Assessment of Ethoxylated Surfactants in Wastewater, Stormwater, and Ambient Water of San Francisco Bay, CA

by

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I. Executive Summary

Ethoxylated surfactants are a broad class of ubiquitous organic environmental contaminants used in a variety of commercial and industrial applications. These compounds have received continued attention over the past several decades, particularly as manufacturing rates increase worldwide and certain sub-classes, such as alkylphenol ethoxylate surfactants and their metabolites, show acute and chronic toxicity concerns, including estrogenic effects. Because of their varying structures, analysis of these compounds in the environment is difficult, and broad-scope analysis of varying alkyl and ethoxymer chain lengths is rarely attempted. Presence of these compounds in surface water is primarily considered the result of contaminated wastewater effluent, however, other sources such as stormwater runoff have not been comprehensively evaluated. This evaluation is especially important for large urban waterbodies that received multiple point and non-point source inputs.

The first objective of this study was to confirm the presence of various alcohol and alkylphenol ethoxylated surfactants in the San Francisco Bay area and quantify concentrations of these contaminants in ambient bay water, stormwater runoff, and wastewater effluent. This study expands on previous evaluations of short chain nonylphenol ethoxylates in San Francisco Bay, and provides a broader scope evaluation of longer chain polyethoxylates. The second objective of this study was to determine the primary pathway or pathways of contamination to the Bay, based on an evaluation of these compounds in stormwater runoff and wastewater effluent. Ethoxylated surfactants were evaluated using novel internal standards developed by the Ferguson Lab at Duke University and high performance liquid chromatography coupled with high resolution mass spectrometry, allowing for detection and quantitation of a broad range of polyethoxylated surfactants.

Analysis revealed that high concentrations of several ethoxylated surfactants of varying polyethoxymer chain lengths were detected in wastewater effluent and stormwater runoff. Ambient Bay water contamination, which was relatively low compared to wastewater effluent and stormwater runoff, is likely the result of both stormwater runoff and wastewater effluent inputs to San Francisco Bay. These results were used to inform management actions and mitigation strategies for the San Francisco Estuary Institute's Regional Monitoring Program for Water Quality.

II. Introduction

A. Uses and Physical Properties of Ethoxylated Surfactants

Surfactants have been quantified and assessed as environmental contaminants in the aquatic environment for over three decades (Alabaster, 1978; Bennett and Metcalfe, 1999; Jardak *et al.*, 2016). Although they have been widely studied with respect to fate and transport, there are many classes and uses of surfactants, which warrants continued investigation of these chemicals in the environment. One specific class, ethoxylated surfactants, are nonionic surfactants applied commonly in industrial and consumer applications as detergents and emulsifiers, used in many products such as paints, cleaning products, personal care products, pesticides, and in textile, paper, and metal industries (Heldmann *et al.*, 1999; Ivanković and Hrenović, 2010; Krogh *et al.*, 2003; Negm *et al.*, 2010; Schramm *et al.*, 2003; Talmage, 1994). They are also used commonly in mixtures with anionic or cationic surfactants as foam and protease stabilizers (Angarska *et al.*, 2007; Russell and Britton, 2002). This class of surfactants includes one of the most well-studied surfactants of concern, nonylphenol ethoxylate. Nonylphenol ethoxylates and primary metabolites such as nonylphenol are known estrogenic pollutants, making them the focus of published literature concerning environmental concentrations of ethoxylated surfactants.

Ethoxylated surfactants are synthesized through the process of reacting alcohol or alkylphenol chains with ethylene oxide, creating a neutrally charged molecule with both a hydrophobic and hydrophilic portion (Ivanković and Hrenović, 2010); a hydrocarbon (or alkyl) chain and an ethoxymer (EO) chain. The process of manufacturing ethoxylated surfactants results in compounds that vary in both alkyl and EO chain length and structure (branched or linear). The two major subclasses are alcohol ethoxylates (AEOs) and alkylphenol ethoxylates (APEOs). Both are classified typically by alkyl chain length, with EO chain length variable as a function of intended use and/or function. Many of the longer-chain polyethoxylates (typically ethoxymer units 3-20) degrade to shorter chain compounds (ethoxymer units 0-2) in aerobic wastewater treatment (Talmage, 1994). The structure of alcohol ethoxylates and alkylphenol ethoxylates are presented in Figure 1, where C_n varies typically from 8-9 for alkyphenol ethoxylates and 11-17 for alcohol ethoxylates and x represents the length of the polyethoxymer chain, ranging generally from 0-20 EO units (DeArmond and DiGoregorio, 2013).

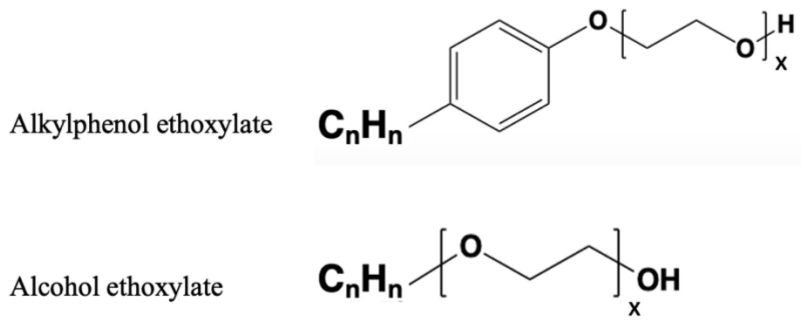


Figure 1. General structures of alcohol and alkylphenol ethoxylated surfactants.

Nonylphenol and octylphenol ethoxylates are two of the most widely studied alkylphenol ethoxylates. Nonylphenol ethoxylate (NPEO) alone makes up about 80%-85% of all alkylphenol ethoxylates and annual use estimates of NPEO as of 2010 are between 123,000 and 168,000 metric tons in the United States (US EPA, 2010). In comparison, the annual use of *all* alcohol ethoxylates in the United States is around 380,000 metric tons (Sanderson *et al.*, 2013). High production and use levels as well as their persistence due to their ring structure has resulted in high detection rates of NPEO and NPEO metabolites in aquatic environments and a focus in the scientific and regulatory community on the toxicity of these specific compounds due to their recognition as endocrine disrupting chemicals (Wu *et al.*, 2017).

B. Presence in the Environment

Because ethoxylated surfactants are widely used and produced on the order of hundreds of thousands of tons per year in the US alone, it is not surprising that they are found in the environment, primarily in aquatic environments and in biosolids (Bennie, 1999). The presence and implications of alkylphenol surfactants in aquatic ecosystems was originally recognized by Giger and colleagues in the 1980s (Giger *et al.*, 1981; Stephanou and Giger, 1982). Their work focused on detection of $NPEO_{1-4}$ and nonylphenol (NP), a primary NPEO degradation product, in wastewater effluent and found that they were present at high concentrations in effluent primarily as NP, $NPEO_1$, and $NPEO_2$ formed from detergents in wastewater treatment. This work was also some of the first to suggest that these compounds readily degrade to alkylphenols and short ethoxymer chain alkylphenol ethoxylates, and these degradation products are persistent in aquatic environments. In contrast to nonylphenol ethoxylate and other alkylphenol ethoxylates, alcohol ethoxylates have not been shown to have a primary degradation product, although shorter alkyl and ethoxymer chain length compounds are more common degradates (Sanderson *et al.*, 2013). Because of these observations, research on alkylphenol ethoxylates primarily focuses on quantification and analysis of the alkylphenol and short chain ethoxymer compounds, whereas AEO research analyzes a wide range of carbon and polyethoxymer chain lengths.

Known uses as detergent ingredients and personal care product additives have led ethoxylated surfactants to be considered "down-the-drain" products: following their household uses, these products are directly routed to wastewater treatment plants in high concentrations. Due largely to this classification and the decades of evaluations conducted on wastewater treatment plant effluent in the United States, surfactant concentrations detected in the environment have generally been attributed to contaminated wastewater treatment plant effluent.

Work in recent years confirms that both AEO and APEO surfactants are still commonly detected in wastewater treatment plant effluent (Jardak *et al.*, 2016). Concentrations of alcohol ethoxylates have been detected at concentrations as high as 15,000 ng/L in municipal wastewater effluent across the United States, with a total-flow-weighted average concentration of 3,640 ng/L across all carbon and ethoxymer chain lengths (Morrall *et al.*, 2006). A comprehensive review of studies conducted across the United States found that alkylphenol ethoxylate metabolites (NP, $NPEO_{1-3}$ and OP) range anywhere from <0.1 to 369 µg/L in US treatment plant effluent (Ying *et al.*, 2002). Looking at specific geographic locations and cities within the United States reveals vast differences in detected concentrations as well. In the midwestern United States between 1999 and 2009, mean NP and $NPEO_{1-4}$ concentrations ranged from 0.05 to 16 µg/L and mean OP and $OPEO_{1-4}$ concentrations ranged from 0.01 to 3.9 µg/L (Barber *et al.* 2015). A study conducted in Los Angeles, CA found 24-hr mean NP concentrations between 0.12 and 0.27 µg/L and 24-hr mean OP concentrations between 0.015 and 0.023 µg/L (Nelson *et al.*, 2011). One study measuring wastewater treatment plant effluent in Stony Brook, NY reported a concentration of 0.31 µg/L for sum $NPEO_{3-15}$ and 0.17 for sum AEOs (Lara-Martín *et al.* 2014).

Recently, stormwater studies have revealed detected concentrations of ethoxylated surfactants in stormwater runoff. This is not surprising due to the broad scope of uses and high production volumes of many ethoxylated surfactants. A study conducted in Paris, France to identify the priority pollutants in stormwater revealed that nonylphenol was found in all stormwater runoff samples. The detected levels in 14 samples ranged from 300 – 9170 ng/L, with a median of 750 ng/L. The authors concluded that the presence in stormwater was due to leaching from urban paint (nonylphenol is used commonly as an emulsifier in paints), cleaning products, and pesticide residues (Zgheib *et al.*, 2012). Björklund *et al.* (2009) detected NP at concentrations up to 1.2 µg/L in more than half of stormwater samples and $NPEO_{1\text{-}4}$ concentrations up to 2.2 µg/L in only one sample. Another French study to identify outdoor sources of alkylphenol ethoxylates that may be contaminating stormwater tested leaching of several construction and automotive materials and found high concentrations of NP and OP in PVC (window shutters and gutters), tire, and drainage material leachate (Lamprea *et al.*, 2018). Concentrations of NPEO in the Lamprea *et al.* (2018) study were also detected in concrete and metallic material leachate.

Minimal research has been devoted to the detection of ethoxylated surfactants in stormwater, especially in the United States; ethoxylated surfactants have typically been detected and quantified when evaluating comprehensive stormwater profiles. A recent study conducted by Masoner *et al.* (2019) evaluating 438 organic chemicals in several stormwater effluent samples across the United States found average $NPEO_1$ concentrations at 1152 ng/L, and average concentrations of OP, $OPEO_1$, and $OPEO_2$ between 108 to 390 ng/L. In a study conducted to identify organic contaminants linked to urban stormwater mortality syndrome in salmon near Seattle, WA, metabolites of various ethoxylated surfactants were detected (Peter *et al.*, 2018). Octylphenol ethoxylate metabolites were specifically identified. OPEOs and their metabolites were not quantified in that study, however OPEOs alone (not including other ethoxylated surfactants that were combined with various polyethylene glycol (PEG) ethers in the paper results) made up 4% and 8% of the analytical signal of the runoff profile in the two creeks sampled. While the authors concluded that ethoxylated surfactants are likely not the primary cause of mortality in salmon, OPEO did make up a significant portion of the profile, and there are toxicity concerns surrounding OPEO and other ethoxylated surfactants.

The concern surrounding ethoxylated surfactants detected in wastewater effluent and stormwater runoff centers mainly on their eventual fate in the environment, particularly in surface waters. As mentioned, detected concentrations of these compounds in the environment are typically considered the result of incomplete removal during wastewater treatment. Therefore, the majority of studies conducted assessing ethoxylated surfactants in surface water are linked to evaluation of these compounds in nearby wastewater treatment plant effluent. In a study by Fendinger *et al.* (1995), three rivers in the Midwestern United States each receiving discharge from a small wastewater treatment plant had down-river concentrations of total alcohol ethoxylates (C_{12-15}) between 0 and 37,000 ng/L, with the highest concentrations typically observed for C_{15} polyethoxylates. Notable in this study was the presence of alcohol ethoxylates upstream of the WWTP outfalls. While not discussed in the paper, detected levels upstream of the plants indicate that there may be other sources of contamination, such as stormwater runoff from urban areas.

In surface waters receiving multiple inputs such as large coastal urban bays, ethoxylated surfactants are ubiquitous but dilute due to the size and mixing of the receiving water. Concentrations of nonylphenol (NP) and alcohol ethoxylates, for example, were detected throughout Long Island Sound near New York City (Lara-Martín *et al.*, 2014) between 1,400 – 4,500 ng/L. Overall, concentrations of short chain polyethoxymers were higher, similar to other studies evaluating ethoxylated surfactants in aquatic systems, and detected concentrations seemed to fluctuate with salinity and tidal movement (Lara-Martín *et al.*, 2014). Lara-Martín *et al.* (2014) also determined that ethoxylated surfactants are common in surface sediments throughout Long Island Sound, although they were detected at higher concentrations near New York City, with concentrations declining rapidly away from the urbanized area and toward the Atlantic Ocean.

Another study conducted in a large urban estuary (Jamaica Bay, NY) by Ferguson *et al.* (2001) showed that short ethoxymer chain NPEO and OPEO were detected in sediments and surface water. Total $NPEO_{0-3}$ ranged from 50 to 30,000 ng/g in sediments, while octylphenol ethoxylates ($OPEO_{0-3}$) had much lower concentrations between 4.5 to 289 ng/g. This same relationship was observed in surface water for total NPEO and OPEO where concentrations ranged from 220 – 1,050 ng/L and 7 – 40 ng/L, respectively (Ferguson *et al.*, 2001). Ferguson *et al.* (2003) published an additional paper focusing on nonylphenol ethoxylate chemistry in sediments, confirming that nonylphenol ethoxylates with shorter ethoxymer chain lengths dominated the sediment profile. Findings by Ferguson *et al.* (2001 and 2003) and Lara-Martín *et al.* (2014) are consistent with the fact that nonylphenol ethoxylate dominates the market for production and use of alkylphenol ethoxylated surfactants, that these compounds degrade to shorter chain ethoxymer units, and that presence in sediment is indicative of presence in water (and vice versa).

C. Toxicity

While the scope of this study does not extend to toxicological evaluation of ethoxylated surfactants, they are well-established in literature as posing both acute and chronic toxicity concerns, driving the need for quantification of environmental concentrations.

Many ethoxylated surfactants and their degradation products are considered persistent compounds, especially nonylphenol and nonylphenol ethoxylates which are considered by the EPA to have persistent, bioaccumulative, and toxic (PBT) properties (US EPA, 2010). This makes their occurrence in the aquatic environment concerning even at low concentrations. Nonylphenol and nonylphenol ethoxylates in particular are toxic to fish, aquatic invertebrates and plants (US EPA, 2010). According to the US EPA, acute toxicity is higher for alkylphenols with fewer EO units, posing a major concern as $NPEO_{0\text{-}3}$ make up the majority of detected environmental polyethoxylates. A toxicity study conducted on fathead minnows and *Ceriodaphnia dubia* resulted in mean LC_{50} values of 218 and 323 µg/L, respectively, for $NPEO_1$ and 328 and 716 µg/L for $NPEO_2$ (TenEyck and Markee, 2007). TenEyck and Markee (2007) also suggested that a mixture of these surfactants (with concentrations converted to toxic units) induce additive effects when co-occurring in the environment. The lowest estimated EC_{50} value for two longer ethoxymer chain NPEO were 2.7 mg/L ($NPEO_6$) (Farré *et al.*, 2001) and 160 mg/L ($NPEO_{9.5}$) (Jurado et.al, 2009), based on assay results. Few toxicity studies of longer chain APEOs exist due to the fact that they have previously been considered to occur at low concentrations in the environment and environmental concentrations have not been well-established.

LC_{50} values for alcohol ethoxylates in aquatic invertebrates, fish, and algae have been observed between 0.05 to greater than 100 mg/L., suggesting that AEOs are less toxic than APEOs. This wide range was due to species variation and differences in structure, alkyl chain length and ethoxymer chain length, where algae were the most sensitive and branched, longer carbon chain compounds with a lower degree of ethoxylation showed increased toxicity (Cowan-Ellsberry *et al.*, 2014). This result was supported by earlier work by Wong *et al.* (1997) who concluded that toxicity increased with increasing alkyl chain length but decreasing number of EO units based on exposure studies. Subsequent QSAR models developed by Wong *et al.* (1997) indicated that average alkyl chain length had a greater effect on toxicity than average number of EO units for alcohol ethoxylates.

