RMP Emerging Contaminant Work Group Meeting
April 3rd, 2008
San Francisco Estuary Institute
DRAFT Meeting Minutes

In Attendance:

Eric Dunlavey (City of San Jose)
Naomi Feger (RWQCB)
Lee Ferguson (University of South Carolina)
Jennifer Field (Oregon State University)
Denise Greig (The Marine Mammal Center)
Jennifer Jackson (EBMUD)
Bruce LaBelle (Cal EPA, DTSC)
Keith Maruya (SCCWRP)
Derek Muir (Environment Canada)
Karin North (City of Palo Alto)
Myrto Petreas (DTSC)
John Prall (Port of Oakland)
Paul Salop (AMS)
David Sedlak (UC Berkeley)
Saskia van Bergen (EBMUD)

Mike Connor (SFEI)
Jay Davis (SFEI)
Letitia Grenier (SFEI)
Katie Harrold (SFEI)
Susan Klosterhaus (SFEI)
Lester McKee (SFEI)
Meg Sedlak (SFEI)
Meredith Williams (SFEI)
Don Yee (SFEI)

Via phone:
Richard Grace (AXYS Analytical)

A. Introductions and Review of Agenda

Meg Sedlak began with introductions and a review of the day's agenda. She began with an overview of the meeting goals: feedback on the updated draft Emerging Contaminants Work Group (ECWG) Five-year Plan, feedback on and ranking of proposed pilot and special studies for 2009, and review and approval of specimen banking protocol outline. She introduced the newest member of the ECWG science advisory panel, Lee Ferguson of the University of South Carolina. Dr. Ferguson has a background in nanoparticles, akylphenol ethoxylates, and organic chemical contaminants. Ms. Sedlak indicated that Dr. Ferguson is a recent recipient of an EPA STAR grant to study nanoparticles – one of the field sites will be San Francisco Bay.

B. Update on 2007/2008 Special Study: PFOS in Seals

Meg Sedlak presented an update on the 2007–8 perfluorinated compounds (PFCs) in seals special study. This work is being conducted in collaboration with Denise Greig of The Marine Mammal Center and is part of a larger three-year study examining the health of harbor seals.

Derek Muir said that a new study on effects of PFCs in mice has been published. The benchmark effects dose is lower than those in previous work. He will send the paper to Meg. Meg said that she knew of two new studies looking at seals and humans that also had lower effects doses. Jennifer Field said that another new paper looked at the estrogenicity of some PFCs. She will send the paper to Meg.

In 2007 seals were captured and sampled at Castro Rocks, near the Richmond Bridge, and Tomales Bay, a reference site outside of San Francisco Bay. There are two other major haul-out sites in the Bay, Mowry Slough and Yerba Buena Island, but these were not sampled. Concentrations of PFCs

(e.g., PFOS, PFDA, PFHxS, and PFNA) were higher in seals captured in San Francisco Bay than Tomales Bay.

PFOS has also been measured in cormorant eggs at three locations: Richmond bridge, which corresponds to the seal Castro Rocks site, Wheeler Island in the Delta, and Don Edwards National Wildlife Refuge in the South Bay. Concentrations of PFOS in cormorant eggs from Don Edwards were greater than the predicted no-effect concentration (PNEC). The closest seal haul-out to Don Edwards is Mowry Slough, which was not targeted as part of the seal study in 2007. Archived 2004 blood samples from seals captured at Mowry Slough will be analyzed this year. The samples will provide an opportunity to see whether there is similar spatial variation in seals.

Jennifer Field asked how Denise Greig compared data from stranded and captured animals. Denise Greig indicated that the issue is complicated and that she remains aware that they are different datasets in her analysis. The PFC element of The Marine Mammal Center study is focused solely on blood from captured (live) animals.

David Sedlak asked if PFC concentrations are standardized to protein content of blood samples because PFCs preferentially bind to proteins. Denise said that they haven't, but that she has the total protein data and could check to see if it makes a difference. Derek said that he has not seen protein corrected data in the literature. Lee Ferguson said that total protein concentrations should remain consistent in serum. He wondered if PFCs preferentially bind to specific kinds of proteins, in which case changes in the ratio of different proteins would have an impact.

In 2008 additional archived samples will be analyzed to better characterize gender, age, and spatial differences. Ten samples will be analyzed from Castro Rocks and Tomales Bay and six from Mowry Slough. Samples from an additional 20 seals will be collected and analyzed in the spring of 2008, dependant on capture success.

