

**RMP Emerging Contaminants Workgroup Meeting  
March 25<sup>th</sup>, 2011**

**San Francisco Estuary Institute  
DRAFT Meeting Minutes**

**In Attendance**

Rachel Allen, SFEI  
Amy Chastain, Bay Area Clean Water Agencies  
Mary Curry, CA Dept of Fish and Game  
Jay Davis, SFEI  
Nathan Dodder, Southern California Coastal Water Research Project  
Eric Dunlavey, City of San Jose  
Naomi Feger, San Francisco Regional Water Quality Control Board  
Lee Ferguson, Duke University  
Jennifer Field, Oregon State University  
Denise Greig, The Marine Mammal Center  
Erika Houtz, University of California - Berkeley  
Susan Klosterhaus, SFEI  
John Kucklick, National Institute of Standards and Technology  
Abdu Mekebri, CA Dept of Fish and Game  
Keith Maruya, Southern California Coastal Water Research Project  
Derek Muir, Environment Canada  
Karin North, City of Palo Alto  
June-Soo Park, Department of Toxic Substances Control/Cal EPA  
David Sedlak, University of California - Berkeley  
Meg Sedlak, SFEI  
Saskia van Bergen, East Bay Municipal Utilities District  
Simret Yigzaw, City of San Jose  
Don Yee, SFEI  
Andrea Kopecky, San Francisco Baykeeper

*Via telephone:*

Richard Grace, AXYS Analytical  
Luisa Valiela, US Environmental Protection Agency

**1) Introductions and Goals for the Meeting**

Meg Sedlak gave a brief overview of the day's agenda.

**2) RMP Planning Overview**

Jay Davis updated the workgroup on the RMP's overall master planning effort. The RMP Steering Committee (SC) has recently outlined priorities for the RMP for the next 5 years, as illustrated in the projected special studies budget in the Master Plan document. The SC has directed the workgroups to develop studies related to these topics, as they will best support the upcoming management decisions. However, if the workgroups identify other important studies that are uniquely suited to the RMP, they will be brought to the Technical Review Committee (TRC) and SC for consideration. The RMP is currently generating proposals for more funding than is available, and if RMP fees remain unchanged, the pool of funding for special studies will shrink. In 2011, the RMP is revisiting the Status and Trends (S&T) program and looking for cost savings, as well as searching for other potential funding sources for special studies.

Jay Davis noted that Contaminants of Emerging Concern (CECs) are a high priority for the Regional Water Quality Control Board, and he anticipates funding to be available for CEC studies in 2013, though the odds of a CEC study being funded in 2012 are low. Small Tributary Loading studies will remain a funding priority in 2012 through 2014. Meg Sedlak noted that the Municipal Regional Permit for Stormwater (MRP) covers some CECs, such as PFCs and nonylphenols. She asked if there are additional specific CECs that should be included in stormwater monitoring. Naomi Feger noted that PFCs and PBDEs were included in the recent small tributary monitoring analyte list, but that the driver for this work was mercury and PCBs. Jay Davis noted that the RMP has dioxin data for fish, bird eggs, water, and sediment, and most recently small tributaries. A synthesis of dioxins in Bay Area matrices will be done in 2013-2014. Eric Dunlavey pointed out that the MRP calls for a longer list of analytes than what has been collected for stormwater loads monitoring, reconnaissance monitoring, and watershed selection to date. Later stages of implementation will include the expanded list that will be monitored less frequently. Lee Ferguson asked for clarification of which analytes will be included in this future stormwater monitoring.

*(Following the meeting, Eric Dunlavey answered Lee's question via email: The details on frequency and number of samples and sampling location are still being finalized through the Small Tributaries Loading Strategy. However two categories of pollutants have been established: high priority and secondary priority, termed Category 1 and Category 2 in the MRP. The high priority ones are mercury, PCBs and associated measurements (SSC, TOC, etc) plus copper. Those analytes have been regularly included in stormwater loads monitoring to date, including the reconnaissance watershed monitoring done in 2010-2011. The expanded (secondary category) list includes: Selenium, PBDEs, PAHs, Chlordane, DDT, Dieldrin, Pyrethroids, carbaryl, fipronil, and nutrients. The actual implementation to date has not been as clean as how it appears in the MRP, but the relative importance of the two lists of analytes (high priority and secondary priority) is consistent with monitoring design to date and the current direction of the implementation plan.)*

In 2011-2012, Susan Klosterhaus will synthesize SF Bay work on CECs and identify priorities for future studies. Following the completion of this document in March of 2012, the ECWG will be better able develop proposals for CEC studies.