Because of the persistent nature of ethoxylated surfactants, and the continuous inputs to aquatic systems, chronic toxicity to aquatic organisms is a concern. For alkylphenols (NP and OP), NOECs vary between 6 and 170 µg/L for fish (33 and 91-day survival endpoint), whereas longer chain alkylphenol ethoxylates ($NPEO_9$ and $OPEO_{10}$) have observed NOECs between 1,800 and 3,300 µg/L for fish (Servos, 1999). Morrall *et al.* (2003) showed that the 21-day NOEC for the survival endpoint for *Dapnia magna* was 187 µg/L for a mixture of C_{12-15} alcohol ethoxylates with EO units 0-15, 110 µg/L for a mixture of C_{13} and C_{15} with EO units 0-19, and 350 µg/L for a mixture of C_{14} and C_{15} with EO units 0-15. Morrall *et al.* also found that the 21-day NOEC for reproductive effects endpoints ranged from 45-83 µg/L for the differing alcohol ethoxylate mixtures.

Endocrine disruption has been an observed effect of exposure to alkylphenol ethoxylates, particularly nonylphenol and short-chain nonylphenol ethoxylates. Lab animals exposed to nonylphenol over several generations have exhibited changes in the estrous cycle and various changes to development of reproductive organs (US EPA, 2010). A more recent study conducted specifically on exposure of 3T3-L1 cells to environmentally relevant concentrations of various ethoxylated surfactants including four alcohol ethoxylates, octylphenol ethoxylate, and five varying ethoxymer chain lengths of nonylphenol ethoxylate found that the majority of compounds impacted metabolic function of for least one study receptor (Kassotis *et al.*, 2018). Study receptors included ATP production, cell proliferation, triglyceride accumulation, and cell viability. This study also showed that alcohol ethoxylates may have similar toxicity as alkylphenol ethoxylates, which contradicts earlier work evaluating toxicity of AEOs and APEOs.

These trends are concerning, but equally concerning is the lack of robust recent toxicity data for more than a handful of these compounds. It is therefore crucial to prioritize additional ethoxylated surfactants for monitoring in order to understand the scope of need for additional toxicity evaluations.

D. Study Objectives

The current study explores ethoxylated contaminant profiles in San Francisco Bay, a large urban estuary that receives multiple wastewater and stormwater inputs and has been previously evaluated for contaminant profiles in other classes and included in non-target evaluations. Thanks to previous research, the San Francisco Bay has been well-studied with respect to occurrence and fate of organic contaminants (Klosterhaus *et al.*, 2013a; Oros *et al.*, 2003; Overdahl *et al.*, 2021).

Much of the previous work on identifying Bay contaminants has been funded by or in collaboration with the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP), which is administered by the San Francisco Estuary Institute (SFEI). The RMP monitors contaminants throughout the estuary to inform management actions to mitigate impacts to the Bay. This study was conducted in close collaboration with SFEI senior scientists and RMP stakeholders.

Previous preliminary studies on a small group of more commonly monitored alkylphenol ethoxylates in the Bay have shown that nonylphenol is present at environmentally relevant concentrations (up to 73 ng/L) in ambient Bay water, while $NPEO_{1-2}$ were not detected (Klosterhaus *et al.*, 2013b). However, both NP and $NPEO_{1-2}$ were detected at moderately high concentrations in sediment (up to 86 ng/g) and mussel tissues (up to 192 ng/g) within San Francisco Bay when they were last evaluated in 2010. Nonylphenol and nonylphenol ethoxylates have been classified by the RMP as "Moderate Concern" contaminants, based on a tiered risk-based framework, which means that data suggest there is "a high probability of a low level effect on Bay wildlife" (Sutton, *et al.*, 2017; Miller *et al.*, 2020). While these specific polyethoxylates have been evaluated, the scope and degree of additional ethoxylated surfactant contamination is unknown. Additionally, little is known about sources and pathways of potential ethoxylated surfactant contamination in the Bay, and thus how these compounds primarily enter ambient Bay water.

The two main objectives in this study are to 1) confirm and quantify presence of a broad range of alcohol and alkylphenol polyethoxylated surfactants in the Bay area and 2) to determine the major pathway or pathways of contamination via stormwater runoff and wastewater effluent. The analytical focus is on longer chain ethoxylates that have rarely been monitored in the environment. Results will indicate the need for further monitoring data to support management decisions for the Bay Area.

Based on analyses conducted during a previous study collaboration (Overdahl *et al.*, 2021), a list of targeted ethoxylated surfactant analytes was generated. The study uses this target list to assess samples for concentrations of each of these analytes. SFEI collected samples of stormwater, wastewater effluent, and ambient Bay water for this study in 2018, 2019, and 2020 and sent these samples to Duke University for analysis. We have utilized HPLC-HRMS to identify and quantify ethoxylated surfactants in wastewater, stormwater, and ambient bay water matrices. The use of high-resolution mass spectrometry allowed for detection, identification, and quantitation of a broad range of polyethoxylated surfactant ethoxymers in the water samples.

Based on previous work on quantification and identification of ethoxylated surfactants, we expect that the highest concentrations of ethoxylated surfactants will be observed in wastewater effluent and will be dominated by shorter ethoxy-chain alkylphenol ethoxylates (NPEO and OPEO).

III. Methods

A. Sample Collection

Wastewater effluent samples were collected from eight wastewater treatment facilities in the Bay Area in August, September, and October 2019. Collection in the dry season eliminates the influence of inflow and infiltration from precipitation on wastewater concentrations. The eight facilities were recruited for the study design to be representative of publicly-owned treatment work (POTW) flows to the San Francisco Bay. Selected POTWs are located across the Bay, and different treatment levels and technologies were included to consider the impact of treatment processes on measured concentrations. Facilities with higher flow rates to the Bay were selected to capture a significant portion of wastewater loadings to the Bay. POTWs included in the study represent approximately 60% of total effluent flows to the Bay and are presented in Table 1, coded by random letter designation to preserve anonymity. Associated information for each POTW is also included in Tables 2 and 3.

Effluent samples from the eight POTWs were collected as 24-hour composite samples on either a flow-weighted or time-weighted basis using auto-samplers that facilities regularly use and maintain for regulatory monitoring purposes. Composite samples are typically collected in a ~5-

gallon container, and samples were collected by transferring ~2L into 2.5L glass bottles. In addition to the primary field samples, one field blank was collected at each site, and a field duplicate was collected at two sites for quality assurance purposes (n=18). The field blank of LC-MS grade water was collected at each of the wastewater facilities by pouring LCMS grade reagent water into a sample container at the sample site.

Urban stormwater runoff samples were collected during the wet season (typically November – March) between November 2018 and January 2020. Sample sites were selected based on 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; and 3) existing sample collection underway as part of other studies to reduce sampling costs. Because the stormwater study includes multiple contaminant of emerging concern (CEC) classes, site selection methods were not specific to ethoxylated surfactants and sampling is still ongoing as part of that CEC evaluation study. In this study, we evaluated 14 samples (including one field blank) from 11 sites (Figure 2). Site details are included in Table 4. Sample containers (2.5L glass bottles) were filled by dipping a pre-cleaned stainless steel bailer into the stormwater channel during a storm event during the rising limb of the hydrograph and directly pouring the sample water into the sample container and filling the sample container at one time. Sample containers were rinsed three times with site water prior to filling the bottle with sample. A field blank was collected by pouring reagent water into the sample container in the field.

Ambient Bay water samples were collected July to August 2019 by SFEI staff. A total of 23 grab samples, including two duplicates and two field blanks, were collected at 19 sites. Each sample contained two liters of water. Sites were selected based on the RMP water sampling program's randomized sampling design that was representative of ambient water concentrations in each sub-embayment.

All samples were kept on ice after sample collection, and shipped overnight on ice from SFEI (Richmond, CA) to Duke University (Durham, NC) within 24 hours of collection. Samples were extracted upon receipt. All analyzed sample site locations are presented in Figure 2.

Table 1. POTW population and flow information. Sites are named by alphabetic letter designations to preserve anonymity.

Facility Code	**Estimated Population**	**2018/2019 Flow to Bay (10^6 L/day)**
A	144,000	58.3
B	482,000	146.1
C	120,000	38.2
D	650,000	219.6
E	153,000	37.9 (2015)
F	150,000	43.9
G	217,000	82.9
H	1,500,000	355.1

Table 2. POTW treatment method information. Sites are named by alphabetic letter designations to preserve anonymity.

Facility Code	Secondary Treatment	Tertiary Treatment	Nitrification	Denitrification	Disinfection
A	Oxidation Tower/Activated Sludge	Y	Y		UV
B	Activated Sludge with Anaerobic Selector				UV
C	Trickling Filter/Solids contact				Sodium Hypochlorite
D	High Purity Oxygen Activated Sludge				Sodium Hypochlorite
E	Trickling Filter/Solids Contact				Sodium Hypochlorite
F	Activated Sludge				Sodium Hypochlorite
G	Trickling Filter/Nitrifying Activated Sludge	Y	Y		UV
H	Activated Sludge/Biological Nutrient Removal	Y	Y	Y	Liquid Chorine

Table 3. POTW influent source industry information. Sites are named by alphabetic letter designations to preserve anonymity.

Facility Code	% Contribution from Residential/ Commercial	% Contribution from Industrial	Agriculture	Automatic Vehicle Washing	Fabricated Metal Products	Industrial Laundries	Leather Tanning and Finishing	Textiles and Carpet Finishing	Pulp and Paper Manufacturing	Other
A	75	25	Yes	Yes	No	No	No	No	No	None
B	96	4	No	Yes	No	Yes	No	No	No	None
C	97.39	2.61	No	Yes	No	No	No	No	No	Marine dry docks; theme park; food processor
D	94	6	Yes	Yes	Yes	Yes	Yes	Yes	No	Municipal fire training areas
E	80	20	No	Yes	Yes	No	No	No	No	Paint manufacturer
F	100	0	No	No	No	No	No	No	No	None
G	90	10	No	Yes	Yes	No	No	No	No	None
H	94	6	No	Yes	Yes	Yes	No	No	Yes	Pharmaceutical manufacturing; Rubber manufacturing; Hospitals; Food processing; Power plants

Table 4. Stormwater runoff watershed characteristics recorded during storm event sampling.

Watershed	**% Residential**	**% Commercial**	**% Industrial**	**% Transportation**	**% Agriculture and Open Space**	**Total Area (km^2)**	**Total Runoff Volume (10^6 m^3)**
Berryessa Creek	6	0	1	1	93	12.6	1.3
Cerrito Creek	57	10	3	18	12	7.1	1.7
Emeryville Crescent North	35	10	10	41	4	3.7	0.9
Ettie Street Pump Station	28	9	26	32	5	4.0	1.0
Meeker Slough	45	11	9	31	3	7.5	2.0
Outfall at Gilman St.	21	8	34	32	4	0.8	0.2
Rodeo Creek	1	0	6	2	91	23.4	4.2
SC-100-CTC-400A	40	5	20	8	27	1.4	0.1
SC-100-CTC-500A	29	11	19	16	24	3.0	0.3
SM-BUR-164A	21	17	40	16	5	1.0	0.2
Temescal Creek/Line12A	40	6	8	25	21	10.5	2.7

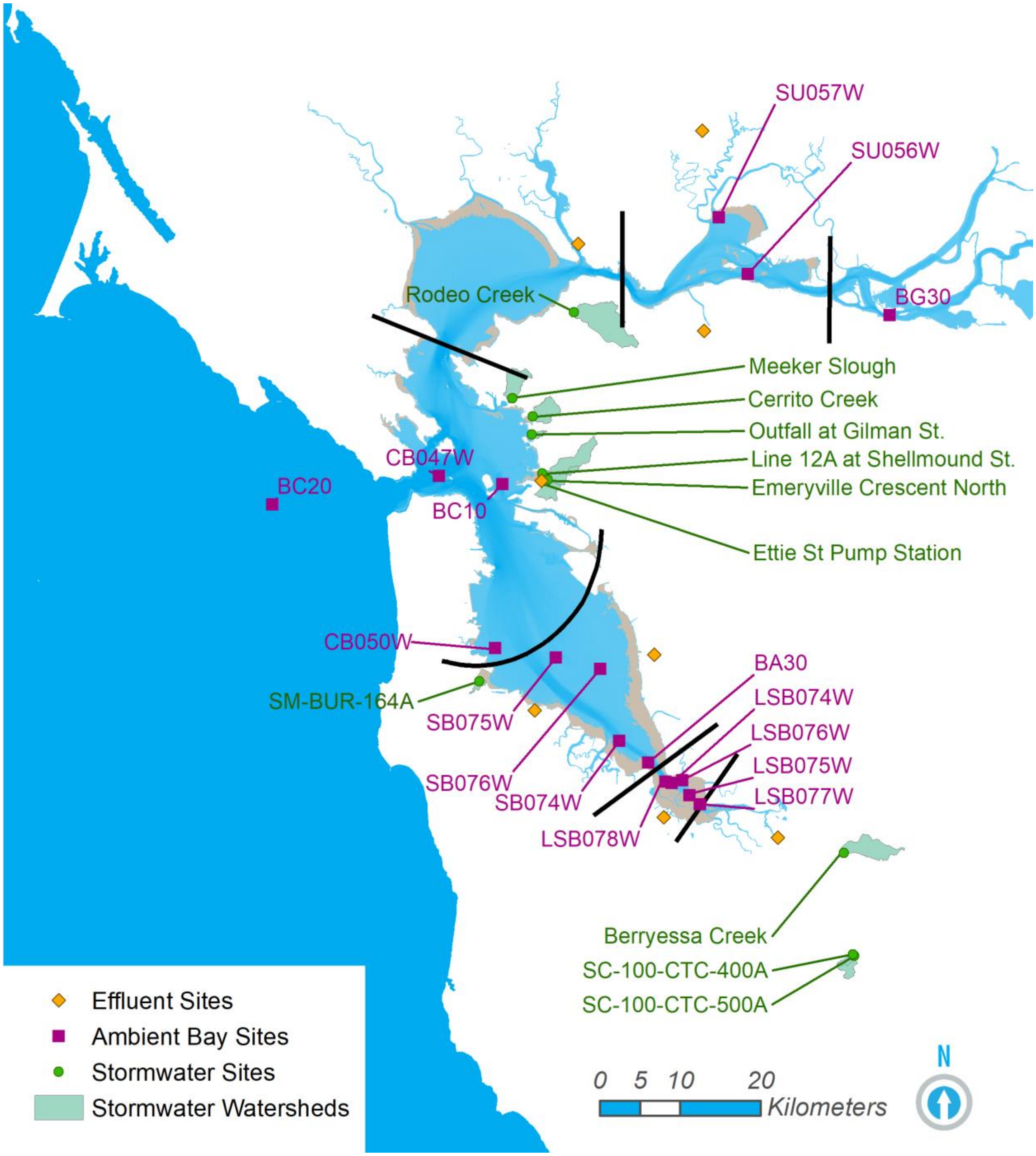


Figure 2. POTW effluent, stormwater runoff and ambient Bay water sites. POTW site labels have been removed to preserve anonymity. Black lines represent boundaries of the various embayments.

B. Sample Preparation

Three of the bottles containing ambient Bay water samples (one sample, one duplicate, and one field blank) and two bottles containing wastewater samples (both blanks) were cracked upon arrival and could not be analyzed, resulting in a total of 20 Bay water, 16 wastewater, and 14 stormwater samples processed through sample preparation (n=50). For all ambient Bay water and stormwater samples, 1 L aliquots of each sample, including all field blanks, were immediately filtered upon receipt (< 0.45µm GF/F, Whatman) for particle removal and processed for solid-phase extraction using an automated SPE system (Dionex Autotrace 280) fitted with Waters Oasis HLB SPE cartridges (500 mg sorbent, eluted with 10% MTBE in methanol). A 1 L laboratory blank was prepared identically. For all wastewater samples, 250 mL aliquots of each sample, including all field blanks, were filtered using identical procedures. Prior to extraction, all aliquots were spiked with isotope-labeled surrogate standards (17β-estradiol-d4, 3,6-dichloro-2-methyl-d3-benzoic acid, atrazine-d5, carbaryl-d7, DEET-d7, imidacloprid-d4, iprodione-d5, mecroprop-d4, metalaxyl-d6, prometon-d14, propanolol-d7, thiophanate-methyl-d6, tramadol-d6; all surrogate standards 10 µg/mL and spiked at 25 µL).

Extracts from SPE elutions were carefully evaporated using a SpeedVac centrifugal evaporator and reconstituted with HPLC starting mobile phase (1 mL volume, 5 mM ammonium acetate in 95%/5% Water:ACN). Due to expected higher concentrations in wastewater samples, 1 mL wastewater samples were then diluted via a 1:4 dilution. Solvent blanks containing LC starting mobile phase (1 mL volume, 5 mM ammonium acetate in 95%/5% Water:ACN) were also prepared for analysis. All samples were then spiked with isotope-labeled internal standards (13C-caffeine, 50 ng/mL).

Glass Hamilton syringes were employed for all spiking and transfers; no plastic was employed during the sample preparation process.

