CALFED Bay-Delta ERP Panel Review

Proposal Number: 129DA

Applicant Organization: San Francisco Estuary Institute, US Geological Survey, and Avocet Research Associates

Proposal Title: Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

Please provide an overall recommendation.

Fund As Is $1,656,569

Conditions: None

Provide a brief explanation of your rating:

The study will investigate mercury cycling in tidal wetlands of the Petaluma River, with emphasis on quantifying and understanding processes that influence the abundance of methylmercury—the highly toxic form that readily bioaccumulates in exposed organisms and can biomagnify to high concentrations in organisms atop aquatic food webs. Many wetlands are sites of active methylmercury production (via microbial methylation of inorganic divalent mercury). It is presently unknown whether wetland-restoration activities will measurably exacerbate the methylmercury problem in the Bay-Delta ecosystem. This investigation is directly relevant to the issue of wetland restoration and methylmercury production in wetlands. The study sites will span a cross-section of wetland age, salinity, and stream order within the watershed. Information from this project will provide a foundation for developing strategies for wetland restoration that could reduce the associated production and bioaccumulation of methylmercury.

This proposal is based on a strong foundation of prior work, and it has been greatly improved and strengthened relative to the previous version. The investigators will apply innovative, state-of-the-science approaches to understanding mercury dynamics in wetland habitats, providing information of direct relevance and utility to ecosystem managers. This study will be conducted at the ecosystem scale, is hypothesis driven, and clearly addresses priority information gaps identified for the Bay-Delta ecosystem, for wetland restoration, and for mercury cycling in general. The results will be transferable to other wetland and estuarine systems, given that much of the proposed work is process-related. The team of investigators is knowledgeable, experienced, and possesses an array of complimentary technical strengths and disciplinary backgrounds. The project goals are ambitious, but the likelihood of successful completion is considered to be very good. The budget is reasonable.

The principal investigators should consider increasing the effort on examination of bioaccumulation and biomagnification in lower trophic levels, processes that could strongly influence the trophic transfer of methylmercury to clapper rails (see comments by Reviewer 1). The Proposal Selection Panel recommends that the principal investigators consider reducing the effort devoted to sampling and analysis of fish (described on pages 11-12 of the proposal), to free project resources for more intensive analysis of the lower benthic food web. It may be desirable to include a co-investigator or collaborator with experience in trace metal bioaccumulation in lower trophic levels of the benthic food web into the overall project.

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CALFED Ecosystem Restoration Program External Review Form

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Below please explain any connection to proposal, to applicant, co-applicant or subcontractor, or to the submitting institution (write "none" if no connection):

I participated in the CALFED scientific review panel and have reviewed a previous version of this proposal. At the time of the assignment, I indicated that I have had a few projects working collaboratively with Dr. David Krabbenhoft, USGS, the fourth author on this proposal. I discussed this potential conflict at the time. It was felt that Dr. Krabbenhoft was more analytical support than project development and that my review would not be a true conflict. I will proceed with that assumption and offer an unbiased review.

Review:

1. **<u>Goals.</u>** Are the project's goals and objectives clearly stated and internally consistent? What ecosystem restoration benefits will it provide?

The project goals are well stated and consistent throughout the body of the proposal. The PIs propose to study a number of different sites within a single watershed in the Bay-delta region. The sites are chosen such that they represent a cross-section of wetland age, salinity and stream order within the watershed. As wetland restoration is a goal of the CALFED program, this project will provide a basis by which a remediation strategy might be developed. In the creation of new wetlands, one must consider the potential effects on the production and bioaccumulation of methyl Hg. This project will certainly provide information pertinent to that decision-making policy.

2. **<u>Approach.</u>** Is the approach well designed and appropriate for the project's objectives? Is it justified by prior site studies or other information documented in the proposal? If additional information is needed to adequately plan and design the project, does the proposal include adequate provisions for obtaining it during the project's design and environmental assessment? If not, what additional information should be gathered?

