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RMP Contaminant Fate Workgroup Meeting February 6th, 2009 San Francisco Estuary Institute Meeting Minutes DRAFT

Attendees:

Shaun Ayers (UC Davis)
Barbara Baginska (RWQCB)
Joel Baker (Univ. of Washington)
Joel Blum (Univ. of Michigan)

Terry Cooke (URS)

Arleen Feng (ACCWP representing BASMAA)

Gretchen Gehrke (Univ. of Michigan) Holger Hintelmann (Trent Univ.) Rusty Holleman (UC Berkeley) Richard Looker (RWQCB)

Rob Mason (Univ. of Conn.) Trish Mulvey (SFEI Board) Tom Mumley (RWQCB)

Darell Slotton (UC Davis) Keith Stolzenbach (UCLA) Jay Davis (SFEI) Ben Greenfield (SFEI) Katie Harrold (SFEI) Michelle Lent (SFEI) Lester McKee (SFEI) John Oram (SFEI)

Meg Sedlak (SFEI)

Don Yee (SFEI)

1. Introductions and Review of Agenda [Don Yee]

Don Yee convened the meeting at 10 am with an introduction of the goals of the meeting. The highest priority items for the meeting were: 1) review progress of Hg strategy pilot studies, 2) develop long-term modeling strategy, and 3) update workgroup on coring project.

Arleen Feng suggested changing summaries of presentations in meeting minutes to consist of a brief summary of highlights of the presentation and a list of action items. Trish Mulvey asked about R. Mason's comment on p. 4 of last CFWG meeting's minutes. Rob Mason noted that the important piece of information in his comment is that Kd is lower in sediment than water. Don Yee asked that any additional comments be emailed to him.

2. Overview of the RMP Mercury Strategy [Jay Davis]

Jay Davis gave an overview of the RMP Mercury Meeting on 2/5/2009. He noted that the Hg meeting was focused on studies addressing Questions 1, 2, and 3, with the main focus being Question 1, which is being addressed by the Small Fish Project.

Discussion:

Trish Mulvey asked what the plan is to address Q5. Jay Davis responded that the strategy is well laid out for Q1-Q2-Q3 for the next few years, but Q4 and Q5 studies will be developed as Q1-Q2-Q3 studies come together. There currently is no plan to address Q5. Arleen Feng suggested that we should be more explicit in how plans will progress or change with new data. Richard Looker stated that he thinks we are making good progress on the Hg studies and that the strategy is good, but the study results are somewhat sobering.

Action Item:

• Jay Davis to lay out plan (brief – 1 page or less) for addressing Question 5

3. Mercury Strategy – Small Fish [Ben Greenfield]

Ben Greenfield presented draft 2008 results from the Small Fish Project and requested guidance for project focus for 2009. He noted that a lot of effort went into developing the study design, which was a stratified random design plus potential hotspots (identified through a conceptual model), last year with significant input from the CFWG and BASMAA. The spatial survey consisted of a probabilistic sampling of entire bay shoreline, with sites designated as enclosed or open-water, and targeted sites including high-/low-elevation wetlands and potential Hg sources. Additionally, some sites were repeat sampling locations from prior years (long-term sites). Both Mississippi silverside and topsmelt Hg data exhibited a North to South trend, with especially high levels in Alviso Slough, which drains to Lower South Bay. The highest small fish Hg levels being found in Alviso Slough are not surprising as it is downstream from a former Hg mining area with features possibly conducive to methylation (wetlands or salt ponds). The highest silverside Hg concentrations were similar to concentrations found in higher trophic level sport fish. Ben noted that this level of Hg in small fish is of concern for protecting wildlife health. Small fish sampled in wetlands did not exhibit a consistently strong elevation signal which was somewhat of a surprise as it had been hypothesized that low-elevation/always-wet marshes would produce less MeHg than higher elevation marshes, which are subject to wetting and drying cycles. Another unexpected result was that silversides sampled in sites downstream of WWTPs generally had lower Hg levels than neighboring sites. Small fish caught in Napa River sites possibly impacted by mining activity also exhibited higher levels of Hg.

