wetlands practices may lessen adverse water quality conditions. In contrast, low winds, hot temperatures, and neap tides render most management efforts ineffective and poor water quality conditions often ensue. Our study identified sixteen management approaches with potential to reduce adverse water

Keywords: dissolved oxygen, methylmercury, wetlands, Suisun, fish

quality conditions.