Special Study Proposal: Contaminants of Emerging Concern (CECs) in Urban Stormwater

Summary: Monitoring during the first, pilot year of a multi-year study on CECs in stormwater is being completed now. The study is designed to provide critical stormwater data needs for four contaminant classes: 1) a new, targeted list of CECs specific to stormwater; 2) per- and polyfluoroalkyl substances (PFASs); 3) organophosphate ester (OPE) plastic additives/flame retardants; and 4) ethoxylated surfactants. A fifth contaminant class, bisphenols, was recommended for inclusion by the Emerging Contaminants Workgroup (ECWG) based on detections of bisphenol (BP) A and S in open Bay samples collected in summer 2017.

Year 2 activities include site selection, sample collection, and analysis for a greater number of samples for this Bay Area-wide screening study. Preliminary review of data will inform the third year of site selection and sample collection; final deliverables at the conclusion of the study will include scientific manuscripts and a summary of results to inform water quality managers. This multi-year study is proposed to provide an intensive and pioneering examination of CECs in urban stormwater.

Estimated Cost: $181,000 for Year 2
(Year 1 $132,000; Year 3 est. $156,000)

Oversight Group: ECWG and SPLWG

Proposed by: Rebecca Sutton (SFEI), Ed Kolodziej (University of Washington), Chris Higgins (Colorado School of Mines), Da Chen (Jinan University), Lee Ferguson (Duke University)

Time Sensitive: Yes (multi-year study already underway)

PROPOSED DELIVERABLES AND TIMELINE

Deliverable (Year 2)	Due Date
Task 1. Site selection and reconnaissance, in coordination with SFEI stormwater and STLS teams; refinement of pilot sampling protocol	Summer 2019
Task 2. Field collection of stormwater samples	Fall 2019 – Spring 2020
Task 3. Laboratory analysis of samples	Spring – Summer 2020
Task 4. Preliminary review and analysis of data to inform Year 3 sample collection	Summer – Fall 2020

Background

An important element of the RMP's CEC Strategy is the application of non-targeted methods to identify unexpected contaminants that merit further monitoring (Sutton et al.

2017). In 2016, the RMP funded a special study to use a type of non-targeted analysis to examine Bay water samples collected from three sites influenced by three different pathways: effluent, stormwater, and agricultural runoff.

Findings from this study indicate that water samples from the stormwater-influenced site, San Leandro Bay, contained a broad array of unique contaminants with strong signals suggesting higher concentrations (Ferguson et al. in prep; Sun et al. in prep). One example of a contaminant identified with high confidence is 1,3-diphenylguanidine (DPG), a rubber vulcanization agent derived from vehicle tires. The European Chemicals Agency has established predicted no effect concentrations (PNEC) for DPG of 30 μg/L in freshwater and 3 μg/L in marine waters (ECHA 2018). While the non-targeted analysis provides only qualitative data, the high relative strength of the DPG signal suggests that this contaminant has the potential to be present at concentrations similar to these PNECs.

These findings indicate that stormwater is a pathway by which unique contaminants from vehicles and roadways make their way to tributaries and near-shore Bay environments. An additional factor contributing to a special interest in emerging contaminants from stormwater is that, unlike wastewater, this pathway generally receives no treatment. As a result, limited degradation or trapping of contaminants occurs prior to their discharge to the Bay. Furthermore, CEC investigations to date in the RMP and elsewhere have focused primarily on wastewater, and CECs in stormwater have received relatively little attention.

Stormwater-derived contaminants have been an especially high concern and research focus in the Puget Sound region, where adult coho salmon (*Oncorhynchus kisutch*) in Puget Sound streams experience acute toxicity and pre-spawn mortality following exposure to urban runoff (Du et al. 2017). This response is not correlated with conventional water chemistry parameters, including temperature, dissolved oxygen, and suspended solids; disease; spawner conditions; or exposure to monitored pesticides, metals, or polycyclic aromatic hydrocarbons (Scholz et al. 2011).

In an effort to identify the potential cause of this acute toxicity in the Puget Sound area, non-targeted analysis of stormwater and tissues from runoff-exposed fish were conducted and resulted in the identification of a number of unique contaminants with sources specific to vehicle traffic. One example is hexa(methoxymethyl)melamine (HMMM), a component of tire resin, which can occur in highway runoff at concentrations exceeding 10 μg/L (Kolodziej, unpublished data). More recent research indicates that aqueous leachates from automobile tires can induce acute toxicity in coho salmon, leading to a focus on understanding the risks of this pollutant source to salmonids and other aquatic organisms. In addition to the acute effects, related ecotoxicology research suggests that stormwater exposure can induce altered growth, decreased immune function, impaired lateral line development, and cardiotoxicity in salmonids (McIntyre et al. 2016; Young et al. 2018), suggesting that a suite of adverse sublethal impacts derived from stormwater exposures are important aspects of water quality in urbanized areas.