Discussion:

In regards to small fish Hg levels being of concern, Richard Looker mentioned a small fish TMDL target of 60 ng/g ww in whole body fish for protecting the Least Tern (a concentration exceeded by many of the fish sampled). Rob Mason asked how different the feeding patterns and life histories of topsmelt and Mississippi silversides are. Ben Greenfield said that in a special study in the Bay they found that topsmelt and silversides in the same area eat the same things, but that topsmelt are more marine and silversides can be found in nearly freshwater, where their diets are probably quite different. Darrel Slotton also noted that the growth rates of the species are quite different with topsmelt growing more quickly, and also foraging over a wider range, which may contribute to their different concentrations. Gretchen Gehrke asked what is known about the hydraulic conditions (e.g. tidal range) at the various sites. She suggested that perhaps the WWTP sites see different water exchange conditions than the other sites. WG members noted that these pelagic fishes could easily travel between adjacent high and low wetland areas, utilizing the same habitat regardless of where caught. Trish Mulvey remarked that some WWTP mixing data exist for the South Bay that might be helpful for estimating flushing characteristics. Joel Blum asked if reactive mercury had been measured in the sediment and said that they would measure it in their sediment samples.

4. Mercury Strategy – Results of the DGT Study [Holger Hintelmann & Ben Greenfield] Holger Hintelmann presented preliminary results from the 2008 deployment of Diffusive Gradient in Thin Films (DGTs). He explained how the DGTs work and how they are deployed.

He showed a two month time series of weekly retrievals which indicated linear MeHg uptake for at least one month; however, due to initial concerns about biofouling, 2008 deployments were only one week in duration. He showed a spatial overview of the MeHg levels seen by DGTs deployed in the water column, which showed a broad-scale north-south gradient, similar to Hg in small fish. However, direct comparison of the water-column DGT MeHg results to small fish THg results by individual sites showed weak correlation. The correlation was weakened by several notable anomalies, namely Pt. Isabel marsh, Kirker Creek, and Alviso Slough. Holger Hintelmann noted that he wouldn't expect perfect correlation given that the DGTs are stationary and sample a local environment for a limited time while mobile fish sample a larger environment over a longer time span. DGTs deployed in sediment to sample pore water registered much higher MeHg levels than their water-column counterparts. In a previous study, sediment DGTs were shown to be very good at identifying high MeHg production areas (tight correlation between MeHg in sediment DGTs and net MeHg production). The sediment DGTs included a section that extended above the sediment-water interface, which showed that the water overlaying sediment has much higher MeHg levels than 'open' water.

While DGTs currently cannot replace small fish Hg sampling due to weak correlation, they offer a complementary tool for identifying hot spots of MeHg production, measuring diffusive fluxes across the sediment/water interface, determining MeHg speciation, and sampling almost any environment in a highly spatially and temporally localized manner.

Ben Greenfield presented a proposed DGT sampling plan for 2009, and requested WG input. Ben Greenfield asked the WG if they supported continuing broad spatial coverage with DGT sampling or if they thought local site "source characterization" (e.g. small-scale spatial variability) was more important. Seasonal sampling for temporal variability was also raised as a possibility. He also brought up the possibility of changing wetland effort to sample resident species and doing a focused DGT study in wetlands.

Discussion:

Joel Baker asked if MeHg desorption/depletion from sediment is actually being measured by DGTs deployed for pore water sampling. Rob Mason suggested comparing methylation and desorption rates to gel uptake rates. It was noted that the data were corrected for temperature. Rob Looker asked about the approximate time it took for MeHg to diffuse across the gel relative to deployment time. Holger Hintelmann responded that the diffusion time is on the order of hours, so it is small relative to the one week deployment time. Richard Looker and Darell Slotton raised concerns about the deployment time being too short relative to time over which fish integrate Hg, as well as potentially missing Hg peaks, and at the wrong time (after and not before fish collection).

