MEMORANDUM

January 20, 2007

To: RMP Steering Committee

From: Meg Sedlak and Mike Connor

Re: Responding to 2003 Program Review: Allocation of Funds for Exposure and Effects Studies and Involving the Academia in the RMP

Every five years, the program is reviewed by an outside panel. In 2003, the panel made several recommendations for improving the program including expanding biological exposure and effects studies and strengthening ties with academia.

The Report of the 2003 Program Review states "RMP should place more emphasis on the biological effects of the contaminants it monitors and on the biological effects of other stressors on the system. Biological effects is the endpoint most relevant to beneficial uses…. We estimate that the effort needs to be funded at least at the $500,000/year level on a sustained basis." In response to this recommendation, the SC extended the Exposure and Effects Pilot Study (EEPS) to 2008, dedicating $200,000 to this study. Implementation of this pilot study is overseen by EEPS workgroup consisting of the following members (areas of expertise noted in parenthesis): Dr. Michael Fry of American Birds Conservatory (birds); Dr. Harry Ohlendorf of CH2M Hill (birds); Dr. Dan Schlenk of UC-Riverside (fish); Ms. Karen Taberski of the SFRWQCB; and Dr. Steve Weisberg, Executive Director of the Southern California Coastal Water Research Project (benthos). At the December 2006 TRC meeting, the TRC requested that the SC discuss funding for exposure and effects studies beyond 2008. The SC could elect to continue the funding of this program at $200,000 as a line item or include biological effects with other pilot and special studies that are evaluated by the TRC in March of every year. The advantage of the former is that the review panel has considerable expertise and is quite active in reviewing the proposals submitted.

The second recommendation by the review panel is that "SFEI/RMP should enhance its linkages with universities. The RMP is presently focused primarily on status and trends with a lesser emphasis on describing the processes that led to past conditions, or will lead to future ones. The RMP monitoring provides a wonderful platform on which to build additional studies that could address these processes…. "

At present, the University of California at Santa Cruz (UCSC) is one of the major recipients of RMP funding through the UCSC analyses of Bay water for trace elements. Dr. Russ Flegal, who oversees these analyses, is recognized a world expert in the field of trace metal chemistry and has developed many of the methods that are in standard use today. When the program initially began, there was a strong rationale for the analyses to be conducted in an academic laboratory. As many of these methods have become more accepted and routine, it may be appropriate to investigate the possibility of a commercial laboratory for conducting these analyses. The TRC, however, feels strongly that Dr. Flegal and other academic colleagues should continue to be involved in the RMP through targeted special studies that address a specific issue of concern to the Regional Water Quality Control Board and to the RMP participants. To that end, Dr. Flegal has proposed a study for 2007 that would determine which sources of mercury are methylated through the use of mercury isotopes. This proposal is described in more detail in the attached appendix.

We would propose that in 2007, the RMP remain cost neutral with regard to the trace metal analysis. During this period, the RMP would explore the use of a commercial laboratory to determine whether similar detection limits and data validation criteria can be achieved as to those we have achieved with UCSC. To facilitate this comparison, a set number of samples will be split between UCSC and a commercial laboratory. Any savings that are achieved through the use of a commercial laboratory will be used by the university to conduct a special study such as the one proposed in the appendix.

Beyond 2007, the SC should consider how academia will be involved in the RMP.

APPENDIX

RMP Research Pre-Proposal
December 11, 2006

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Hypothesis: Variations in stable mercury isotopic compositions may be used to resolve sources and mixing rates of different natural and industrial inputs of mercury to San Francisco Bay, as have variations in stable lead isotopic compositions.

Background: Variations in stable lead isotopic compositions have been used to chronicle temporal fluxes on natural and industrial lead to San Francisco Bay in dated sediment cores (Ritson et al., 1999). These analyses show the first perturbation of the natural lead isotope ratio occurred from 1852-1914 when sediment loads in the Sacramento River increased 10-fold due to the influx of hydraulic mining sediment from the foothills of the Sierra Nevada. The analyses show subsequent perturbations from deposits from the Selby smelter (beginning prior to the turn of the previous century – late 1800s) and then from leaded gasoline emissions that became apparent in the 1940s and have been dominant since then.