A direct outcome from these non-targeted analytical efforts in Puget Sound was the development, by Dr. Kolodziej, of a list of target analytes to assess the stormwater pathway as major contaminant inputs. While there are a number of targeted CEC lists designed around the influence of wastewater (e.g., focused on pharmaceuticals and other compounds typically disposed of down the drain), this is the first major effort to develop a CEC list targeting the influence of urban runoff in aquatic habitats with a concerted analytical effort. While the endangered coho salmon, the focus of the Puget Sound research effort, are now absent from tributaries discharging to the Bay, steelhead (*Oncorhynchus mykiss*), a threatened species, are observed in some Bay streams (e.g., Guadalupe River, Alameda Creek) and may also be susceptible to these contaminants.

In addition to this newly developed list of urban stormwater CECs, four other classes of emerging contaminants have been identified in recent RMP studies and ECWG discussions as critical data gaps for stormwater, and are included as part of this pioneering exploration of CECs in stormwater.

<u>Per- and polyfluoroalkyl substances (PFAS)</u> – PFOS, PFOA, and other long-chain perfluorocarboxylates are classified as Moderate Concerns for the Bay, while other PFAS are considered Possible Concerns. A conceptual model of sources of PFAS to stormwater includes outdoor textiles, plastic items, paints, and urban litter (e.g., food packaging), as well as industrial products such as fire-fighting foams. Atmospheric deposition is also possible. The RMP's draft PFAS Synthesis and Strategy (Sedlak et al. 2017) reviewed two studies of stormwater that have been conducted in the Bay Area: a seven site study conducted in water year 2010 (October 2009 through September 2010), and a 10 site study conducted in water year 2011. A relatively small number of PFAS were monitored; in addition, the watersheds monitored were not specifically selected to provide representative data for these contaminants in the Bay Area. The PFAS Synthesis and Strategy recommends stormwater monitoring as an RMP priority for future work.

<u>Organophosphate ester (OPE) plastic additives/flame retardants</u> – OPEs were recently classified as Moderate Concerns for San Francisco Bay. A conceptual model of sources of these contaminants to stormwater includes outdoor products such as construction and building materials, as well as volatilization from a far broader assortment of consumer goods to the air followed by deposition to urban streams. Samples collected during two storms (water year 2014) at two Bay Area stormwater sites indicate the presence of OPEs at concentrations generally comparable to those found in wastewater (Sutton et al. 2019). An RMP report that reviews available data for this class of CECs recommends stormwater monitoring as a priority for the RMP (Lin and Sutton 2018).

<u>Ethoxylated surfactants</u> – Ethoxylated surfactants include alkylphenol ethoxylates (classified as Moderate Concerns for the Bay), as well as alcohol ethoxylates and others. A conceptual model of sources of ethoxylated surfactants to stormwater includes outdoor use and automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, and many other products. The non-targeted analysis of San Francisco Bay sites described previously also identified a number of ethoxylated surfactants with strong signals in the stormwater-influenced site, San Leandro Bay (Ferguson et al. in prep; Sun et al. in prep). The RMP has funded a 2019 special study to screen Bay water, sediment, and wastewater for ethoxylated surfactants; results from the two studies will be complementary.

<u>Bisphenols</u> (New ECWG recommendation) – Bisphenols are a class of high production volume, endocrine-disrupting chemicals that are used in the manufacturing of polycarbonate

plastics and epoxy resins, as well as various other products. Bisphenol A (BPA), the most widely used and studied bisphenol, is one of the highest production volume chemicals in the world (estimated at 8 million tons per year), and can be found in products ranging from automotive and electrical equipment, polycarbonate plastic products, linings for food containers and drinking water pipes, and thermal paper receipts. A conceptual model of bisphenol sources to stormwater includes outdoor use plastics and coatings, as well as litter, including plastic items and thermal paper receipts. During the April 2019 ECWG meeting, the Workgroup reviewed detections of BPA and BPS in open Bay water samples collected in 2017 (Shimabuku et al. in prep). Levels of BPA at some sites approached an available PNEC of 60 ng/L (Wright-Walters et al. 2011); PNECs are not available for BPS or any other bisphenol. Cumulative impacts of these endocrine-disrupting compounds are poorly understood. The Workgroup reclassified bisphenols as Moderate Concerns for the Bay, and recommended follow-up monitoring of the full set of bisphenol analogues in stormwater, wastewater effluent, and archived margin sediment.