*(Eric Dunlavey indicated after the meeting that the current version of the MRP does not call for monitoring of PFCs and nonylphenol during this permit term. It calls for permittees to develop a work plan and schedule for initial loading estimates and source analysis for emerging contaminants. The workplan is to be submitted with the 2014 annual report and implemented in the next permit term, starting in 2015 at the earliest.)*

### **3) Pro Bono Brominated Dioxins Pilot Study and Flame Retardants in Oyster Bay Sediments**

Susan Klosterhaus presented the results from a pilot study on brominated dioxins in Bay Area sediment, white croaker, and harbor seal blubber and another study on flame retardants in sediment from Oyster Bay.

Brominated dioxins and furans are the brominated analogues of the well-studied chlorinated dioxins and furans. They are present as impurities in some brominated flame retardant commercial mixtures and may be formed via the combustion of products containing these mixtures. Available information suggests they have toxicity equal to or greater than their chlorinated analogues. Six samples from each of the three matrices were collected from SF Bay between 2006 and 2010, and analyzed pro bono by AXYS Analytical for brominated dioxins and furans. In sediment, brominated dioxins and furans were not detected at levels higher than the blanks, which were 0.1-0.5 pg/g dry weight. Some compounds were detected in sportfish, though they are all considered estimates as they are near the limits of detection. TEFs are not available for brominated dioxins, so TEQs were calculated using TEFs from the chlorinated dioxins. Maximum risk estimates (using nondetects equal to method detection limits) for brominated dioxins and furans in sportfish were 0.3-0.4 pg/g wet weight TEQ. One brominated dioxin congener (1,2,3,7,8-PentaBDD at 1 pg/g wet wt) was detected in one seal blubber sample above the blank value, and this concentration was also considered an estimated value. Susan Klosterhaus suggested that brominated dioxins only be monitored under special circumstances, as they do not appear to be accumulating in the Bay.

Richard Grace clarified that the MDL is computed by 1.5 times the signal to noise ratio, based on the full method detection limit. Blanks for brominated dioxins and furans tend to be higher than those for the chlorinated dioxins and furans because they are much less frequently analyzed and have fewer controls.

A separate study focused on PBDEs and alternative flame retardants in sediments from Oyster Bay, which were analyzed pro bono by Heather Stapleton at Duke University. Oyster Bay Regional Shoreline is downstream of the only foam manufacturing facility in the Bay Area. It no longer produces foam at the facility, instead importing from China; however there is still a large amount of foam processing that occurs at the facility.

In the Oyster Bay sediment samples, the pentaBDE mixture dominated, and the concentrations of PBDEs and other flame retardants tended to decrease towards the Bay, suggesting that transfer of these chemicals to the Bay from the creek may not be

substantial. Karin North suggested further studies test the blood of workers at the plant. Lee Ferguson added that the flame retardants in imported foam are unknown, and do not necessarily match the locally produced mixtures.

#### **4) RMP 2009-2010 PFC Sources Special Study**

Meg Sedlak presented the results from the 2009 RMP pilot study on sources of perfluorinated compounds (PFCs) to SF Bay. Between wastewater treatment plant effluent, stormwater, sediment and water around the bay margins, and ambient bay water, she found that PFC concentrations can vary greatly. The stormwater results suggest that PFOA is more quickly mobilized (perhaps due to its higher solubility) than PFOS, because it is higher during the river rise than the peak, relative to PFOS. The levels in wastewater treatment plant effluent are on par with other regions around the world.

Meg Sedlak clarified that the analyses were done on whole water samples, not filtered.