C. Sample Analysis

All samples (1 mL, in muffled amber glass LC-MS vials) were analyzed by UHPLC (ThermoDionex Ultimate 3000) coupled to high-field orbital trapping mass spectrometry

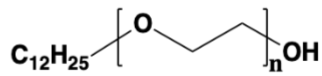
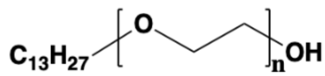
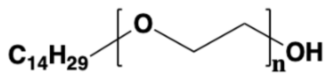
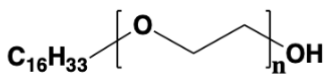
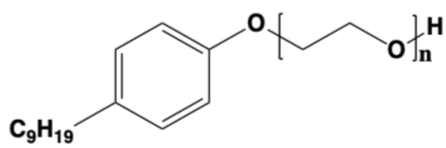
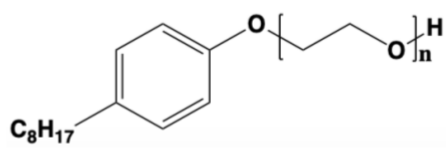
(ThermoFisher Orbitrap Fusion Lumos). Specifically, samples were separated using reversed phase UHPLC (Thermo Hypersil Gold column, 1.9 µm particle size, 2.1 x 100 cm) over a 37 minute multi-step gradient (mobile phases water [5mM ammonium acetate] and acetonitrile [5 mM ammonium acetate]) prior to introduction to the mass spectrometer through the electrospray ion source. The gradient was increased from 5% to 95% acetonitrile over the first 30 minutes; held at 95% acetonitrile for five minutes; then brought from 95% back to 5% over the last two minutes.

The Orbitrap Fusion Lumos was operated at 240,000 mass resolution from 200Da to 2000Da with internal mass calibration to achieve < 1 part per million (ppm) mass accuracy across the mass range of interest. All masses of ethoxylated compounds of interest were prioritized for data-dependent MS/MS spectral acquisition via mass inclusion lists created from known polyethoxylated surfactant masses. High-resolution detection of analytes in MS mode was performed by the Orbitrap analyzer, with subsequent data-dependent MS/MS performed in the Orbitrap at 30,000 mass resolution via higher energy collisional dissociation (HCD) after selection of precursor ions in the quadrupole assembly. Ions for MS/MS analysis (top speed, one second per total scan) were dynamically chosen on a per-scan basis, with priority given to accurate mass values in the inclusion list.

D. Data Processing

We quantified ethoxylated compounds in all samples via in-house purified and characterized reference standards for the alcohol ethoxylate series $C_{12\text{-}14}EO$, $C_{16}EO$, and the alkylphenol ethoxylates NPEO and OPEO. Compounds were chosen based on the list of target analytes developed from 2018 preliminary data, as mentioned above. Names and chemical structures are presented in Table 5. Ethoxylate units 1-16 were analyzed for each ethoxylate. Calibrated standards of alcohol polyethoxylates were prepared from commercial surfactant mixtures by separation of these mixtures into component ethoxymers via mixed-mode size exclusion chromatography with charged aerosol detection (CAD). Alkylphenol ethoxylate mixtures were separated using the same strategy, with quantitative ethoxymer characterization accomplished by UV-VIS detection. A nine-point calibration curve for each ethoxylate was created, with concentrations of highest-abundant ethoxymer ranging from 0 ng/mL to 1000 ng/mL in 95:5 water[5 mM ammonium acetate]:acetonitrile[5mM ammonium acetate]. 13C-caffeine was used as the internal standard in each sample (50 ng/mL). Analytes were quantified using TraceFinder software [ThermoFisher, version 5.0].

Table 5. Target list of alcohol and alkylphenol ethoxylated surfactants analyzed. Ethoyxmer units 1-16 were analyzed for each ethoxylate.

Ethoxylate Series	**Ethoxylate Category**	**Structure**	**Alkyl chain isomers**
$C_{12}EO$	alcohol		linear
$C_{13}EO$	alcohol		branched
$C_{14}EO$	alcohol		linear
$C_{16}EO$	alcohol		linear
NPEO	alkylphenol		branched
OPEO	alkylphenol		branched

IV. Results

Six alcohol and alkylphenol ethoxylate series were quantified in ambient Bay water, stormwater runoff, and wastewater effluent. Two ambient bay water samples were removed from further evaluation due to poor internal standard response and an inability to match the analyzed sample to a valid site location based on documentation. For each ethoxylated surfactant, we used an authentic reference standard containing 1-16 EO units in distribution to quantify individual ethoxymers. For each ethoxymer, an instrument limit of quantitation (LOQ) was determined as the lowest-concentration calibration point that demonstrated reproducibility and signal-to-noise separation (1:10) for three replicate calibration samples. Per ethoxymer, the method detection limit (MDL) was then determined as the ethoxymer LOQ plus three times the standard deviation of average ethoxymer detection in six instrument blanks. It should be noted that there were detected concentrations of individual polyethoxylates (0.001 - 12 ng/L) in at least one of each of the six instrument blanks for almost all polyethoxylates. This resulted in the loss of low concentration data, which particularly impacted ambient Bay water analysis as many of the Bay water samples had concentrations less than the MDL. Final reporting limits (RL) for each ethoxymer were determined by calculating the average ethoxymer concentration across field blanks per sample matrix (ambient Bay water, stormwater, and wastewater); in cases where no ethoxymer was detected in the field blanks, the RL was considered equivalent to the MDL. Significant blank contamination was observed for C_{16}EO ethoxymers across nearly all wastewater field blank sites, with detected field blank concentrations of individual ethoxymers as high as 160 ng/L and total ethoxymer concentrations between 29 and 1,321 ng/L, which are above the effluent sample concentrations for most facilities (Appendix A, Table A-2 and Appendix C, Figure C-1). Therefore, C_{16}EO was not included in reporting or figures for wastewater effluent analysis. For C_{12}EO, C_{13}EO, C_{14}EO, NPEO, and OPEO, some polyethoxylate contamination in field blanks was observed above the MDL, primarily in the stormwater field blank (<MDL – 12 ng/L, with one statistical outlier of 53 ng/L) and wastewater field blanks (<MDL – 28 ng/L, with 10 statistical outliers > 37 ng/L). Table A-1, listing LOQs, MDLs, and RLs for each ethoxymer, is included in Appendix A. In all cases, we were able to quantify surfactant ethoxymers with EO units three through 15; surfactant ethoxymers with EO units of length one, two and 16 were rarely quantifiable due to either abundance or low electrospray response efficiency. With the exception of C_{14}EO and

$C_{16}EO$, ethoxylated surfactant concentrations were detected in more than 84% of stormwater samples and more than 30% of wastewater samples. The majority of ethoxylated surfactants were detected in only 2 of the 17 ambient Bay water samples. Specific N values along with summed concentration ranges are displayed in Table 6.

NPEO was detected in stormwater, wastewater, and ambient Bay water samples at sum polyethoxylate concentration ranges 30 – 2,998 ng/L, 95 – 36,296 ng/L, and 2 – 708 ng/L, respectively; OPEO was detected in stormwater, wastewater, and ambient Bay water samples at sum concentration ranges 20 – 1,506, 10 – 7,855 ng/L, and 0.1 – 49 ng/L, respectively. $C_{13}EO$ had the highest summed ethoxylated surfactant concentration in both stormwater and wastewater, detected in stormwater at concentration ranges 37 – 4,731 ng/L and in wastewater at concentration ranges 31 – 45,361 ng/L. This was not observed in ambient Bay water, where $C_{13}EO$ had lower concentrations than most other compounds (7 – 21 ng/L). $C_{12}EO$ was detected at summed concentrations 14 – 770 ng/L in stormwater, 12 – 1,620 ng/L in wastewater, and 0.4 – 490 ng/L in Bay water samples. $C_{14}EO$ and $C_{16}EO$ were detected only in select samples for all matrices. $C_{14}EO$ sample concentrations in stormwater, wastewater, and ambient Bay water ranged from 4 – 155 ng/L, 3 – 1920 ng/L, and 22 – 339 ng/L), respectively. $C_{16}EO$ stormwater concentrations above reporting limits were detected only in one stormwater (sum = 154 ng/L) and one Bay water (sum = 14 ng/L) sample.

Table 6. Concentration ranges and N values for the various ethoxylated surfactant series in each matrix. All concentrations are in ng/L. N values represent the number of samples with detected concentrations out of a total of 10 samples for wastewater, 13 for stormwater, and 17 for ambient Bay water (this excludes field blanks). *Due to detected high field blank concentrations, values are not displayed for C_{16}EO wastewater sites.

	C_{12}EO			**C_{13}EO**			**C_{14}EO**			**C_{16}EO**			**NPEO**			**OPEO**		
	Min	Max	N	Min	Max	N	Min	Max	N	Min	Max	N	Min	Max	N	Min	Max	N
Wastewater	12	1620	3	31	45361	7	3	1920	2	*	*	*	95	36296	6	0.1	7855	7
Stormwater	14	770	11	37	4731	11	4	155	6	154	154	1	30	2998	12	20	1506	12
Bay Water	0.4	490	3	7	21	2	22	339	2	14	14	1	2	708	3	10	49	4

A. Evaluating Total Ethoxylated Surfactant Concentrations Within Wastewater, Stormwater, and Ambient Bay Water

In order to compare ethoxylated surfactant distributions in each of the sampling matrices, concentrations at or above RLs were summed across EO units to obtain a total ethoxylated surfactant concentration for each series in each sample matrix. Figure 3 shows a comparison of ethoxylate distributions among the three sampling matrices, with more detailed figures for each of the ethoxylated surfactant series included in Appendix B. Summed ethoxylated surfactant concentrations for each site are provided in Appendix A, Table A-2. Data were nonparametric and were therefore log transformed for statistical analysis and visualization. Data were analyzed via one-way ANOVA (Kruskal-Wallace) and Tukey post-hoc comparison tests to determine significant relationships of ethoxylated surfactant concentrations among sample matrices. Because C_{16}EO was detected at only one Bay water and stormwater site, and wastewater was excluded due to field blank contamination, no meaningful statistical analyses could be performed for this ethoxylate.

A comparison of the three sampling matrices revealed that ethoxylated surfactant concentrations (across all ethoxylates, except C_{16}EO) were significantly higher in both stormwater and wastewater samples compared to ambient Bay water (p-value < 0.01). The median ethoxylated surfactant concentration in stormwater samples was 11 times greater than the median concentration in Bay water; the median ethoxylated surfactant concentration in wastewater samples was 23 times greater than the median ambient Bay water concentration. Stormwater and wastewater concentrations were not significantly different from each other (p-value = 0.29).

Summed ethoxymer concentrations for each ethoxylated surfactant across each matrix were compared to determine ethoxylated surfactant series differences among matrices. Sum NPEO concentrations for wastewater sites were significantly higher than those in ambient Bay water (p-value = 0.01), but no difference was found between wastewater and stormwater or stormwater and Bay water (p-values $\geq$ 0.08). OPEO concentrations were found to be significantly higher in stormwater samples compared to OPEO in Bay water (p-value = 0.01) but showed no significant difference between stormwater and wastewater samples or wastewater and Bay water (p-values $\geq$ 0.12). C_{13}EO concentrations in wastewater were found to be significantly higher than C_{13}EO concentrations in both stormwater (p-value = 0.05) and ambient Bay water (p-value < 0.01), but there was no significant difference between stormwater and Bay water summed concentrations (p-value = 0.08). Concentrations of C_{12}EO and C_{14}EO were found not to be significantly different between Bay, stormwater, or wastewater samples (C_{12}EO p-values $\geq$ 0.57, C_{14}EO p-values $\geq$ 0.75).

A comparison between summed polyethoxylated surfactant concentrations within each of the three matrices revealed that while no significant differences existed between any ethoxylated surfactant series concentrations in wastewater samples or in Bay water samples (p-values $\geq$ 0.1), differences did exist in stormwater. NPEO summed concentrations in stormwater were significantly higher than C_{12}EO and C_{14}EO (p-values $\leq$ 0.05). OPEO and C_{13}EO concentrations were also significantly higher than C_{14}EO in stormwater (p-values $\leq$ 0.04). No other ethoxylates in stormwater differed significantly from one another.

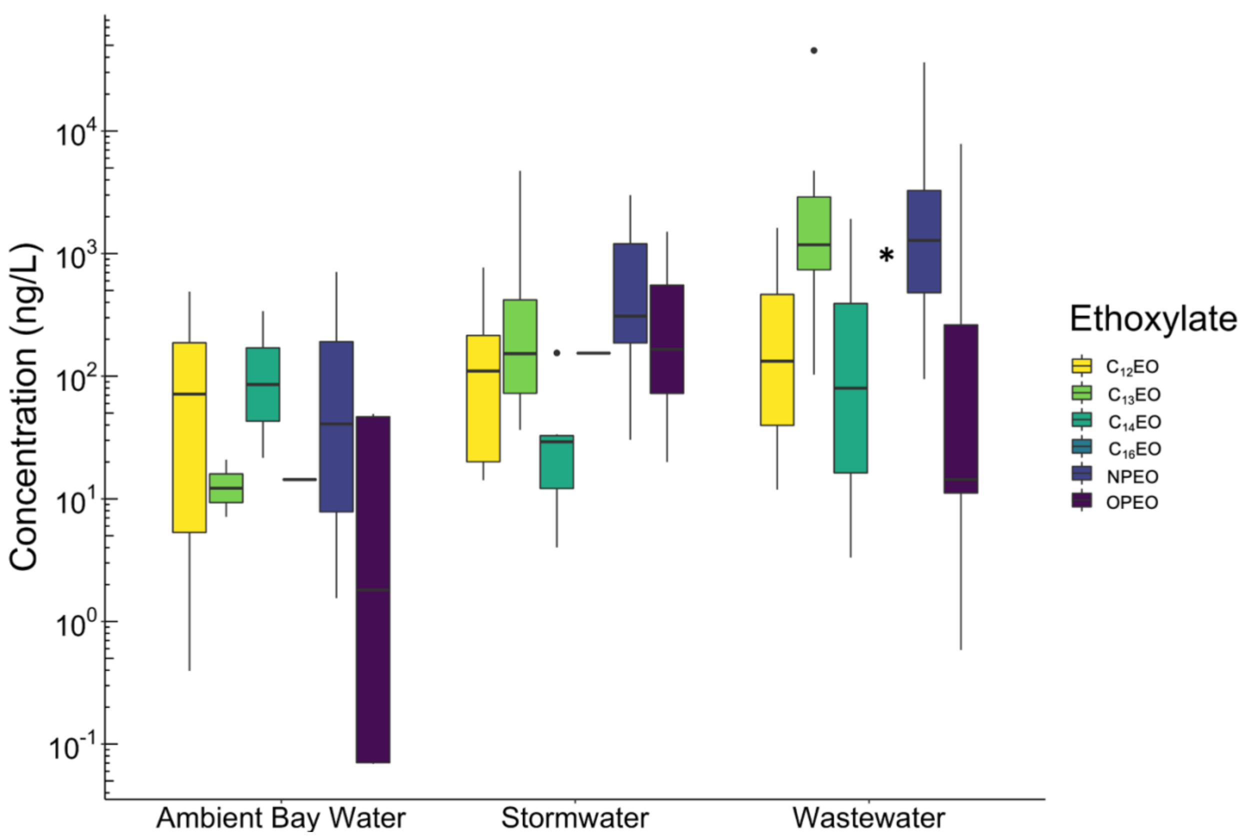


Figure 3. Log-transformed distribution of total ethoxylated surfactant concentrations across different matrices. Only individual ethoxymer concentrations above reporting limits were included in the sum total for each ethoxylated surfactant series. A table of individual summed concentrations for each site can be found in Appendix A, Table A-2. *C_{16}EO has been removed from wastewater due to field blank contamination.

B. Evaluating Ethoxylated Surfactant Concentrations Among Sites Within Sampling Matrices

We analyzed relationships of ethoxylated surfactants among all sampling sites within each sampling matrix, plotting concentrations of each polyethoxylate per ethoxylated surfactant series per sampling site. Results, shown in Figure 4, 5, and 6, indicated that of the quantified ethoxylated surfactants, NPEO, OPEO, and $C_{13}EO$ dominated the surfactant profiles for both wastewater and stormwater. Within wastewater sampling sites, $C_{13}EO$ was predominant, closely followed in abundance by NPEO. Site E POTW effluent contained the highest wastewater ethoxylated surfactant concentrations, with peak ethoxymer concentrations in the most abundant ethoxylate roughly ten times higher than peak ethoxymer concentrations for the most abundant ethoxylated surfactants at any other site (Figure 4). $C_{13}EO_6$ and $NPEO_3$ were present at highest peak concentrations at site E (13,321 ng/L and 23,814 ng/L, respectively); $OPEO_3$, $C_{12}EO_4$ and $C_{14}EO_5$ were the individual polyethoxylates with highest peak concentrations, also at site E (2,611 ng/L, 256 ng/L and 342 ng/L, respectively).

While stormwater samples (Figure 5) demonstrate more profile variability than wastewater samples, NPEO and OPEO generally dominated the polyethoxylate profile at each site, followed by $C_{13}EO$. One notable exception to this trend was site SM-BUR-164A, where $C_{13}EO$ concentrations were higher than other compounds (peak concentration = 551 ng/L for $C_{13}EO_{10}$). NPEO was detected at highest peak concentration ($NPEO_3$ > 600 ng/L) at the Outfall of the Gilman St. site, with various OPEO, $C_{12}EO$ and $C_{14}EO$ polyethoxylates detected at highest peak concentrations at the same site (234 ng/L, 144 ng/L, and 38 ng/L, respectively). Two stormwater sites selected as reference sites with a lower level of surrounding urbanization showed low to no detected concentrations of ethoxylated surfactants. For the Rodeo Creek stormwater reference site, concentrations of $C_{12}EO$, $C_{13}EO$, NPEO and OPEO were detected, with peak concentrations not exceeding 35 ng/L for the most abundant compound ($NPEO_3$). Concentrations for $C_{16}EO$ were low, with peak polyethoxylate concentrations less than 18 ng/L for all sites. Berryessa Creek had no detected concentrations of polyethoxylates above the MDL.

