

## **2005 List of Ideas for Potential RMP Pilot and Special Studies**

**Number:** 2005-1

**Topic:** **Monitoring bio-available mercury in the San Francisco Estuary open-water habitats: using the food web to assess interannual and spatial trends**

**Proposed by:** Letitia Grenier, SFEI

**Workgroup Rating:** NA

**Description:** This project advanced to the Conceptual Scope of Work stage last year, but did not make the final cut. The TRC instructed SFEI to develop the idea further for reconsideration in 2005. The revised Conceptual Scope is provided as another handout.

**Estimated Cost:** \$64,000 (composited samples) - \$172,000 (individual samples)

**Proposed start date:** 2006

**Number:** 2005-2

**Topic:** Causes of Sediment Toxicity and Benthic Impacts in San Francisco Estuary

**Proposed by:** Bruce Thompson

**Workgroup Rating:** NA

**Description:** The objective of this study is to determine to the extent possible, which contaminants, or mixtures of contaminants, at what levels, are responsible for sediment toxicity and benthic impacts observed in San Francisco Bay. This year (2005), in-depth analyses of relationships between sediment chemistry and toxicity and benthic impacts will be conducted for the State SQO project. Those analyses are correlational and are based on field measurements of sediment mixtures, and will probably narrow down the list of possible causative agents, and may implicate some individual contaminants, but will not provide convincing evidence for cause. This will require additional field and lab studies. The RMP has supported investigations into causes of sediment toxicity for several years at a low level of funding. With the advent of SQO, there will be a need to complete our understanding of what is causing sediment toxicity. Using the information from the SQO analyses, we will identify sampling locations with gradients of implicated individual- and mixtures of contaminants. Sediment toxicity lab studies would verify implicated chemistry building upon the MPL studies of cause of sediment toxicity. Those studies require field verification and additional analyses at more locations where sediment toxicity occurs. Lab tests may use resident species and will also test effects thresholds identified in the SQO analyses. Benthic studies along selected gradients would also clarify or narrow down causes of benthic impacts. Field experiments or mesocosm studies, where sediment is dosed with one chemical / mixture at a time could be included, if existing gradients can't be found. These studies would also be used to test effects thresholds determined for SQO. These kinds of focused field and lab studies are the only way this problem can be solved, and these studies are essential to properly direct clean-up and loading reduction efforts towards chemicals / mixtures definitively demonstrated to cause biological effects in sediments.

**Estimated Cost:** Guessing... a level of \$50-75K / year is reasonable.

**Proposed start date:** Three year special study beginning in 2006.

**Number:** 2005-3

**Topic:** Investigation of the Presence of Fluorinated Alkyl Substance of San Francisco Bay

**Proposed by:** Meg Sedlak, SFEI

**Workgroup Rating:** NA

**Description:** In the last 50 years, fluorinated alkyl substances have been used extensively in a variety of commercially available products including fire-fighting foams, refrigerants, stain repellants in textiles, and coatings for paper used in contact with food products. Their popularity in commercial and industrial applications in part results from their unique ability to be both hydrophobic and oleophobic, that is able to repel both water and oil.

Fluorinated alkyl substances are synthesized from perfluorinated sulfonyl fluoride and carbonyl fluoride intermediates by electrochemical fluorination process (ECF) or telomerization fluorination processes. Because these processes are not selective, numerous by-products are produced in the manufacture of these intermediates such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

As a result of their chemical stability and widespread use, fluorinated alkyl substances such as PFOS and PFOA have been detected in marine mammals and aquatic organisms throughout the world including relatively pristine environments such as the Arctic. PFOS and related perfluorinated compounds have been associated with a variety of toxic effects including mortality, carcinogenicity, and adverse development. Their widespread dispersal throughout the globe and their potential toxicity has caused increasing concern among scientists and regulators. In response to this concern, 3M Corporation initiated a voluntary phase out of PFOS; however, PFOA continues to be produced in the manufacture of fluoropolymers.