A draft article will be distributed to the ECWG for review within the next few months. Meg Sedlak proposed additional sampling of seals and birds in 2012, because the current data on sources do not explain the high levels of PFCs seen in these organisms. She also suggested that future stormwater sampling could include PFCs, along with nonyl-phenol and other emerging contaminants.

Jennifer Field asked about the relatively high concentrations of PFCs detected in sediment at Cooley Landing and Palo Alto. Karin North noted that the Palo Alto Landfill (near the sampling site), is unlined and still in use. Dr. Field noted that the presence of short chain PFCs in landfill leachate is consistent with other locations. She noted that landfill leachate tends to contain lots of 4-6 chain-length carboxylates, while wastewater is typically higher in the 8 carbon PFCs.

Karin North noted that Chris Higgins studied the Palo Alto wastewater treatment plant, and because PFC concentrations are occasionally higher in the effluent than in the influent, it looks like the plant is creating PFCs. Jennifer Field noted that this is a common effect, and is usually attributed to the degradation of precursors to PFOS and PFOA, most commonly, in activated sludge.

June-Soo Park asked about sediment cores – he noted that PFDS can be greater than PFOS in sediment cores. Richard Grace indicated that AXYS had developed a new method for biosolids that does include analysis of PFDS. To date, they have seen similar levels of PFDA and PFDS.

David Sedlak noted that the concentrations in sources in the Bay Area are similar to levels seen around the world, but some of the biota have extremely high PFC concentrations. He wondered if this implies that bioaccumulation is occurring differently here, or if there are other sources that have not been investigated.

Denise Greig asked about the half-life of PFCs in seals, which Meg Sedlak confirmed was short (weeks to months in seals and birds). She indicated that some seals migrate to the South Bay during pupping season, but that that region may not be their primary source of food.

Derek Muir asked about the PFOA level in seals. Because it is low, it indicates that they are not being exposed directly from contaminated food. Denise Greig confirmed this interpretation, noting that if the food supply were the only source more overlap would be expected between the concentrations seen in the South Bay and in Richmond. *(Following the meeting, Denise Greig indicated that recent work by Corinne Gibble in her Moss Landing Marine Labs masters thesis suggests that different prey is consumed by harbor seals in the north bay versus the south bay. Therefore, it may make sense that differences are observed in chemicals with short half lives in the blood of seals, while one would not expect such differences in the chemicals that persist in the blubber.)*

David Sedlak noted that the question of unique food web vs. anomalous source has management implications, and should direct the next PFC studies that are proposed.

Naomi Feger asked if the PFC signature in Cooley Landing sediments was similar to that in the South Bay seals. Meg Sedlak indicated that there was no correlation.

Jennifer Field noted that based on on-going research in landfill leachates, she does not expect levels to decline over the next few decades because of the large reservoirs of sources.

#### **5) PFCs and Precursors in Urban Watersheds RMP 2010-2011**

Erika Houtz gave a presentation on her study investigating PFC precursors in stormwater samples. She worked with SFEI during the 2010-2011 wet weather season to collect samples at 16 watersheds around the Bay Area, and is in the process of analyzing them for PFCs and PFC precursors. She measures precursor concentrations by oxidizing the samples, and comparing the PFOS and PFOA levels before and after oxidation. Based on lab studies, she expects the oxidation technique to convert most precursors to PFOS or PFOA. Results to date show PFOA and PFOS concentrations in stormwater up to about 20 ng/L, and up to 40 ng/L PFOA after oxidation, suggesting significant potential for precursors. There were no large differences between the concentrations seen in the watersheds investigated to date.

Lee Ferguson, Jennifer Field, Derek Muir, and Erika Houtz discussed some of the techniques used in the analytical method.