C. Update on 2008 Special Study: Alternative Flame Retardants

Susan Klosterhaus presented an update on the 2008 alternative flame retardants special study. She is planning to analyze bioaccumulative compounds in archived samples of harbor seal blubber (~10 samples; various sites; 2007-2008), croaker and surfperch (~10 samples; various sites; 2006), cormorant eggs (6 samples; 2 composites at 3 sites; 2006), and sediment (~10 samples; South Bay, Central Bay; 2007). Additionally, she plans to analyze surface water from the Lower South Bay (10 1-L grab samples; 5 sites; 2 replicates/site) for non-bioaccumulative compounds.

David Sedlak asked if hydrolysis of DEHP has been observed in seawater. Derek Muir said that a study of DEHP in Vancouver did not find bioaccumulation in marine foodwebs. Dr. Muir indicated that this was because they hydrolyze.

It was noted that the hydrolysis of the brominated benzoate and brominated phthalate could form a paraben. Jennifer Field said that some of the concern about parabens is due to the initial exposure to humans prior to their entry into marine systems and the foodweb. Richard Grace indicated that the metabolites of the parabens can be quite high (10 times higher than the measured concentration). Mr. Grace indicated that he is preparing a manuscript on this subject that should be available in two months.

Lee Ferguson said that there may be some protection from hydrolysis by sorption to particles if the K_{OW} is high.

Karin North asked if Susan would like to analyze effluent samples. She noted that biosolid concentrations will not provide any information about potential effluent concentrations. She said that the City of Palo Alto would be willing to provide effluent samples and may be able to assist with the analytical costs.

David Sedlak asked Susan Klosterhaus if she was planning on analyzing reference samples. Susan said that she had reference samples for seal blubber, but was not sure if there are reference samples available for the other matrices because they are archived samples. Jay Davis said that it may be possible to get reference fish samples, but that eggs would be harder. Denise Greig said that she might have contacts with researchers collecting eggs in Monterey, but it may not be a good reference site as significant DDT contamination has been identified in the sloughs near Monterey.

David Sedlak asked why the water was being analyzed for a suite of compounds including triphenyl phosphate (TPP) as he wasn't sure that they would be detected and wasn't sure that they would accumulate. Derek Muir indicated that the compounds were fairly stable. In a prior RMP pilot study, Daniel Oros detected some compounds in surface water samples.

Lee Ferguson asked if it would be possible to add benthic samples. Susan said that the RMP has not routinely sampled the benthos, limiting the availability of archived samples. She said that this study would serve as a first cut to determine if the compounds are present. Future studies could look at the benthos. Derek Muir stated that phthalates may not biomagnify. Lee noted that sampling benthic biota, where many of the compounds are expected to be, would be very valuable. Karin North said that USGS collects benthic samples near the Palo Alto WWTP discharge point. She suggested that they may have archived samples or be willing to collect extra samples. Jay said that there are archived bivalve samples which could be analyzed.

Lee Ferguson concurred with David's suggestion of reducing the number of water samples.

Lee asked what other analyses had been done on the archived samples. He suggested that some results, such as silver, could be useful to correlate with and possibly indicate sources.

Myrto Petreas asked what the likelihood of detecting the analytes was.

Derek Muir suggested that the results from blubber samples may be disappointing.

ACTION ITEMS:

- Susan Klosterhaus to revise the 2008 Alternative Flame Retardants study and send back out to the group for informational purpose.

D. Discussion of Five-year Plan

Meg Sedlak presented the draft Five-year Plan for EC. She asked for feedback from the workgroup on the priority question, strategy for identifying chemicals, and the five-year plan and budget. She said that there is the option to add additional priority questions and noted that the other workgroups

each have several. The current EC priority question is "what emerging contaminants have the greatest potential to adversely impact beneficial uses in the Bay?"

Derek Muir and Lee Ferguson said that the current approach to identifying chemicals for consideration is consistent with approaches of similar groups and is appropriate.

Meg suggested evaluating the list of top chemicals identified in the Great Lakes National Program Office Report (Howard and Muir 2007) and available analytical capabilities as a potential future pilot study. The list is based on an evaluation of the Canadian Domestic Substance List (DSL), the U.S. EPA High Production Volume (HPV) list, and the Toxic Substance Control Act (TSCA) Inventory Update Rule. The threshold for the Canadian DSL list was much lower than for the TSCA list (i.e., 100 kg vs 10,000 kg).