The objective of this study will be to determine concentrations of PFOS and related compounds in San Francisco Bay. At present, little information is available regarding the presence of PFOS and perfluorinated compounds in the Estuary. A research group at Stanford University has recently analyzed South Bay sediment and water samples for PFOS and its precursors; however, a comprehensive study of the concentrations of these compounds in the Estuary has not been conducted. It is anticipated that this study would build upon the research currently being conducted at Stanford. We propose conducting additional sediment and water analyses to provide a complete picture of the Bay and to investigate the potential for PFOS and other perfluorinated compounds to accumulate in the food web. It is anticipated that tissue from biota that are relatively high in the food chain (e.g., birds or fish) will also be analyzed.

**Estimated Cost:** \$60,000

**Proposed start date:** 2006

**Number:** 2005-4

**Topic:** Evaluation of Pesticides in San Francisco Bay Tributaries

**Proposed by:** Daniel R. Oros, SFEI

**Workgroup Rating:** NA

**Description:** The objective is to determine the identities, concentrations, and distributions of agricultural and urban use pesticides in San Francisco Bay tributaries. The results of a recent RMP special study, "Identification and Evaluation of Previously Unknown Organic Contaminants in the San Francisco Estuary 1999-2001" SFEI Technical Report #45), showed that a variety of pesticides were present in estuary water samples collected by the RMP in 2002. The pesticides that were identified using full scan GC-MS included atrazine, chlorpyrifos, dichlobenil, metolachlor, molinate, oxadiazon, propanil, terbutylazine, thiobencarb, and piperonyl butoxide. Three of these pesticides, molinate, thiobencarb and propanil, are general use herbicides that are applied in rice production. The detection of pesticides in estuary water samples is evidence that reasonable effort should be focused on determining the levels and distributions of these and other agricultural and urban use pesticides in the estuary and, if their concentrations are at levels that could deleteriously impact resident aquatic species. Information derived from a pesticide study will be useful for evaluating the potential causes of observed episodic toxicity in the estuary. Water and sediment samples will be collected during the wet and dry seasons in major tributaries and urban creeks. A list of agricultural and urban use pesticides will be generated and a subset of specific pesticides families (e.g., pyrethroids, carbamates, organophosphates, etc.) will be identified for analysis based on level of use (tonnage) and potential to induce toxicity at the low levels (ppt) that are expected in the estuary. Sample analysis will be conducted using high performance liquid chromatography-mass spectrometry (HPLC-MS) and high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) instrumentation. The deliverable will be a RMP Technical Report and a paper to be submitted for publication in a peer reviewed scientific journal.