The PIs have presented an innovative approach to understanding Hg dynamics in a single, well-characterized watershed in the Bay-Delta area. They have definitely strengthened their approach relative to their previous version of this proposal. There are several innovative approaches that make this a strong research project. First, they have built their proposal on a strong foundation of previous work and assemble a team that brings together many different strengths and backgrounds. Second, they identify key sites within the watershed to use as indicator sites for future restoration efforts based on wetland physiography and contrasting physical-chemical characteristics. Third, the use of stable isotopic techniques to study hg transformation proceses at near-ambient levels is cutting-edge research and a real plus to this proposal. Finally, the authors have described an approach to use stable isotopic approaches to better understand the food web structure that leads to bioaccumulation of Hg in the endangered clapper rail. It is an ambitious proposal, but one that should prove beneficial to future restoration efforts.

3. **Feasibility.** Is the approach fully documented and technically feasible? Is the scale of the project consistent with its objectives? Does it reflect "best practices" for this type of project? If not, how should the project be revised to reflect "best practices"? Is it likely to attain the ecosystem restoration objectives it seeks?

As presented, the approach is feasible, given the number of sampling sites and the technical abilities of the group assembled for the research project. The group will conduct seasonal sampling at each of their sites. As an aside, it would be extremely beneficial to conduct a mass balance for a few tidal cycles on some of the sub-wetlands studied. The link with USGS researchers and the ability to gage a portion of this watershed could yield valuable information on source/sink relationships in these wetlands. These are critical measurements if one is dealing with Hg that is predominantly transported downstream and deposited into a wetland. Knowing whether particular portions of the complex wetland watershed are sources or sinks of methyl Hg would be valuable information for restoration efforts. The PIs should also do a better job understanding and sampling Hg and MeHg in the lower food web. Benthic invertebrates are mentioned, but better details of which organisms are important and the frequency of sampling needed to define Hg and MeHg content would have strengthened the proposal.

4. **Capabilities.** What is the applicants' track record in terms of past projects? Is the project team qualified to efficiently and effectively implement the project? Does the proposal describe how additional expertise and other support necessary to successfully accomplish the project will be obtained? If not, what additional expertise or support is needed?

The PIs are well-qualified to participate in this research. While the main PI does not have an extensive publication record in Hg processes and pathways, the collaborators provide the strong background in trace metal cycling in the environment. This project could benefit by the inclusion of a PI with more extensive experience in trace metal bioaccumulation in the lower food web. Simply measuring MeHg in a variety of organisms may not be the best way to determine trophic transfer. Phytoplankton, algal mats and grazers may all be important for bioaccumulation, but may not be apparent in analysis of clapper rail diets.

5. **Cost/Benefit Comments.** Is the budget reasonable and adequate for the work proposed?

The budget appears to be reasonable for the level of work proposed.

Additional comments:

Please provide an overall evaluation summary rating: Excellent: outstanding in all respects; Good: quality but some deficiencies; Poor: serious deficiencies.

<table>
<tr><th>Overall Evaluation Summary Rating</th><th>Provide a brief explanation of your summary rating</th></tr>
<tr><td>Excellent X</td><td rowspan="3">If there were a category of “Very good”, I would have assigned it to this proposal. This revision of the proposal addresses some of the weaknesses of the previous version. The only concern that I have with this proposal is that the lower portion of the food web is not well described and may be one of the most important aspects in estimating the extent of bioaccumulation for predictive models. The PIs have a strong track record in geochemistry, microbiology and avain biology, but there appears to be a slight weakness in understanding lower food web processes. For this reason, it falls a bit short of the “excellent” level.</td></tr>
<tr><td>Good X</td></tr>
<tr><td>Poor</td></tr>
</table>

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I have worked collaboratively with Dr. David Krabbenhoft on past projects, and have co-authored a grant proposal submitted to the US Geological Survey several years ago. I do not believe that this affiliation affects my review in any way.

