Special Study Proposal: Ethoxylated Surfactants in Ambient Water, Margin Sediment, and Wastewatwer

Summary: Ethoxylated surfactants are nonionic surfactants that are widely used in industrial and household products, including cleaning products. Previous Bay studies have focused on nonylphenols (NPs) and key nonylphenol ethoxylates (NPEs), which have been ubiquitously detected in Bay water, sediment, and bivalve samples. Currently, NPs and NPEs are classified by the RMP as Moderate Concern compounds. Additionally, preliminary results from a 2016 RMP special study of Bay water samples via non-targeted analysis suggest that Bay samples contain a broad, complex mixture of ethoxylated surfactants in addition to NPEs. These compounds have not been targeted for monitoring in the Bay.

This proposed study will analyze a broad suite of ethoxylated surfactants in three Bay matrices: ambient water, sediment, and wastewater. Analysis of ethoxylated surfactants in stormwater is being proposed in a complementary 2019 Special Study proposal. This study would provide information to help determine whether ethoxylated surfactants should be classified as Moderate Concern contaminants. The data will also guide development of a monitoring and management strategy for this class of contaminants that has been prioritized by ECWG.

Estimated Cost: $123,200

Oversight Group: ECWG

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PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Coordinate sampling protocol with wastewater treatment facilities	April 2019
Task 2. Complete wastewater effluent sample collection	August 2019
Task 3. 2019 Status and Trends Water Cruise	August 2019
Task 4. Laboratory method development	July 2019
Task 5. Complete laboratory analysis of samples	January 2020
Task 6. QA/QC and data management	February 2020
Task 7. Preliminary results presentation for ECWG meeting	April 2020
Task 8. Draft manuscript and summary for managers	August 2020
Task 9. Final manuscript and summary for managers	January 2021

Background

Ethoxylated surfactants are a broad class of nonionic surfactants with a wide range of potential consumer and industrial applications, including cleaning products, pesticide formulations, textile and paper processing, paints and coatings, with very high volume consumptions on the order of millions of kilograms per year. Nonylphenol ethoxylates (NPEs), a family within the broader class of alkylphenol ethoxylates, are used in industrial and household laundry detergents, although voluntary phase-outs may have reduced this particular use significantly (Maruya 2015, EPA 2010). However, demand for NPEs is driven by growth in industrial and institutional cleaning, paints, and agrochemical sectors (DTSC 2018).

Ethoxylated surfactants are manufactured by reacting a hydrophobic alkyl chain (for example AP for alkylphenol) with ethylene oxide to form a hydrophilic ethylene oxide chain (EO) of varying lengths, e.g., APnEO, where n refers to the length of the EO group. The ethoxylation process forms mixtures of compounds with varying chain lengths, which are usually described by only the main or average compound's ethylene oxide length. Longer-chain ethoxylates can degrade to shorter-chain products, for example, nonylphenol diethoxylates (4-NP2EO) to nonylphenol monoethoxylates (4-NP1EO) to nonylphenol (NP).

Nonylphenols are persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (USEPA 2010). A small set of NPE and NP compounds, specifically 4-NP, 4-NP1EO, 4-NP2EO, have been analyzed in Bay surface water, sediments, bivalves, small fish, and aquatic bird eggs (Klosterhaus et al. 2013). Currently, NPs and NPEs are classified as Moderate Concern compounds. Although NP concentrations in the Bay are well below most toxicity thresholds, previously measured concentrations in the surface water were above concentrations that impacted barnacle settlement in a laboratory study (Billinghurst et al. 1998). NPEs and their degradation product are estrogenic and can impact the growth, reproduction, and development of fish and aquatic invertebrates at low concentrations (DTSC 2018). And of particular concern is that studies have also shown the potential for synergistic effect of alkylphenols and alkylphenol ethoxylates in combination with other contaminants such as pesticides, which could elicit estrogenic effects on fish (Schlenk et al. 2012) at concentrations measured in the Bay.

Importantly, preliminary results from a non-targeted analysis of Bay water and effluent samples reveal the ubiquitous presence of a much larger class of ethoxylated surfactants than monitored via previous targeted analysis of NPEs (L. Ferguson, personal communication). This means that there are many additional ethoxylated surfactants present in Bay water that have never been the subject of targeted monitoring in the Bay. The qualitative data from this non-targeted analysis suggests that residential wastewater effluent may not be the only pathway for ethoxylated surfactants to the Bay, and that stormwater discharges may also be an important pathway. Therefore, ambient Bay concentrations for this broader class of ethoxylated surfactants may be higher than previously anticipated.

Moreover, the Department of Toxic Substance Control's (DTSC) Safer Consumer Products program is proposing to list NPEs in laundry detergent as a Priority Product under its Safer Consumer Products regulation due to concerns for the contaminants' persistence and toxicity in the aquatic environment (DTSC 2018). Data from this study may provide useful findings to support DTSC's evaluation by supplying more current monitoring data on the presence of NPEs and other ethoxylated surfactants in wastewater effluent, as well as ambient water and sediment concentrations.

