



RMP
Emerging Contaminants Workgroup
April 15th, 2014
San Francisco Estuary Institute
Meeting Summary

Attendees:

Tom Mumley (SFB RWQCB)	Becky Sutton (SFEI)
Karin North (City of Palo Alto)	Meg Sedlak (SFEI)
Mike Connor (EBDA)	Ellen Willis-Norton (SFEI)
Eva Agus (EBMUD)	Don Yee (SFEI)
Simret Yigzaw (City of San Jose)	Keith Maruya (SCCWRP)
Derek Muir (Environment Canada)	Richard Grace (AXYS)
David Sedlak (UC Berkeley)	Jonathan Benskin (AXYS)
Ian Wren (SF Baykeeper)	June-Soo Park (DTSC)
Lee Ferguson (Duke University)	Erika Houtz (DTSC)
Luisa Valiela (US EPA)	Heather Peterson (SFPUC)
Eric Dunlavey (City of San Jose)	Nancy Denslow (University of Florida)
Kelly Moran (TDC Environmental)	Daniel Schlenk (UC Riverside)
Philip Gschwend (MIT, UC Berkeley)	Michael Fry (Fish and Wildlife - Hawaii)
Denise Greig (The Marine Mammal Center, California Academy of Sciences)	Sara Hoover (OEHHA)
Jay Davis (SFEI)	Andria Ventura (by phone)

I. Information: Update on Bioanalytical Tools Study [Nancy Denslow]

Nancy Denslow began her presentation by stating that bioanalytical assays are useful if you are unsure what chemicals are affecting aquatic biota. She then listed the year one and year two goals for the San Francisco Bay bioanalytical tools study. Nancy stated that by June 2014 the molecular biomarkers for *Menidia beryllina* will be developed, laboratory tests in early life stage (ELS) and juvenile exposures will be run, and in vitro bioassays will be completed. The model chemicals that will be used in the laboratory exposures include E1, 4-NP, BPA, and galaxolide. Survival, growth, and 5 molecular biomarkers were analyzed for ELS and juveniles during the laboratory exposures. In addition, vitellogenin (Vtg), estrogen, and testosterone were analyzed in juveniles.

High throughput estrogen and androgen receptor assays (InVitrogen assay) were also run for BPA, E1, NP, and bifenthrin. The response curve of the 17-beta estradiol (E2) was compared to the four chemicals to calculate the bioanalytical equivalent concentration. Nancy found that 17-beta estradiol was the most sensitive, followed by E1, 4-NP, and BPA. When the assay is run in antagonist mode, E1 is still a weak estrogen while NP and

bifenthrin act as antagonists at low levels. NP and bifenthrin act as antagonists because they occupy the ligand binding domain and don't let E2 bind to the estrogen receptor. Nancy thinks that galaxolide will also act as antagonist in the high throughput assay.

Nancy discussed the *in vivo* work that has been completed including a 7-day ELS *Menidia* toxicity test using 10-day old *Menidia* larvae. The endpoints for the test were survival and growth. For E2, E1, and NP there were no significant differences for survival and growth as the concentrations increased. Nancy stated that molecular endpoints are more sensitive; therefore, the samples have been preserved for targeted gene expression analysis.

Nancy described the 21-day juvenile *Menidia* toxicity test using 50-day old *Menidia* fry. The endpoints were growth, condition factor, liver RNA, and the carcass to verify sex. Four fish were used as backups to measure Vtg and steroids. The 21-day test has been completed for E2 and E1 and there were no significant differences in weight or length; the test is still running for NP, BPA, and galaxolide. Nancy noted that she is letting some fish grow longer to determine if any changes in sex occur.

Menidia PCR primers were validated for ERa, ERb, AR, Vtg, Growth hormone receptor, doublesex and mab-3 related transcription factor 1 (DMRT1, indicates genetic sex), and others to ensure the primers were working. Subsequently, juvenile E2 exposure was tested. The 10 and 20-day exposed juveniles only had Vtg expression with E2 levels of 100 ng/L; Choriogenin (Chg) appeared to be more sensitive with expression occurring at 30 ng/L E2. Nancy stated that for *Menidia* Chg was a more sensitive biomarker.