Review:

1. **<u>Goals.</u>** Are the project's goals and objectives clearly stated and internally consistent? What ecosystem restoration benefits will it provide?

   The project goals and objectives are clearly stated, and fulfill many of the critical gaps in information that CALFED has identified. If successful, the authors will provide critical information as to how inorganic and methylmercury (MeHg) cycles relative to specific wetland characteristics, including age, salinity, chemistry, food web structure, time, and space. Very little is known about Hg cycling in wetlands world-wide, much less in the Bay-Delta system—the fact that much of the proposed work is heavily process-related means that the results should be transferable to other wetland, terrestrial, and estuarine systems. Such benefits include:

   - relation of methylation and demethylation rates relative to pore water chemistry, especially sulfate/sulfide content—a point of active debate
   - confirmation as to whether benthic organisms are good indicator species for spatial distribution of Hg and MeHg
   - information for managers as to the sensitivity of varying wetland environments to changes in Hg/MeHg

   The principal strengths of the proposal are the experience and abilities of the authors, who are very well suited to carry out the proposed research, as well as the focus on benthic-biota coupling and process-oriented studies.

   I would have liked to see a goal that examines the relative bioavailability of mining-derived (mineral phase) Hg to that of atmospheric or more reactive aqueous inputs in a controlled experiment. Perhaps these studies could be worked in as the project progressed.

   The project is ambitious in that it is investigating everything literally from the ground up to the rails. These studies can have inherent drawbacks such as dilution of resources and labor, and undersampling/aliasing. Also, how representative is the Petaluma system to other local wetlands in terms of hydrology, Hg inputs, and vegetation?

Overall, I believe that the information gained is likely to outweigh these concerns.

2. **Approach.** Is the approach well designed and appropriate for the project's objectives? Is it justified by prior site studies or other information documented in the proposal? If additional information is needed to adequately plan and design the project, does the proposal include adequate provisions for obtaining it during the project's design and environmental assessment? If not, what additional information should be gathered?

   As mentioned, the study approach is ambitious in its spatial and temporal scales. The authors acknowledge this by proposing frequent compositing of samples, and eschew the need for assessing meter-scale sediment patchiness. Their approach assesses wetlands with gradients in age and salinity along the Petaluma River, with between- and within marsh comparisons from five wetland systems. Water, sediment, benthos, and fish will be collected over time and space. I find these samples to be adequate to the objectives and hypotheses, but would recommend that several other points along the age/salinity continuum could be sampled to a much lower extent (and perhaps one in the Bay). Further, perhaps an additional gradient in vegetation could be investigated, using these pre-chosen sites. While certainly not an expert, the rail work seemed like it could quickly get out of hand in terms of labor and time, particularly linking prey items and egg characteristics to Hg/MeHg concentrations. I would like to see better constraint and detail on these approaches.

   The authors will use multiple regressions to establish controls on MeHg, which is sufficient for a study like this where so little is known about the system or its controls. Several of the objectives, such as photo-demethylation rates, have focused experiments planned. Of particular importance is the MeHg to sulfate/sulfide concentration dependence, and it is good to see that all of these ancillaries are being measured. How about additional incubation experiments that add sulfate or sulfide to porewater to benthic organisms? Also, I would like to see focused experiments examining the relative bioavailability of mine tailing mineral Hg to that of non-mineral (perhaps atm-derived) Hg. I have included a list of questions and concerns relating to the approach:

   - (not knowing much about rails) are rails year-round integrators of a certain marsh or sub-marsh, or will off-site effects mask the signatures of local wetland sites?
   - Should we be concerned about small-scale patchiness, particularly when evaluating sediment patterns and benthic organisms? 8-10 samples per site may not be enough to characterize it.
   - What about diel variation in aqueous MeHg and water chemistry? The Everglades work demonstrated that things can happen quickly, and easily aliased. Perhaps a winter and summer diel study could be included.
   - My accounting says (max.) 2 locations x 10 samples x 3 seasons x 5 sites = 300 samples for water and sediment. The budget says 140 per year. Is this a concern? Also, samples are budgeted for analysis in year 3, but with no sample collection—is this analysis of back-logged samples?

