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Continued Investigation of Mercury Stable Isotopes in San Francisco Bay

Estimated Cost: $120,000 over 2 years. Can be scaled with scope of work.

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Proposed Deliverables and Timeline:

Sample Collection	Sept. 2010 to May 2011
Sample Analysis	Jan 2011 to Jan 2012
Data synthesis and Report Writing	Feb 2012 to June 2012
Final Reports (publications)	Aug 2012

Background

During the past two years we carried out a study of mercury stable isotopes in sediments, young-of-year fish and atmospheric samples from throughout San Francisco Bay with the goal of constraining the source of bioavailable mercury to fish. We believe that this study approach has been very successful and that additional work is warranted and will be fruitful (see Final Report). The most important findings are that sediments in south San Francisco Bay carry a strong isotopic fingerprint of mercury released from the New Almaden mercury mining district and that this mercury can be seen to mix gradually into a second source of mercury coming from north San Francisco Bay, which is likely the mercury used in gold mines in the Sierras and in industry in the north Bay. This spatial variation in mercury isotope signal observed in the sediments is passed on to young-of-year fish at each locality after some isotopic fractionation caused by microbial methylation and both microbial and photochemical demethylation. The strong correlation in mercury source between sediments and fish continues from the South Bay to the Carquinez Straight, but breaks down somewhat in the Sacramento River Delta, suggesting a more complex mixture of methyl mercury sources in this area. Based on low concentrations of mercury in precipitation and runoff, and on limited isotopic data, we suggest that atmospheric mercury is not likely to be a major source of mercury to sediments or young-of-year fish in San Francisco Bay. However, additional work is need to allow further evaluation of our present interpretations and to expand the Hg isotope approach to address additional questions related to Hg biogeochemistry in the San Francisco Bay Estuary.

Additional Work Needed

There are a number of areas that we have identified in the current study where additional mercury isotope data would be extremely beneficial to the understanding of mercury sources and biological uptake. Most of these analyses were not possible to carry

out two years ago and are now made possible by considerable efforts at method development in our laboratory made possible by this project and a similar project funded by the State of Florida. We propose to carry out:

1. Hg isotope analyses of reactive inorganic mercury extracted from sediments.
2. Hg isotope analyses of sediment from additional sample sites in the Sacramento River Delta region.
3. Hg isotope analysis of large-volume urban run-off samples.
4. Hg isotope analysis of co-located samples of dry deposition, wet deposition and gaseous elemental mercury at a single location in the Bay area.
5. Hg isotope analyses of sport fish and sea-bird egg shells to gain information on Hg sources to these organisms.

The first area where we propose additional work is a study of mercury isotope compositions of sequential extractions of the same sediment samples from San Francisco Bay and the rivers emptying into the Bay that we have already studied for bulk properties in the first two years of the study. There have been numerous analytical schemes developed to examine Hg-contaminated sediment with respect to the various forms of mercury that exist within the sediment matrix. Most recently, a comparatively simple approach was developed as a surrogate measure of the fraction of total mercury that is most readily available to bacteria for conversion to MeHg, referred to as 'reactive' inorganic mercury ($Hg(II)_R$). This method operationally defines this fraction as the fraction of the total inorganic mercury (Hg(II)) pool in whole sediment that is readily reduced to elemental mercury by an excess of stannous chloride ($SnCl_2$) under weakly acidic and anaerobic conditions, during a standard (15-minute) time period. Extensive experimentation with this approach across many sediment types from many different ecosystems has shown this generally separates the sediment mercury fraction that is available to the Hg(II)-methylating microbial community (Marvin-DiPasquale, pers. comm.). We have only recently developed the methodology to separate mercury from sediments with the high yields necessary to accurately measure mercury isotopes in this fraction. Adding information on the mercury isotopic composition of this fraction would enhance our understanding of the linkages between sediment mercury and fish mercury that we investigated in the first two years of this study.

The second area where we propose additional work is tracing the sources of mercury to sediments in the Sacramento River Delta, where we have determined from our initial two-year study that mercury sources are more complex than in San Francisco Bay proper. We suspect that mercury is transported from both gold mines in the Sierras and mercury mines in the Coast Ranges and that these sources differentially contribute to bioavailable mercury in the Sacramento Delta region. We propose to investigate the downstream transport and biogeochemical processing of sediment-adsorbed Hg derived from hydraulic gold mining in the Sierra Nevada and mercury mining in the Coast Ranges within and through the Yuba-Feather-Sacramento River system. We will document the mercury isotopic composition of primary sources (Coast Range v. Sierra Nevada) of Hg contamination to lowland ecosystems where methylation potential is high in the Sacramento Valley and Bay-Delta and the relative contribution and bioavailability of each. We plan to assess how Hg bioavailability changes along sediment transport pathways, irrespective of total Hg concentrations, and by identifying/quantifying the controlling processes at the intersection of sedimentation and biogeochemical modifications of Hg speciation.

The third areas were we propose additional work is in the measurement of Hg isotopes in urban runoff. Concentrations of Hg were found to be very low and isotopic

measurements were not possible with the sample sizes collected. We have improved our methods of analysis to allow smaller samples but we still need large samples for high precision analyses. We propose a large volume sampling and field pre-concentration sampling effort for a small number of samples to place some constraints on the Hg isotopic composition of this source of Hg to San Francisco Bay.