The WG discussed the expected spatial scale of sediment vs. water column DGTs. Specifically, sediment DGTs pick up a highly localized MeHg signal (which can vary greatly on short spatial scale). In contrast, water DGTs exhibit a more spatially integrated MeHg signal. Fish might be eating benthic organisms, but it is an open question as to how much benthic fish MeHg levels are influenced by sediment MeHg levels.

Jay Davis stated that he is not surprised by the low level of correlation between small fish MeHg concentrations and DGT MeHg concentrations due to temporal and spatial sampling differences, but the real question is "Are DGTs a useful tool, i.e. for identifying MeHg hotspots?"

With regard to the 2009 DGT plan, Darell Slotton suggested deploying DGTs first, for four weeks, then collecting DGTs and fish together at the end of the DGT deployment, so the temporal sampling is similar. Several issues were noted for longer deployment: increased likelihood of losing DGTs, increased fouling, data not comparable to 2008 data (1 wk deployment), and more difficult fieldwork logistics.

Regarding the potential wetland effort, Richard Looker remarked that wetland signature might be blurred by species that are being sampled, but changing to wetland-specific species will limit inter-comparability of data. Jay Davis noted that from a traditional RMP perspective, wetlands are studied with regard to their impacts on the Bay, so lack of a true understanding might be okay; however, if perspective is changing, then we should rethink study design. Arleen Feng commented that wetland discussion merits its own study, so we should finish this study first, and then move into wetlands. Darell Slotton mentioned that obligate wetland fish biomonitoring species (e.g., longjaw mudsucker) are likely not easy for Terns to eat, so they might be less relevant to management endpoints. Tom Mumley noted the need to incorporate new information to update/revise strategy and conceptual models, and he asked if there is any formal reporting/revision structure for doing this. Jay Davis responded that we will develop a means of tracking progress in implementing the RMP strategies and revising the strategies. This will be done as part of the annual process of evaluating the strategies and the RMP Master Plan.

For the DGT 2009 sampling plan, the WG came to the consensus that expanding comparisons with small fish was the highest priority, with seasonal characterization being a secondary priority. "Source characterization" spatially intensive studies at individual sites are to be considered a low priority. The WG also agreed that changing the deployment strategy to 4 weeks prior to fish sampling (as suggested by Darrel Slotton) was necessary. The WG recommended using any remaining funds to do a spatial and temporal (seasonal) characterization at SFEI's local MLK site. The WG also suggested that multiple DGTs be deployed a set distance (e.g., 10 m) apart to investigate how variable the concentrations are.

Action Item:

• Ben Greenfield to send memo to WG incorporating the WG's feedback on 2009 DGT sample design and outlining cost options for increased DGT effort at Small Fish sites

5. Mercury Strategy – Results of the Isotope Study [Joel Blum]

Joel Blum presented preliminary results of the Hg Isotope study, and requested WG input on study plans for 2009. The goal of the study is to better understand which processes, sources, and pathways contribute disproportionately to food web Hg accumulation. The study looked at Hg isotope variation in sources (current data: bedrock, mine waste, dry deposition; pending data: precipitation, urban run-off, wastewater effluent), sediments, and fish. Joel Blum showed results for 10 sediment sites paired with fish (silverside) samples. Each sample was plotted as its mass-dependent fractionation (MDF) against its mass-independent fractionation (MIF). The sediment data were tightly clustered in its isotopic composition except for sediment from Pt. Isabel which

exhibited a lower MDF. The silverside data were somewhat spread along the MDF axis showing a North/South signal, but tightly clustered along the MIF axis except for two MIF anomalies: Pt. Isabel and Kirker Creek. Joel Blum also presented isotopic composition data for some Hg sources, including dry deposition, pre-anthropogenic marine, urban precipitation, industrial Hg products, Hg mining ore & waste. The data were somewhat clustered, and only calcine really stood out with having a higher MDF. Joel Blum then presented several ways the isotopic composition of Hg can change: 1) microbial demethylation, which shifts the MDF, 2) photochemical demethylation, which shifts both MDF and MIF, and 3) photochemical reduction, which shifts both MDF and MIF. He then showed how the MDF and MIF shift from sediment to estuary to open ocean as the percent photochemically degraded MeHg increases.