#### **6) AXYS/RMP Study on CECs in San Francisco Bay Mussels, Water, and Sediment**

Susan Klosterhaus presented the results from the 2010 CEC pilot study in San Francisco Bay.. The analysis of 104 pharmaceuticals and personal care products (PPCPs), alkylphenol ethoxylates (APEs), and PFCs was performed pro bono by AXYS, and the study was designed in support of the NOAA Mussel Watch CEC pilot study in California. About 40 PPCPs were detected in water, sediment, and/or mussel tissue. The concentrations detected were comparable to concentrations in other marine environments. In general, levels were highest in the South Bay. Nonylphenol (NP) was detected in water, sediment, and mussel tissue and the nonylphenol mono- and di-ethoxylates (NP1E and NP2E, respectively) were detected in sediments and mussel tissue. Susan Klosterhaus noted that where comparisons could be made, the levels from this study were similar to those for PPCPs in the 2006 South Bay study.

David Sedlak indicated that he was surprised at the number of wastewater-derived compounds and asked what the salinity at the sites was. Susan Klosterhaus noted that the sites were saline, but the salinity was not recorded. David Sedlak noted that these concentrations would not be expected in water with 20-30 ppt salinity, but rather in less diluted waters, close to WWTP outfalls. He is suspect of the veracity of the data based on the reported concentrations and the expected dilutions.

Lee Ferguson noted that though the APEs data for the sediments and mussels look reasonable, he is concerned with the water results. He stated that it is very rare to observe "only" NP in water at significant concentrations and we should detect both NP1E and NP2E in the water column as well, typically at higher concentrations than NP. He suggested that it may be a detection limit problem. In wastewater treatment, the NPE mixture is de-ethoxylated and often oxidized to form short ethoxy-chain NPEs (typically up to ~3EO), and NP is not appreciably formed during aerobic wastewater treatment. Typically, NP is formed during anaerobic sludge digestion or within anoxic sediments (through terminal de-ethoxylation). In the water column, the oxidized NPE metabolites are often the most important species quantitatively. These would be NP1EC and NP2EC. Lee stated it is possible (though unlikely) that all of the NPE species in the water column were oxidized to form carboxylated, acidic forms. This would remove all NPEs from the analytical window that AXYS had available. Oxidation to acid metabolites cannot easily happen for NP, so that compound would remain. He stated that it is also possible that there's another (non wastewater) source of NP to the Bay, which does not derive from NPEs (NP is used alone, in non-ethoxylated form, in plasticizers). If this was the case though, you'd expect to see the pattern repeated in the sediment, which it does not seem to be. Lee noted that generally speaking the concentrations are reasonable, believable, and quite low, but the patterns are not easily explainable. *(Lee Ferguson's comments were clarified and elaborated upon in an email after the meeting. His complete remarks are summarized here.)*

Susan Klosterhaus will discuss these concerns with AXYS and notify the group of the outcome.

**Action Items:**

- Susan Klosterhaus to discuss concerns about the PPCP and NPE data with AXYS and update the workgroup with the outcome.

#### **7) 2010-2011 NOAA Mussel Watch CEC California Pilot Study and Water Board Advisory Panels Update**

Keith Maruya updated the workgroup on the status of the Advisory Panel CEC report to the State Water Board. As part of the process, a number of case studies in Southern California coastal receiving waters are being conducted. Results from the first sampling efforts suggested that CECs were present in higher concentrations at the farthest point downstream for a case study of a river in San Diego. However, stormwater concentrations were still about 10 times lower than concentrations seen in wastewater. The project is currently focusing on occurrence and fate in effluent-dominated rivers in the LA region, biological effects testing, and expansion to inland freshwater systems. The final recommendations on monitoring CECs in discharges to coastal and marine systems is expected by September 2011. (*Dr. Maruya indicated after the meeting that this report would likely be delayed until early 2012.*)

Keith Maruya also discussed the status of the 2009-2010 NOAA Mussel Watch CEC California Pilot Study. The project is focusing on CECs and is utilizing the analytical capabilities of specialized labs across the US. Currently, data are being formatted and reviewed, and will be stratified by land use and proximity to point sources. The results will be presented at a future conference, likely SETAC 2012 in Long Beach. Susan Klosterhaus indicated that a special session on this project is in initial discussions for the SETAC 2012 conference.

Since the program is considering expanding to media other than mussels, Jennifer Field suggested that plastic pellets found in marine debris could also serve as a passive sampler. Keith Maruya noted that a group at SCCWRP is looking into this idea.