Ambient Bay water ethoxylated surfactant concentrations were generally an order of magnitude lower than stormwater and wastewater (Figure 6). The majority of ethoxylated surfactants were only detected at two ambient Bay sampling sites: SB075W and LSB074W. As shown in Fig. 5, NPEO dominated the polyethoxylated surfactant profile at SB075W (peak concentration = 117 ng/L for $NPEO_3$), while $C_{12}EO$ and $C_{14}EO$ dominated the profile at LSB074W, with peak concentrations of 96 ng/L and 60 ng/L for $C_{12}EO_4$ and $C_{14}EO_5$, respectively.

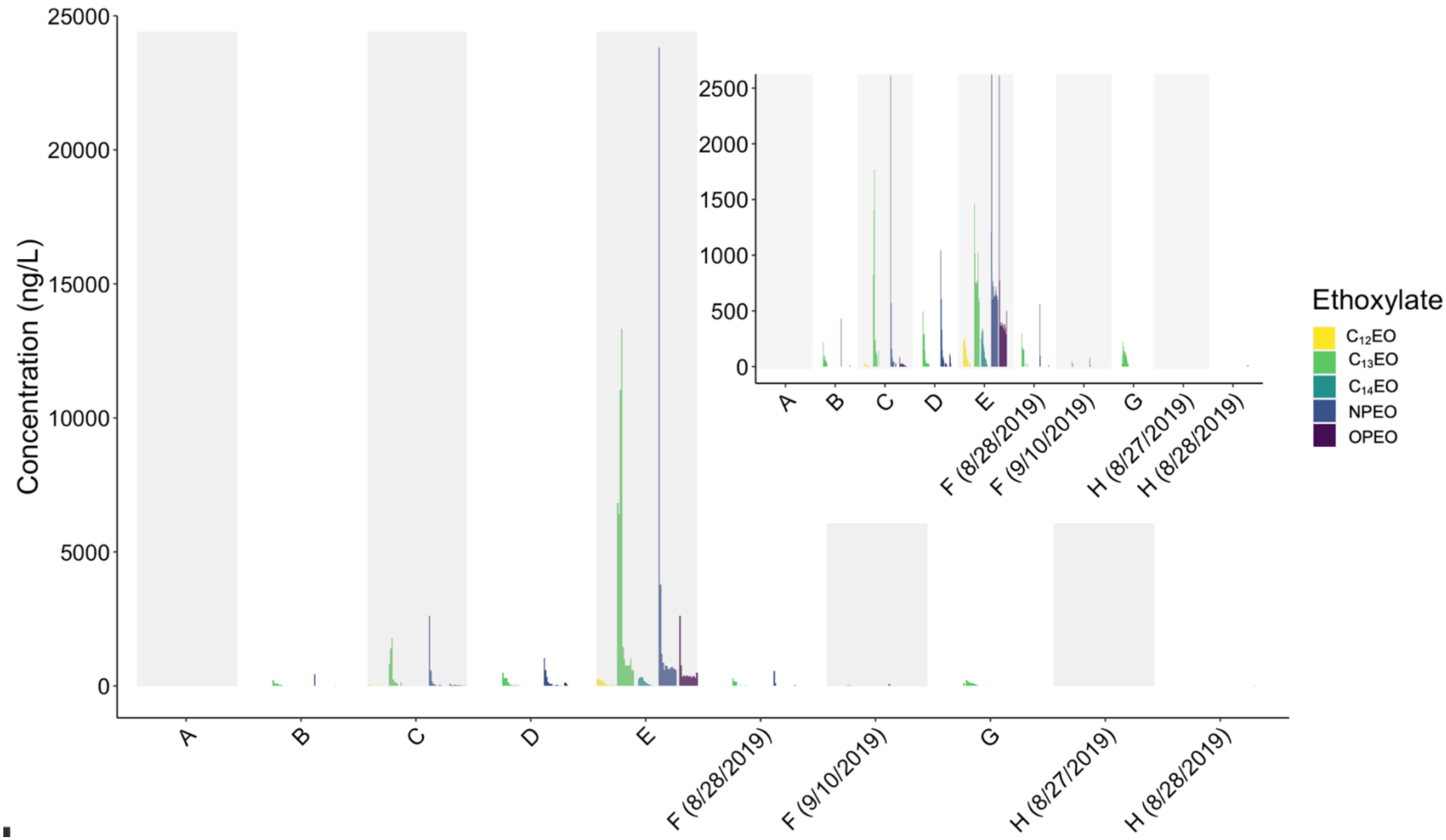


Figure 4. Concentrations of ethoxylated surfactants resolved at the ethoxymer level in each wastewater effluent sample. Individual ethoxymers are plotted from smallest to largest EO unit. Inset shows concentrations of ethoxymers in POTW effluent for sites with concentrations <3000 ng/L (this is all sites except E). C_{16}EO is not shown due to few detected concentrations above field blank concentrations (see Appendix C, Figure C-1).

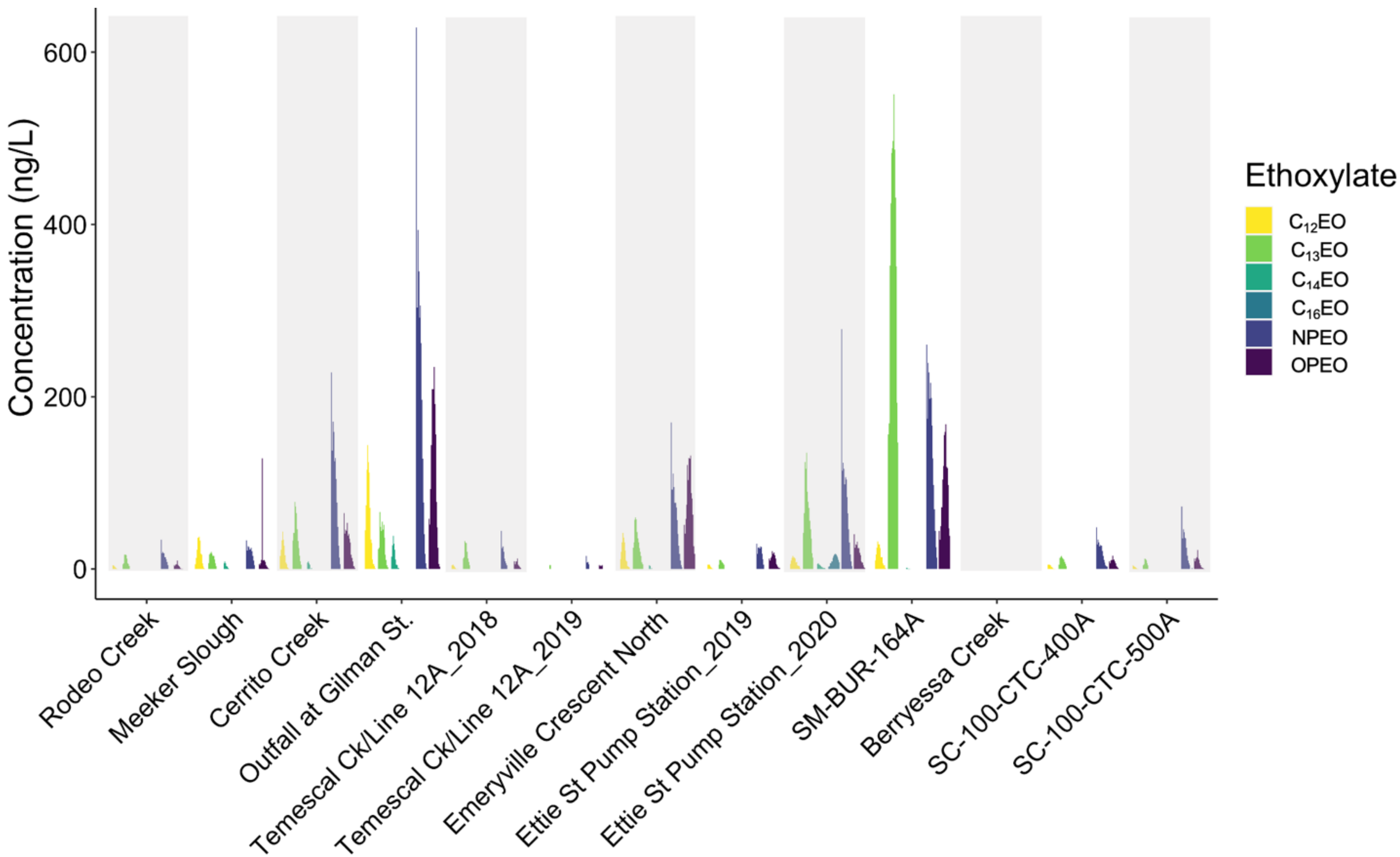


Figure 5. Concentrations of ethoxylated surfactants resolved at the ethoxymer level in each stormwater runoff sample. Individual ethoxymers are plotted from smallest to largest EO unit.

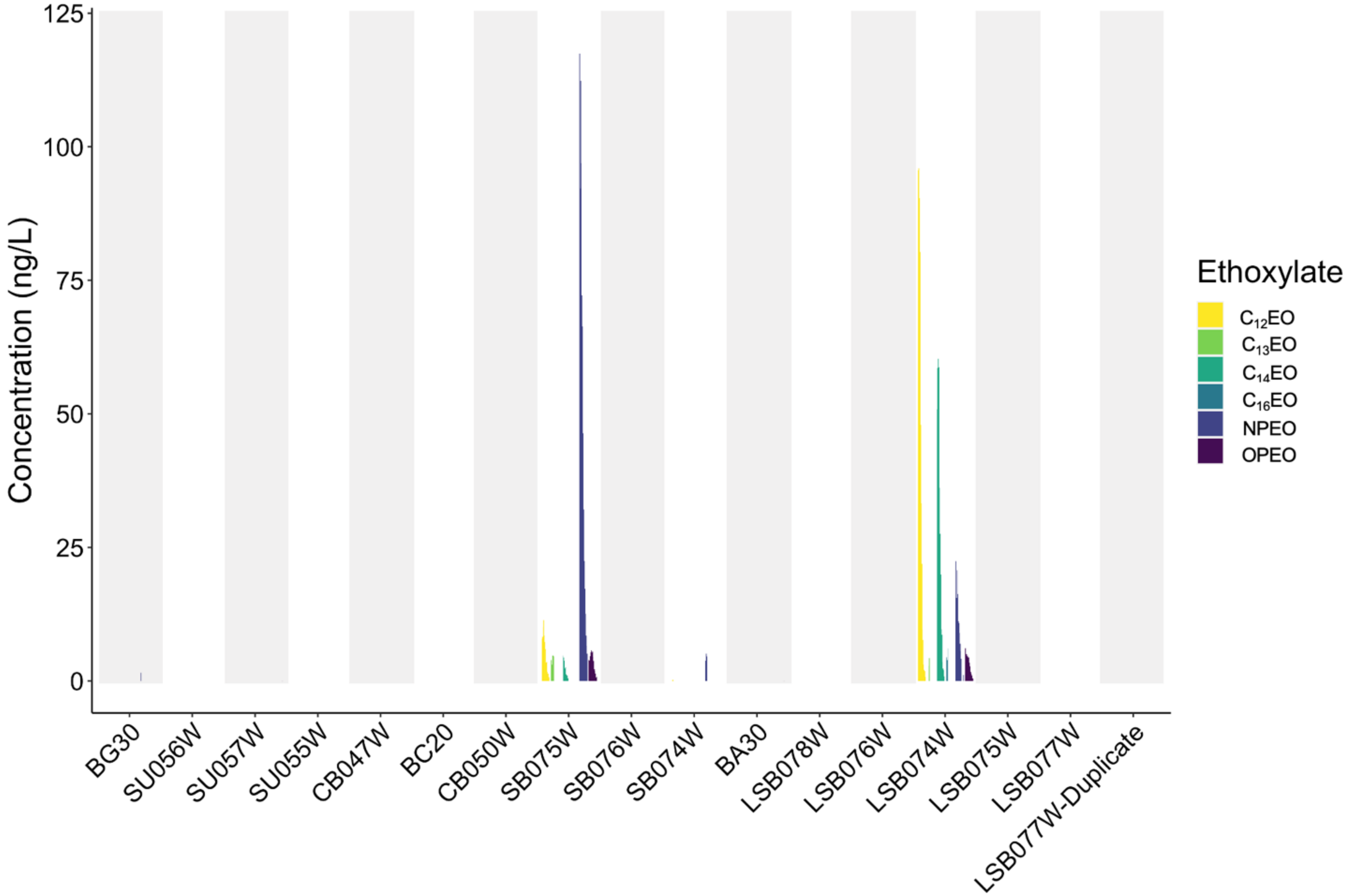


Figure 6. Concentrations of ethoxylated surfactants resolved at the ethoxymer level in each ambient Bay water sample. Individual ethoxymers are plotted from smallest to largest EO unit.

C. Comparing Average Ethoxymer Unit Distributions as an Indicator of Degradation and Primary Contamination Pathway

Average number of ethoxymer (EO) units for each compound at each sampling site were calculated using concentrations of individual ethoxymers at or above RLs to compare the distribution of EO units for ethoxylates among sampling sites. For each ethoxylate, the average EO number was calculated by first determining the mol fraction for each individual ethoxymer (calculated as the ratio of ethoxymer concentration to total ethoxylate concentration); mol fraction was then multiplied by ethoxymer number to determine an EO-weighted mol fraction in percent, and EO-weighted mol fractions were summed and divided by 100 to determine the average EO number for the ethoxylate. Average EO numbers are indicative of degradation of ethoxylates at matrix sites and provide comparisons for degradation observed in Bay water that may indicate primary pathway(s) of contamination (stormwater runoff and wastewater effluent). In general, highly degraded profiles in surface water suggest that contamination is the result of biologically-treated wastewater effluent due to the fact that ethoxylated surfactants are metabolized to their shortest chain lengths during microbial degradation in secondary wastewater treatment. A higher average EO number for Bay water sites would suggest stormwater pathway, as less degradation is likely to occur compared to wastewater and the ethoxymer distribution should approximate that of a surfactant in as-used formulation. Individual ethoxymer concentrations for each ethoxylated surfactant are shown as bar plots in Appendix C; these plots contain the same data as Figures 4, 5, and 6 but are separated according to ethoxylated surfactant series to highlight EO distribution for the various ethoxylated surfactants. Average EO numbers for each ethoxylated surfactant at each site are shown in Appendix A, Table A-2. In order to most accurately show EO distribution trends, bar plots represent all data above MDLs, even if values were below RLs. Average EO distributions were assessed only for quantifiable ethoxymers. Across all samples, results showed that the median average EO number was generally left-skewed for all matrices for each ethoxylate (Table 7 and Appendix C), where the median is the median average EO number across all sites in each matrix. The median average EO unit number for C_{12}EO, C_{13}EO, and NPEO are lowest in wastewater and highest in stormwater (Table 7). Inversely, the median average EO number for C_{14}EO was highest in wastewater, although the difference was small (Table 7). For OPEO, median average EO unit number was highest in ambient Bay water due to the presence of long chain ethoxymers detected at low concentrations at two sites (Table 7 and Appendix A: Table A-2).

Statistical analyses (ANOVA and Tukey post-hoc comparison tests) were also conducted to determine significant differences in average EO numbers for each polyethoxylated surfactant between ambient Bay water and stormwater and wastewater. For NPEO and OPEO, average EO numbers among Bay water samples were significantly higher than average EO numbers in wastewater samples (p-value $\leq$ 0.04). There was no significant difference between stormwater and Bay water average EO number (p-values $\geq$ 0.07). For C_{12}EO, C_{13}EO, and C_{14}EO, no significant differences in average EO number were observed between ambient Bay water and stormwater or ambient Bay water and wastewater (p-values $\geq$ 0.31). Figure 7 shows that average EO number for Bay water sites falls generally somewhere between wastewater and stormwater average EO unit number. The main exception is OPEO, which is due to the fact that for ambient Bay water sites SU057W and BA30, only the 15 ethoxymer had detected concentrations (<1 ng/L).

Average EO numbers for surfactants present in wastewater samples were generally lower than for other matrices. This was expected based on what is known about ethoxylate surfactant degradation in wastewater treatment plants. As mentioned, Site E yielded the highest concentrations for all ethoxylated surfactants, and average EO unit numbers ranged from 4.0 to 5.9. Average EO unit numbers for site B, site C, and site D were comparable to site E, ranging from 3.0 – 6.1. Site G and site F had a more varied distribution of average EO unit number (7.8 – 10 and 3.0 – 11, respectively). This shift toward higher average EO unit at these sites is due to the fact that the only detected concentrations of C_{14}EO and C_{12}EO were for the longer chain ethoxymers (EO_{10-15}) (Appendix A: Table A-2).