Summary of what isotopic composition shows:

MDF: A difference in bio-available Hg sources to sediments (need to measure)

MIF: A difference in the extent of demethylation of MeHg (or photoreduction of methylatable Hg2+???) prior to incorporation into the food web

Discussion:

Richard Looker asked, in regard to atmospheric mercury transported across the Pacific, if there is any correlation between Hg transport distance and species fractionation. Joel Blum responded that nothing has been published on this topic, but he suspects that there would be distance-dependence of fractionation due to oxidation.

Lester McKee noted that most Hg used by humans has been 'roasted' during post-mining processing and asked if this would change isotopic signature. Joel Blum responded that the isotopic signature of Hg from roasting is not necessarily different than that of Hg mined directly as Hg. But the tailings from roasting will have a different isotopic signature because the Hg has been preferentially separated to only leave the heavy isotopes behind.

Lester McKee pointed out that much South Bay Hg is from erosion (natural deposits and mining tailings) and should have a different isotopic signature. Joel Blum agreed, and said that the Hg from erosion would be heavier than the processed Hg shipped to the Sierras. It was noted that we would expect a North-South Hg isotope gradient due to processed Hg coming in through Delta and mining waste Hg entering Bay from Lower South Bay watershed, although gradient may be complicated by former Hg mines in coastal range of north Bay area. Richard Looker commented that the sediment cores might show Hg mining signal versus gold mining signal.

Lester McKee asked if photo transformation is more important in the Delta then the Bay, noting that the site sampled closest to the Delta had the highest MIF. Joel Blum remarked that photochemical degradation rate is impacted by light penetration. Darrel Slotton noted that Pt. Isabel and Kirker Creek sites are less turbid than other sites, which could explain the high photochemical degradation signal in MeHg at those sites. He remarked that they could use a Secchi disk to measure water transparency this year. Joel Blum and Gretchen Gehrke were keen to explore this possible explanation for their results.

Joel Blum and Gretchen Gehrke asked for topsmelt samples for the same sites they tested silverside to check for species uptake differences and see if habitat differences are reflected in isotope ratios.

Action Items:

- Joel Blum indicated that he would finish the 2008 analyses that are outstanding including reactive mercury in sediment, atmospheric wet deposition from the four sites, wastewater treatment samples and the Zone 4 Line A wet weather samples. The results from the 2008 work will be presented in a progress report to CFWG. Joel will also include a proposal for the work for 2009. Both documents will be circulated to the CFWG for review.
- Lester McKee/SFEI staff will assist Joel Blum in collecting urban runoff samples
- Darell Slotton/Shawn Ayers and Gretchen Gehrke will coordinate shipping of topsmelt samples for appropriate sites
- Darell Slotton to consider taking Secchi disk readings in future sampling.

6. Modeling Strategy [John Oram]

John Oram presented the draft modeling strategy, and asked for guidance/feedback from the WG. The intent of the modeling strategy is to develop capacity to predict impact of management efforts on Estuary water quality. The strategy was developed on the premise that we have good hydrodynamic understanding of bay and surrounding watersheds, but lack good sediment transport understanding needed to understand transport of some contaminants.

Strategy:

- 1. Increase coordination by establishing a Bay Area Modeling Forum
- 2. Develop a flexible resolution Bay and Margin Model
- 3. Develop Regional Watershed Model(s)

After outlining the overall strategy and showing some example flexible grid models, John Oram outlined the tasks and a timeline to create a Bay and Margin model. The modeling would start with a literature review to develop a conceptual model of Bay margin, then a South Bay hydrodynamic model would be developed and extended to include sediment transport, hotspots and tributaries. Then the South Bay hydrodynamic model would be extended to the entire Bay, and finally contaminants and biota would be added to the Bay Model. Currently only the Margins Conceptual Model is funded.