**RMP Objectives and Management Question Addressed:** 1c, 1d, 2a, 2b, 2c, 3c, 4a, and 5a-c.

**Time Sensitivity:** This project will not exceed 1 year.

**Estimated Cost:** \$85,000

**Proposed Timing:** 2006

**Number:** 2005-5

**Topic:** Evaluation of Pharmaceuticals in the San Francisco Estuary

**Proposed by:** Daniel R. Oros, SFEI

**Description:** Pharmaceuticals such as anti-biotics (e.g., erythromycin and trimethoprim), analgesics (e.g., ibuprofen and acetaminophen), anti-inflammatories (e.g., diclofenac and naproxen), anti-depressants (e.g., Prozac and lofepramine), anti-hypertensives (e.g., atenolol and propranolol), anti-cancers (e.g., paclitaxel and tamoxifen), and sexual performance enhancers (e.g., Viagra and Levitra), among other drugs, are used to treat illness, disease, and medical conditions in humans and animals. They enter the environment from consumer use and actions and, in the case of industrial confined animal feedlots where antibiotics are used, from waste effluents. The primary pathway is ingestion followed by subsequent excretion into the municipal sewage system, while the secondary pathway is disposal of unused and outdated medications directly into the sewage system. These biologically active compounds and their metabolites are not completely removed by current wastewater treatment technologies and are often found in treated effluents and receiving waters. For example, the analgesic, acetaminophen, was found in the San Francisco Bay at a maximum estimated concentration of 390 ng/L [Marine Pollution Bulletin, 46, 2003, 1102-1110]. The fact that wastewater treatment plants discharge approximately 230 billion gallons of treated effluents into the Bay each year, this could represent a significant loading of pharmaceuticals to the Bay. Discharged pharmaceuticals are diluted and even mixed with other pharmaceuticals from multiple discharge sites in the Bay. Concentration levels are expected to peak during the dry season when freshwater flow into the Bay is at its lowest. The RMP does not monitor for pharmaceuticals in the Bay, so it is not known which pharmaceuticals are currently present and at what concentrations. Several key questions that could be addressed in this proposed special study include: What pharmaceuticals are present in the Bay? Are they present at concentrations that cause toxicity (e.g., LOEC, LC<sub>50</sub>) to aquatic biota? What are the sources and transport pathways on input? The deliverable will be a RMP Technical Report and a paper to be submitted for publication in a peer reviewed scientific journal.

**RMP Objectives and Management Question Addressed:** 1c, 1d, 2a, 2b, 2c, 3c, 4a, and 5a-c.

**Time Sensitivity:** This project will not exceed 1 year.

**Estimated Cost:** \$85,000

**Proposed Timing:** 2006

**Number:** 2005-6

**Topic:** Food-web monitoring for mercury in tidal marshes

**Proposed by:** Letitia Grenier

**Workgroup Rating:** NA

**Description:** The objective of this study is to monitor methylmercury accumulation in the tidal marsh food web. We propose to use habitat-specific indicator species to monitor mercury in tidal marsh food webs to provide information on methylmercury bioaccumulation on spatial and temporal scales of interest. Stratifying across habitats (tidal channel and marsh plain) is important to reduce noise, because abiotic conditions and microbial processes relating to methylation rates, as well as food web structure and species composition, vary across habitats. Predatory fish and birds are useful monitoring tools, because they integrate small-scale variation in methylmercury production over space and time. Furthermore, these vertebrates accumulate mainly methylmercury, so only total mercury in their body tissues need be measured. Fish muscle and bird feathers would be sampled, so birds would not be sacrificed. The cost would depend on the scope of the desired monitoring project, both in terms of geography and of marsh habitats. The full set of proposed indicator species is detailed in the table below. Ideally, all habitats and bays within the Estuary would be sampled initially to develop a picture of spatial and habitat-based variation in mercury in tidal marsh biota. Following this initial effort, the monitoring could be scaled back if certain areas or habitats were deemed not problematic for mercury accumulation. Similarly, monitoring would ideally be annual, but could be scaled back if necessary. This project would produce standard protocols for monitoring mercury in the tidal marsh food web that could be used Estuary-wide by other monitoring efforts to produce a regional set of comparable data. Because these species have such small home ranges (inside of tidal channels for fish and along tidal channels for sparrows), we could also use them to test whether accumulation of methylmercury varies between small and large tidal channels.

Habitat Element	Species	Characteristics
Tidal channels	Longjaw mudsucker	<ul style="list-style-type: none"> <li>• Resident in tidal marsh channels</li> <li>• Abundant in <b>saline marshes</b></li> <li>• Territorial (small home range)</li> <li>• Predatory (high in resident food web)</li> </ul>
	Shimofuri goby	<ul style="list-style-type: none"> <li>• Resident in tidal marsh channels</li> <li>• Abundant in <b>brackish to fresh marshes</b></li> <li>• Sedentary (small home range)</li> <li>• Predatory (high in resident food web)</li> </ul>
Marsh plain	Song sparrow	<ul style="list-style-type: none"> <li>• Resident in tidal marsh plain</li> <li>• Abundant across the Estuary in marshes of all salinities</li> <li>• Territorial (small home range)</li> <li>• Predatory (high in resident food web)</li> </ul>