Trends in stormwater samples showed that for all ethoxylated surfactants except C_{14} and C_{16} (for which no comparisons could be made), median average EO number was slightly higher than wastewater (Table 7). C_{13}EO across all stormwater samples was present with a median average EO number of 6.5. Except at site SM-BUR-164A, C_{13}EO concentrations did not dominate site profiles. NPEO had a median average EO number of 5.9. C_{13}EO and NPEO ethoxylated surfactants were present at roughly five times the concentration of C_{12}EO and OPEO. C_{12}EO yielded a median average EO unit number of 7 while OPEO yielded a median average EO unit number of 6.4. C_{14}EO displayed similar median average EO unit number as that of C_{12}EO (7.6). C_{16}EO had a high median ethoxymer number (9.8) compared to C_{12} and C_{14}.

As mentioned, SB075W and LSB074W were the only sites with prominent quantifiable concentrations of ethoxylated surfactants, and C_{12}, C_{14}, and NPEO dominated the profiles at these sites. However, low detected concentrations of individual polyethoxylates (<10 ng/L) were measured for some additional sites. Median average EO unit number for NPEO was 5.4 across all ambient Bay water sites. The median average EO number for C_{12}EO across all ambient Bay water sites was 6.2 and median average EO number for C_{14}EO was 7.3. C_{13}EO, C_{16}EO, and OPEO had low detected concentrations at both SB075W and LSB074W, with median average EO numbers between 4.0 and 11.1.

Table 7. Median average number of EO units for each ethoxylated surfactant series across each matrix. Median is the median number of EO units across all sites in each matrix. N is the number of sites included in the median for each matrix. *Due to high field blank concentrations, average EO number was not calculated for C_{16}EO wastewater sites.

	C_{12}EO		**C_{13}EO**		**C_{14}EO**		**C_{16}EO**		**NPEO**		**OPEO**	
	Median	N	Median	N	Median	N	Median	N	Median	N	Median	N
Wastewater	6.1	3	4.9	7	7.8	2	*	*	3.3	6	3.6	7
Stormwater	7.0	11	6.5	11	7.6	6	9.8	1	5.9	12	6.4	12
Bay Water	6.2	3	5.3	2	7.3	2	4.0	1	5.4	3	11.1	4

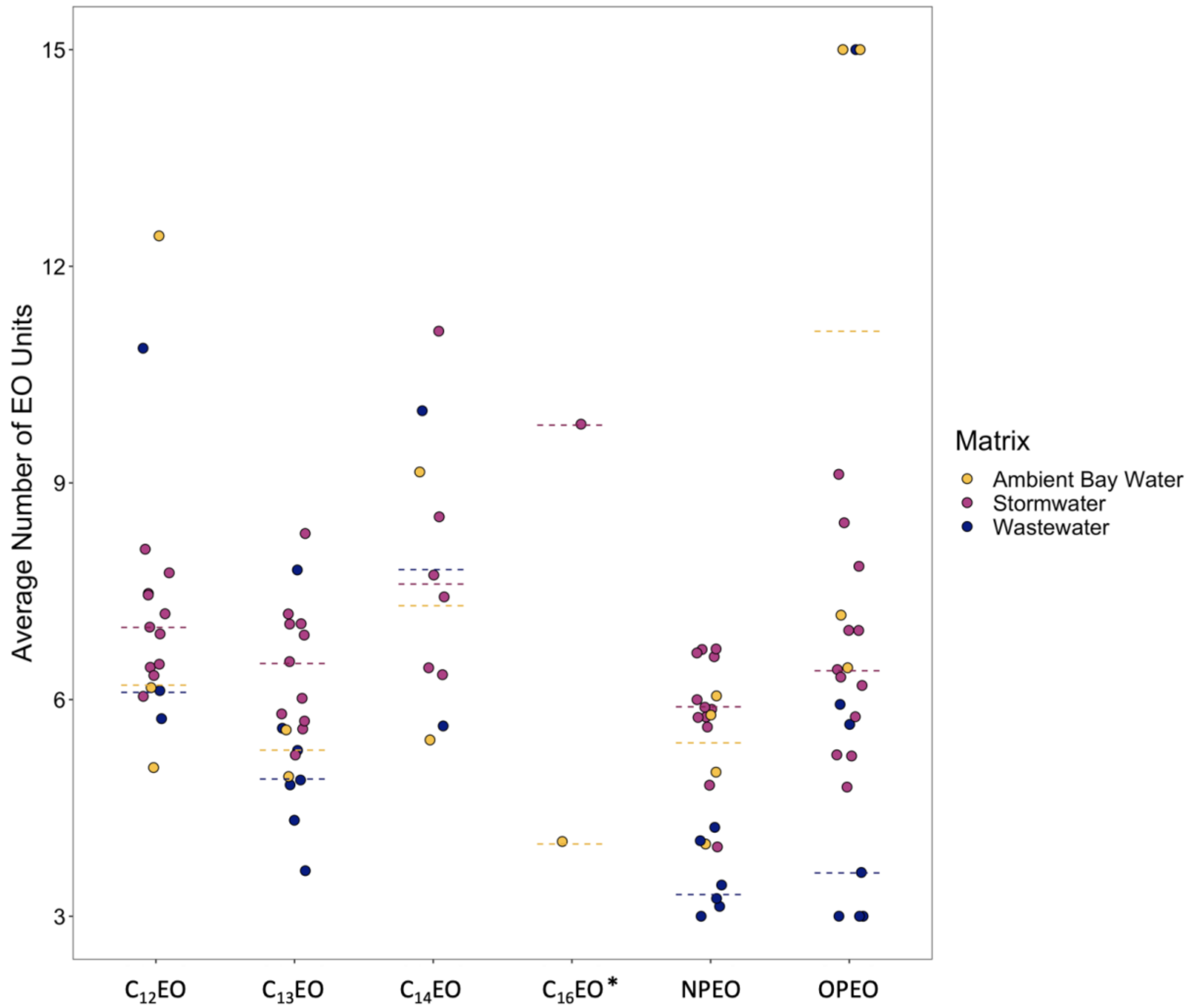


Figure 7. Distribution of average EO number by compound and matrix for each site. Dashed lines represent median average EO number, colored by corresponding matrix. *Due to high field blank concentrations, average EO number was not calculated for any $C_{16}EO$ wastewater sites.

D. *Ethoxylated Surfactant Profiles For SB075W and LSB074W and Surrounding Wastewater and Stormwater Sites*

Contributions from stormwater and wastewater to ambient Bay water were discussed above with respect to the potential of treated vs. untreated ethoxylated surfactant pathways to contribute influences on average EO number observed in samples. Here, profile comparisons were made to determine potential site-specific pathways of contamination to each of the Bay water sites that were measured to have elevated concentrations of ethoxylated surfactants (Figures 8 and 9). Due to the fact that concentrations were rarely quantifiable in other Bay water sites, it is possible that specific stormwater outfalls or POTWs had an immediate or significant influence on observed ambient Bay water concentrations for SB075W and LSB074W. This is especially relevant for LSB074W, where the dominance of C12 and C14 alcohol ethoxylates indicate a "snapshot" of recent inputs (not long term accumulation).

At SB075W, 81% of the total ethoxylated surfactant profile was dominated by NPEO, where C_{12}, C_{13}, C_{14} and OPEO made up the remainder, between 2-8% of the profile. In contrast, proximal stormwater and wastewater sites to SB075W were dominated by both NPEO (25-55%) and C_{13}EO (39-57%), with OPEO making up the majority of the remainder (1-16%). These proportions and sum concentrations of each ethoxylated surfactant are shown in Figure 8.

LSB074W had a more variable profile than SB075W, where C_{12}EO accounted for 48% of the total ethoxylate profile, C_{14}EO accounted for 33%, and NPEO accounted for only 13%. The remaining proportion was made up primarily by OPEO (4%). Stormwater and wastewater sites surrounding LSB074W had low to no detected concentrations of C_{12}EO and C_{14}EO, accounting for only 0-5% of the total ethoxylated surfactant profile at these sites. Stormwater and wastewater sites proximal to LSB074W were instead dominated by NPEO, OPEO, and C_{13}EO at stormwater sites (62-69%, 18-19%, and 9-15%, respectively) and OPEO and C_{13}EO, respectively, at each of the two wastewater sites. These relationships are shown in Figure 9.

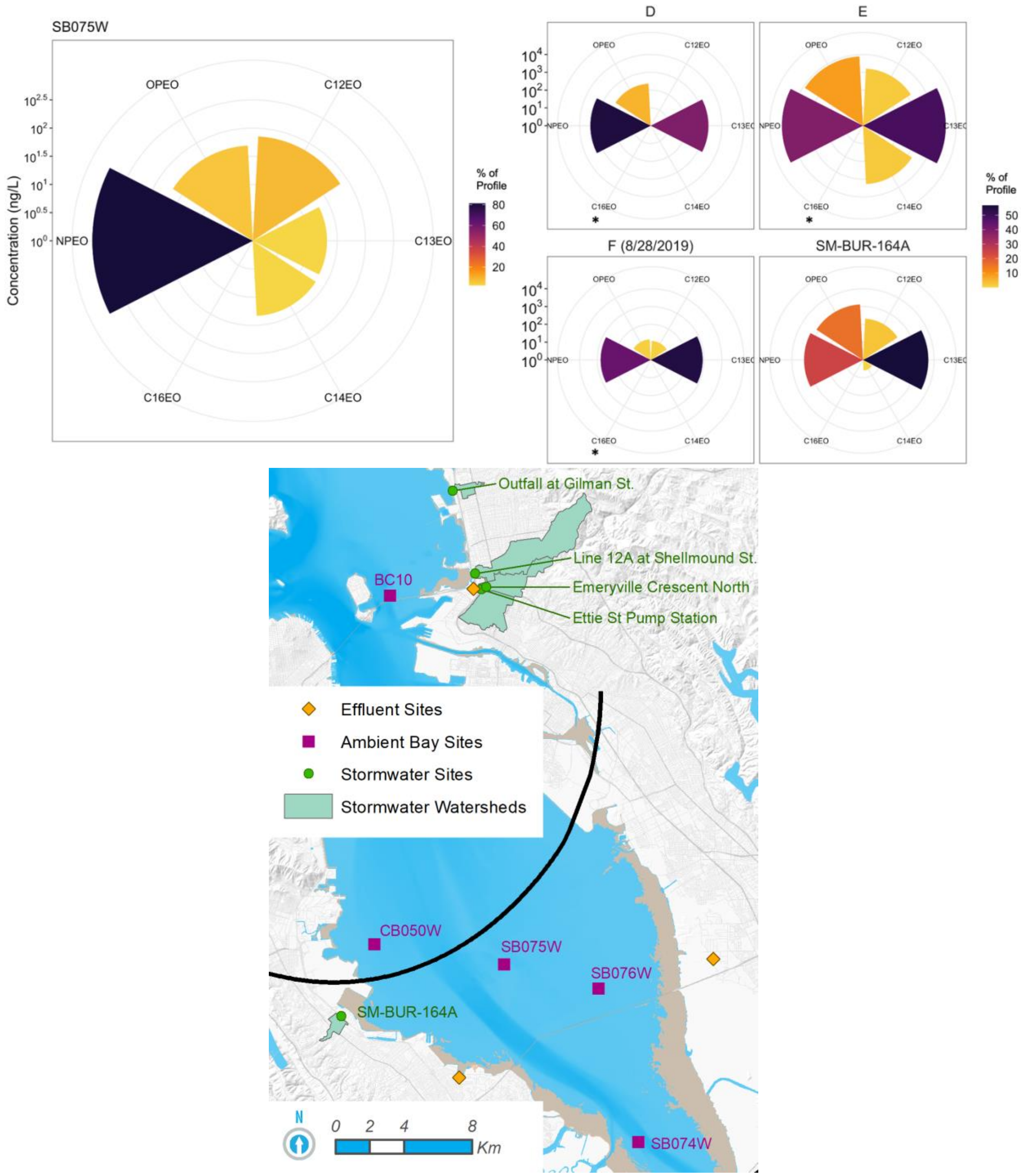


Figure 8. Summed ethoxylated surfactant concentrations for SB075W and nearby POTW and stormwater outfall sites. Rings correspond to each concentration value presented on the y-axis. Ethoxylated surfactants are colored based on the percent of total ethoxylate profile that they make up. Summed ethoxylate concentrations are based on values only above the RL and shown in Appendix A: Table A-2. Data is log transformed. Site map shows SB075W and adjacent sites. *C_{16}EO sums and proportions in wastewater effluent sites have been removed due to field blank contamination.

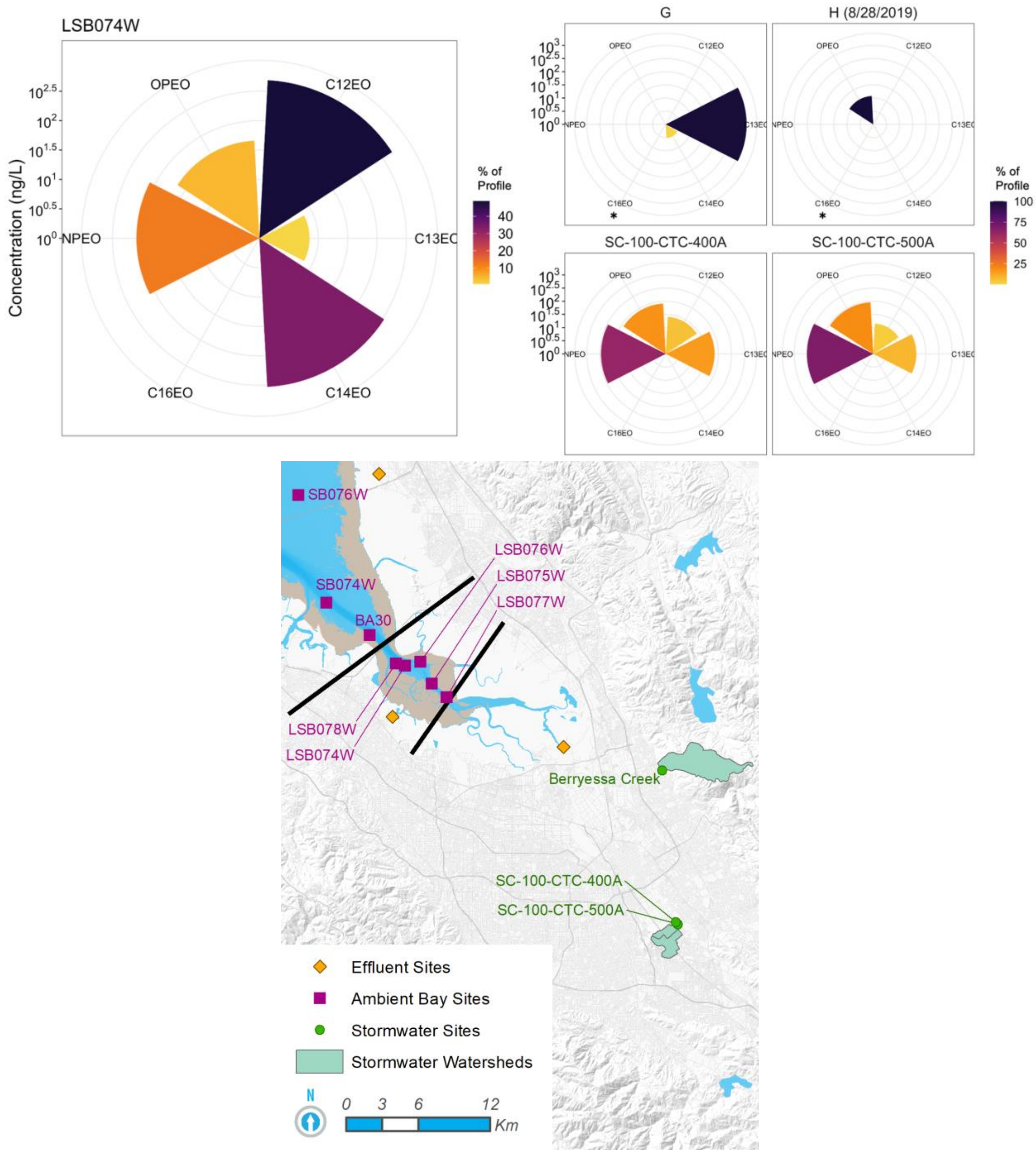


Figure 9. Summed ethoxylated surfactant concentrations for LSB074W and nearby POTW and stormwater outfall sites. Rings correspond to each concentration value presented on the y-axis. Ethoxylated surfactants are colored based on the percent of total ethoxylate profile that they make up. Summed ethoxylate concentrations are based on values only above the RL and shown in Appendix A: Table A-2. Data is log transformed. Site map shows LSB074W and adjacent sites. *C_{16}EO sums for wastewater effluent sites have been removed due to field blank contamination.

V. Discussion

Quantitative analysis of ethoxylated surfactants in this study has provided a valuable glimpse into the scope of ethoxylated surfactant contamination in San Francisco Bay water and the potential pathways by which these compounds enter the Bay. Results showed that POTW effluent contained the highest peak concentrations of ethoxylates of the three matrices. However, this observation is dominated by site E. Concentrations of ethoxylated surfactants in wastewater effluent measured in this study were variable among the POTWs sampled, likely due to variations in influent concentrations and treatment technologies. Summed concentrations of ethoxylated surfactants in wastewater effluent were generally not statistically different from summed concentrations of these compounds in stormwater. Accordingly, stormwater sites were contaminated with ethoxylated surfactants at the majority of target sites and with similar summed concentration ranges compared to wastewater sites, apart from site E. This observation reflects trends observed in a previous non-target evaluation of San Francisco Bay waters, where concentrations of ethoxylated surfactants were present at relatively high abundances in both stormwater and wastewater-influenced sites, indicating that both water types may be important pathways of ethoxylated surfactant contamination in the Bay (Overdahl *et al.*, 2021).