Discussion:

Tom Mumley suggested pulling together a summary of sediment transport knowledge. Jay Davis responded that the TRC had discussed this idea and decided it was not high enough priority to fund in 2009.

Arleen Feng asked if the model will meet the needs of the WB in a timely fashion, and noted that we need to look ahead to data needs for regulation. Tom Mumley responded that the model is necessary for the WB to be better informed. Arleen Feng stated that she is fully in support of a modeling forum, but that it should have a narrow RMP focus. Barbara Baginska commented that we would need to review the results of the Margin Conceptual Model before we truly know how to proceed and that there needs to be a feedback loop with check-ins. Joel Baker said that

successful models are clearly driven by management objectives. Barbara Baginska agreed and noted that it is also the WB's responsibility to establish management questions.

Joel Baker expressed a concern with the modeling strategy and cautioned against stepwise additions of model capabilities (i.e. water first, sediment next, contaminants after that); suggested instead adding contaminants "early and often." He stated that if biota are the main concern, we need to rethink the strategy, e.g. for PDBEs in birds, need to accurately model plankton, organic carbon, and other food web components, so is sediment transport really the focus? He noted that there are lots of good reasons to model water and sediment, but need to focus on what will answer management questions. Successful modeling efforts have been driven by well-articulated questions. For example, in New York Harbor, a \$10 million effort focused on answering "where are the contaminants in this bucket of mud coming from?" General discussion followed regarding needing to define question(s) to be answered by modeling in order to determine necessary capabilities and resolution of the models. In response, Lester McKee commented that we might not be able to predict what will be the important management question(s) as we do not know what will be important in five years, e.g. emerging contaminants are constantly coming online and so we'll need flexibility in model to address these new contaminants.

Tom Mumley said that the model seemed like a good deal for its cost, but where will the funds come from? Meg Sedlak responded that the funds can come from pilot and special studies RMP fund. Arleen Feng remarked using those funds would not leave much money for any other pilot or special studies, so need to consider priorities. She also raised the concern about equity in the RMP funding allocation process, vis a vis, CFWG requests vs. requests from other work groups. Jay Davis mentioned he, John Oram, and Josh Collins are looking into additional funding opportunities (e.g., USFWS).

Keith Stolzenbach said this type of modeling is becoming routine and that other locations in CA are doing these types of modeling, e.g. for Marine Protected Areas. He recommended collaborating with these other modeling efforts, as well as with USGS sediment modeling program. He cautioned that there's no point in doing 2D modeling and that we need to do 3D modeling to get real capabilities. He recommended connecting watersheds to Bay model early on, as a parallel and integrated effort, as opposed to connecting watershed model later. He suggested possibly incorporating a wind model and wave model.

Arleen Feng stated that we need to think about a RMP product that gives useful information to stakeholders, e.g. interactive websites (like the Prop 13 website) that provide usable information.

John Oram summarized the issues raised as being 1) Is this the right approach to the modeling? and 2) What are the management questions? In regard to management questions, Richard Looker commented that we will need to refine them as we generate data and learn more, so we will need an iterative process with check-ins. Barbara Baginska requested more refined description of the various modules in the model and suggested evaluating what is already available for each module (and how customizable the modules are) so that we know which modules would need to be developed. Richard Looker said he thought the draft strategy is good, but that, if we want to make a regulatory product, we need to phrase management questions in terms of TMDLs.

Trish Mulvey commented to Arleen Feng that dischargers seem of two minds about actually wanting a management tool that they may be required to use. Arleen Feng responded that dischargers want management tools once they know something is going to be regulated, so it's important to have tools ready for them.