- Will water samples include filtration to assess non-particle fractions?
- Why are Hg radio isotopes used rather than stable ones? Not a major issue, just curious.
- Photo-demethylation: the budget says 60 samples/yr—what are the sampling specifics?
- I didn't find much specifics on the rail surveys (perhaps this needs to be worked out as the study progresses)…how many birds do you plan to tag and track, and for how long—is there a statistical number that need to be tracked? It was difficult to assess cost/benefit on this one. The budget lists ca. 3000 man-hours of labor for rail studies in yr 3, though no year 3 sampling is planned in the timeline.
- Lower taxa will be composited at each site—will any of these taxa be analyzed separately if enough tissue is available?
- What is the "reference site" for comparing rail egg data? What will the isotope and gut analysis data tell us about MeHg contamination in rails? It seems like a lot of work for an endpoint (rail MeHg) that has so many other compounding effects and controls.
- The QA/AC procedures seem fairly standard. Is it appropriate to analyze in duplicate, as apposed to triplicate (for error analysis)? Also, what % of field and lab samples will be routinely analyzed with replication?
- Is there the need and resources for a 3rd winter sampling in 2005-06 (see timeline). The last field trips end during the middle of year 2.
- The study performance measures are typical and adequate.

3. **Feasibility.** Is the approach fully documented and technically feasible? Is the scale of the project consistent with its objectives? Does it reflect "best practices" for this type of project? If not, how should the project be revised to reflect "best practices"? Is it likely to attain the ecosystem restoration objectives it seeks?

   I have no doubts that the authors will apply the best possible technical capabilities to this project. Particularly on the geochemical side, the authors employ the most up-to-date and proven methods for Hg analysis and microbial study. All aspects of this research have been performed before on other projects, so method development is likely a minimum effort.

   The scaling of the experimental design is appropriate to the objectives, though the project has the potential to get out of hand in terms of numbers of samples collected (spatial/temporal considerations) and the undefined labor estimates associated with the rail work. The authors should stay flexible and modify the amount of composite samples taken as the study progresses.

4. **Capabilities.** What is the applicants' track record in terms of past projects? Is the project team qualified to efficiently and effectively implement the project? Does the proposal describe how additional expertise and other support necessary to successfully accomplish the project will be obtained? If not, what additional expertise or support is needed?

To my knowledge, the authors Davis, Martin-DePasquale, and Krabbenhoft are at the top of their fields, and there is no reason to believe that they and the others will not produce high quality results and recommendations. The diversity and experience of the authors compliments their stated objectives extremely well. I do not believe that outside expertise is required.

5. **Cost/Benefit Comments.** Is the budget reasonable and adequate for the work proposed?

   The budget is adequate for the proposed research, with the stated concerns over the potential discrepancy between sample collections and analyses for MeHg in sediments and water. Also, I am not sure that the amount of labor associated with the rail work is adequate, as there was little detail on rail numbers, cost of effort per bird, etc.

   Generally speaking, the benefits from this study could be quite high relative to cost, as very little is known about mercury in these ecosystems. Also, much of the knowledge gained (rate constants, pathways, controls) may potentially be applied to other systems.

Additional comments:

Please provide an overall evaluation summary rating: Excellent: outstanding in all respects; Good: quality but some deficiencies; Poor: serious deficiencies.

Overall Evaluation Summary Rating	**Provide a brief explanation of your summary rating**
Excellent X	The study will investigate an understudied ecosystem that gets to the very heart of the wetland restoration debate. It is heavily process-oriented and wide in scope—an ambitious effort. I believe that it is well-worth funding at the proposed level.
Good	
Poor	