Nancy then tested how E2 exposure would induce AR and ERb mRNA. Interestingly, At 100 ng/L AR mRNA increased, but then decreased at 300 ng/L, which Nancy thought could be due to feedback inhibition.

Nancy ended her presentation by describing the field exposure experiment that will occur this coming year. The experiment will include exposing ELS and juvenile *Menidia* to effluent from various sample sites and running assays and identifying molecular biomarkers. The effluent will come from Bay Area WWTPs, collected by SFEI, and from Southern California WWTPs. An initial ER assay was completed using WWTP effluent and with dilutions there was a very clear response; Nancy noted that the same results were not observed with an AR assay.

Discussion:

Lee Ferguson asked about the how bifenthrin acts as an estrogen, if it is through basic binding to the estrogen receptor (ER). Nancy replied that bifenthrin causes Vtg to increase *in vivo*. But, bifenthrin may act on the hypothalamus, rather than directly binding to the ER. Tom Mumley asked if work has been completed on other pyrethroids. Dan Schlenk responded that studies on permethrin have been completed which show that the pyrethroid causes estrogenic activity.

Dan asked if the duration of the exposure was long enough; in his experiments, using a different fish, the fish are dead within a week in 300 ng/L E2. He noted that it would be useful to have a similar endpoint, or threshold, concentration. He agreed with Nancy that Chg is a more sensitive biomarker. Finally, Dan stated that the ability to see DMRT1 was useful in distinguishing phenotypic from genetic sex. Nancy agreed, stating that the *Menidia* she receives comes in two different sizes and it would be useful to determine if the size differences indicate their sex or a difference in age/growth. Dan responded that the tanks should be divided by *Menidia* size class before the exposures are performed.

Derek Muir asked if the “round robin” ER assay that Nancy described at the end will be performed for the four model chemical assay; Nancy responded affirmatively. Derek wondered if there was inter-lab variability; Nancy replied that all of the labs listed the same waters as estrogenic.

David Sedlak asked about how various water quality parameters, such as high ammonia levels, may affect the results. Nancy replied that by changing the pH, ammonia can be removed from the water. David also wondered if *Menidia*'s sensitivity to the chemicals changes in saltwater. He stated that there is a known estrogenic response in fish exposed to the model chemicals and wondered about the causative agent if the effluent concentrations do not trigger a response. Nancy replied that all of the treatments were performed in saltwater. She added that *Menidia* is more sensitive than sheepshead minnow but less sensitive than fathead minnow in fresh water. She stated that estuarine type fish may not be as responsive to estrogens and suggested completing a similar experiment with adult *Menidia*.

Denise Greig asked if estrogenicity is expected to increase or decrease growth. Nancy responded that estrogens could do both and she will examine the human growth receptor after exposure to the four chemicals. Michael Fry asked if Nancy could determine the stage of sexual maturity based on the gonads. Nancy replied that her team has performed the histology and the ovaries and oocytes were visible; however, the testes were not. Nancy is planning on taking sagittal sections to view the testes. Meg Sedlak ended the discussion by stating that the ECWG will receive the year one progress report on June 1 and she will ask the workgroup if they support year two of the study.

Action Items:

1. Meg Sedlak will send the year one progress report on June 1 and will ask the workgroup if they support year two of the study.

II. Update on CEC Strategy [Meg Sedlak]

Meg Sedlak provided an update on 2013 CEC activities including the completion of the CEC Synthesis, the CEC Strategy, and the PBDE Summary Report (with a manuscript in progress). Meg noted that there are other CEC activities occurring across the state including statewide recommendations for CEC monitoring in estuaries, an expert panel to advise recycled water use, and the creation of a Green Ribbon Science Panel to advise the Department of Toxic Substance Control on reducing adverse health and environmental

impacts of CECs. Meg noted that Kelly Moran and Becky Sutton are both members of the Green Ribbon Panel.