#### **8) CEC Profiles and Triclosan Fact Sheet**

Susan Klosterhaus updated the workgroup on the work on the CEC profiles, which have been created for triclosan and triclocarban, alkylphenol ethoxylates, and carbamazepine. Recently, a “recommended next steps” section was added to all the profiles, and a shorter fact sheet on triclosan was developed. The group was asked for their thoughts on the general format and content of the profiles, as well as next steps in this project: should more profiles or factsheets be developed, and if so, for which CECs?

Jay Davis noted that the triclosan factsheet was developed as part of the RMP effort to distribute more information to a larger audience. He envisions an RMP web page with access to a suite of factsheets.

David Sedlak suggested including a pre-amble at the beginning of the fact sheets to contextualize them, as they may become separated from SFEI as they are distributed

more widely. He also suggested that the “recommended next steps” section be renamed “uncertainties”, so that if they are not followed up on, it will not appear to be a fault.

Eric Dunlavey, Jay Davis, Lee Ferguson and Susan Klosterhaus discussed the format of the fact sheet and its intended audience. Susan Klosterhaus will revisit the “recommended next steps” section to address the comments.

Naomi Feger, Lee Ferguson, Jay Davis, Jennifer Field and David Sedlak discussed the efficacy of using CEC profiles to drive the emerging contaminants strategy. David Sedlak pointed out that profiles are inspired by questions from stakeholders and the public, rather than the forefront of science. Jennifer Field added that emerging contaminants require a balance of information designed to address stakeholder needs, such as “which new chemicals are harmful and how can they be controlled?” and information on the whole ecosystem, such as “what important effects may be caused by CECs?”. Jay Davis indicated that the contaminant by contaminant approach will not necessarily drive future funding, but serves as a piece in developing the CEC strategy.

Derek Muir suggested that “Antimicrobials” is a more appropriate title for the triclosan and triclocarban profile, as it highlights their mode of action, makes it more broadly applicable to compounds such as chloro-3 methyl phenol, and implies a role in the market – as soon as one is regulated or removed, another will be developed to fill the role. Lee Ferguson suggested including “Potential Future Actors” to illustrate this possibility.

Karin North and Amy Chastain suggested that the Water Board would be the appropriate entity to develop a management fact sheet that outlines what the public can do about these contaminants.

David Sedlak suggested that the profiles also include recommendations to wastewater treatment facilities for changes in their processes that could improve removal of the contaminants. Karin North added that the wastewater facilities are currently going through master planning efforts, so such recommendations would be timely.

Lee Ferguson proposed monitoring for CECs, especially alkylphenols and their derivatives, in stormwater.

#### **Action Items:**

- Revisit the “Recommended Next Steps” section of the CEC profiles and factsheet, rename to “Information Gaps”.
- Discuss with the SC the development of management fact sheets by the Water Board, based on the RMP scientific fact sheets.

#### **9) Broadscan Screening of Bay Wildlife for Anthropogenic Pollutants (Year 2)**

Nathan Dodder provided an overview of the analytical methods being applied by SCCWRP and Eunha Hoh at San Diego State to perform untargeted screening of wildlife

tissues from the East coast and southern California. This study is designed to identify chemicals that bioaccumulate in wildlife and have not been previously targeted for analysis. So far, the technique has been successful at identifying new contaminants, most of which are halogenated. David Sedlak pointed out that there are rarely bioaccumulative compounds that have effects that are not halogenated, so the skew towards detection of halogenated compounds may not be troublesome.

John Kucklick provided an overview of his progress to date on the untargeted analysis of chemicals in San Francisco Bay harbor seals. Six harbor seal samples have been collected and sent to NIST, along with mussel samples from two of the RMP mussel deployment sites in the Bay and the time zero mussels from Bodega Bay. Method development for the seal blubber samples is coming along well though additional work is still needed. John stated that he expects to complete the analysis of the CA seal blubber by the end of May, and from there will begin method development for the mussel samples. Additional year two objectives include building a library of new chemicals to augment the existing NIST/EPA/NIH Mass Spectral Library and quantify the nontarget compounds. He expects to have the mussel sample analysis and a manuscript completed by the end of 2011. In early 2012 he will focus on building the mass spec library and quantifying nontarget compounds in the samples.