A. Dominant Ethoxylated Surfactant Series Concentrations

Highest observed concentrations of individual ethoxylated surfactants were typically for NPEO and C_{13}EO in the various matrices. OPEO concentrations were also high, but generally lower than NPEO. Both of these results were expected based on the fact that alkylphenol ethoxylates are persistent compounds and NPEO comprises the majority of the commercial market for alkylphenol ethoxylate surfactants in the United States (US EPA, 2010). Wastewater effluent presence and relative concentrations of NPEO in this study were consistent with previous work on evaluation of ethoxylated surfactants across the US, and higher than other studies evaluating effluent concentrations specifically in highly populated coastal California cities (Jardak *et al.*, 2016; Nelson *et al.*, 2011). Concentrations of NPEO detected in stormwater were also similar to previous work in the United States (Masoner *et al.*, 2019) and in Europe (Zgheib *et al.*, 2012). Interestingly, the previous wastewater and stormwater studies mentioned above evaluated short chain ethoxymers for NPEO ($NPEO_{1-4}$, including NP), which are typically considered to occur at higher concentrations than the longer chain NPEO ethoxymers. In our study, we observed concentrations of the longer chain ethoxymers (primarily $NPEO_{3-4}$) similar to those of shorter chain ethoxymers for NPEO in these previous studies. NPEO ethoxymer concentrations in ambient Bay water were lower than individual NPEO ethoxymers evaluated in previous urban estuary studies (Ferguson *et al.*, 2001; Lara-Martín *et al.*, 2014). However, concentrations of $NPEO_{3-16}$ evaluated in this study were higher than those detected for short chain ethoxymers (NP and $NPEO_{1-2}$) in previous work in San Francisco Bay (Klosterhaus *et al.*, 2013b).

High concentrations of $C_{13}EO$ were also measured in many samples. For most wastewater sites, $C_{13}EO$ was measured at concentrations two times higher than that of NPEO, and at concentrations above those measured for all alkyl and ethoxymer chain lengths combined (Morrall *et al.*, 2006). Unlike alkylphenol ethoxylates, information is not readily available for alcohol ethoxylates that dominate in commercial products, as they are often produced as complex mixtures. It is known that alcohol ethoxylates often appear as mixtures of numerous isomers and alkyl chain lengths; thus, measured concentrations of $C_{13}EO$ may be due in part to the wide peak areas attributable to branched isomer hydrophobes, compared to linear C_{12}, C_{14}, and C_{16} alcohol ethoxylated surfactants evaluated in this study. This, however, does not explain why $C_{13}EO$ would be higher than NPEO. This may be due to changes in use of ethoxylated surfactants in certain industries. NPEO, while still used and produced in the United States, has the potential to be banned or phased out, similar to the current restriction of these chemicals in Europe (ECHA, n.d.). Producers of ethoxylated surfactants and industries that use these compounds in high volumes may be anticipating this change or reacting to European bans on imported products containing NPEO by converting to use of alcohol ethoxylated surfactants. Inconsistent with wastewater and stormwater profiles, $C_{13}EO$ had low detected concentrations in ambient Bay water.

B. Wastewater Effluent

Several factors are important to consider when evaluating presence or absence of ethoxylated surfactants in wastewater effluent. These compounds are ubiquitous in consumer use and therefore present to some extent in most wastewater treatment plant influent and effluent (Cowan-Ellsberry *et al.*, 2014; Jardak *et al.*, 2016). However, wastewater treatment plants often have differing treatment technologies that influence removal efficiency and final effluent concentrations of ethoxylated surfactants (Klečka *et al.*, 2012; Morrall *et al.*, 2006). Another consideration is influent type: if the majority of influent is derived from particular sources, there may be different proportions of ethoxylated surfactants corresponding to use patterns from those sources. The differing inputs could result in variations in effluent ethoxylated surfactant concentration, even if treatment types are similar between POTWs.

Effluent at POTW site E had the highest observed concentrations for ethoxylated surfactants in this study. The site E facility estimates that 20% of their influent is derived from industrial sources, which is higher than all other POTWs in our study except site A (25%), which had no detected concentrations of ethoxylated surfactants above the reporting limit. The industrial input types they receive do not differ greatly from other POTWs in this study, with one notable exception. Site E receives influent from a paint manufacturer, which could be a major source of ethoxylated surfactants due to their common use as emulsifiers in commercial paints. These factors may have contributed to relatively high concentrations of ethoxylated surfactants observed in site E POTW effluent in this study.

Additionally, site E applies trickling filter/solids contact secondary treatment and no tertiary treatment. Previous studies have indicated that trickling filter treatment is less effective at removing both alcohol and alkylphenol ethoxylated surfactants compared to alternative methods such as activated sludge (Morrall *et al.*, 2006, Petrie *et al.*, 2013), so use of trickling filter treatment may also have contributed to the high effluent concentrations observed for the site E POTW. This possibility is further substantiated by the fact that site C, the POTW with the second highest observed concentrations of ethoxylated surfactants, also uses trickling filter/solids contact treatment with no tertiary treatment. Site C has a low proportion of influent that comes from industry but is the only other POTW in this study that uses the same secondary treatment method as site E. Site G also uses trickling filter secondary treatment, but it is coupled with nitrifying activated sludge and tertiary treatment, possibly explaining the lower concentrations of ethoxylated surfactants measured in site G effluent, detected only for C_{13}EO and C_{14}EO. Other facilities with notable concentrations of ethoxylated surfactants included site B, site D, and site F. These facilities have varying proportions of influent from industry, but along with site E and site C, represent all of the POTWs examined in this study that do not utilize any form of tertiary treatment.

Site H, the POTW serving the largest population and variety of industries included in this study, had low to no detected concentrations of various ethoxylated surfactants. This may be due to the low proportion of influent flow derived from industry (6%) and the more advanced treatment methods employed. Site H uses activated sludge/biological nutrient removal secondary treatment and tertiary treatment methods including nitrification and denitrification; it is the only POTW in this study that uses tertiary treatment and both nitrification and denitrification.

A comparison of ethoxylated surfactant concentrations detected in this study and these concentrations normalized for population size was conducted to determine the influence of industry versus residential inputs on the various POTWs. Per capita concentrations were calculated by first determining concentration in nanograms per day using flow information for each treatment plant, then dividing this value by the population size served to find a per capita estimation of nanograms per person per day. Site E was removed from analysis for NPEO, OPEO, and $C_{13}EO$ as a statistical outlier. This comparison revealed that similar high variability (based on standard deviation) exists for both non-normalized and per capita normalized sum concentrations across POTWs for each compound (Table 8), indicating that observed concentrations are not the result of ubiquitous watershed contamination. However, this analysis would be more effective in determining POTW watershed characteristics if conducted on influent, as effluent is already influenced by treatment to an unknown degree.

Based on the analytical results and assessment of POTW operations, treatment method and specific industrial influent sources influenced final effluent concentrations in this study, rather broad use throughout the POTW watersheds.

Table 8. Non-normalized and per capita normalized mean and standard deviation of sum concentrations across the 10 POTW samples (excluding field blanks). N represents the number of samples included, with outlier sites excluded.

Ethoxylated Surfactant	**Concentration (ng/L)**		**Per Capita Concentration (µg/person/day)**		**N**
	Mean	St. Dev.	Mean	St. Dev	
$C_{12}EO$	588	896	148.9	219.1	10
$C_{13}EO$	1,548	1,666	505.5	532.8	9
$C_{14}EO$	962	1,356	238.2	335.1	10
NPEO	1,451	1,511	466.5	493.8	9
OPEO	94	133	30.5	43.6	9

C. Urban Stormwater Runoff

To date, minimal published research exists evaluating both alkylphenol and alcohol ethoxylate surfactants in urban stormwater, particularly for longer chain ethoxymers. The focus on short chain NPEO ethoxymers and lack of comprehensive studies in the United States make direct comparison to our study results difficult (Bergé *et al.*, 2012).

Profiles of dominant hydrophobe classes and concentrations of ethoxylated surfactants in stormwater runoff were somewhat variable across sites. This could be representative of a combination of use patterns across a wide range of consumer products and differential transport mechanisms. The Outfall at Gilman St. site, with the highest sum concentrations for most ethoxylated surfactants, was the smallest runoff watershed in our study (0.8 km^2). However, it had a higher proportion of watershed area that is industrial (34%) compared to most sites. Some specific industries include a forging company, an autobody repair shop, and a metal fabricator. There is also a recycling center, turf soccer fields, and Hwy 80/580 which runs directly upstream of the sampling site. Construction materials were also observed near the sampling site. Ethoxylated surfactants are widely used in metalworks in oil-water emulsions (Negm *et al.*, 2010), and on-site use and storage of these oil-water emulsions may result in outdoor leaks or spills that make their way into stormwater. Automotive supplies, including tires, and construction materials have also been identified as key sources of alkylphenol ethoxylate contamination in the outdoor environment (Lamprea *et al.*, 2018). The industries and construction materials observed are likely sources of contamination and could be representative of broader land use in the area, exacerbating the contamination issue in the Outfall at Gilman St. watershed. Further investigation of the recycling center activities and potential for ethoxylated surfactants leaching from artificial turf is required to determine if these are likely sources of contamination. The only site with a higher proportion of industrial land cover was SM-BUR-164A (40%), which had the highest concentration of C_{13}EO and relatively high concentrations of NPEO and OPEO. SM-BUR-164A also had a relatively small watershed area (1 km^2) but includes Hwy 101 immediately upstream of the sampling location and tennis courts near the sampling site. The tennis courts could be a source of ethoxylated surfactants from sealant coating, concrete, and paint (Heldmann *et al.*, 1999; Karsa, 2003). Specific industries in this area were not identified in the sampling plan. Ettie Street Pump Station, another site with higher measured surfactant concentrations, also had a higher proportion of industrial land cover compared to other sites (26%). Two other sites, Cerrito Creek and Emeryville Crescent North, had lower proportions of industrial land cover but still relatively high concentrations of surfactants. At Emeryville, the difference could have been explained by the fact that a high proportion of land cover was transportation-derived (41%). The Outfall at Gilman St. and Ettie St. Pump Station also had higher relative proportions of transportation (e.g., road surface) land use. Interestingly, higher concentrations of ethoxylated surfactants were observed at Ettie St. Pump Station in 2020 than in 2019. Temporal differences for this site and others warrant further investigation in future studies.

It is not surprising that industrial land use would be related to surfactant contamination, given the uses of these compounds and relationship observed between industry and surfactant contamination in the wastewater effluent evaluation. In addition to industry sources, it is well established that many contaminants found in stormwater are derived from roadways due to primary uses and increased area of impervious surface (Burant *et al.*, 2018; Müller *et al.*, 2020; Peter *et al.*, 2018). This may also be the case for surfactants based on measured concentrations of surfactants in stormwater in our study as well as other studies (Peter *et al.*, 2018; Tian *et al.*, 2020). In fact, studies have shown high levels of alkylphenol ethoxylate surfactants leaching from tires and concrete (Lamprea *et al.*, 2018). Contributions to stormwater from roadways may also come from sealants and coatings applied to roadways, and from surfactants used as emulsifiers in vehicle products such as antifreeze, washing fluids, and paint (Karsa, 2003; Kuwabara *et al*., 2014; Schramm *et al.*, 2003). Sites with low measured ethoxylated surfactant concentrations had high proportions of agriculture and open space, including the two reference sites included in this study: Rodeo Creek and Berryessa Creek. There were no detected concentrations of any target ethoxylated surfactants at the Berryessa Creek reference site, where 93% of the runoff watershed area is classified as open and agriculture space. Rodeo Creek, however, did have detected concentrations of NPEO, OPEO, C_{12}EO and C_{13}EO. These concentrations were lower than many other stormwater sites but not insignificant, with detected sum concentrations higher than one to three non-reference sites (depending on hydrophobe class). Rodeo Creek has a high percentage of runoff watershed classified as agriculture and open space (91%); however, this site is located just downstream of Hwy 80 and could be influenced by roadway runoff. Overall, these results suggest that stormwater contamination by ethoxylated surfactants is driven by land use type, not watershed size. This same observation is well-documented in studies that classify pollution from varying land use and land cover (Tong and Chen, 2002; Wilson, 2015). Higher proportions of transportation and industrial land use in the Bay Area appear to correlate with higher concentrations of ethoxylated surfactants in stormwater samples.

D. Ambient Bay Water

Ambient Bay water concentrations of all surfactants were low compared to wastewater and stormwater concentrations, with peak concentrations generally lower than those of ethoxylated surfactants measured in other studies examining large urban estuaries (Ferguson *et al.*, 2001; Lara-Martín *et al.*, 2014), although these studies focused on the short chain ethoxymers. Notably, concentrations of longer chain NPEO ethoxymers in this study were higher than those of short chain NPEO evaluated in previous studies, where no concentrations of $NPEO_{1\text{-}2}$ and low concentrations of NP were detected in San Francisco Bay water (Klosterhaus *et al.*, 2013b). Low detected concentrations compared to wastewater and stormwater were consistent with dilution and degradation processes and potential partitioning to sediment, a matrix that was not evaluated in this study but has been assessed in other studies (Ferguson *et al.*, 2001; Ferguson *et al.*, 2003; Lara-Martín *et al.*, 2014).

Concentrations of ethoxylated surfactants above the MDL were detected at SB075W and LSB074W. SB075W is in the middle of the area designated as South Bay, near the San Mateo (Hwy 92) bridge. LSB074W is located at the very southern end of the Bay near the Hwy 84 bridge. The Lower South Bay embayment is relatively shallow and has a longer hydraulic residence time compared to other embayments (Smith and Hollibaugh, 2006). Therefore, contaminants in stormwater and particularly wastewater were expected to be higher in Lower South Bay compared to other embayments. It might have been expected that nearby Bay water sites would also have had comparable surfactant concentrations and profiles, given that samples in each embayment were collected on the same day. However, this was not observed, as several sample sites proximal to SB075W and LSB074W had much lower or no detected concentrations of ethoxylated surfactants.

The observed SB075W profile may have been due to persistence of NPEO and accumulation of ethoxylated surfactants from several pathways. As observed for site SB075W, none of the surrounding POTW effluent or stormwater profiles matched the observed profile of ethoxylated surfactants at the LSB074W site. This profile appeared to be somewhat irregular, with high concentrations of C_{12} and C_{14} alcohol polyethoxylates. This site was also surrounded by wastewater and stormwater sites that had low measured concentrations of ethoxylated surfactants, indicating these sites do not have an immediate influence on Bay water concentrations, although this conclusion is difficult to make as wastewater, stormwater, and bay water samples were not collected on subsequent days. This is a particularly difficult comparison for stormwater, as those sample were collected during the wet season (November – January) and Bay water and wastewater samples were collected during the dry season, when stormwater is less influential. There were many more POTWs and potential stormwater inputs present in the Bay Area than we were able to evaluate in this study (Appendix D), so it is possible that this observed Bay water profile was influenced by another source or pathway that was not captured in sampling. More advanced modeling and more comprehensive sampling would be needed to evaluate specific polyethoxylate profiles and concentrations at these sites.

Based on our evaluation of ethoxylated surfactant contamination in wastewater effluent, stormwater runoff, and ambient Bay water, it is likely that observed Bay water contamination is the result of both stormwater and wastewater pathways. No significant differences in summed concentrations were observed between stormwater and wastewater samples, for both total ethoxylated surfactant concentrations (across all ethoxylated surfactants combined) and individual ethoxylated surfactants between the different matrices, apart from C_{13}EO. Additionally, Bay water sites in this study had EO number distributions consistent with a mixture of both stormwater and wastewater pathways for alcohol ethoxylates, as there was no significant difference observed for average EO number between ambient bay water and either stormwater or wastewater. Ambient Bay water samples had significantly higher average EO numbers than wastewater, but no significant difference was observed between Bay water and stormwater for the alkylphenol ethoxylates, suggesting that the main pathway of NPEO and OPEO contamination may be stormwater as opposed to wastewater. For OPEO, this conclusion is also supported by statistically higher concentrations of OPEO that were detected in stormwater compared to bay water and a trend of higher OPEO concentrations in stormwater compared to wastewater. Figure 7 shows that the distribution of average EO number, at least in the most prevalent compounds (C_{13}EO, NPEO, and OPEO), was lowest for most wastewater sites, slightly higher at stormwater sites, and ambient Bay water sites were interspersed among the range observed. One exception to this is OPEO, where two Bay water sites had detected concentrations in only one ethoxymer: $OPEO_{15}$. The concentrations of OPEO at these two sites were less than 1 ng/L, and no other polyethoxylated surfactants were detected at either of the sites. This conclusion that ethoxylated surfactant concentrations in San Francisco Bay ambient water are influenced by both stormwater and wastewater pathways is in agreement with recent work evaluating broad-spectrum Bay contamination and potential pathways of pollution (Overdahl *et al.*, 2021).