Derek Muir presented a summary of how he and his colleagues evaluated the lists and identified the probable persistent and bioaccumulative substances that should be considered for further study and measurement in the Great Lakes region. They identified the top ten chemicals within several classes (brominated, chlorinated, fluorinated, non-halogenated, and siloxane-related) and recommended that these be analyzed in environmental media as part of chemical contaminant monitoring programs.

Derek Muir indicated that there were a number of challenges working with siloxanes. There are no commercially available chemical standards and analytical methods are not well developed. Blank contamination is a huge issue. There is not much ecological toxicity data; several of the siloxanes have been identified as carcinogens (e.g., D-4 which is widely used). Phasing out silicones in society would be a huge effort.

Derek Muir also said that no compounds regulated by the FDA were included in the evaluation. Derek said that the QSAR model (structure activity model used to predict chemical/physical properties) biased the results toward halogenated compounds.

Jay Davis asked if the Great Lakes Commission is planning to conduct a follow up study based on the results of the evaluation. Derek said that there were no plans yet. He said that they are facing the same question as the ECWG, if compounds are being targeted because they can be measured or because they are of concern.

Denise Greig asked if analytical methods have been standardized for many of these compounds. Derek said that standardization is occurring slowly. Don Yee said that Environment Canada is hoping to have a method available by 2010 and that a conference on this issue was recently held in Canada.

Lee Ferguson said that screening for many compounds could be done with LC-MS and high-resolution MS. He said that metabolites are not included in Derek's evaluation and that they may be valuable. He asked what the end product of PFC degradation is and said that it may be important to evaluate.

Lee Ferguson suggested that the RMP consider including cationic surfactants. He said that they have not been measured in the US except by Bruce Brownawell at Stony Brook University. They have been detected in concentrations up to 100 $\mu g\ g^{-1}$ in sediment in Jamaica Bay, New York. The analysis is analytically difficult, but they are deliberate biocides/microbicides. They are extremely

persistent, although they may not be bioavailable because they strongly adsorb to particulates. Jennifer Field suggested that the availability and toxicity from particulate bound compounds be evaluated prior to analysis. David Sedlak said that New York has more combined sewers and combined overflows than the Bay Area, which may impact concentrations.

David suggested that the ECWG consider looking at compounds in wastewater and develop a method for identifying the next generation of urban pest controls (i.e., pyrethroid replacements). He suggested that because the Bay is home to several major ports, the ECWG should look for the next tributyl tin and consider other shipping-related compounds. He also said that Silicon Valley is close to the Bay and that the ECWG should consider evaluating water-based cleaners.

Jennifer Jackson said that she was concerned about nanoparticles, particularly with regard to issues regarding the discharge by nanoparticle manufacturers to wastewater treatment facilities. Eric Dunlavey and Karin North agreed. Lee Ferguson said that the analytical methods for nanoparticles are very challenging and specific to each kind of nanoparticle. He said that the production information is proprietary and that because nanoparticles are not reportable substances there is little available information on their composition. Jennifer Field said that there are significant problems with standards for nanoparticles.

Karin and Jennifer Jackson said that they were concerned about the perceived threat of pharmaceuticals. Karin asked that a statement be added to the Five-year Plan that the effects of long-term exposure to low concentrations of pharmaceuticals are not known. Jennifer Field said that eventually illicit drugs will be detected in waterways. She has detected 2 $\mu g\ L^{-1}$ of methamphetamine. Illicit drugs are bioactive and frequently undergo very little degradation, and the developmental and behavioral toxicities at low concentrations are not known.

Derek Muir mentioned that he anticipates revising the table of chemicals to include additional toxicity information.

E. Proposals for 2009 Pilot and Special Studies

i. Pharmaceuticals Part II

Katie Harrold presented a brief summary of the 2007 pharmaceuticals special study and presented several potential options for next steps. Concentrations of the compounds detected generally decreased: influent > effluent > Bay surface water. Concentrations of the six compounds detected in the Bay decreased with increased distance from WWTP discharge points and frequently were below detection.