Meg then briefly reviewed the RMP's CEC Strategy, focusing on the tiered risk based screening approach to monitoring. Meg stated that approach is iterative; there is the potential for removing contaminants from certain tiers with increased information or new management strategies. Meg reviewed the contaminants listed as of moderate concern, Tier III (PFOS, Fipronil, Nonylphenol, and PBDEs), informing the ECWG of ongoing monitoring and potential special studies for each CEC.

PFOS is currently being monitored in bird eggs, sportfish, and sediment. Meg noted that apex predators continue to possess high PFOS concentrations. Today, the 2013 PFC precursor results will be discussed as well as the potential for measuring PFCs in effluent and harbor seal blood. PBDEs will continue to be monitored in sediment and tissue; water sampling will no longer occur because it is not an effective matrix for PBDE monitoring. Meg noted that Nonylphenol and Nonylphenol Ethoxylates (NP/NPE) are not included in S&T, which is consistent with the recommendations of the State CEC panel report. However, they are included as part of the bioanalytical tools project. Today, Becky Sutton will discuss the option for monitoring NP/NPE in WWTP effluent. Fipronil is currently measured in Bay stormwater, sediment, and was measured in ambient Bay water in 2013 (all non-detects). Fipronil monitoring will continue in Bay sediment because there is an increasing trend as well as in stormwater; Bay water monitoring will be discontinued. In the afternoon, Becky will discuss the inclusion of Fipronil in a special study on effluent monitoring.

Meg then noted that Tier II and Tier I contaminants will also be addressed today when 2015 special study proposals are presented including pharmaceuticals and personal care products (Tier II), alternative flame retardants (Tier I), and current use pesticides (Tier I). Outside of the tiered risk framework, the RMP is identifying CECs using bioanalytical tools and NIST broadscan work. Meg was encouraged that not many CECs were identified in the broadscan work.

Meg ended her presentation that the SC supported a placeholder of \$100,000 for 2015 CEC special studies. Tom Mumley noted that there are competing priorities in the RMP; therefore, the goal of today's meeting is to review and prioritize the proposed special studies and recommend study designs.

III. Information: Update on Alt Flame Retardant Monitoring [Becky Sutton]

Becky Sutton began her presentation on alternative flame retardant monitoring by stating that the change to TB117 is now in effect, instead of products needing to withstand an open flame, they now just need to withstand a smolder test. Becky noted that another bill, AB127, was recently approved by the Governor requires the California Fire Marshal to review the current flammability standards for insulation material. The Fire Marshal has created a review panel to address the possibility of changing the standard.

Becky then stated that the RMP is monitoring for flame retardants in surface water, stormwater, WWTP effluent, sediment, bivalves, and seal blubber. Da Chen, a professor at Southern Illinois University, has developed methods for phosphate, brominated, and Dechlorane plus-related analytes. He is expanding his phosphate method to include metabolites, and adding a few more target chemicals to the method for brominated flame retardants.

Becky presented general trends in ambient Bay and stormwater alternative flame retardant concentrations. Phosphate flame retardant concentrations were ten times higher in stormwater than in ambient bay water, indicating that stormwater is a source of flame retardants to the Bay. However, the concentration ratios of the various phosphates differed between stormwater and ambient Bay water. Becky ended the presentation by listing the 2014 sampling timeline: effluent is being sampled in April, seals will be sampled in June, sediment in August, and bivalves in September.

Discussion:

Mike Connor asked Becky for an estimated mean concentration for ambient Bay water; Becky replied around 300 ng/L. Derek Muir responded that the concentration she mentioned is globally on the high end. Becky noted that she does not have all of the ambient Bay sample results; therefore, the average concentration may change. Naomi Feger asked if all of the products were flame retardants. Becky replied that the products could also be plasticizers. Lee Ferguson asked if the RMP was measuring tracers (e.g. caffeine) along with the alternative flame retardants. Becky replied that PCBs are being measured, but not in the same 4 L bottle.