Given the potentially wide range of sources of ethoxylated surfactants, analysis of a broad set of ethoxylated surfactants in Bay samples would provide information to determine whether ethoxylated surfactants should be classified as Moderate Concern contaminants. At the spring ECWG meeting (April 12-13, 2018), stakeholders and experts expressed strong support for a study of ethoxylated surfactants in the Bay. This proposal will analyze a broad suite of ethoxylated surfactants, including previously identified alkylphenol and alcohol ethoxylates in Bay water, sediment, and wastewater. Funding for the stormwater analysis is being proposed in a separate, complementary study of contaminants of emerging concern in stormwater. The two studies will allow comparison of the wastewater effluent pathway and the stormwater runoff pathway, and support a more complete answer to study questions listed in Table 1.

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 ethoxylated surfactant occurrence data with toxicity information reported in the scientific literature. Evaluate future monitoring needs and toxicity data gaps.	What are current concentrations of ethoxylated surfactants in Bay water and sediment? Which newly identified contaminants merit further monitoring? Do findings suggest ethoxylated surfactants should be classified as high, moderate, low, or possible concern within the RMP's tiered framework?
2) What are the sources, pathways and loadings leading to the presence of individual CECs or groups of CECs in the Bay?	Investigate the influence of different pathways based on ethoxylated surfactant concentrations in wastewater effluent vs. stormwater, as well as patterns in ambient Bay sample locations (e.g., comparison of ambient water and sediment concentrations near stormwater vs. wastewater discharges).	Do sites influenced by different pathways show different patterns of contamination?

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?	Compare ethoxylated surfactant profiles in pathways vs. ambient samples.	Which ethoxylated surfactants appear to be persistent and bioaccumulative in the Bay?
4) Have the concentrations of individual CECs or groups of CECs increased or decreased in the Bay?	Compare ethoxylated surfactant concentrations with previous monitoring data for a limited number of analytes.	Have concentrations of nonylphenol and nonylphenol ethoxylates in the Bay increased or decreased from previous measurements?
5) Are the concentrations of individual CECs or groups of CECs predicted to increase or decrease in the future?	Compare detected ethoxylated surfactant analytes in wastewater and stormwater to those subject to proposed management actions.	Will management actions targeting nonylphenol ethoxylates in wastewater have an effect on the main pathways entering the Bay?
6) What are the effects of management actions?	N/A	N/A

Approach

<u>Ambient Water Sampling</u>
Bay water sample collection will take place in the summer of 2019 as part of the RMP's regular Status and Trends water monitoring cruise. Grab samples of ambient Bay water will be collected at all 22 Bay sites. A second field replicate will be collected at two sites and a field blanks will be collected at two sites for a total of 26 samples (22 field samples + 2 field replicates + 2 field blanks). The expected sample volume required is about 2.5 L per sample.

<u>South Bay Margin Sediment</u>
Margin sediment samples were collected from the RMP margin sediment sampling cruise in South Bay and Lower South Bay in the Summer 2017. Samples from 14 sites were archived for future analysis using clean protocols for alkylphenol ethoxylate analysis. Samples were collected using a Van Veen sediment grab. A field blank and two duplicates were also collected and archived. These locations include wastewater and stormwater influenced sites, as well as sites without clear influence that may serve as "background sites."

<u>Wastewater Effluent</u>
Eight volunteering wastewater treatment facilities will be targeted for study. An ideal group of participants will include regionally diverse facilities using secondary treatment as well as more advanced treatment; those facilities with larger discharges to the Bay will be particularly valuable. 24-hour composites of final effluent will be collected using automated sampling equipment regularly in use at the facility. It is expected that on-site sampling equipment that is regularly in use and constantly flushed with final treated effluent will have lower risk of contamination from cleaning detergent residue. A blank will also be collected at each site in order to detect contamination from the facility setting. A replicate from two facilities will be collected to evaluate variability in wastewater effluent. If collection of a 24-hour composite

without contamination is determined not to be feasible, then a grab sample may be collected during peak flow instead. The expected sampling volume required for analysis is about 300 mL per sample.

<u>Stormwater</u>

A total of 50 stormwater samples (including field duplicates and field blanks) will be characterized over two years in a separately proposed 2-year study. The analyte list will include ethoxylated surfactants using similar analytical methods. 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 our conceptual model of sources of ethoxylated surfactants to stormwater, which includes outdoor use and automotive cleaners, lubricants and other fluids, as well as pesticides, plastics, paints, and many other products.