The fourth area where we propose additional work is a study of atmospheric dry deposition in the Bay Area. In the first phase of this work we measured Hg concentration and isotopic composition in wet precipitation and from tree moss from a series of sites surrounding San Francisco Bay. We found that wet precipitation deposited a relatively small amount of Hg and we were able to characterize its isotopic composition. We had also assumed, based on the literature, that Hg accumulating in tree lichen would be a good approximation of the isotopic composition of total wet plus dry deposition. Since that time we and several other research groups have learned that tree moss and lichen do not accurately capture the isotopic composition of atmospheric deposition because isotope fractionation occurs on the plant surfaces presumably due to photochemical reduction. Therefore, we propose to collect and measure Hg dry deposition, wet deposition and gaseous elemental mercury (GEM) simultaneously using a newly developed dry deposition surrogate surface collector and GEM collector that we have deployed and tested during the past year in a project funded by the State of Florida.

The fifth and final area where we propose additional work is a study of Hg isotopes in sea-bird eggs and in San Francisco Bay sport fish. We have learned a tremendous amount about the Hg isotope systematics of Hg sources for young-of-year fish and we wish to apply that knowledge to a study of seabirds and sport fish. From the study of deeper water sport fish we can evaluate whether they derive Hg from the same foodweb as the shallow-water young-of-year fish that we have studies previously. We know that Pacific Salmon, for instance, have highly contrasting Hg isotope compositions and Hg sources compared to San Francisco Bay coastal fish (Blum, submitted). From a study of egg-shells that were collected in another RMP-funded study (Forster's Terns, Ackerman and Eagles-Smith) we plan to evaluate the proportion of Hg to which birds are exposed that is derived from coastal fish in San Francisco Bay versus other sources of Hg exposure including deep water fish and terrestrial sources.

Applicable RMP Objectives and Management Questions

2. Which processes, sources, and pathways contribute disproportionately to food web accumulation?

The result of this study should provide useful information to support water quality management decisions by placing further constraints on the sources of bioavailable Hg to San Francisco Bay food webs. It is well know that the bioavailability of Hg in different materials can vary dramatically and that bioavailability is often difficult to predict. By isotopically tracing Hg sources and bioavailable fractions and comparison to previous work on young-of-year fish we expect to be able to provide guidance on which Hg sources to SFB are most easily converted to methyl-Hg and taken up by biota. This would allow managers to more strategically limit Hg inputs (and/or exposure) that would most directly reduce Hg concentrations in fish and seabirds.

Task Descriptions

Task 1: Sample collection. Two members of the University of Michigan research group will sample sediment at additional sites in the Sacramento River Delta. They will also set up atmospheric precipitation, dry deposition and GEM collectors on the roof at SFEI.

Finally, several large urban run-off samples will be collected for isotopic analysis. Samples will all be shipped to the University of Michigan.

Task 2: Sample analysis. Samples will be digested, separated from matrix components and pre-concentrated when necessary by reduction of Hg with $SnCl_2$, purging of Hg(0) with Ar, and trapping of Hg(II) in potassium permanganate traps. All samples will then be analyzed for $\delta^{202}Hg$, $\Delta^{201}Hg$ and $\Delta^{199}Hg$ by MC-ICP-MS. Concentrations of Hg will be determined by $SnCl_2$ reduction/gold trap/atomic absorption spectrophotometry (AAS), and both yields and blanks will be determined for each Hg separation for isotopic analysis. Our MC-ICP-MS mass spectrometry method utilizes matrix and concentration matching, on-peak zero blank correction, use of Tl to correct for instrumental mass discrimination and sample-standard bracketing with NIST SRM 3133 (Blum and Bergquist 2007). External quality control standards are run with each set of ten samples and 3 replicate analyses are made on most samples (as long as there is enough Hg in the particular sample).

Task 3: Data synthesis and report writing. $\delta^{202}Hg$, $\Delta^{201}Hg$ and $\Delta^{199}Hg$ data will be interpreted within the context of other scientific studies of Hg and Hg isotopes in SFB and globally. A final report will be prepared and after review a condensed version of that report will be submitted to a peer-reviewed journal.

Task 4: Preparation and submission of manuscripts for peer reviewed journals (such as Environmental Science & Technology).

BUDGET

The estimated cost of the project is $120,000, which includes $109,091 in direct costs and $10,909 in indirect costs. Per sample analytical costs cover the expenses for lab expendable supplies, senior technician support of the AAS and MC-ICP-MS, and hourly recharge expenses for MC-ICP-MS maintenance. The study will be directed by Joel Blum, for whom one week summer salary per year is included, and a PhD student or postdoc who will be recruited from several incoming students and postdocs. Senior Lab technician Marcus Johnson will be supported for one month per year to conduct QA/QC, training, lab management and data synthesis. An itemized budget is presented below.

High precision Hg isotope analyses: 100 samples x $400	40,000
Hg concentration analyses: 100 samples x $40	4000
Atmospheric particulate, precip and GEM collectors for Hg	2000
Travel expenses for 2 persons on 2 sampling trips:	4000
Six months per year for 2 years graduate student stipend	
or 3 months per year for 2 years postdoc salary	24000
One month per year for 2 years senior lab tech for QA/QC	11315
One week summer salary per year for 2 years for PI	8600
Fringe at 30%	13176
Shipping:	2000
Total Direct Cost	109,091
Indirect Cost (SFEI rate of 10% of direct)	10,909
TOTAL	120,000