Mike Connor stated that the concentrations Becky mentioned would put alternative flame retardants above PBDEs in the tiered risk framework. Becky responded that phosphate flame retardants are metabolized quickly, unlike PBDEs. Derek replied that phosphates should be measured in blood, which is a matrix Becky is considering sampling in seals. June-Soo Park stated that DTSC is considering measuring phosphate flame retardants in human urine samples

IV. Information: Update on AXYS PFC Precursor Pro Bono Study [Jonathan Benskin]

Jonathan Benskin gave the ECWG an update on PFC precursors in San Francisco Bay. Jonathan began by providing background on PFCs, a diverse class of anthropogenic chemicals. He noted that recent studies have found that PFC precursors could be a significant source of PFOS and PFOA, the two most common PFCs, in the environment.

Jonathan stated that in San Francisco Bay, PFOS precursors are sometimes greater than PFOS concentrations in sludge and sediment concentrations. Additionally, precursor concentrations were similar to perfluoroalkyl acid (PFAA) concentrations in stormwater runoff. Based on the evidence that precursor concentrations are elevated in the Bay, Jonathan wondered if elevated levels of PFOS in the Bay can be explained by exposure to precursors. Additionally, if perfluorooctane sulfonyl fluoride (PFOSF) is being phased out, will telomer-based substances become a source of PFAAs in Bay wildlife? The

objective of the study was to measure concentrations of conventional PFAAs, PFCA and PFOS precursors, and emerging phosphorous containing PFAAs in sediment and WWTP effluent in South Bay.

At all three effluent sampling sites, perfluorinated carboxylic acids (PFCA) and perfluorinated sulfonic acids (PFSA) were the dominant classes. However, PFOS and PFOA were not always the main PFCs observed. The PFC profiles differed between all three effluent locations; at sites 1 and 2 the two main contaminants were PFOS and PFOA; at site 3 it was PFPeA and PFHxA. In sediment, the highest concentration of PFOS precursors was observed at Alviso Slough, where the highest concentration of PFOS was also measured. In sediment, diPAP concentrations were an order of magnitude greater than both PFCA and PFSA concentrations. PFCAs were only observed at Cooley Landing.

Discussion:

Derek Muir stated that it would be worthwhile to monitor for precursors in water; one study found high levels of PFOS precursors in the North Sea, indicating they are water soluble. Lee Ferguson found the concentrations of diPAPs in the sediment interesting and asked if it would be useful to also monitor triPAPs. Jonathan responded that the triPAPs are usually not the main ingredients in products and also hydrolyze to diPAPs. Phil Gschwend asked about the production of PAPs over time. Jonathan replied that PAPs became the major surfactant in the food packaging and paper industry starting in 2002; the concentrations in the environment have increased considerably over the past decade. David Sedlak mentioned PAPs' hydrophobicity and Jonathan responded that PAPs partition onto suspended sediments. The concentrations of PAPs are low in effluent, indicating they may be entering the Bay via stormwater runoff.

V. Information: California Safer Consumer Products Regulations and the Green Ribbon Science Panel [Becky Sutton]

Becky Sutton began her presentation by stating that the Green Ribbon Science Panel was formed to help implement the Safer Consumer Products Regulations, which requires alternative assessments for priority products (products that contain a chemical of concern). The regulations will address the question of if a chemical is necessary. RMP advisor Kelly Moran and Becky are both serving on the 15 member Panel and will provide guidance to the Department of Toxic Substance Control (DTSC).

DTSC created an initial candidate chemical list (n=153), which is based on the chemicals' hazard and exposure. An initial priority products list was created based on whether they possessed any of the candidate chemicals. So far, three priority products have been announced: Children's foam-padded sleeping products containing TDCPP; spray polyurethane foam systems containing unreacted diisocyanates; and paint/varnish strippers, surface cleaners containing Methylene Chloride.