Study Objectives and Applicable RMP Management Questions

Table 1. Study objectives and questions relevant to RMP ECWG management questions

Management Question	Study Objective	Example Information Application
1) Which CECs have the potential to adversely impact beneficial uses in San Francisco Bay?	Compare new occurrence data for stormwater CECs with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	Do any stormwater CECs merit additional monitoring in the Bay or a specific classification in the tiered risk framework? What are the potential risks of these CECs? Is a need for management actions indicated?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Compare concentrations observed at different sites in the Bay Area to glean possible insights regarding the influence of sources or land use types. Compare Bay Area concentrations to other measurements of other urban areas.	What are the key sources or land uses that are associated with individual CECs or CEC classes in stormwater?
3) What are the physical, chemical, and biological processes that may affect the transport and fate of individual CECs or groups of CECs in the Bay?	N/A	

4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare concentrations with previous monitoring data for a limited number of analytes.	The data from this study can establish baseline data for stormwater CECs in the Bay Area. Instructive comparisons are possible for a subset of analytes previously examined in Bay Area stormwater, though robust trends cannot be inferred due to data limitations.
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	N/A	
6) What are the effects of management actions?	N/A	

Approach

Stormwater Sample Collection

Site selection will occur prior to sample collection, in consultation with the stormwater team at SFEI and the RMP's Small Tributaries Loading Strategy (STLS) team. Lessons learned from the pilot sample collection and analysis will inform site selection. Sites will be selected based on multiple factors including: 1) greater relative urban land use in the watershed, with an emphasis on proximity to roadways; 2) unique land uses associated with potential contaminant sources, such as airports; and 3) reduced sample collection costs due to existing sample collection underway as part of other studies. Site selection will be informed by the conceptual models of potential sources of the CECs to stormwater, with sites located in proximity to these sources being of particular interest.

Up to 20 samples (including field blank and duplicate samples) will be collected as part of Year 2 sample collection. Samples will consist of grabs or composites. Composites collected using an ISCO pump are preferred for the new stormwater CECs analyte list developed by Dr. Kolodziej. For the other types of contaminants, the ISCO pump may lead to procedural contamination. For these contaminants, one or more grab samples will be collected at each site, and may be combined in the field or in the analytical laboratory to produce a composite.

Particular focus will be placed on capturing the first fall flush at one or more sites of interest, using STLS storm size criteria. At least one site will be revisited during a later storm as an initial means of assessing variability. QA/QC samples collected will include at least one field duplicate and two field blanks.

Chemical Analysis

Up to 20 stormwater samples (including field duplicates and field blanks) will be characterized by four different academic laboratories with specialized expertise.

Stormwater CECs: Unfiltered samples will be analyzed by the Kolodziej Laboratory (University of Washington) with a newly developed, targeted analytical method using multi-residue solid phase extraction (SPE) and liquid chromatography with tandem mass spectroscopy (LC-MS/MS). Approximately 35 compounds will be monitored, including pharmaceuticals, pesticides, and several vehicle-specific analytes such as DPG and HMMM. A description of the analytes is provided as a separate attachment. This suite of representative tracers for urban runoff includes a broad range of contaminants with different physical-chemical parameters (e.g., various chemical functionalities, wide range of polarities and biodegradation potential). The compounds were selected to represent three primary urban sources: residential use, roadways, and wastewater.

PFASs: Unfiltered samples will be analyzed by the Higgins Laboratory (Colorado School of Mines) using quadrupole time-of-flight mass spectrometry (LC-Q-ToF-MS). The samples will be extracted and cleaned up using established protocols for the analysis of PFASs in soils and sediments (McGuire et al. 2014; Barzen-Hanson et al. 2017). Each sample will be split, with one aliquot being subjected to the TOP assay (oxidation followed by LC-QToF-MS; Houtz and Sedlak, 2012) and the other aliquot being directly analyzed by LC-QToF-MS. The stormwater extracts will be injected and separated on a C18 column prior to analysis by both ESI+ and ESI- LC-QToF-MS. Quantitative analysis will be performed on 45 PFASs, including different long- and short-chain perfluoroalkanoic acids, perfluoroalkane sulfonates, perfluoroalkane sulfonamides, fluorotelomer sulfonates, and fluorotelomer alkanoic acids. This list includes PFASs on the UCMR3 list along with many others.

Organophosphate Ester (OPE) Plastic Additives/Flame Retardants: Both dissolved and particulate phase samples will be analyzed by the Chen Laboratory (Jinan University). Samples will be extracted in the U.S. by a partner laboratory, then shipped to China where Dr. Chen will characterize contaminants within the aqueous and solid phases using highly sensitive liquid chromatography–triple quadrupole mass spectrometry (LC-QQQ-MS/MS) based analysis methods (Chen et al. 2012; Chu et al. 2011). Dr. Chen has agreed to undertake method development to add recently identified OPEs, including isopropylated and tert-butylated triarylphosphate esters (ITPs and TBPPs; Phillips et al. 2017) to his extensive list of target analytes.