<u>Analytical Method</u>

Bay water, sediment, and final wastewater effluent will be analyzed for ethoxylated surfactants by the Ferguson laboratory of Duke University, using mixed-mode high-performance liquid chromatography with electrospray mass spectrometry, modified from methods published previously (Ferguson et al., 2001) to include a broader range of ethoxylated surfactants in addition to the alkylphenol ethoxylates. The analyte list is expected to include the following surfactant families: nonylphenol ethoxylates, octylphenol ethoxylates, and C9, C10, C12, C13, C14, and C16 alcohol ethoxylates. Analytes for each family will include compounds with a broad range of ethoxylate chains, typically ranging from 1 – 20. Isotopically labeled standards are only available for a few of these analytes (i.e., the nonylphenol ethoxylates); however, the uncertainty in precision associated with quantitation was deemed acceptable by the ECWG for screening purposes. The expected analytical method detection limits for analytes are expected to be at least in the 1 - 40 ng/g range depending on the ethoxymer for sediment, and in the 1 - 50 ng/L range for water. These detection limits are below reported effects concentration in water in the 1 μg/L range (Billinghurst et al., 1998), and in the range of reported PNEC for NPs in freshwater sediment (WHO 2004). Water and effluent samples are expected to be analyzed as total water (unfiltered).

<u>Data Interpretation</u>

This study would establish a baseline for ethoxylated surfactant concentrations in sediment, water, effluent, and stormwater (covered by a separate ECWG study). The measured concentrations of a broad suite of ethoxylated surfactants in Bay water and sediment will be used to determine the risk tier category of this broad class of contaminants. Comparison to published toxicity thresholds will help determine whether alkylphenol ethoxylates should continue to be classified as Moderate Concern. This study may also identify new ethoxylated surfactants that have not previously been targeted for analysis in the Bay; an evaluation of these ethoxylated surfactants compared to available thresholds will allow for classification in the tiered risk framework for CECs. Observed increase or decrease in NPEs previously monitored in ambient waters may indicate whether voluntary management actions are having the intended effect. Additionally, comparison of contaminant profiles in pathways versus ambient samples may indicate degradation or persistence of specific contaminants, particularly within an ethoxylate family.

This study will also provide insights regarding contaminant profiles in pathways, as well as at margin sediment sites influenced predominantly by wastewater effluent or stormwater runoff. Understanding the sources and pathways of ethoxylated surfactants can inform what management decisions may be effective in reducing future concentrations.

Budget

Budget Justification

Project Staff
Ambient water sampling field costs are minimal because samples will be collected during the RMP's 2019 Status and Trends water sampling cruise, and 26 staff hours is allocated to cover additional time needed to plan, collect, and ship samples during the water sampling cruise. Sediment sampling field costs are minimal because samples have already been collected and archived. An additional ten staff hours are allocated to retrieve and ship samples. The largest field cost is associated with collecting wastewater effluent samples from eight participating facilities. Most of the sampling collection costs are based on staff hours needed to collect wastewater effluent samples from 8 participating facilities (developing sampling plan, coordinate sample collection, sample collection, sample shipment).

Data Management Costs
Data services will include QA/QC review and upload to CEDEN.

Analysis and Reporting
Preliminary results will be reported to and reviewed by ECWG. Preparation of draft manuscripts for publication in a peer-reviewed journal will be led by the analytical partner. After the manuscripts are complete, RMP staff will produce a summary document for managers that describes the results and their implications for stakeholders.

Laboratory Costs
Analytical costs are expected to be around $500/sample for ambient water and wastewater effluent samples, and $1,000/sample for sediment samples. Twenty-six ambient water samples (22 sites + 2 duplicates + 2 blanks), 18 wastewater effluent samples (8 sites + 8 field blanks + 2 duplicates), and 17 sediment samples (14 sites + 2 field duplicates + 1 field blank) are planned.

Direct Costs
Direct costs include equipment, travel reimbursement, and shipping costs. Shipping costs are estimated to be $300/cooler and twelve cooler shipments needed to ship field samples, and an additional eight shipments needed to ship cleaned empty sample containers from the laboratory. One cooler shipment is estimated for the sediment samples, three coolers for wastewater samples (18 x 500 mL bottles), and eight coolers for the for the ambient water samples (26 x 2.5 L bottles).

The following budget represents estimated costs for this proposed special study (Table 2). Efforts and costs can be scaled back by reducing the number of sites sampled.

Table 2. Proposed Budget.

Expense	Estimated Hours	Estimated Cost
Labor		
Sample Collection	240	29,500
Data Technical Services		24,700
Analysis and Reporting	140	22,000
Subcontracts		
Name of contractor		
Ferguson/ Duke U.		38,000
Direct Costs		
Equipment		2,000
Travel		1,000
Shipping		6,000
Grand Total		123,200

Reporting

Deliverables will include: a) preliminary results presentation during the ECWG spring 2020; b) draft manuscript[1] that serves as RMP technical reports, due fall 2020; c) a summary for managers describing the results and their implications, due fall 2020; and d) additions to other RMP publications such as the Pulse.

[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.

References

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