Becky's role will include helping DTSC establish means for assessing how the chemicals and associated products may affect ecological health. She noted that the current candidate chemical list is mainly based on human health concerns. She stated that the RMP can

help by encouraging DTSC to consider ecological exposure and toxicity lists; informing DTSC of the CECs the RMP has discovered in the Bay; suggesting that DTSC complete ecological alternatives assessments; helping increase knowledge about products that are in use today; and providing DTSC ideas on potential priority products.

Discussion:

Lee Ferguson stated that many products are imported from China and the chemicals that are in them are not on TSCA and some don't have CAS numbers. Becky responded that DTSC can ask importers to complete the assessment; Lee responded that importers may not know what is in the product. Becky noted that the Panel will begin to address data gaps in the near future. Denise Greig asked if the regulations require increased labelling; Becky replied that required actions will only be determined after the alternatives assessments. The alternative assessments will begin in late 2015. The company that is producing a priority product will first be required to conduct a preliminary, short alternatives assessment report within 180 days of being notified. DTSC will review the preliminary assessment and determine if a longer assessment is needed.

Ian Wren asked why only five products were on the priority products list. Tom Mumley responded that DTSC did not want to take on too many products at the beginning of the program. In the future, more than five products will be included on the list.

Derek Muir wondered if a chemical was only considered hazardous if a study on the chemical had been published. He noted that many high production chemicals have not been studied, but may still be hazardous. Kelly Moran responded that the State was not given the authority to require new data, so chemicals that have not been studied are not included. She added that the State is in the process of developing a three-year workplan for its priority product selection; therefore, it would be timely and help DTSC if the RMP can help advise DTSC on pollutants and/or products that are of concern to Bay biota.

VI. Special Study 2015: Monitoring Wastewater Effluent for CECs [Becky Sutton and Meg Sedlak]

Becky Sutton stated that there are a number of effluent studies the RMP is already completing including evaluating effluent for alternative flame retardants and endocrine disruptor compounds (EDCs; from one WWTP). Becky proposed adding PFOS and PFOS precursors, Fipronil and its degradates, and EDCs to the list of compounds the RMP evaluates in effluent. The study would include collecting grab samples from at least 3 South Bay and Lower South Bay WWTPs, at least 2 Central Bay WWTPs, at least 1 Suisun or San Pablo Bay WWTP, and include 2 WWTPs that discharge to wetlands. The samples would be collected in Fall 2014 and would include a variety of treatment methods. The budget is currently \$64,000; however, ECWG members may want to consider also including microplastics and other pharmaceuticals and personal care products in the sampling effort.

Discussion:

Lee Ferguson asked if all the polyethoxylates would be included in monitoring, or just nonylphenol (NP). Nancy Denslow replied that only NP is part of the bioanalytical tools

study. Lee responded that it might be interesting to monitor E1, E2, and E3 polyethoxylates as well as carboxylated NPs. Becky responded that currently the study only includes the essential EDCs, but Keith Maruya is interested in completing a broader screen of EDCs to inform the bioanalytical screening results and to fulfill data gaps identified by the Statewide Expert Panel. David Sedlak noted that he does not consider NP an emerging contaminant and would only suggest monitoring the EDCs in multiple WWTP's effluent if it is critical to the success of the bioanalytical tools study. Derek Muir argued that Environment Canada is worried about hindered phenols, which are structurally related to NP and are highly used. He suggested that Keith create a list of hindered phenols that have not been monitored before and including them in a broader screen of EDCs. Derek agreed to give Keith a list of hindered phenols that would be useful to monitor and added that he would be willing to measure hindered phenols in a few RMP effluent samples.

David stated that he was concerned that the variability in Fipronil concentrations throughout the day will be lost if a grab sample is collected; he suggested collecting Fipronil as a composite sample instead.