Katie noted that the initial study was preliminary and only included the compounds for which there were commercially available analytical methods. There are other compounds of interest due to their persistence and/or toxicity, which can now be analyzed. Additionally, pharmaceuticals are in the public awareness especially with the recent AP article on pharmaceuticals in drinking water.

There are several options for future studies: 1) a white paper that includes a literature review of concentrations in effluent and other environmental matrices and a dilution model, 2) a survey of concentrations Bay-wide, which would include additional compounds for which there are now analytic methods, 3) a survey of concentrations in water, sediment, and biota, potentially including metabolites. Katie also asked for input from the workgroup on ideas for potential studies. She

presented a proposal by Mark Benotti of the Southern Nevada Water Authority to study bioaccumulation of pharmaceuticals and compare bioaccumulation and/or sediment partitioning to log K_{OW} values.

Lee Ferguson said that the pharmaceutical study had well characterized effluent concentrations. Karin North noted that Lower South Bay has tertiary treatment unlike much of the rest of the Bay and therefore the concentrations may not be applicable Bay-wide.

Karin suggested conducting a study on estrogenicity. David Sedlak said that estrogenicity from WWTPs is always dominated by steroid hormones. Lee said that pharmaceuticals and endocrine disrupting compounds are evaluated using different methods.

ii. Nonylphenol Ethoxylate Degradation Products

Katie Harrold presented a proposal to study nonylphenol ethoxylate degradation products. She said that nonylphenol was analyzed as part of the RMP Status and Trends monitoring in 2002 and 2003. It was subsequently dropped from the list of analytes because the concentrations were not believed to be of concern. However, there are many degradation products that are also estrogenic and are more likely to be present in the Bay.

Lee Ferguson said he was surprised that nonylphenol was not detected in sediment. In general concentrations of nonylphenol, which is hydrophobic, are higher in sediment than water. He asked what methods were used and noted that it is very important to be careful when selecting analytical methods.

Jennifer Field suggested adding carboxylated degradation products to the list of analytes. She noted that they are the more abundant species. Chlorinated and brominated alkylphenols are generally present at much lower concentrations.

Jennifer Field also noted that Stanford researcher Martin Reinhard has been involved in a study of using recycled water to augment groundwater supplies in the South Bay and that it might be helpful to look at this work.

iii. Sources of Perfluorinated Compounds to the Bay

Meg Sedlak presented a proposal to study the sources of perfluorinated compounds (PFCs) to the Bay. Concentrations of PFCs in Bay biota, seals, and cormorant eggs are elevated relative to reference sites and concentrations worldwide. There are many potential sources of PFCs including fire fighting foams (from refineries, military bases, airports), aviation hydraulic fluids, and industrial and consumer uses. She proposed testing surface water from the RMP Status and Trends cruise, tributary surface water that is being collected as part of RMP Special Studies, WWTP influent and effluent, and small fish.

Jennifer Field asked if there were unlined landfills that have been in existence since the 1960s and discharge to the Bay. The group indicated that there were many unlined landfills around the Bay. Jennifer said that she found high concentrations of PFCs at 10 landfills tested, including some located near San Francisco Bay. Karin said that the City of Palo Alto is number 5 in the study that Jennifer performed. Jennifer also suggested looking at historical reports of fuel fires and locating fire training centers as they may be significant point sources of PFCs. She said she did not know

what the effects of tertiary treatment would be on effluent concentrations. She said that she did not think that including influent from secondary WWTPs would be valuable because of low rates of removal.

Both the City of Palo Alto and City of Redwood have unlined landfills. Karin said that the Palo Alto WWTP treats the leachate from their unlined landfill.

Derek Muir suggested including some of the acetic acids. He will send Meg the analyte list.

Including decane sulfonate in biota was suggested.

ACTION ITEMS:

- Meg Sedlak to revise PFC sources proposal based on feedback from the workgroup.

iv. Polychlorinated Naphthalenes

Susan Klosterhaus presented a proposal to study polychlorinated napthalenes (PCNs). PCNs were widely used until the 1980s and have been detected in Great Lakes biota and in breast milk from people in Sweden. PCNs have dioxin-like toxicity and have similar potencies as some of the coplanar PCBs. Because there is a potential connection between PCBs and PCNs as impurities in PCB mixtures and they are dioxin-like, PCNs may be of concern in San Francisco Bay. The goals of the study are to assess whether PCNs are present in the SF Bay foodweb at concentrations that have the potential to cause adverse effects to wildlife and provide a preliminary assessment of whether there are particular areas of concern within the Estuary.