Ethoxylated Surfactants: Stormwater samples will be analyzed for ethoxylated surfactants by the Ferguson Laboratory (Duke University), using a method to be developed. The matrix is likely to be total water, and the analyte list is expected to include the following surfactant families: nonylphenol ethoxylates, octylphenol ethoxylates, and C12, C14, and C16 alcohol ethoxylates. Analytes for each family will include compounds with a broad range of ethoxylate chains. Isotopically labeled standards are only available for a few of these analytes; however, the uncertainty associated with quantitation was deemed acceptable by the ECWG for screening purposes.

Bisphenols: Both dissolved and particulate phase samples will be analyzed by the Chen Laboratory (Jinan University) using a highly sensitive liquid chromatography–electrospray ionization(-)-triple quadrupole mass spectrometry (LC–ESI(-)-QQQ-MS/MS) based analysis method. This method will include analysis of bisphenol A, as well as suite of alternative bisphenol compounds, including bisphenols S, B, C, AF, AP, BP, M, E, P, F, PH, Z, G, TMC, and C-dichloride.

Data Interpretation
We anticipate that most of these contaminants will be widely observed in urban areas but have lower concentrations in non-urban areas. Therefore, screening data will be evaluated based on land-use type. Specific indicators of source types, such as road density, will be used for an initial investigation into key sources or land uses associated with these CECs.

In some cases, results can be compared with prior studies. For example, comparison to previous studies of PFAS in stormwater (Houtz and Sedlake 2012) may suggest increased prevalence of short-chain relative to long-chain (phased-out) PFAS, a potential result of shifting manufacturing practices. Results for the Bay Area will also be compared to levels observed in other urban regions.

Levels in Bay Area stormwater will also be compared to available toxicity thresholds. Findings may highlight concerns, data gaps, and the need for further research.

Budget

Budget Justification
The budget provided is specific to Year 2 of a multi-year study design and budget. The Year 2 budget emphasizes sample collection and analysis, with limited funds for data management and reporting. The majority of data review and reporting will occur during Year 3.

Planning and Stakeholder Engagement Costs
In consultation with RMP and STLS stormwater experts, we will establish a Year 2 study design that specifies site selection. Study design discussions and preliminary data reports will require regular participation in monthly calls with the STLS team.

Field Costs
The Year 2 budget includes $70,000 devoted to stormwater sample collection. Every effort will be made to minimize field costs by leveraging existing stormwater monitoring activities of the RMP. Based on the pilot year sampling experience, we anticipate that two-thirds of the sites visited in Year 2 will leverage RMP monitoring of legacy contaminants, while one-third of the sites will be specific to CECs.

Data Management Costs
Data services will include quality assurance review and upload to CEDEN during Year 3. Preliminary data management activities will occur during Year 2 and be supported by the Year 2 budget, including field collection data entry and communications with laboratories.

Table 2. 2020 CECs in Stormwater budget (Year 2 only)

Expense	Estimated Hours	Estimated Cost
Labor - Year 2		
Study Design, Stakeholder Engagement	70	10000
Stormwater Sample Collection	500	70000
Data Technical Services		12000
Analysis and Reporting	130	18000
Subcontracts - Year 2		
Stormwater CECs: Kolodziej, U. Washington		10000
PFASs: Higgins, Colorado School of Mines		12000
Organophosphate Esters: Chen, Jinan U.		14000
Ethoxylated Surfactants: Ferguson, Duke U.		11000
Bisphenols: Chen, Jinan U.		12800
Direct Costs - Year 2		
Equipment		2700
Travel		2000
Shipping		6500
Grand Total		181000

Analysis and Reporting Costs
Preliminary results will be reported to and reviewed by ECWG, STLS, and SPLWG. This activity would be supported by the Year 2 budget.

Preparation of draft manuscripts for publication in a peer-reviewed journal (stormwater-themed special issue) would occur following Year 3 sampling and analysis, and generally be led by the analytical partners. RMP scientists may be lead authors of one of the manuscripts, and coauthors of others. After the manuscripts are complete, RMP staff will produce a summary document for stakeholders, which describes the results and their implications for water quality management. Funding for this reporting would be part of the Year 3 budget.

Laboratory Costs
Each laboratory is receiving a budget sufficient to analyze up to 20 samples. Additional funding is provided to the Chen laboratory to cover the cost of analyzing bisphenols in stormwater samples collected in year 1 of the study (2019). Laboratory QA/QC samples will be analyzed at no charge, while field blanks and field duplicates will be considered part of the 20 samples charged to the RMP.

Reporting

Deliverables will include: a) draft manuscripts[1] that serve as RMP technical reports, due spring 2022; b) a summary for managers describing the results and their implications, due spring 2022; and c) additions to other RMP publications such as the Pulse.

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[1] The draft manuscript will be distributed to RMP stakeholders for review by email, not published on the website, so as to not jeopardize publication of the manuscript in a peer-reviewed journal.

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