Phil Gschwend asked if Becky considered monitoring for inorganics that are associated with the electronics industry. Mike Connor responded that he thought that the RMP has monitored for Osmium in the past. Mike thought it would be useful to have a rough understanding of the inorganics Phil mentioned and supported sampling for them at a few ambient water stations and in WWTP effluent. Naomi Feger asked if influent data would also be necessary; David Sedlak and Eric Dunleavy responded affirmatively. Naomi stated that more research and data gathering is necessary before pursuing a special study.

Action Items:

2. Derek Muir will send Keith Maruya a list of hindered phenols that would be useful to monitor.

VII. Special Study 2015: Pharmaceuticals and Personal Care Products [Rebecca Sutton]

Becky Sutton stated that pharmaceuticals and personal care products (PPCPs) are listed in Tier II (Low Concern) in the CEC Strategy and plasticizers are listed as Tier I (Possible Concern). Despite their inclusion in Tier II there are still many PPCPs for which the level of concern is unknown. Concern for a chemical was evaluated by looking at toxicity thresholds, environmental detections, its chemical properties, and use and loading trends. Becky explained the methodology for identifying high priority PPCPs; high priority PPCPs were defined as chemicals for which environmental concentrations are above the PNEC, or chemicals that do not readily biodegrade and may be harmful for aquatic ecosystems.

Becky listed six PPCPs that were identified as high priorities for monitoring. The first being sulfamethoxazole because three out of 15 detections of sulfamethoxazole in the Bay were above the PNEC. Each sulfamethoxazole sample will cost \$535 to \$1,910 to

analyze, depending on whether the RMP is interested in analyzing a smaller or larger suite of PPCPs at the same time.

Bisphenol S (BPS) was the next PPCP Becky included as being of high concern. BPS is a replacement for Bisphenol A (BPA) and has not been measured in the Bay. BPS is not likely to degrade and has estrogenic activity and reproductive toxicity. Becky noted that AXYS Analytical Services Ltd. does not analyze BPS; however, Environment Canada does have a method to perform BPS analyses. BPA was the next PPCP on Becky's list because it has high estrogenicity. BPA has been monitored in Bay water and sediment, but was not detected. Keith Maruya noted that in effluent BPA concentrations were around 10-20 ng/L and the PNEC is 60 ng/L.

The fourth chemical Becky described was Butyl benzyl phthalate, a plasticizer. The concentration in Bay sediment was higher than the low apparent effects threshold; however, the Bay water concentrations were 1000 fold below the water PNEC. Becky noted that use of Butyl benzyl phthalate substitutes are increasing and suggested completing AXYS's general screen for phthalates. Mike Connor noted that butyl benzyl phthalate was a priority pollutant and Jay Davis added that the detection limits for the chemical are high.

The next PPCPs on the list were ADBAC and DTDMAC. Becky stated that some river environments contain levels greater than the freshwater PNEC; however, an estuarine sediment PNEC does not exist. The final PPCP was octocrylene, a widely used chemical that is found in many sunscreens. A PNEC does not exist, but there is concern that the chemical is persistent and bioaccumulative. AXYS Analytical does not analyze octocrylene and it has not been monitored in the Bay. Mike Connor thought it would be more interesting to monitor octocrylene in a lake where people swim.

Discussion:

Naomi Feger asked why sulfamethoxazole was listed as low concern if it was detected. Meg Sedlak replied that the values used to be estimates, but the RMP has received more accurate data recently. Derek Muir noted that if a larger suite of PPCPs are analyzed alongside sulfamethoxazole, the detection limits will increase. David Sedlak asked if the PNEC was a legitimate threshold for an estuarine system. If the PNEC is appropriate, then sulfamethoxazole may need to be ranked in a higher tier.

Lee Ferguson stated that ADBAC and DTDMAC are not very bioavailable and will be strongly bound to sediments. Lee noted that ADBAC and DTDMAC have never been measured in stormwater suspended sediment and thought it would be interesting to monitor. Kelly Moran added that ADBAC is a pesticide that could enter stormwater runoff; she will forward the EPA review of ADBAC to Becky. Mike Connor suggested a small monitoring study near AT&T Park and having Bruce Brownawell analyze the samples.