Susan laid out two sampling options. Cormorant eggs (3 egg composites at three sites) will be collected in 2008 as part of RMP Status and Trends monitoring. The funding for sampling and analysis of dioxins and dioxin-like PCBs is already secured. The eggs could also be analyzed for PCNs, which would allow for the calculation of sum dioxin TEQs and the relative contribution of PCNs. In 2009, sport fish will be collected as part of Status and Trends. White croaker, which generally have the highest concentrations of organic chemical contaminants, could be analyzed for PCNs. However, they are not currently slated to be analyzed for dioxin or dioxin-like PCBs. Analysis of croaker would complement previous sport fish studies of dioxin-like toxicity (1994-2006) and provide data on the risk of exposure to fish-eating wildlife and people.

David Sedlak asked what the management options would be if PCNs were detected in high concentrations. He said that the current strategy for PCBs is to wait for them to degrade. Susan noted that the data may be valuable to the dioxin TMDL that is being developed.

Susan was asked what the volume of PCN production was.

Richard Grace suggested that if the full suite of PCNs is analyzed the source may be identifiable. He said that there are significant signatures for point sources.

Derek Muir said that if there are archived PCB extracts they could likely be analyzed for PCNs.

John Prall asked if there is a model for entry into the Bay. Susan said she expected it was similar to PCBs. Derek Muir said that PCNs can be an impurity in PCBs.

Jennifer said that oxy-PAHs can have high toxicity and have been found in the LA Basin. They can be in soils, as metabolites of PAHs, and are produced by white rot.

ACTION ITEMS:
- Susan Klosterhaus to revise PCN proposal based on feedback from workgroup.

F. Specimen Banking Protocol

Susan Klosterhaus presented the preliminary plans for a specimen banking protocol. She asked for feedback from the workgroup on relative priorities for archiving different classes of samples and appropriate storage conditions to insure sample integrity over time.

Derek Muir said that changes in the lipid concentrations have been detected at -20 °C by de Boer. Lee Ferguson said that enzyme activity doesn't go to zero, it is just decreased, so there will still be some activity at -20 °C.

Paul Salop described the current conditions of the archived samples. The facility is at -20 °C and records the temperature, but does not have back up generators. However, it would likely stay cold for a few days in the event of power failure. The facility is not secured, but he puts tape on the coolers every time he stores samples and the tape has never been disturbed. An advantage of the current facility is that he can access the samples whenever there is a need.

Derek Muir asked if the samples are stored in plastic or glass. Paul said that the storage container varies depending on the sample.

Myrto Petreas said that DTSC stores samples in glass at -20 °C. She said that CDC uses polypropylene for their samples. Lee Ferguson said that glass can be used at -80 °C, but that care must be used. He said that samples cannot be overfilled and that Pyrex is less likely to break than untreated glass. He also said that seals can be damaged or compromised at -80 °C.

David Sedlak again voiced his support for chemical analyses of samples from reference sites and the archiving of this material. He also noted that samples will need to be purged every so often because of degradation and lack of space. Planning for indefinite storage of samples is fine for now, but in another 40 years it may not make sense. It was suggested that the oldest samples are often the most valuable and it might be foolhardy to get rid of them.

Denise Greig said that everything can go wrong, as the Marine Mammal Center has found out. She said she would be happy to share all the information they've learned from their archive.

Lee said he supported long-term storage at -80 °C. He said that the ThermoFisher quote for freezer storage was quite high since a unit could be purchased for $5,000. Jennifer suggested getting a Toshiba unit, which moderates power surges. Freezers can be set up to call a phone number when they lose power.

Derek suggested -40 °C walk-in freezers.

Combining storage with another institution was suggested.

G. Science Advisory Panel Closed Session

A memorandum summarizing the science advisory panel closed session will be sent to the workgroup separately.

H. Next Meeting

The next ECWG meeting will be Friday October 17th, 2008.

Summary of Action Items

- Meg Sedlak to revise PFC sources proposal based on feedback from workgroup.
- Susan Klosterhaus to revise PCN proposal based on feedback from workgroup.
- Susan Klosterhaus to summarize changes to the 2008 Alternative Flame Retardants study.
- Meg Sedlak to write pilot and special study proposal for a white paper on contaminants of potential concern in wastewater.