Denise Greig offered to pass along to John Kucklick information about what compounds were injected into the seals before the blood sampling occurred.

#### **10) CEC Strategy Development'**

Meg Sedlak opened the discussion on the development of the CEC Strategy with a few ideas for future CEC studies. She proposed further monitoring of PFOS in seals, targeted monitoring for CECs such as triclosan, triclocarban, and alkylphenols in stormwater, and reporting assistance for the California CEC Mussel Watch pilot study. Jay Davis noted that none of these studies are being strongly recommended for 2012, but that the RMP wants to spend its money most efficiently, and is looking for input from the ECWG.

Derek Muir asked if the effects studies could help define the priority contaminants, and Naomi Feger suggested holding a joint meeting with the ECWG and the Exposure and Effects Workgroup.

David Sedlak pointed out that the RMP is most effective when it leverages concern amongst the larger scientific community about a specific issue to drive the collection of local data. He suggested that PFCs present a large area of uncertainty, primarily with regard to their sources and accumulation within the food web. An isotope study may be able to help address some of these questions. Denise Greig and Meg Sedlak will talk with David Senn about developing a hypothesis driven study on sources and pathways of PFCs using isotopes.

Lee Ferguson noted that studies have detected BPA at 50 ng/L concentrations in stormwater, concentrations close to the levels at which it causes estrogenicity. Karin North noted that BPA has more public interest.

Karin North and Eric Dunlavey noted that there are no pressing information needs on CECs from the wastewater agencies.

David Sedlak asked if there was a protocol for removing a compound from the “list of concern” in the MRP. For example, if loading from stormwater is less than 10% of loading from wastewater after four rounds of sampling, it should be removed from the list.

Derek Muir suggested that siloxanes may be an upcoming concern, and that Canada has led research efforts in this area. They are persistent and bioaccumulative, and can occur at high levels in the environment. To be proactive, the RMP should sample receiving waters and fish near wastewater outfalls, along with sewage sludge. Meg Sedlak suggested working with Environment Canada, and sending them small fish samples collected near WWTP outfalls.

David Sedlak suggested that working with SCCWRP to write up the Mussel Watch data is not a high priority for the RMP.

Meg Sedlak and the RMP will write up study proposals for the following ideas, and send them out to the ECWG for comment:

- 1) Isotope study on sources of PFCs
- 2) Emerging Contaminants in Stormwater, leveraging the MRP small tributary studies
- 3) Siloxanes
- 4) Flame Retardants in Oyster Bay

**Action Items:**

- Consider holding a joint ECWG and EEWG meeting that is focused on effects of CECs on biota.
- Develop a follow-up study on PFCs in the foodweb. Discuss the possibility of using isotopes with David Senn.
- Discuss developing proposals for future studies on siloxanes, CECs in stormwater, and flame retardants in Oyster Bay.

#	Action Items – March 2011	Who?	When?	Status 6/6/2011
1	Susan Klosterhaus to discuss concerns about PPCP and NPE data with AXYS, and update the workgroup with the outcome.	Susan Klosterhaus		

2	Revisit the “Recommended Next Steps” section of the CEC profiles and factsheet, rename to “Information Gaps”.	Jay Davis, Susan Klosterhaus		
3	Discuss with the SC the development of management fact sheets by the Water Board, based on the RMP scientific fact sheets.	Jay Davis/ Meg Sedlak		
4	Consider holding a joint ECWG and EEWG meeting that is focused on effects of CECs on biota.			
5	Develop a follow-up study on PFCs in the foodweb. Discuss the possibility of using isotopes with David Senn.	Meg Sedlak	June 2011	PFC study (not including isotopes) proposed to TRC for 2012.
6	Discuss developing proposals for future studies on siloxanes, CECs in stormwater, and flame retardants in Oyster Bay.			