Phil Gschwend stated that he doubts octocrylene is used in mass quantities. He added that many compounds are quickly replaced with alternatives and would suggest looking at

families of compounds. For example, there are a large number of bisphenols that could be analyzed at one time. Becky responded that a complete methodology for analyzing bisphenols has not been developed. Lee noted that the chemicals Becky listed as plasticizers, such as BPA, should be called polymer additives.

Andria Ventura wondered how the effects of the compounds play into what contaminants the RMP chooses to monitor. Becky responded that concentrations are compared to toxicity thresholds when available. Kelly Moran ended the discussion by suggesting monitoring for antimicrobial chemicals that the EPA recently registered, there are clear pathways to the Bay and some level of toxicity data is available. .

Action Items:

3. Kelly Moran added that ADBAC is a pesticide that could enter stormwater runoff; she will forward the EPA review of ADBAC to Becky.

IX. Special Study 2015: Current Use Pesticide (CUPs) [Ellen Willis-Norton and Kelly Moran]

Ellen Willis-Norton began her presentation by stating that the RMP monitors legacy pesticides as part of the Status and Trends (S&T) program. Use of these legacy pesticides ended between 40 and 50 years ago and the RMP has observed a slow decline in concentrations since 1993. As many S&T contaminant concentrations begin to decline or stabilize, the RMP has begun focusing efforts on Contaminants of Emerging Concern (CECs), including current use pesticides (CUPs).

The RMP's CEC Strategy includes ranking the relative risk of CECs to the Bay based on a tiered risk framework. All CUPs are ranked in Tier I (Possible Concern), excluding Fipronil and Pyrethroids (Moderate Concern and Low Concern respectively). However, Ellen noted that CUPs are considered of special concern because they are designed to kill organisms.

CUPs can enter the Bay via stormwater runoff, in bay application, and WWTP effluent. The CEC Strategy suggests screening level monitoring efforts for Tier I contaminants to help determine their concentration in ambient Bay water and sediment, effluent, runoff, and biota.

There are over 1,000 CUPs in existence; therefore, prioritizing which CUPs to monitor in the Bay is essential. The RMP developed a comprehensive monitoring priority list for agricultural CUPs. The list was created using spatially-explicit use data provided by the Department of Pesticide Regulation's California Pesticide Information Portal. Only agricultural pesticides, rather than both urban and agricultural, were included in the list because agricultural use data is reported to the township level. The RMP took the top 50 highest use pesticides within the Region 2 Water Quality Control Board boundary and determined their risk ratio (total use/lowest aquatic life benchmark).

The 20 agricultural pesticides with the highest risk ratio were: Naled, Oxyfluorfen, Flumioxazin, Pyraclostrobin, Mancozeb, 1,3-dichloropropene, Dimethoate, Imidacloprid,

Paraquat Dichloride, Metam-Sodium, Thiophanate-Methyl, Cyprodinil, Trifloxystrobin, Methomyl, Pendimethalin, 2,4-Dichlorophenoxyacetic acid, Diquat Dibromide, Oryzalin, PCNB, and Triflumizole. The use data for all 20 pesticides was mapped to determine where pesticide use was concentrated. The majority of the pesticides were applied in Napa County indicating agricultural pesticide concentrations are likely highest in the Napa River and subsequently San Pablo Bay.

Ellen proposed monitoring the following seven CUPs at three locations within the Napa River in this special study: Oxyfluorfen, Pyraclostrobin, Mancozeb, Imidacloprid, Paraquat Dichloride, Metam-Sodium, Diquat Dibromide. The sediment and water samples will be sent to North Coast Laboratories Ltd., a laboratory with expertise in pesticide analyses.

Discussion:

Mike Connor stated that Diuron has a lot of urban uses and wondered if it should be included in monitoring; Kelly Moran responded that this is an urban contaminant that is being addressed through DPR urban monitoring. Naomi Feger wondered why Naled was not included in the monitoring plan; Kelly replied that Naled should be included since its degradate is of high concern. David Sedlak then noted that he completed a study that demonstrated high estrogenicity in the Napa River. He wondered if the CUPs described in the presentation could be contributing to the estrogenicity.