**Estimated Cost:** Cost depends on geographic scope and range of habitats: \$30,000 - \$70,000 per year.

**Proposed start date:** Three-year special study starting in 2006.

**Number:** 2005-7

**Topic:** Identifying sources of food-web mercury in the Bay ecosystem: a retrospective wildlife study

**Proposed by:** Letitia Grenier

**Workgroup Rating:** NA

**Description:** The objective of this study is to identify the source(s) of food-web mercury in the Bay ecosystem. The approach comprises two steps: (1) Quantify the temporal pattern of mercury concentrations in wildlife over the past century using museum specimens, and (2) Compare the pattern in wildlife to known temporal patterns of mercury inputs from different sources (e.g. temporal pattern of mine-related-mercury deposition from sediment core data). The source of the mercury that enters the Bay food web is not known. Although mine-related sediments comprise the most massive mercury source in the Bay ecosystem, the amount of mercury inputted from atmospheric deposition and subsequent runoff may be more bio-available and is sufficient in mass to cause the observed concentrations of methylmercury in wildlife. These two mercury sources, as well as other potential sources, differ in the pattern in which they were inputted to the Estuary. For example, sediment cores show that mine-related mercury inputs from the Gold Rush peaked near the middle of the 20<sup>th</sup> century, while atmospheric mercury rose throughout the century. We propose to identify the sources of food-web mercury by comparing temporal patterns of mercury bioaccumulation in wildlife over the past century to known temporal patterns of mercury inputs to the ecosystem. Excellent specimen series at the Museum of Vertebrate Zoology, University of California, Berkeley and the California Academy of Sciences will allow for statistically rigorous comparison of concentrations in wildlife from different decades of the 20<sup>th</sup> century. A hair or feather sample can be taken from these specimens for mercury analysis, and the museum curators are willing to allow destructive sampling for this study. Previous studies have shown that exogenous mercury is not a problem in museum specimens, but methylmercury could be analyzed if exogenous mercury became a concern. From the Bay ecosystem, the species with the best specimen series are the song sparrow, the clapper rail, and the salt marsh harvest mouse. For a pilot study with limited funding, a series of up to 50 specimens of one species would be sampled from one geographic area (e.g. west side of the South Bay) over the past 100 years. The species and geographic area would be chosen based on interest and available specimens. Steven Schwarzbach (USGS) is interested in collaborating on a clapper rail retrospective study and has begun to collect samples for this purpose. Similarly designed retrospective studies in other parts of the world have successfully identified food-web mercury sources using museum specimens of wildlife. For example, in the Everglades, historical wading bird specimens were used to identify local incineration plants as the source of food-web mercury.

**Estimated Cost:** \$30,000 (for 50 specimens of one species from one geographic area)

**Proposed start date:** The study would start in 2006 and could be extended in subsequent years to other parts of the Bay.



**Number:** 2005-8

**Topic:** Sources and Quality of Tidal Marsh Sediments

**Proposed by:** Josh Collins, SFEI

**Workgroup Rating:** NA

**Description:** There is growing interest in knowing what sources of inorganic sediment contribute to tidal marsh and tidal flat development and natural maintenance, what is the quality of those sources, and how has that changed over time.

For any given marsh location, possible immediate sediment sources include adjoining tidal channels, the flats themselves (by their erosion), and local watersheds. Where the sediments come from has much to do with its quality, and that can strongly influence wetland restoration designs and management. If local watersheds are really as important as some of us think, then watershed management for sediment quality and quantity has direct impacts on intertidal habitat restoration.

I suggest SFEI take the lead in a collaborative effort with UCB (Lynne Ingram's group) to (1) develop a reference set of geo-chemical fingerprints for local watersheds, tidal flats, and arterial channels; (2) core existing marshes to profile their sediment sources over time (last 250-300 years); (3) better characterize the existing quality of marsh surface sediments involved in local food webs of protected wildlife species. We could start in South Bay to support the SBSPPR.

**Estimated Cost:** \$xx

**Proposed start date:** 2006