The recycling of those historic inputs of lead to the system, along with ongoing inputs, has been documented with lead isotopic composition analyses of surface waters throughout the Bay (Dunlap et al., 2000; Steding et al., 2000; Dunlap et al., ms. in review). These measurements substantiate mass balance calculations that indicate leaded gasoline emissions account for ~90% of industrial lead atmospheric depositions throughout California over the past century. They also indicate that ongoing inputs of historic leaded gasoline deposits in the estuarine watershed will persist for decades - if not centuries. [This documentation is a principal piece of evidence in current litigation on funding the California Childhood Lead Prevention Program (Shell et al. v. State of California)].

While we have been repeatedly asked if we can do the same type of analyses for mercury, we have not had either the instrumentation or the expertise to conduct those analyses. However, with our acquisition of a Finnegan Neptune multi-collector high resolution inductively coupled plasma mass spectrometer (MC HR ICP-MS) with a grant from the Keck Foundation the former limitation has been addressed; and we have recently demonstrated our ability to measure differences in stable mercury isotopic compositions. Therefore, we are now poised to conduct analyses of stable mercury isotopic compositions that parallel our analyses of stable lead isotopic compositions in the Bay.

Methods: In contrast to our previous measurements of trace metal concentrations and speciation in Bay waters, sediments, and biota that are now routine, methodology for

measuring stable mercury isotopic compositions are still in the developmental stage – as our analyses of trace metals in Bay waters were when we initiated RMP sampling in 1989. Therefore, the initial set of mercury isotopic composition analyses will be made with reference materials and sediments (from age dated sediment cores) from the Bay to test our hypothesis that there are measurable differences in mercury isotopic compositions in historic inputs of mercury to the Bay. Assuming that hypothesis is confirmed, we will then measure spatial gradients of mercury in surface sediments within the Bay and its watershed.

Interpretation of these isotopic data will be complicated. While there is no measurable environmental (biological, chemical, geological or physical) fractionation of lead isotopes, the degree – if any – of environmental fractionation of mercury isotopes is not known. Moreover, there is no data base of natural or industrial mercury sources, as there is for lead, so sourcing mercury fluxes to the Bay and its recycling within the Bay will be more difficult. Fortunately, we have acquired numerous samples from the New Almaden and New Idria mercury mines that may be used to characterize the isotopic compositions of those two sources, and we have age-dated cores from the Bay that may be used to characterize sources of pre-industrial mercury inputs to the Bay. And we are collecting atmospheric depositions from both local (San Francisco Bay area) and trans-Pacific industrial sources that may be used to characterize contemporary aeolian fluxes to the Bay. Therefore, we may be able to distinguish natural, historic industrial, and contemporary industrial mercury fluxes to and within the Bay.

Personnel: The proposed research will involve individuals with complementary expertise. These include Dr. Celine Gallon, whose doctoral thesis research chronicled natural and industrial lead fluxes in lacustrine sediments using stable lead isotopic composition; Dr. Kit Conaway, whose doctoral thesis chronicled temporal and spatial variations in mercury concentrations and speciation in the Bay; Dr. Jugdeep Agaarwal, who has developed an expertise in MC HR ICP-MS – including some preliminary analyses of variations in mercury isotopic composition of reference materials. Genine Scelfo and Sharon Hibdon, who have been the principal analysts in our portion of the RMP program for more than a decade will also participate in the project, as will Russ Flegal, who also has been involved in all of the preceding types of analyses, will direct the research project.

Summary: The preliminary proposal is designed to duplicate the lead isotopic composition studies in the Bay that have proven so useful in identifying the sources and cycling of natural and industrial lead in the Bay. Those analyses have provided information on those sources and processes that could not be obtained with any other methodology. Analyses of mercury isotopic compositions in the Bay may provide similar information, which may then be used to optimize remediation efforts for this persistent and principal pollutant in the Bay.

References:

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