Jay Davis asked the WG if they think funding the development of the South Bay Hydrodynamic Model (\$30,000) is a priority. It was noted that \$30,000 is a relatively small buy-in. Jay Davis stated that an outline of the Bay Margin Conceptual Model report will be circulated. Joel Baker suggested also circulating results of CARP (NY Harbor) model to show what has been/can be done. This project did a good job of distilling the output into final products. For Conceptual Model development, Barbara Baginska requested being clear about what is possible and what is not, as well as what we already do.

Action Items:

- WG given 2 weeks for additional comments on strategy. John Oram will circulate revised version with workgroup suggestions.
- Develop and circulate outline of Bay Margin Conceptual Model Report
- Circulate results of CARP model (http://www.carpweb.org/main.html)

7. RMP Sediment Coring Project – Next Steps [Don Yee]

Don Yee presented results to date for the Sediment Coring Project. The Sediment Coring Project inventories contaminants distribution (spatially and historically) in sediment around the Bay and provides data for contaminant model development and validation. To determine pollutant loading history from sediment cores, Don Yee matched sediment layers to associated time period through bathymetric history, or radioisotope-dating (complete dataset not yet available). For each region of the Bay. Don Yee showed several examples of core dating using bathymetry. Cs137 presence (known 1960s peak) and Pb210 decay, establishing approximate timeframes for sediment layers. For each of the core sites, he showed metal and PCB concentrations over the length of the core and discussed the timing of pollutant concentration peaks, comparing them to known historical loadings. Don Yee found that bathymetry and isotope dating qualitatively gave generally similar sedimentation results: Suisun Bay and San Pablo Bay are eroding, Central Bay and South Bay are neutral/eroding and Lower South Bay is accreting. Cores from wetland sites more directly track pollutant loading history, but results from Bay cores were difficult to interpret as some sites had eroded or the sediment was well-mixed. Also, for Bay cores, the bathymetric history, isotope dating and expected/known pollutant signal did not always match up, again making interpretation difficult. A major highlight of Don Yee's results is that there are few 'ticking time bombs' in the Bay as historical pollutant loads have mostly eroded or already been dispersed. After presenting results, Don Yee discussed next steps, including analyzing pending samples (radio-dating, PCBs, OC pesticides), potentially adding more analytes (e.g. dioxins), working with USC researcher (Doug Hammond) modeling accretion versus mixing for radioisotopes, and developing strategy for potential future coring.

Discussion:

The WG was generally surprised that the core from Coyote Creek showed a Hg peak ~1960, while the core from Alviso Slough does not. Lester McKee noted that Hg use was up after WWII, so a 1960 peak is not that surprising. Trish Mulvey mentioned that the mouth of the Guadalupe River was moved from Guadalupe Slough to Alviso Slough ~1900, and she suggested looking at Robin Grossinger/Historical Ecology's history of development data for Lower South Bay to better understand core taken from Coyote Creek.

Rob Mason noted that Ar-Cl interferes with Se ICP-MS analysis in seawater, so he suggests disregarding Se data (signal too noisy). Someone asked if Se analysis was done with DRC (dynamic reaction cell) ICP-MS which may be less subject to interference. Tony Rattonetti (of CCSF lab asked after the meeting) later confirmed DRC was used.

Richard Looker commented that the results show that bathymetric history cannot be relied on for core age, which brings into question John Oram's sediment calibration of the PCB multibox model. Rob Mason said that he believes isotope dating over bathymetric history. Joel Baker suggested integrating Pb age over entire core. Erosive areas should have less Pb210 (little new accumulation), compared to well mixed areas which might have similar surface Pb210 but more at depth.

Joel Blum asked if there are military bases with antifouling metals use that have been cored. Craig Jones' work at Hunters Point was mentioned as was the Mothball Fleet work done by NOAA recently, and Alameda Naval Station.

Action Items:

• Re-circulate Craig Jones' reports on sediment work and coring

Next CFWG Meeting: The date for the next CFWG has not been set yet and will be chosen via email.