E. Toxicity Implications

Bay water concentrations of individual alcohol and alkylphenol ethoxylate surfactants were below the range of concern for laboratory-determined acute and chronic toxicity to aquatic organisms for longer chain ethoxylated surfactants (Cowan-Ellsberry *et al.*, 2014; Lechuga *et al.*, 2016; Acir and Guenther, 2018). However, some ethoxylated surfactants exhibit persistent and bioaccumulative properties (e.g., the alkylphenol ethoxylates), making continued loading of these contaminants to the Bay a concern for chronic exposures and potential toxicity. Varying concentrations of multiple ethoxylated surfactants in Bay water samples were observed, so there is the potential that ethoxylated surfactants present in the Bay may produce additive effects – from both the contaminants quantified in this study as well as those potentially present but not included on our target list. Total concentrations of all ethoxylated surfactants present may combine in toxicity to cause adverse effects, even though lower individual ethoxylated surfactant concentrations were observed (TenEyck and Markee, 2007). It should be recognized that this study was not able to quantify the short chain (0-2) NPEO and OPEO ethoxymers, which are considered the more toxic alkylphenol ethoxylated surfactants. It will be important to continue monitoring these contaminants, including follow-up evaluations of short-ethoxymer chain polyethoxylates and sediment concentrations to help assess presence and potential accumulation of the more toxic alkylphenol ethoxylates.

F. Study Limitations, Areas of Improvement and Future Research

Ethoxylated surfactants are ubiquitous, and some analytes were detected in isolated field blanks and instrument blanks, limiting analysis to concentrations above calculated reporting limits, or eliminating potential analysis entirely (as was the case for $C_{16}EO$ in wastewater effluent samples). This limited the statistical evaluations and profile comparisons to a smaller subset of data, especially for ambient Bay water, where a significant portion of low measurement values were excluded based on MDLs and RLs. Field blank contamination at instrument-detectable levels was generally detected for nearly all ethoxylated surfactant series and several ethoxymers within those series. Contamination also tended to scale relative to matrix (i.e., field blank contamination was highest for wastewater blanks and lowest in the ambient Bay water blank). This likely indicates field collection contamination, but could also indicate instrument contamination through sample carryover, although this is less likely considering that samples were not run in matrix series order. This underlines the importance of proper sampling and sample prep procedure when evaluating surfactant contamination in environmental samples in the future.

Spatial comparisons were based solely on comparing ethoxylated surfactant profile and EO distributions of our ambient Bay water samples to those of POTW outfalls and stormwater sites geographically adjacent to the Bay sites with detected concentrations. Hydrology in large estuaries is complex and there may be other factors such as mixing, flushing, temperature, and salinity that influence concentrations, as observed by Lara-Martín *et al.* (2014) in another large urban bay. Those variables were not accounted for in this study. Additionally, ambient Bay water samples were taken during the dry season, which likely influenced our ability to determine immediate stormwater runoff contribution to Bay contamination.

There are several opportunities for future research on ethoxylated surfactants in the Bay area. One primary evaluation should focus on quantifying ethoxylated surfactant sediment concentrations in the Bay. In this study, we observed what appeared to be snapshot concentrations of ethoxylated surfactants in ambient Bay water, based on the limited site detections and differing hydrophobe class profiles. Therefore, ambient Bay water concentrations may be temporally-dependent based on increases in stormwater runoff contribution during the wet season and certain monthly, weekly, or even daily changes in POTW effluent concentrations. Sediment analysis will provide context for continued or baseline loading of ethoxylated surfactants to Bay water, as ethoxylated surfactants tend to accumulate in sediment (Ferguson *et al.*, 2001; Lara-Martín *et al.*, 2014). This analysis could also provide useful information regarding degradation and spatial accumulation patterns.

Subsequent analyses may also consider using methods to capture concentrations of long and short chain (1-2) ethoxymers in all three matrices to determine if long chain ethoxymers are present in sediment or if short chain polyethoxylates are the only compounds accumulating over time. Although previous Bay studies showed no detected concentrations of $NPEO_{1\text{-}2}$ and low concentrations of NP in ambient Bay water (Klosterhaus *et al.*, 2013a), additional analysis could be used to verify or refute those results, thereby providing support for continued monitoring of alkylphenol ethoxylate concentrations. These analyses will also provide baseline information for $OPEO_{1\text{-}2}$ and OP concentrations in ambient Bay water as well as short chain alkylphenol ethoxylate concentrations in stormwater and wastewater.

Additional wastewater monitoring is suggested to highlight any temporal variation in concentrations as well as to isolate sources of contamination based on influent concentrations. As mentioned, POTW E had concentrations an order of magnitude higher than other sites, and while we hypothesize that this is partially the result of overall industrial influent proportion (20%), there were no detected concentrations at site A, which has the highest proportion of influent from industry in our study (25%). Additionally, site F had notable concentrations of ethoxylated surfactants, and their estimated proportion of influent from industry is 0%. This indicates that detected concentrations in wastewater effluent are driven by specific influent sources, not ubiquitous contamination from one general influent type. Although per capita concentration normalization suggested that contamination was not widespread in POTW watersheds, residential uses cannot be discounted as sources of contamination in wastewater effluent. Further analysis of wastewater treatment plant characteristics and influent could highlight why these variations in concentrations were observed.

Based on ethoxylated surfactant profiles detected at only two sites in the Bay with no surrounding sites showing the same trends, evaluation of specific contributions to those two site areas could be conducted to determine whether the observed concentrations in this study are reproducible. The spatial component of Bay water contamination may be aided by the sediment analysis and advanced modeling of loading, mixing, and degradation, which was beyond the scope of this study. Additional sampling of Bay water during the wet season and comparison of wet season profiles and concentrations to the dry season profiles evaluated in this study may also be useful. This analysis could provide more context and evidence for whether or not stormwater is a major contributor to Bay contamination, and if contaminant loading for ethoxylated surfactants exhibits seasonal trends.

Follow-up studies also need to evaluate toxicity concerns for the Bay, based on a more comprehensive literature review of observed toxicity to aquatic systems from long-chain ethoxymer ethoxylated surfactant contamination and analysis of ethoxylate mixture toxicity for both alcohol and alkylphenol ethoxylate surfactants.

VI. References

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Appendix A. Supplementary Tables

Table A-1. Limit of Quantitation, Method Detection Limit, and Reporting Limit values used. For any blank cells in the RL columns, the RL is equal to the MDL for that ethoxymer and matrix. All units are ng/L.

Compound	**LOQ**	**MDL**	**Ambient Bay Water RL**	**Stormwater RL**	**Wastewater RL**
C12EO1	NA	NA	NA	NA	NA
C12EO2	NA	NA	NA	NA	NA
C12EO3	2.37	5.35			27.90
C12EO4	0.53	3.73			14.88
C12EO5	0.56	3.78			15.12
C12EO6	0.61	3.78			15.12
C12EO7	0.44	2.52			12.23
C12EO8	0.37	1.79			8.48
C12EO9	0.28	1.27			5.08
C12EO10	0.14	0.59			2.38
C12EO11	0.13	0.49		0.54	1.98
C12EO12	0.05	0.20		0.24	0.80
C12EO13	0.04	0.14		0.17	0.55
C12EO14	0.16	0.24			0.95
C12EO15	0.07	0.11			0.42
C12EO16	NA	NA	NA	NA	NA
C13EO1	NA	NA	NA	NA	NA
C13EO2	0.31	0.31			
C13EO3	0.88	1.40			5.60
C13EO4	1.26	1.82		3.31	7.27
C13EO5	2.43	3.29		6.82	13.18
C13EO6	2.95	3.57		8.27	16.99
C13EO7	3.42	4.21		9.90	16.86
C13EO8	3.38	4.04		9.93	16.16
C13EO9	3.39	3.88		10.45	15.50
C13EO10	3.50	4.20		11.62	16.82
C13EO11	2.96	3.51		10.91	14.02
C13EO12	2.59	3.11		9.82	12.46
C13EO13	2.12	2.52		8.02	10.10
C13EO14	1.25	1.52		3.70	6.08
C13EO15	1.15	1.51		2.63	6.02
C13EO16	NA	NA	NA	NA	NA

C14EO1	NA	NA	NA	NA	NA
C14EO2	NA	NA	NA	NA	NA
C14EO3	6.03	6.43			25.74
C14EO4	2.69	6.31			25.23
C14EO5	1.42	5.49			21.95
C14EO6	1.55	5.78			23.11
C14EO7	1.11	3.72			14.88
C14EO8	0.93	3.20			12.82
C14EO9	1.44	3.14			12.54
C14EO10	0.36	0.40			1.61
C14EO11	0.32	1.06			4.22
C14EO12	0.13	0.44			1.78
C14EO13	0.09	0.31			1.22
C14EO14	0.08	0.23			0.93
C14EO15	0.17	0.18			0.72
C14EO16	NA	NA	NA	NA	NA
C16EO1	NA	NA	NA	NA	NA
C16EO2	NA	NA	NA	NA	NA
C16EO3	0.30	1.79			13.23
C16EO4	0.33	2.36			13.11
C16EO5	0.48	4.37			19.19
C16EO6	0.62	5.14			16.41
C16EO7	0.74	6.70			20.54
C16EO8	0.83	9.96			25.64
C16EO9	0.88	12.57			28.12
C16EO10	0.97	14.84			
C16EO11	1.02	16.00			
C16EO12	0.94	14.22			
C16EO13	0.87	12.37			
C16EO14	0.82	10.11			
C16EO15	0.71	7.97			31.86
C16EO16	0.53	0.53			24.73
NPEO1	NA	NA	NA	NA	NA
NPEO2	NA	NA	NA	NA	NA
NPEO3	2.99	2.99			10.21
NPEO4	0.20	1.40		4.09	5.62
NPEO5	0.45	2.52		6.00	10.10
NPEO6	0.60	3.29		6.64	13.17
NPEO7	0.69	3.55		6.24	14.20
NPEO8	0.95	4.69		7.71	18.78

NPEO9	1.00	4.54		8.09	18.14
NPEO10	0.97	3.96		6.55	15.84
NPEO11	0.88	3.29	2.50	5.71	13.14
NPEO12	0.72	3.18	3.67	4.37	12.72
NPEO13	2.89	4.06			16.23
NPEO14	2.09	3.03			12.11
NPEO15	1.45	2.41			9.64
NPEO16	0.18	0.95			3.79
OPEO1	NA	NA	NA	NA	NA
OPEO2	54.12	54.12			
OPEO3	0.39	1.26		2.14	6.14
OPEO4	0.56	1.81			7.22
OPEO5	0.76	2.35		2.43	9.41
OPEO6	0.91	2.60		3.22	10.40
OPEO7	1.00	2.57		4.29	10.26
OPEO8	0.86	2.00		4.86	7.98
OPEO9	0.78	1.70		6.34	6.80
OPEO10	0.55	1.15		6.53	4.58
OPEO11	0.41	0.83		6.70	3.32
OPEO12	0.20	0.39		4.54	1.56
OPEO13	0.14	0.27		4.47	1.06
OPEO14	0.09	0.18		3.84	0.70
OPEO15	0.04	0.07		1.56	0.27
OPEO16	0.14	0.14		1.22	0.58

Table A-2. Summed ethoxymer concentrations and average number of EO units for each ethoxymer at each sample site. Red numbers indicate that the sites were statistical outliers among wastewater field blank concentrations and were not included in the averaging of field blank concentrations to determine the Reporting Limit. *Average EO number was not calculated for C_{16}EO wastewater sites due to high field blank contamination.

Site	**C_{12}EO**		**C_{13}EO**		**C_{14}EO**		**C_{16}EO**		**NPEO**		**OPEO**	
	Sum (ng/L)	Avg. #EO	Sum (ng/L)	Avg. #EO	Sum (ng/L)	Avg. #EO	Sum (ng/L)	Avg. #EO	Sum (ng/L)	Avg. #EO	Sum (ng/L)	Avg. #EO
Ambient Bay Water												
BA30											0.1	15.0
BC20												
BG30									1.6	4.0		
CB047W												
CB050W												
LSB074W	490.4	5.1	7.1	5.6	339.0	5.4	14.4	4.0	123.7	6.1	45.9	6.4
LSB075W												
LSB076W												
LSB077W												
LSB077W-Duplicate												
LSB078W												
SB074W	0.4	12.4							13.4	5.0		
SB075W	71.5	6.2	20.9	4.9	21.6	9.2			708.3	5.8	49.2	7.2
SB076W												
SU055W												
SU056W												
SU057W											0.1	15.0
Field Blank												
Stormwater												
Berryessa Creek												
Cerrito Creek	206.8	6.0	408.9	6.0	28.3	6.3			1226.3	5.8	437.7	6.4
Emeryville Crescent North	220.5	6.4	412.7	6.9	9.2	7.7			851.2	5.9	1114.7	8.4
Ettie St Pump Station_2019	22.8	7.8	36.5	5.6					206.5	6.6	141.5	7.0
Ettie St Pump Station_2020	110.2	7.0	889.9	7.1	33.7	7.4	154.1	9.8	1194.8	5.9	261.0	6.3

Meeker Slough	230.1	7.2	121.4	7.2	30.1	8.5			226.5	6.7	193.2	7.0
Outfall at Gilman St.	770.2	6.3	426.8	7.0	154.8	6.4			2997.9	5.8	1506.2	7.8
Rodeo Creek	15.6	7.5	73.2	5.7					137.3	5.6	27.9	5.2
SC-100-CTC-400A	25.7	8.1	71.8	6.5					288.6	6.7	82.0	6.2
SC-100-CTC-500A	14.2	7.4	43.5	5.2					331.4	6.0	91.7	5.8
SM-BUR-164A	209.2	6.9	4731.5	8.3	4.0	11.1			2060.1	6.6	1324.0	9.1
Temescal Ck/Line 12A_2018	17.6	6.5	152.6	5.8					135.3	4.8	49.9	5.2
Temescal Ck/Line 12A_2019									30.2	4.0	20.0	4.8
Field Blank												
Wastewater												
A												
B			651.4	4.8			230.2		430.4	3.0	10.3	3.0
C	132.7	6.1	4755.8	5.6			345.5		3587.7	3.4	296.5	5.7
D			1760.5	4.9					2479.6	4.2	232.0	3.6
E	1620.2	5.7	45361.3	5.3	1920.5	5.6	1404.7		36296.1	4.0	7855.1	5.9
F (8/28/2019)	11.9	10.9	835.8	4.3			227.5		661.1	3.1	14.4	3.0
F (9/10/2019)			102.8	3.6					94.7	3.2	0.6	15.0
G			1180.7	7.8	3.3	10.0	757.0					
H (8/27/2019)							566.8					
H (8/28/2019)							542.1				12.1	3.0
A Field Blank												
B Field Blank			30.5				1321.6					
C Field Blank							407.7					
E Field Blank												
F Field Blank							239.9					
H Field Blank	210.9						28.9				11.6	

Appendix B. Supplementary Boxplots

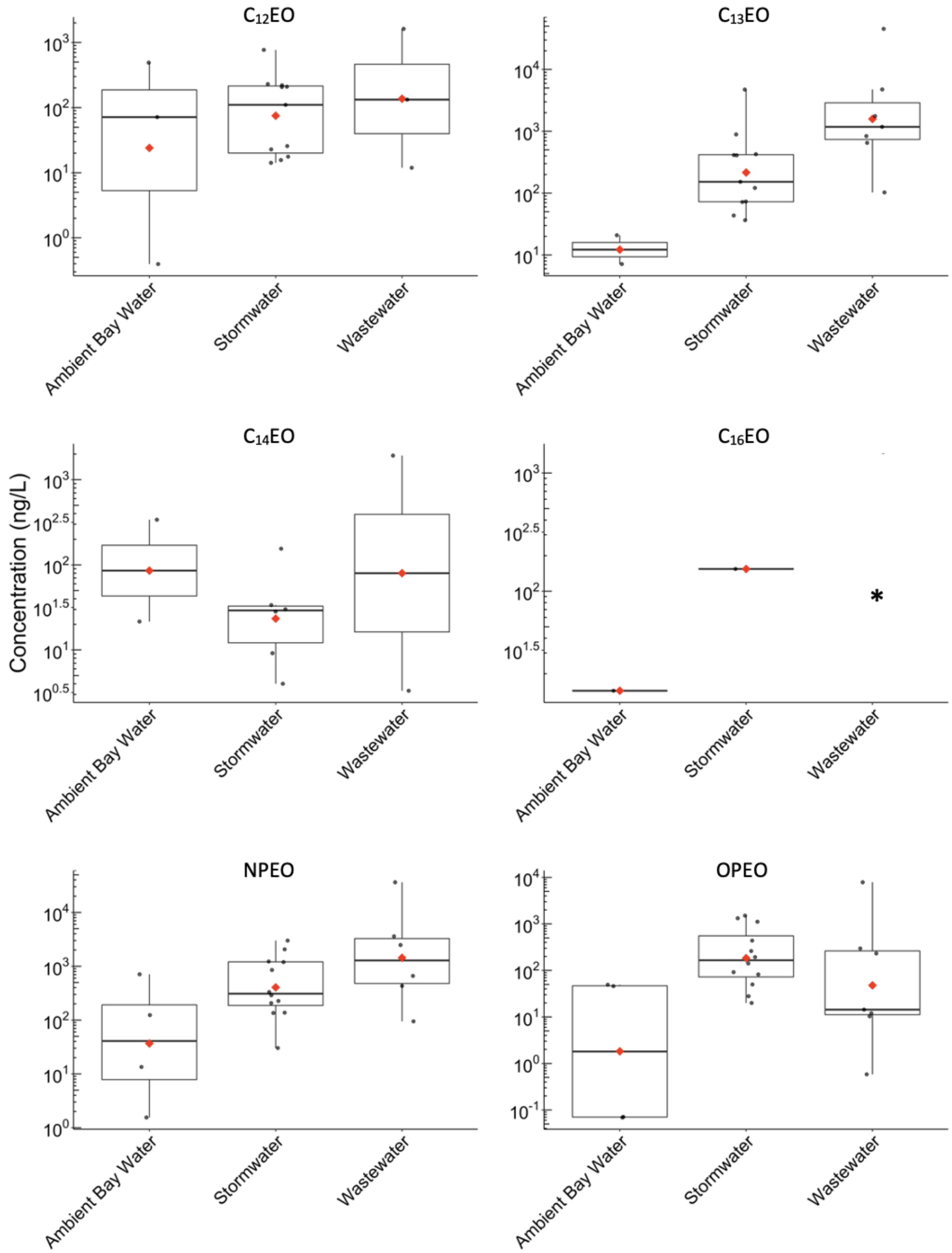

Figure B-1. Distribution of total ethoxylate concentrations (summed across EO unit) for different matrix sites for each ethoxylate. These plots represent the same information as Figure 3. Individual matrix sites included in each boxplot are represented by the points. Geometric means are displayed as red diamonds. Only individual ethoxymer concentrations above reporting limits were included in the sum total for each ethoxylate. Data is displayed on a logarithmic scale. *$C_{16}EO$ has been removed due to field blank contamination.