Kelly Moran suggested timing sampling in the Napa River with pesticide application. She can help retrieve the pesticide application dates to inform monitoring efforts. Kelly added that urban use data was not included because only the total quantity of use is sent to DPR; there is a lack of spatially-explicit urban use data.

Lee Ferguson asked about using passive samplers in addition to collecting grab samples. Phil Gschwend stated that using passive samplers in sediment would be useful. Kelly Moran noted that some of the CUPs are very soluble and may be found in both sediment and water. Nancy Denslow stated that she has been a collaborator on a project that uses a passive sampler in both sediment and water. David Sedlak agreed that the current proposal only gives a narrow view of the CUPs found in the Napa River. He suggested using broadscan techniques or Orbitrap mass spectrometry. Lee Ferguson offered to complete a broadscan screen of some of the samples using his MS/MS. Mike Connor stated that it would be useful to collect both types of samples and to also have Lee run a subset of the samples.

X. Special Study 2015: Microplastics [Ellen Willis-Norton]

Ellen Willis-Norton explained that microplastic is a term used to describe fragments of plastic that are less than 5mm. Microplastics can be pellets that are used as precursors for industrial products, microbeads used in consumer products (e.g. exfoliants), or fragments/fibers of plastics that are the breakdown products of larger plastic materials. Microplastics can enter the aquatic environment through wind, stormwater runoff, or effluent. It is important to note that both California and New York have proposed bans on microplastics found in cosmetics and many companies have already have pledged to

phase out the use of microbeads in their skin cleansers. Therefore, the concentrations entering wastewater may decrease in the future.

Studies have found that microplastics are also to adsorb to organisms, blocking their feeding appendages. Ingestion of microplastics can block the digestive tract, reduce growth rates, block enzyme production, lower steroid hormone levels, affect reproduction, and cause the adsorption of toxins. The potential for ingesting toxins occurs because microplastics readily accumulate hydrophobic organic compounds, due to their high surface area to volume ratio.

Ellen stated that multiple regions have monitored for microplastic pollution including in Chesapeake Bay, Puget Sound, the Los Angeles River, Santa Monica Bay, and the Great Lakes. Ellen noted that the study in the Great Lakes is on-going and the researchers, including the project lead Sherri Mason (SUNY Fredonia), are currently considering adding effluent sampling to the monitoring effort.

Ellen noted that microplastics were sampled in San Francisco Bay surface waters in 2011. The study determined the mass of microplastic at sites in Central Bay that were suspected to be most influenced by trash. The concentration of microplastics was similar to the concentration range observed in Puget Sound and the San Gabriel River. However, the study only measured the mass of the microplastics, rather than the abundance and composition. Additionally, effluent has not yet been monitored in San Francisco Bay.

Ellen recommended sampling for microplastics at 10 S&T ambient water and sediment sites as well as sampling effluent to help identify whether personal care products were a significant source of microplastic pollution in the Bay. Ellen stated the samples would be analyzed by Dr. Sherri Mason, the project lead for the Great Lakes microplastic study, and the study would cost approximately \$5,000 to complete.

Discussion:

Lee Ferguson asked if chemical composition was included in the analyses. Ellen responded that she will check with Dr. Sherri Mason. Ian Wren noted that the study could be separated into two different studies based on the plastic fragments size; microbeads are likely found mainly in effluent while other fragments would be primarily found in stormwater. Ian wondered if this study should focus on microbeads. Kelly Moran suggested partnering with a student of Dr. Swee Teh at UC Davis, who is analyzing the effects of microbead ingestion on fish. Jay Davis responded that because the cost to complete the study is so low it may be easier to complete the study without a partnership with UC Davis.

Action Items:

4. Ellen Willis-Norton will ask Dr. Sherri Mason if chemical composition was included in the analyses of microplastics.