Appendix C: Supplementary Bar Plots

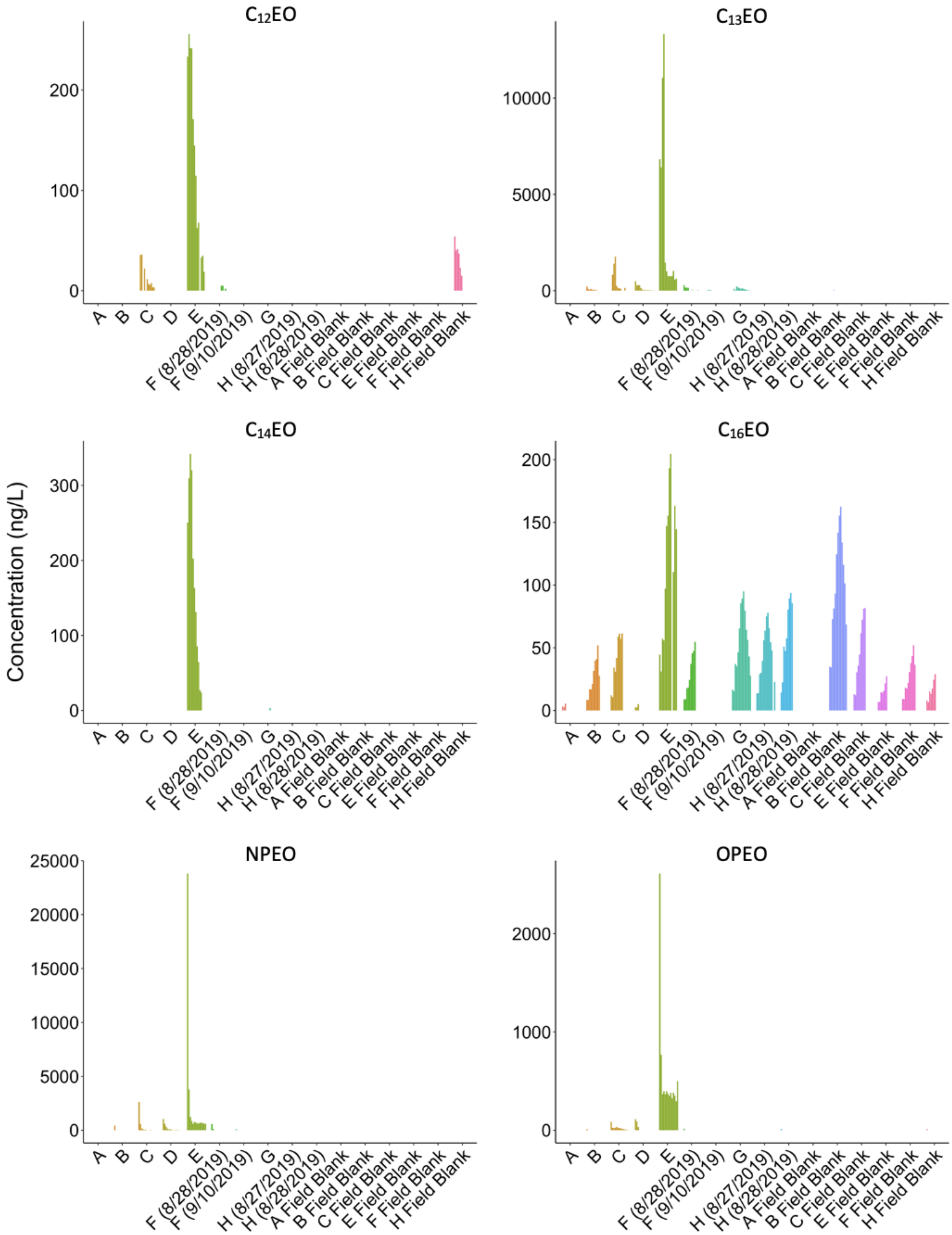

Figure C-1. Concentrations of individual polyethoxymers for each ethoxylated surfactant in POTW effluent samples (including blanks).

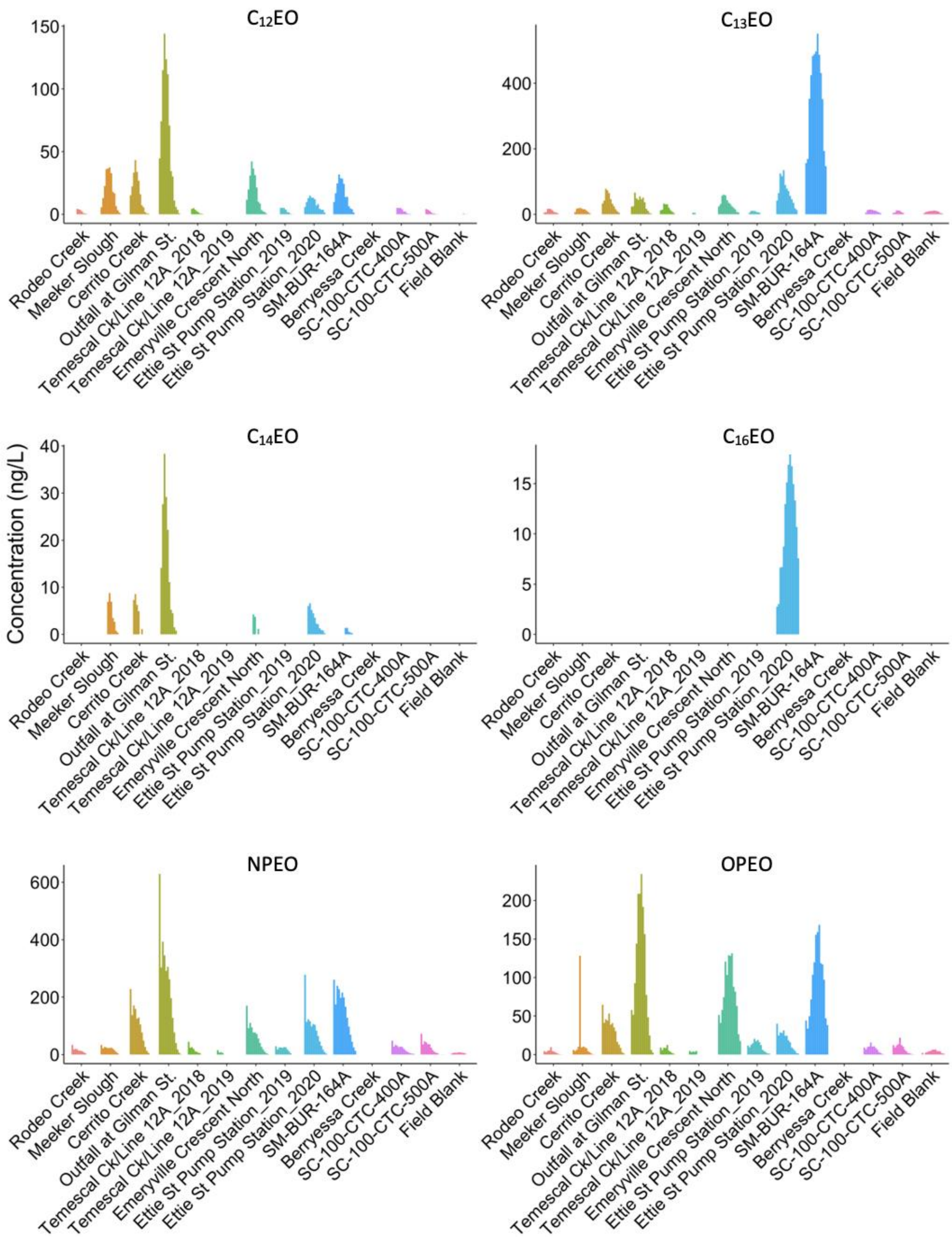

Figure C-2. Concentrations of individual polyethoxymers for each ethoxylated surfactant in stormwater runoff samples (including blanks).

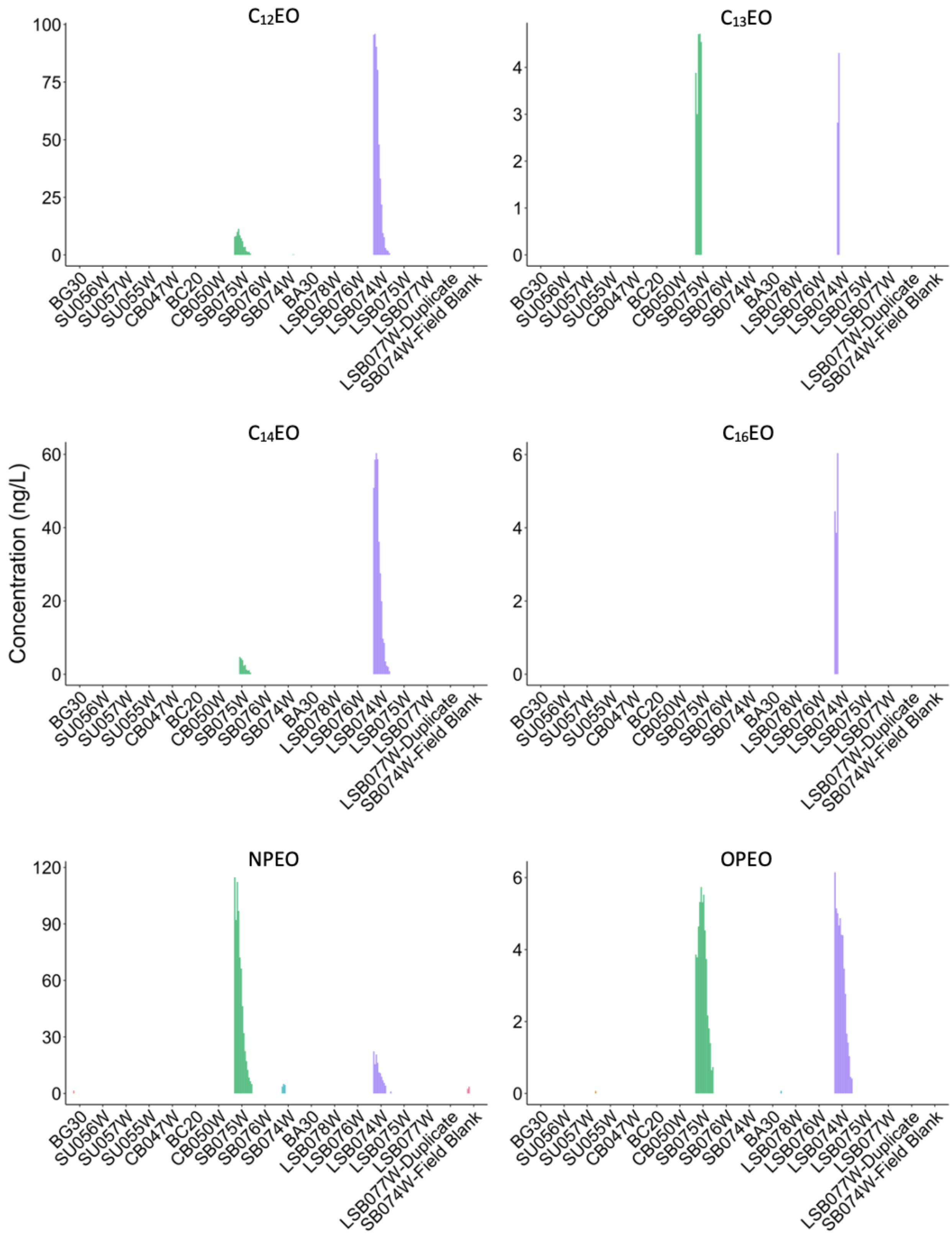

Figure C-3. Concentrations of individual polyethoxymers for each ethoxylated surfactant in ambient Bay water samples (including blanks).

Appendix D: Supplementary Site Maps

Figure D-1. Additional POTWs in the San Francisco Bay area.

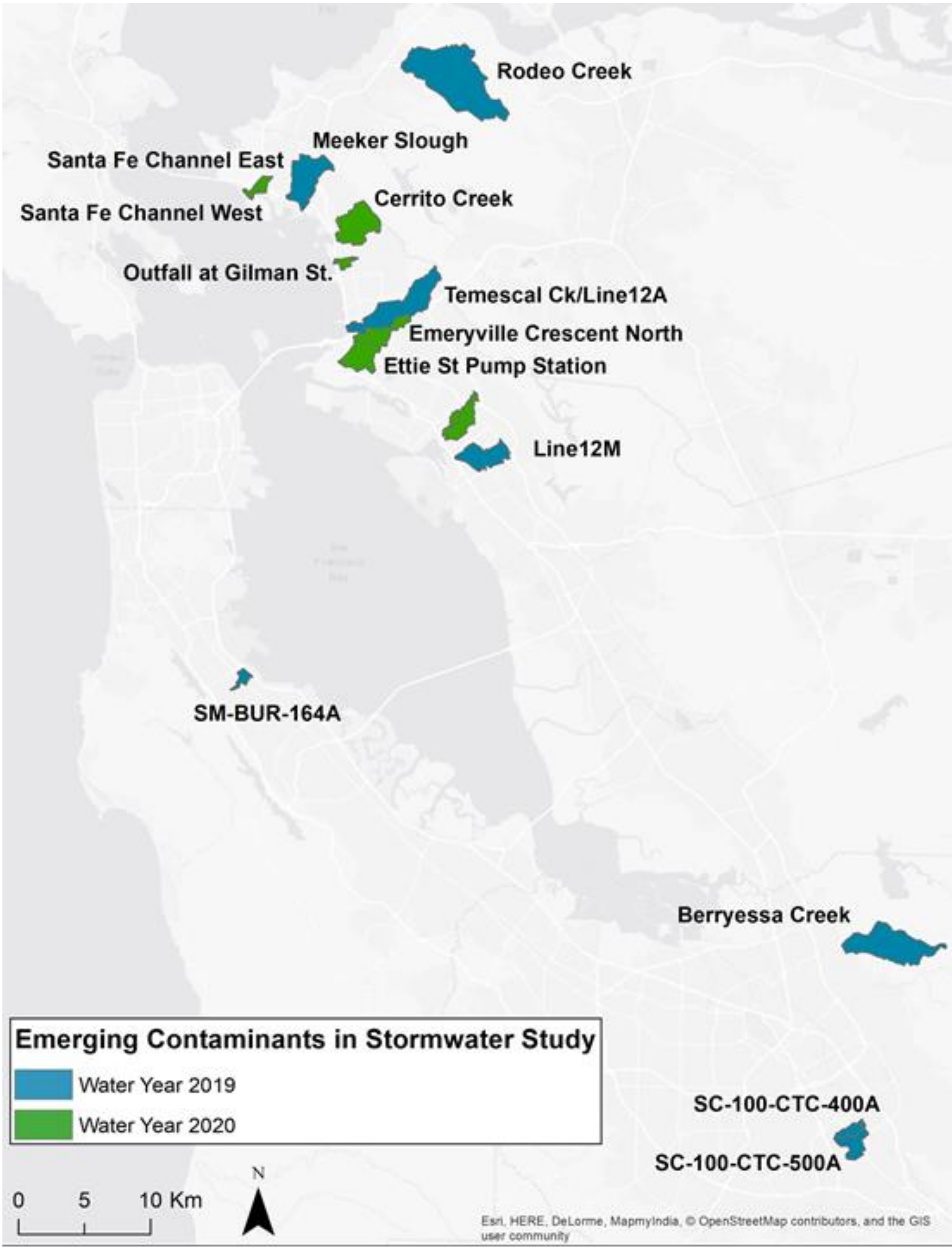

Figure D-2. Additional urban stormwater runoff sites identified by SFEI in their Special Study proposal.